[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE LEAD DIOXIDE-LEAD SULFATE ELECTRODE[1]

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Although the lead storage cell has been extensively studied from the practical side, the value of the lead dioxide–lead sulfate electrode, which is generally considered to form the positive electrode of the storage cell, is known only approximately. Gerke[2] gives 1.7 v. for the value of this electrode, the second figure being considered uncertain. This value is based on the work of Kendrick.[3] Vinal[4] has tabulated the values of different observers for the electromotive force of the lead storage cell. There is an average variation from the mean of 0.02 v. in the values for cells with the same acid concentration when all the results tabulated are considered.

In this investigation the electromotive force of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2SO_4},\ \mathrm{PbSO_4},\ \mathrm{H_2SO_4}\ (a = x) \mid \mathrm{H_2SO_4}\ (a = x),\ \mathrm{PbO_2},\ \mathrm{PbSO_4} \mid (\mathrm{Pt}) \qquad (1)$$

was measured. The lead dioxide and lead sulfate were prepared chemically or, in the case of a few preparations of the former, by an electrolytic process different from that used in forming the positive plates of storage cells. From the electromotive force of Cell 1 the value of the lead dioxide–lead sulfate electrode was calculated.

By combining the electromotive force of Cell 1 with that of the cell[5]

$$\mathrm{Pb} \mid \mathrm{PbSO_4},\ \mathrm{SO_4^{--}} \mid \mathrm{SO_4^{--}},\ \mathrm{PbSO_4},\ \mathrm{Hg_2SO_4} \mid \mathrm{Hg} \qquad (2)$$

the electromotive force of the cell

$$\mathrm{Pb} \mid \mathrm{PbSO_4},\ \mathrm{H_2SO_4}\ (a = x) \mid \mathrm{H_2SO_4}\ (a = x),\ \mathrm{PbO_2},\ \mathrm{PbSO_4} \mid (\mathrm{Pt}) \qquad (3)$$

was calculated.[6] This was found to agree as well as could be expected with the observed electromotive force of the lead storage cell.

Materials

Mercury.—Commercial redistilled mercury was purified by passing it repeatedly through a column of mercurous nitrate solution, and by fractionally redistilling it at least twice under reduced pressure in a current of air.

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[1] Condensed from a major portion of the dissertation submitted by D. Norman Craig to the faculty of the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Gerke, *Chem. Reviews*, **1**, 390 (1925).

[3] Kendrick, *Z. Elektrochem.*, **7**, 53 (1900).

[4] Vinal, "Storage Batteries," John Wiley and Sons, New York, **1924**, p. 166.

[5] (a) Henderson and Stegeman, THIS JOURNAL, **40**, 84 (1918); (b) Mellon and Henderson, *ibid.*, **42**, 676 (1920).

[6] The electromotive force of Cell 3 could not be measured directly on account of the difficulty of reproducing the lead sulfate–lead amalgam electrode when the electrolyte was a sulfuric acid solution. Lewis and Brighton, THIS JOURNAL, **30**, 1908 (1917), have reported this difficulty, and their observations were confirmed in this investigation.

Lead Amalgam.—The lead amalgam was prepared electrolytically from purified mercury and twice recrystallized lead nitrate. It contained 10% of lead by weight.

Mercurous Sulfate.—The mercurous sulfate was prepared by adding at a slow rate a mercurous nitrate solution, made from twice recrystallized mercurous nitrate, to a hot 2 *M* sulfuric acid solution, which was made from c. p. acid. The precipitated mercurous sulfate was digested for nineteen hours on a steam-bath under 2 *M* sulfuric acid solution.[7]

Lead Nitrate.—Lead nitrate of c. p. quality was recrystallized twice by the addition of concd. nitric acid to a hot concentrated solution of the salt. In the second recrystallization redistilled nitric acid and redistilled water were used.

Lead Sulfate.—Five hundred cc. each of a 0.5 *M* lead nitrate solution and 0.5 *M* sulfuric acid solution were added simultaneously drop by drop with constant stirring to 2 liters of boiling 0.1 *M* sulfuric acid solution. The lead sulfate was digested for twelve hours on a steam-bath under 2 *M* sulfuric acid solution.

