ON THE CHANGES OF WEIGHT OF THE ELECTRODES OF THE LEAD-ACID STORAGE CELL IN THE COURSE OF DISCHARGE.

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Introduction. More than seventy years have elapsed since Gaston Planté made the first lead storage cell in 1859. Many authors studied this cell, yet there remains some ambiguity in the chemical change involved in the charge and discharge of the cell. It may be considered to be rather complicated matters.

The double sulphation theory was proposed by Gladstone and Tribe⁽¹⁾ for the fundamental chemical reaction of the cell, which then was supported by many investigators. Dolezalek⁽²⁾ made an important contribution to the theory, by treating it thermodynamically and applying the Gibbs-Helmholz equation to this problem. On the other hand Féry⁽³⁾ held a different opinion against the double sulphation theory, which is usually called Féry's theory. Chéneveau⁽⁴⁾ measured the changes of weight of the electrodes of the storage cell and obtained the results in favour of Féry's theory, while Denina's results of the similar experiment supported the double sulphation theory.⁽⁵⁾

These two theories can be expressed by the following chemical equations:

$$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O \text{ (double sulphation theory)};$$

$$2Pb + Pb_2O_5 + H_2SO_4 = 2PbO_2 + H_2O + Pb_2SO_4 \text{ (Féry's theory)}.$$

Changes of weight of the positive and negative electrodes calculated from these theories are given in Table 1. This table shows the increases of weight of the electrodes in the discharge of 1 ampere hour of the electricity.

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(1) Vinal, "Storage Batteries," (1930), 152.

(2) Dolezalek, "Die Theorie des Bleiaccumulators," (1901).

(3) Féry, *Bull. soc. chim.*, **25** (1919), 223.

(4) Féry and Chéneveau, *Bull. soc. franç. élec.*, (1926), 13-32.

(5) Denina, *Giorn. chim. ind. applicata*, **12** (1930), 67; c.f. Jumau, *Rev. gén. élec.*, **28** (1930), 311.

Table 1.

	Double sulphation theory	Féry's theory
Positive electrode	+ 1.196 g.	− 0.294 g.
Negative electrode	+ 1.791 g.	+ 1.791 g.

In the case of positive plate it is expected that the weight increases in discharge from the double sulphation theory, while decreases from Féry's theory. The change of weight of the negative plate is expected to be the same for both of these theories. The present author has made some experiments on this subject and the results are described in this paper.

Experimental Procedures. A small pasted type electrode of the lead-acid cell, being dipped in dilute sulphuric acid, was hung from one of the arms of a thermobalance by a hook made of a glass capillary. The cell was placed in a thermostat maintained at 25°C. The thermobalance is provided with a small mirror at the top of its arm and the inclination of the arm can be observed by means of a telescope and a scale. Besides the mirror, it possesses a pointer and a scale as in the ordinary chemical balance. Both of these devices have been used in the present experiments. The sensibility of the balance was lessened by the damping effect due to the immersion of the electrode in the solution of the cell, and was about 0.02 g.

The electrodes used in the experiments were made by Nippon Tikudenti K. K. The dimensions of the plates were about 20 mm. × 96 mm. × 3 mm., and their capacity was about 1 ampere hour. The discharge current was maintained to 250 milli-amperes throughout the experiments, and the change of weight was measured every 1/4 a.h. of discharge. A glass vessel of about 800 c.c. was used as the container of the solution. By using such a large vessel the variation of the density of the solution before and after the discharge was only 0.001 in specific gravity. The volumes of the electrodes used for the experiments were found to be about 4-5 c.c., accordingly the variations of buoyancy due to the change of the density of solution do not need to be taken into consideration.

Results of the Experiments. **(1) The Positive Plate.** The measurements of the positive plate were made first. In this case the change of weight accompanied in the process of discharge must have the opposite signs according to the two theories cited above. Ten cycles of charge and discharge were made, and the results of measurements are given in Table 2 and Table 3. The weight always increases in the course of discharge.

