mount and Spring Garden pools often deteriorates to a point below the maximum limit of admissible impurity. And whilst the evidence afforded by the single analysis of the water in the Roxborough pool, which was only incidentally made in the course of this investigation, is much in favor of the latter, yet the relative character of the Roxborough water can only be established with certainty by more extended research.

THE CHEMISTRY OF THE PLANTÉ AND FAURE ACCUMULATORS.*

By J. H. GLADSTONE and ALFRED TRIBE.

(Continued from vol. cxv, page 68.)

PART V.—1. INFLUENCE OF STRENGTH OF ACID.

In the second part of this communication, see this *Journal*, vol. cxiv, p. 223, when treating of the charging of the cell, we pointed out that in the electrolysis of dilute sulphuric acid between lead electrodes, two totally different reactions might be obtained. The positive metal becomes thinly coated with lead sulphate when the current employed is of small density, but with lead peroxide when the density of the current is of greater magnitude. This latter action is, of course, what takes place in the ordinary formation of a Planté battery. The chemical change, therefore, which goes on at the positive electrode is to a certain extent dependent upon the strength of the current. It appeared also of both theoretical and practical interest to determine whether the chemical change was also influenced by the strength of the acid employed. Our experiments consisted in passing a current of uniform strength, about 1 ampere, between electrodes of lead, 12 square inches in size, in varying strengths of sulphuric acid, and estimating in each case the amount of oxygen fixed by the positive electrode. We determined this for successive five minutes of time, and as such actions are not always very uniform, we made in each instance more than one experiment. The results are given in the following table:

* From *London Nature*.

Strength of acid.	Expt.	Percentage of oxygen fixed.				
		First 5 mins.	Second 5 mins.	Third 5 mins.	Fourth 5 mins.	Total.
1 to 5.....	I.	38.1	28.6	28.6	33.3	128.6
	II.	39.5	30.2	25.6	30.2	125.5
1 to 10.....	I.	43.4	38.7	29.2	34	145.3
	II.	44.1	39.3	29.3	31.9	147.6
1 to 50.....	I.	48.3	39.6	35.3	22.4	145.6
	II.	46.2	43.9	23	30	143.1
	III.	54	40	35.3	35.5	165
1 to 100.....	I.	42	38.3	33.9	29.5	143.7
	II.	42.4	40	37.8	35.5	155.7
	III.	51.4	41.2	34.9	34.9	165.1
1 to 500.....	I.	46.6	32.6	27	27	132.6
	II.	46.4	27	27	18	118.4
1 to 1,000.....	I.	90.6	81.1	76.4	57.5	305.6
	II.	90.8	77	72.3	63.1	303.2

It appears from this that the strong sulphuric acid (1 to 5) is not quite so favorable to the action as the more dilute (1 to 10), but that between this latter proportion and 1 to 500 there is no great difference in the amount of oxygen fixed, and therefore of corrosion of the plate. The appearance of the plate in every instance indicated the formation of peroxide lead only. With sulphuric acid diluted with 1000 parts of water, the amount of oxygen fixed, and therefore of corrosion, was at least doubled, while the chemical action was very different. On parts of the electrode, streaks of a mixture apparently of the yellow and puce-colored oxides were seen. On other parts a white substance formed and was easily detached, falling in clouds into the liquid. Where this latter action took place, the plate was visibly the most corroded. This white substance gave on analysis SO_4 , equivalent to 73.6 per cent. of lead sulphate, suggesting the idea that it was a basic sulphate of the composition $2\text{PbSO}_4 \cdot \text{PbO}$, which would require 73.1 per cent. As the peroxidation of the lead is required, and the corrosion

WHOLE NO. VOL. CXVI.—(THIRD SERIES, Vol. lxxxvi.)

of the plate is to be avoided as much as possible, it is evident that this extremely dilute acid must be avoided. It has already been shown that if the sulphuric acid is entirely removed from solution, as sometimes happens in an accumulator, the lead is simply converted into the hydrated protoxide, and therefore corroded without any good effect.

2. FUNCTION OF HYDROGEN.

In the formation of a secondary cell, after the complete reduction of oxide or sulphate to metallic lead, bubbles of hydrogen gas are seen to escape from the lead plate. It has been assumed that a portion of this is occluded by the lead, or in some other way enters into association with it, and it has been supposed that this hydrogen compound may play an important part in the subsequent production of electromotive force. It therefore appeared desirable to obtain experimental evidence as to whether hydrogen is so absorbed. The process we adopted for this purpose was founded upon the observation of Graham that hydrogen associated with palladium reduced ferri- to ferro-cyanide of potassium, and that generally in the occluded condition the element was more active chemically. We had previously ascertained that hydrogen associated with other elements, as platinum, copper and carbon, was capable of reducing potassium chlorate to chloride. This method seemed to give trustworthy results, and therefore we applied it in this instance. As the result of several trials, however, we found that the amount of hydrogen associated with the reduced lead was almost inappreciable. Small as this quantity is, however, it is by no means impossible that it may be the cause of the exceedingly high electromotive force observed for the first few moments on joining up a completely formed cell immediately after its removal from the circuit of the charging current. This, however, may be due, as Planté imagined, to the gaseous hydrogen itself. The principal if not the only function of the hydrogen of the water or sulphuric acid is therefore that of reducing the lead compounds.