Sulfuric Acid Solution.—The sulfuric acid solutions to be used as electrolytes in the cells were made by diluting concentrated c. p. acid to the required concentration with redistilled water.

The concentrations were determined by titrating a known weight of the solution with a standard carbonate-free sodium hydroxide solution. The latter was standardized by titrating in a similar manner a known weight of a hydrochloric acid solution, which in turn had been standardized gravimetrically by the silver chloride method. Duplicate determinations agreed within one part in a thousand. The method of Randall and Scalione[8] was tried also as a check. Duplicate determinations did not agree quite so well, but the mean values agreed within an average of less than two parts in a thousand with the results of the first method. The concentrations given below are expressed in moles per 1000 g. of water.

Preparation of the Lead Dioxide

Several methods for the preparation of lead dioxide were tried because agreement of preparations made by different methods can be considered as evidence that the material is of sufficient purity and has a stable physical form.

Method 1.—Lead hydroxide was prepared by precipitation from a dilute lead nitrate solution by means of sodium hydroxide. It was well washed and then dissolved by means of sodium hydroxide solution. The resulting sodium plumbite solution was maintained at about 93°, stirred mechanically and bromine or sodium hypobromite solution added. It made little difference whether the oxidizing agent was bromine carried in by a current of air, bromine water or sodium hypobromite solution. In all cases the addition of the oxidizing agent was continued until the precipitate which was formed had turned dark brown or black.

Method 2.—The second method was similar to the first except that gaseous chlorine was used as the oxidizing agent. The chlorine was generated by the action of concd. hydrochloric acid on potassium permanganate and was washed by bubbling through water.

Method 3.—The third method consisted in hydrolyzing sodium plumbate. Lead dioxide was prepared by electrolysis and dissolved with hot concentrated sodium hydroxide solution. The solution was filtered and added drop by drop to a large volume of water kept at about 93° and mechanically stirred.

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[7] See Vosburgh and Eppley, THIS JOURNAL, **46,** 110 (1924).

[8] Randall and Scalione, *Met. Chem. Eng.*, **13,** 787 (1915).

Method 4.—Lead dioxide was also prepared by the electrolysis of a solution of 100 g. of lead nitrate and 400 cc. of concd. nitric acid in a total volume of three liters with a platinum gauze anode. The cathode was a platinum wire sealed into glass and was surrounded by a porous cup. The current density was kept in the vicinity of 2.5 amperes per square decimeter and the temperature was 93°.

A few preparations were made with the solution at room temperature. This material was not as satisfactory as that made at the higher temperature.

Lead dioxide was also deposited electrolytically directly on coils of platinum wire to be used later as cell electrodes. The electrolysis was carried out in hot solutions with various concentrations of lead nitrate and nitric acid and various current densities. Smooth as well as previously platinized wires were used. These electrodes were not satisfactory.

Other Methods.—Lead dioxide preparations made by hydrolyzing sodium plumbate with cold water and by oxidizing sodium plumbite with hydrogen peroxide were not satisfactory.

Digestion of the Lead Dioxide.—Two advantages may be gained by digesting lead dioxide with sulfuric acid at an elevated temperature. The lead dioxide may be brought to a more stable physical form[9] and any lead monoxide present may be converted to lead sulfate. Since lead sulfate was to be mixed with the lead dioxide in setting up the cells it was not an objectionable impurity.

The lead dioxide used in all but the preliminary experiments was digested under 3 *M* sulfuric acid solution on a steam-bath for several days. The color of the digested lead dioxide was nearly black, even in those cases in which the color was dark reddish-brown before digestion.

Apparatus

The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer, which was calibrated by the method described by the manufacturers.[10]

The standard cells were of the saturated type and were kept in an oil thermostat at 25°. They have been previously described.[11]

The experimental cells were kept in an oil thermostat. During the measurements at temperatures other than 25° two thermostats were used, one at 25° for the standards and the other containing the experimental cells. The temperatures were measured by a thermometer checked by the Bureau of Standards and are probably accurate to ±0.03°.