Table 2. Increases of Weight of the Positive Plate (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
1	—	0.44	—	0.54
2	—	—	—	0.55
3	—	—	—	0.55
4	0.13	0.29	0.44	0.54
5	—	0.31	—	0.61
6	0.13	0.30	0.45	0.55
7	0.14	0.30	0.45	0.55
8	0.13	0.29	0.43	0.53
9	0.13	0.29	0.44	0.55
10	0.13	0.30	0.46	0.55
mean	0.13	0.32	0.45	0.55

Table 3. Increases of Weight of the Positive Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
4	0.13	0.16	0.15	0.10
6	0.13	0.17	0.15	0.10
7	0.14	0.16	0.15	0.10
8	0.13	0.16	0.14	0.10
9	0.13	0.16	0.15	0.11
10	0.13	0.17	0.16	0.09
mean	0.13	0.16	0.15	0.10

Table 2 gives the changes of weight due to the discharge of 1/4 a.h., 1/2 a.h., 3/4 a.h., and 1 a.h., while Table 3, changes of weight per 1/4 a.h. of discharge. From Table 2, we can see that the changes of weight by discharge of 1/4 a.h., 1/2 a.h., 3/4 a.h., and 1 a.h. give well reproducible values. In Table 6 changes of weight per 1 a.h. of discharges measured by the author are compared with the values observed by Chéneveau.(4) It is remarkable that Chéneveau's values are always a little larger than author's values. It is noticeable, from Table 3, that the weight increases per 1/4 a.h. discharge at different stages are not equal, the initial and the final being smaller than the middle. The increases of weight corresponding to the first, second, third, and final discharge of 1/4 a.h. are 0.13 g., 0.16 g., 0.15 g., and 0.10 g., respectively. Such an unequality of the weight change is probably due to some secondary reaction, the occurrence of which being considered from the evolution of gas bubbles especially at the beginning and at the final stages of discharge.

(2) **The Negative Plate.** Five cycles of discharge were made in the experiment. The specific gravity of the electrolyte solution was taken to be 1.262 (at 27.5°C.). Experimental results are tabulated in Table 4 and Table 5.

Table 4. Increases of Weight of the Negative Plate (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
1	0.29	0.56	0.81	1.08
2	0.29	0.58	0.85	1.13
3	0.30	0.59	0.87	1.14
4	0.29	0.59	0.87	1.16
5	0.30	0.60	0.89	1.16
mean	0.29	0.58	0.86	1.13

Table 5. Increases of Weight of the Negative Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity			
	1/4 a.h.	1/2 a.h.	3/4 a.h.	1 a.h.
1	0.29	0.27	0.25	0.27
2	0.29	0.29	0.27	0.28
3	0.30	0.29	0.28	0.27
4	0.29	0.30	0.29	0.29
5	0.30	0.30	0.29	0.27
mean	0.29	0.29	0.28	0.27

Thus the changes of weight of the negative electrode give fairly well reproducible values. In Table 7 author's results of the changes of weight per 1 a.h. of discharge are compared with Chéneveau's values, the former being a little smaller than the latter.

Discussion of the Results. In Table 6 and Table 7 author's results are compared with Chéneveau's data and with the theoretical values calculated from both of the two theories cited above.

Table 6. Comparison of Observed Values with Theoretical Values (g.) (Positive Plate).

Observed values		Theoretical values	
Kinoshita	Chéneveau	D. S. theory	Féry's theory
0.54	0.69	1.196	−0.294
0.55	0.73		
0.54	0.73		
0.61	0.63		
0.55	0.78		
0.55	0.51		
0.53			
0.55			
0.55			

Table 7. Comparison of Observed Values with Theoretical Values (g.) (Negative Plate).

Observed values		Theoretical values	
Kinoshita	Chéneveau	D. S. theory	Féry's theory
1.08	1.26	1.791	1.791
1.13	1.47		
1.14	1.37		
1.16	1.27		
1 16	1.23		
	1.35		

From these tables we see that the weight changes of the electrodes during the course of discharge do not agree well with the theoretical values calculated from the double sulphation theory or Féry's theory. The weight increase is actually observed both by the present author and Chéneveau in the case of positive plate, while the weight decrease must be expected from Féry's theory. As the explanation for the discrepancy of Chéneveau's measurements from the theory, Féry assumed the existence of a side reaction which takes place at the negative electrode side by side with the formation of Pb_2SO_4, and the migration of Pb-ion from negative to positive electrode.(4)

On the other hand observed values for both positive and negative electrodes were found to be smaller than the values calculated from the double sulphation theory, being about 51–46% for the positive, and 65–57% for the negative electrode. These experimental results give no decisive conclusion for the two theories mentioned above. The present data, however, are rather coincident with Chéneveau's values, and show very good constancy among themselves.

As already stated, the effect of buoyancy change due to the variation of the specific gravity of sulphuric acid is very small, and the principal causes of error may be the effect of gas bubbles in the pores of the electrodes. Further investigations have been undertaken on this point.