By a totally different process Prof. Frankland has very recently come to the same conclusion as ourselves in regard to the exceedingly small amount of occluded hydrogen.

3. EVOLUTION OF OXYGEN FROM THE PEROXIDE PLATE.

Planté noticed a small escape of gas from the negative plate of his cell immediately after its removal from the influence of the charging

current. This he attributed to a decomposition of water by means of local circuits between the peroxide and the subjacent lead plate in contact with it.

The explanation we gave in our first paper (this *Journal*, vol. cxiv, p. 219) of the local action which goes on at the negative plate does not account for the escape of any gas—either oxygen or hydrogen. We therefore thought it of interest to ascertain the nature, and if possible the origin of the gas noticed by Planté.

We found that the escape of gas from a Planté negative plate was very slight, and soon ceased; but we observed that it became much more pronounced when the temperature of the electrolytic liquid was raised. In order to get a sufficient quantity of the gas for examination, we prepared a negative plate according to the procedure of Faure, and then heated it in dilute acid, with an arrangement for collecting the gas as it was evolved. The amount of gas was still very small in comparison with that of the peroxide, but a sufficient quantity was collected to enable us to ascertain that it was oxygen. We next heated some of the electrolytic peroxide apart from the lead plate, and again noticed a similar evolution of gas, which was also found to be oxygen. This shows, therefore, that it was not a result of local action.

The gas has generally some odor of ozone, and on testing the dilute acid between the plates of a Planté cell we always found traces of something that bleached permanganate of potassium, and which might be either ozone or peroxide of hydrogen.

The origin of the gas noticed by Planté may be easily attributed to the oxygen which always passes off in quantity from the peroxide plate during the process of "formation." It is only necessary to suppose that some of this becomes condensed on the peroxide, and is gradually eliminated from it when the surrounding conditions are changed. But the matter is capable of another explanation. If peroxide of hydrogen be really formed in the liquid, it will exert its well-known influence on higher oxides, namely, that of reducing them and itself at the same time. As a matter of fact, if peroxide of lead is dropped into peroxide of hydrogen, oxygen is evolved.

4. TEMPERATURE AND LOCAL ACTION.

Planté has recently pointed out that an elevation of temperature facilitates the formation of his secondary cell (*Comptes Rendus*, August, 1882). The character of the chemical changes which took place at the

negative plate led us to think it exceedingly probable that this increase in the rate of formation arose from an augmentation in the amount of local action. Experiment showed such to be the case. Pairs of similar negative plates on Planté's model were allowed to remain in repose at 11°C. and 50°C. respectively, and the formation of the white sulphate was visibly more rapid at the higher than at the lower temperature. The same is also true with negative plates prepared by Faure's process. Thus we found that two similar plates kept in repose for an hour, the one at 11°C. and the other at 50°C., formed by local action 2.6 and 7.4 per cent. of lead sulphate respectively. On two other plates the proportions were 7.6 and 9.5 per cent. respectively. These observations of course by no means exclude the idea that an increase of temperature may facilitate the other chemical changes that take place in the formation of a lead and lead-oxide cell.

PEMBERTON'S METHOD FOR THE VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID.

By PROF. G. C. CALDWELL.

[From advance sheets of the Second Report of the Cornell University Experiment Station.]

Mr. H. Pemberton, Jr., has described (*JOURNAL FRANKLIN INSTITUTE*, March, 1882, p. 184) a new method for the volumetric determination of phosphoric acid, especially in fertilizers, by a standard solution of ammonium molybdate; he adds the precipitant to the suitably prepared solution of the fertilizers as long as a precipitate is produced, the final tests for further precipitation being made with small filtered portions of the solution under examination. He prepares his standard solution by dissolving 89.543 grams of ordinary ammonium molybdate in 1000 cc. of water; each cubic centimetre of such a solution precipitates 3 milligrammes of phosphoric anhydride. The solution of the phosphate is freed from silica and organic matter, then made up with as little excess of acid as possible, and just neutralized with ammonia; 2 cc. of nitric acid (sp. gr. at least 1.4) and 10 grams of ammonium nitrate are added, and the solution is heated to 60° Cent., or above, preparatory to adding the molybdate; it is necessary to apply the filtration test only towards the end of the operation, when it becomes difficult to discern the effect of further addition of the molyb-