Preliminary Experiments

A number of separate lead dioxide–lead sulfate electrodes were set up in order to find out which methods of preparing lead dioxide gave the best results. They were combined, by means of an intermediate vessel containing some of the electrolyte, with two mercurous sulfate electrodes and the

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[9] (a) Vosburgh and Eppley, ref. 7, found that digestion of the mercurous sulfate with a sulfuric acid solution at boiling temperature helped in the preparation of reproducible Weston standard cells. The digestion probably brought the mercurous sulfate to a more stable physical form. See also (b) Cohen, "Physico-Chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, **1926**, p. 50 and (c) Vosburgh, THIS JOURNAL, **50**, 2391 (1928).

[10] Leeds and Northrup Company, Bulletin No. 755, **1923**, p. 22.

[11] Ref. 9 c, p. 2389.

resulting cells were measured at room temperature. The electrolyte was 0.1 *M* sulfuric acid solution throughout. The lead dioxide–lead sulfate electrodes were made by mixing lead dioxide and lead sulfate with the electrolyte and allowing this paste to flow around a coiled platinum wire in the electrode vessel. The platinum wire, which was 0.4 mm. in diameter (No. 26) and 4-cm. long, was sealed into a glass tube and connected with a copper wire terminal by means of mercury.

The preliminary experiments showed that different samples of undigested lead dioxide prepared by the same method gave cells differing by as much as 5 mv. Samples prepared by different methods gave cells differing by 10 to 15 mv. in some cases. When the lead dioxide was digested with a sulfuric acid solution on a steam-bath for several days, samples prepared by different methods gave cells agreeing within 2 mv. or better. The concentration of the sulfuric acid in which the lead dioxide was digested was of some influence. The best results were obtained when the acid concentration was from one to six molar. Nine-molar acid led to some erratic results. Therefore three-molar acid was used in digesting the lead dioxide for the final cells.

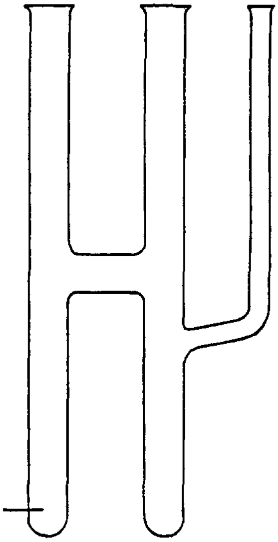

Fig. 1.—Cell vessel.

The preliminary experiments also led to the choice of Methods 1, 2, 3 and 4 described above as the best methods of preparing lead dioxide. When lead dioxide was deposited directly on the platinum coils by electrolysis, the resulting cells decreased in electromotive force steadily over periods of several weeks and were never observed to become constant.

The Cell Hg | Hg_2SO_4, $PbSO_4$, H_2SO_4 | H_2SO_4, PbO_2, $PbSO_4$ | Pt

Preparation of the Cells.—The final cells were set up in vessels of the type shown in Fig. 1. The leg bearing the sealed-in platinum wire was used for the mercurous sulfate electrode and that with the side arm was used for the lead dioxide electrode. The sulfuric acid solutions used had been carefully standardized as described above. The lead dioxide had been digested in all cases.

In preparing some of the mercurous sulfate electrodes. air-free solutions were used. These had been standardized after freeing from air. Precautions were taken also to protect the mercurous sulfate from air by means of an atmosphere of carbon dioxide while the cell was being set up.[12] Others, as indicated in the tables below, were set up without protection from oxygen. Some lead sulfate was mixed with the mercurous sulfate paste and the layer of this mixture in the cell, at least 1 cm. deep, was covered with a layer of lead sulfate.

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[12] Vosburgh, This Journal, **47,** 1258 (1925).