Experiments on the Different Conditions of Cell. Now the conditions of the cells such as the concentration, temperature and the viscosity of the electroyte are altered and the effect on the weight change is studied.

To determine the viscosity and the specific gravity, a small amount of the electroyte solution was taken out into an Ostwald pycnometer or a viscosimeter, respectively. In discharging the cell, current was maintained to 250 milli-amperes throughout the experiments, and change of weight was measured every 1/4 a.h. of the discharge.

(1) **Experiments with the Very Dilute Sulphuric Acid.** At first the specific gravity of the sulphuric acid in the cell was reduced to 1.111 by dilution with water. Owing to the dilution of the electrolyte the capacity of the cell diminished to about 1/2 a.h. Accordingly measurements were made only for the discharge capacities of 1/4 a.h. and 1/2 a.h. The results obtained for the positive electrode are tabulated in Table 8 and Table 9.

The discharges from the first to the 9th cycle were made at room temperature (about 15°C.), and from the 10th to the 16th cycle at 30°C., the cell being kept in a water thermostat.

In Table 8 and Table 9 we notice that there are no remarkable effects of the dilution of the solution, though slightly smaller values were obtained in the case of dilute electrolyte solution. Moreover, increase of the values was noticed at the temperature raised to 30°C.

Table 8. Increases of Weight of the Positive Plate (g.).

Cycle	Discharge capacity		Temperature (°C.)
	1/4 a.h.	1/2 a.h.	
1	0.19	0.38	
2	0.13	0.30	
3	0.11	0.26	
4	0.13	0.29	
5	0.11	0.23	
6	0.12	0.25	
7	0.13	0.25	
8	0.12	0.25	
9	0.11	0.24	
10	0.17	0.34	30
11	0.15	0.33	30
12	0.14	0.32	30
13	0.14	0.30	30
14	0.13	0.27	30
15	0.15	0.29	30
16	0.20	0.40	30
mean	0.14	0.29	

Table 9. Increases of Weight of the Positive Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity		Temperature (°C.)
	1/4 a.h.	1/2 a.h.	
1	0.19	0.19	
2	0.13	0.17	
3	0.11	0.15	
4	0.13	0.16	
5	0.11	0.12	
6	0.12	0.13	
7	0.13	0.12	
8	0.12	0.13	
9	0.11	0.13	
10	0.17	0.17	30
11	0.15	0.18	30
12	0.14	0.18	30
13	0.14	0.16	30
14	0.13	0.14	30
15	0.15	0.14	30
16	0.20	0.20	30
mean	0.14	0.15	

(2) **Experiments with the Concentrated Sulphuric Acid.** Concentration of the electrolyte was increased to the specific gravity of 1.540. In this case the active materials of the plate fell out of the grid in the initial charge, so the experiments could not be continued.

(3) **Experiments with the Viscous Electrolyte Solution.** Viscosity of the electrolyte solution may be one of the most important factors which affect the existence of the gas bubbles in the pores of the electrode. The viscosity of the liquid will prevent the escaping of the gas bubbles from the pores.

In order to increase the viscosity gelatin and glycerin were added to the solution. The viscosity was measured by the Ostwald viscosimeter. The solution of the cell was made by dissolving 2 grams of gelatin in 1000 c.c. of the sulphuric acid of the specific gravity 1.240. The change of weight of the positive electrode was measured with this cell. The experimental results are tabulated in Table 10 and Table 11.

Table 10. Increases of Weight of the Positive Plate (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.13	0.47	1.962/25°C.
2	0.13	0.30	
3	0.16	0.30	

Table 11. Increases of Weight of the Positive Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.13	0.24	1.962/25°C.
2	0.13	0.17	
3	0.16	0.14	

The capacity of the cell decreased to about one half of the normal value by the increase of viscosity of the electrolyte solution. The measurements were only made at 1/4 a.h. and 1/2 a.h. of discharge. The weight increases at 1/4 a.h. and 1/2 a.h. are tabulated in Table 10 and those for every 1/4 a.h. of discharge are tabulated in Table 11.

Next, the viscosity was increased by the addition of glycerin. Thus 260 c.c. of glycerin was added to 1000 c.c. of sulphuric acid (specific gravity of 1.240). The specific gravity of this mixture was found to be 1.2461 at 25°C. and its relative viscosity was 3.143 / 25°C. By using such solution the capacity of the cell decreased seriously, probably by the lack of supply of the electrolyte to the active material, and the cell could scarcely stand a discharge of 250 milli-amperes during a few minutes.