In setting up a lead dioxide–lead sulfate electrode, the tube bearing the platinum coil was first fixed in place. The glass tube was passed through a hole in a paraffined cork disk and the disk was pushed into the tube of the cell vessel for a distance of two or three centimeters. Melted beeswax was poured on top of the cork disk. Then a paste of about equal parts of lead sulfate and lead dioxide was introduced through the side arm. Enough was introduced to cover completely the platinum coil. This mixture was covered with a layer of lead sulfate. The opening of the vessel on the mercurous sulfate electrode side and the opening of the side arm were closed with paraffined cork disks pushed in for some distance and covered with a layer of beeswax. The finished cells were mounted on racks and connected as described by Vosburgh.[11]

Effect of Dissolved Oxygen.—Randall and Young,[13] whose paper appeared while this investigation was in progress, have shown that the presence of dissolved oxygen has an appreciable effect on the electromotive force of a calomel electrode with an acid electrolyte. Vosburgh[14] found that in setting up Weston standard cells protection from the air was of less importance when the electrolyte contained some sulfuric acid than when it was nearly neutral. Therefore, the effect of dissolved oxygen in the present cells is of interest. Table I gives a comparison of four cells prepared with and four prepared without precautions against dissolved oxygen.

Table I

Effect of Dissolved Oxygen

PbO_2	H_2SO_4, M	E.m.f.[b] 1 day, v.	Change of e.m.f. 5 days, v.	2 wks., v.	4 wks., v.
1A	0.1000[a]	0.82587	0.13	0.23	....
2	.1000[a]	.82593	.06	.05	....
1A	.1035	.82874[c]	− .37	− .70	−0.85
2	.1035	.82833[c]	− .30	− .78	− .98

[a] Oxygen was excluded in the preparation of these cells by means of an atmosphere of nitrogen.

[b] Each value is the average value for two cells.

[c] On the basis of these values the value for a 0.1000 M electrolyte would be 0.82687 v.

The electromotive forces of cells made with oxygen present decreased, while the electromotive forces of the cells made in the absence of air[15] increased slightly but were more nearly constant than the others. The average initial electromotive forces of the two groups differed by about 1 mv. when that of the second group was calculated to an acid concentration of 0.1000 M. Tables II and III indicate that the presence of oxygen has a smaller effect on the constancy when the acid concentration is larger. In Table II a group of cells made without protection from the air and with 1.036 M acid as the electrolyte is compared with a group made with protection from the air and with an electrolyte of 1.964 M acid. In this table also each electromotive force value is an average of the values of duplicate cells.

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[13] Randall and Young, This Journal, **50**, 993 (1928).

[14] Ref. 12, p. 1266.

[15] Nitrogen was used rather than carbon dioxide in these cells.

TABLE II

EFFECT OF DISSOLVED OXYGEN. CONSTANCY

PbO_2	H_2SO_4 *M*	Electromotive force at 25°				
		2 wks., v.	5 wks., v.	7 wks., v.	12 wks., v.	16 wks., v.
1	1.036	.....	.....	0.95255	0.95253	0.95247
2	1.036	.....	.....	.95256	.95254	.95250
1	1.964[a]	1.00129	1.00132	1.00133	1.00126	
2	1.964[a]	1.00118	1.00123	1.00123	1.00120	

[a] Oxygen was excluded from the electrolyte of these cells.

The values of the electromotive forces were not measured at 25° previous to the measurements recorded in Table II. Measurements at higher temperatures indicated that the electromotive forces increased slowly during the first week or two. In the case of the last group of cells, at least, constancy was attained within two weeks and the electromotive forces remained constant for at least ten weeks. Table III will show that values for the cell with unit sulfuric acid activity calculated from the two groups agreed within 0.3 mv. It is to be concluded, therefore, that the effect of dissolved oxygen is largest in the cells with the most dilute electrolytes, and that it causes an uncertainty in the electromotive force of not more than 1 mv.

Electromotive Force.—The electromotive forces of all the cells set up were measured frequently over a period of several weeks. From the series of values so obtained the best value for the electromotive force was selected. In the case of the cells with the more dilute electrolytes from which oxygen was excluded, the initial values were taken as the best. In the case of cells with oxygen-free electrolytes in which the concentration was 1 *M* or larger, constancy was attained within a week or two after the cells were set up and the constant value was taken as the best one. For the other cells also the constant values were accepted as the best. Table III summarizes

TABLE III

CELL Hg | Hg_2SO_4, H_2SO_4 | H_2SO_4, PbO_2, $PbSO_4$ | (Pt)

H_2SO_4 *M*	Electromotive force at 25°					E°_{25}
	PbO_2 1[b] v.	PbO_2 2 v.	PbO_2 3 v.	PbO_2 4 v.	Av., v.	
0.05355[a]	0.7956	0.7954	....	....	0.7955	1.0580
.1000[a]	.8258	.8264	0.8264	0.8270	.8264	1.0577
.1035	.8287	.8283	....	....	.8285	1.0582
.2579[a]	.8747	....	....	....	.8747	1.0593
.5154	.9106	.9105	....	.9113	.9108	1.0597
1.036	.9526	.9526	....	....	.9526	1.0600
1.065[a]	.9550	....	.9551	.9550	.9550	1.0607
1.964[a]	1.0013	1.0012	....	....	1.0013	1.0597
2.206[a]	1.0121	....	....	....	1.0121	1.0590
3.499[a]	1.0638	1.0639	....	....	1.0639	1.0573

[a] Oxygen was excluded from the electrolytes of these cells.

[b] The numbers 1, 2, 3 and 4 refer to the method by which the lead dioxide was prepared.

the best electromotive force values for each acid molality and for lead dioxide prepared by the four different methods. Each value in the table is an average value for at least two cells, and in a few cases for four cells.

The different lead dioxide preparations gave cells agreeing within about 1 mv. at most, and in the case of the 1.065 *M* acid to within 0.1 mv. Commercial lead dioxide even after digestion gave cells with electromotive forces about 4 mv. higher than the others but of good reproducibility and constancy.

Cells with electrodes made by electrolytic deposition of lead dioxide on the platinum wire electrodes from hot solutions of lead nitrate agreed fairly well with each other, though not with the other cells, but were never satisfactory as to constancy. They showed a continuous decrease in electromotive force which did not come to an end during the two months' period of observation. Consequently their electromotive forces are not included in the table.

In the next to the last column of Table III is given the average value for each acid molality. From these the values of $E°$ given in the last column were calculated by means of the equation

$$E° = E + \frac{RT}{F} \ln \frac{a_{H_2O}}{4\gamma^3 m^3}$$

where m is the molality of sulfuric acid, γ is its activity coefficient and a_{H_2O} is the activity of the water. Values for the activity coefficients of sulfuric acid were obtained by graphic interpolation from the values of Lewis and Randall.[16] The values for the activity of water were calculated by the method described by Randall and Young.[17] The values so obtained agreed with corresponding values calculated from the vapor pressure data of Grollman and Frazer.[18]

The cells with the smallest acid concentrations were the least reproducible and the most variable when made with oxygen-free electrolytes. The $E°$ values for these cells are therefore to be given less weight than the others. The activity coefficients of sulfuric acid have been less well established for the larger concentrations than for concentrations in the vicinity of 1 or 2 *M*. Therefore, the last value may be considered questionable. The others give $E^{\circ}_{25} = 1.060 \pm 0.001$ v. as the best value for Cell 1.

The electromotive force of the cell

$$H_2\ (Pt)\ |\ H_2SO_4\ (a = 1)\ |\ H_2SO_4\ (a = 1),\ PbO_2,\ PbSO_4\ |\ (Pt) \qquad (4)$$

which on the basis of the usual conventions can be called the potential of the lead dioxide–lead sulfate electrode, can be calculated from the electromotive force of Cell 1 and that of the hydrogen–mercurous sulfate cell.

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 357.

[17] Ref. 13, p. 1002.

[18] Grollman and Frazer, THIS JOURNAL, **47**, 712 (1925).

The electromotive force of the latter when the sulfuric acid electrolyte has unit activity is given by Gerke[19] as 0.6213 v. Therefore the electromotive force of Cell 4 at 25° is $E^{\circ}_{25} = 1.681 \pm 0.001$ v.