Experimental results obtained with the negative electrode were tabulated in Table 12 and Table 13.

Table 12. Increases of Weight of the Negative Plate (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.38	0.66	2.034/25°C.
2	0.30	0.59	
3	0.31	0.61	
4	0.28	0.57	
5	0.28	0.60	
6	0.28	0.51	
7	0.28	0.57	
8	0.27	0.56	
9	0.27	0.55	
mean	0.29	0.58	

Table 13. Increases of Weight of the Negative Plate per 1/4 a.h. of Discharge (g.).

Cycle	Discharge capacity		Relative viscosity
	1/4 a.h.	1/2 a.h.	
1	0.38	0.28	2.034/25°C.
2	0.30	0.29	
3	0.31	0.30	
4	0.28	0.29	
5	0.28	0.32	
6	0.28	0.23	
7	0.28	0.29	
8	0.27	0.29	
9	0.27	0.28	
mean	0.29	0.29	

A solution made from 10 g. of gelatin and 1000 c.c. of sulphuric acid (specific gravity of 1.240) was used in this experiment. The discharge capacity of the electrode also diminished to about one half of the normal value.

Conclusion. From the results described above the changes of weight of the electrodes during the course of discharge do not agree well with the calculated values from both double sulphation theory and Féry's theory. The changes of weight of the electrodes show no remarkable differences by the alteration of conditions such as the concentration or the viscosity of the electrolyte solution. On the other hand the capacities of the electrodes, both positive and negative, were affected seriously by the alterations of such conditions, especially by adding glycerin to the solution. In this case the terminal voltage of the cell fell to about 1.0 volt for a several minutes of discharge. These may lead to the considerations that the effect of gas bubbles in the pores of the electrodes are considered to be rather small. The active materials of the both positive and negative electrodes are submitted to the chemical change during the course of discharge, and therefore there occurs the volume change of these materials. So that Jumau(6) and Tomii(7) proposed the necessity of the correction for the buoyancy change of the electrode before and after the discharge. Such a correction was made to author's results. The densities of the active materials assumed in Féry's theory, i.e. Pb_2O_5 and Pb_2SO_4, are not known, so the corrections of the buoyancies cannot be done in this case. The densities and the molecular volumes of lead, lead peroxide, and lead sulphate are shown in Table 14. The required amounts of Pb and PbO_2 for the discharge of 1 a.h. are 3.866 g. and 4.463 g., respectively.

Table 14.

	Density	Mean density	Molecular volume	Difference of molecular volume
Lead	11.37	11.37	18.2 c.c.	30.4 c.c.
Lead sulphate	6.23	6.23	48.6 c.c.	22.6 c.c.
Lead peroxide	8.91–9.50	9.21	26.0 c.c.	

It follows that the volume changes of the electrodes for the discharge of 1 a.h. are $(30.4 \times 3.866 / 207.2) = 0.567$ c.c. for the negative plate and $(22.6 \times 4.463 / 239.2) = 0.422$ c.c. for the positive plate. Assuming that the

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(6) Jumau, *Rev. gén. élec.*, **20** (1926), 235.

(7) Tomii, *J. Soc. Chem. Ind., Japan*, **34** (1931), 59 C.

density of the solution does not change throughout the course of discharge and is 1.261, the corrections for the buoyancy change for the discharge of 1 a.h. are 0.71 g. for the negative plate and 0.53 g. for the positive plate. These correction values are added to author's results described already, and the corrected values are compared with Chéneveau's values, which are also corrected (Table 15).

Table 15.

Increases of Weight per 1 a.h. of Discharge (g.) (Negative plate).

Observed values (corrected)		Theoretical value from D.S. theory
Kinoshita	Chéneveau	
1.79	1.97	1.791
1.84	2.18	
1.85	2.08	
1.87	1.98	
	1.94	
	2.06	

Increases of Weight per 1 a.h. of Discharge (g.) (Positive plate).

Observed values (corrected)		Theoretical value from D.S. theory
Kinoshita	Chéneveau	
1.07	1.22	1.196
1.08	1.26	
1.07	1.26	
1.14	1.16	
1.08	1.31	
1.08	1.04	
1.06		
1.08		
1.08		

As seen from Table 15 the corrected values are somewhat larger for the negative plates and about 10% smaller for the positive plates than the calculated values. In spite of these discrepancies, the results obtained in the present experiments are in favour of the double sulphation theory.

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