Temperature Coefficients

The electromotive forces of a number of representative cells were measured at five-degree intervals of temperature between 20 and 40°. The temperature was changed successively from 25 to 20, 30, 35, 40, 35, 30 and 25°. The cells were maintained at each temperature for a period of three or four days, except at 20° at which temperature they were kept for two days. Readings were taken at frequent intervals. The standards were kept at 25° in a separate bath. In general the cells showed no change greater than 0.01 mv. after the third day. The values given in Table IV are the averages for all cells with the same acid molality. The changes in the electromotive force of the individual cells with the same acid concentration showed an average variation from the mean of ±0.02 mv.

TABLE IV

CHANGE OF ELECTROMOTIVE FORCE WITH TEMPERATURE

H_2SO_4, *M*	No. of cells	E_{25}, v.	$E_t - E_{25}$, mv.						
			20°	30°	35°	40°	35°	30°	25°
0.1000	11	0.82617	+1.98	−1.92	−3.81	−5.59	−4.03	−2.02	−0.15
.5154	6	.91076[a]	....	....	....	−2.32	−1.57	−0.79	....
1.036	6	.95267	+0.30	−0.26	−0.47	−0.66	−0.47	−0.25	−0.00
1.964	4	1.00128[a]	....	....	....	....	+0.35	+0.18	....
3.499	4	1.06378[a]	....	....	....	....	+0.62	+0.34	....

[a] These values at 25° are the values obtained after the series of temperature changes rather than before. In the first case (0.5154 *M* electrolyte) the cells appeared to be variable during the early part of the run, while in the other two cases the cells were set up only shortly before the second measurements at 35°.

It is to be noted that the temperature coefficient varies with the molality of the electrolyte. It is negative in the cells with the most dilute electrolyte, passes through zero as the molality increases and becomes positive for cells with electrolytes having a molality larger than about 1.5 *M*.

The change of 0.15 mv. in the electromotive force of the cells with 0.1000 *M* electrolyte was permanent. Such a change might be expected in cells with dilute electrolytes. For cells with 1.036 *M* electrolyte the change in electromotive force with temperature as determined with rising temperature showed excellent agreement with corresponding values determined with decreasing temperature. These cells had apparently attained constancy at 25° before the temperature was changed. Furthermore, the electromotive forces returned to their original 25° values soon after the temperature was lowered and showed constancy for some time thereafter. Their temperature coefficients are probably the most reliable of all.

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[19] Ref. 2, p. 385.

The Lead Storage Cell

The electromotive force of Cell 3

$$\text{Pb} \mid \text{PbSO}_4, \text{H}_2\text{SO}_4\ (a = 1) \mid \text{H}_2\text{SO}_4\ (a = 1), \text{PbO}_2, \text{PbSO}_4 \mid (\text{Pt})$$

can be calculated by combining the electromotive forces of Cell 1, Cell 2 (with a lead amalgam electrode) and the cell[20]

$$\text{Pb} \mid \text{Pb}^{++} \mid \text{Pb(Hg)};\ E = 0.0057 + 0.000165\ (t - 25) \qquad (5)$$

For the cell with an electrolyte of unit activity the calculated electromotive force is $E^\circ_{25} = 1.060 + 0.9648 + 0.0057 = 2.0305$ v.

Cell 3 represents the lead storage cell according to the double sulfate theory[21] of the action of the storage cell. It would not, however, represent the action of the storage cell on the basis of the higher oxide theory of Féry.[22]

To facilitate comparison of the electromotive force of Cell 3 with that of the lead storage cell, the acid molalities were converted to specific gravities. Then electromotive force was plotted against the specific gravity of the electrolyte and electromotive forces for certain specific gravities were read from the graph. These electromotive forces are compared in Table V with the most concordant of the values compiled by Vinal[4] for the lead storage cell, and also with the values of Kendrick.[3]

TABLE V

COMPARISON OF THE ELECTROMOTIVE FORCE OF CELL 3 WITH THAT OF THE LEAD STORAGE CELL

Sp. gr. 25°/25°	1.040	1.050	1.100	1.150
Gladstone and Hibbert, v.	1.898	1.913	1.963	2.003
Kendrick, v.	1.890	1.905	1.957	2.000
Dolezalek, v.	...	1.906	1.965	2.010
Vinal and Altrup, v.	1.890	1.903	1.956	2.000
Cell 3, v.	1.894	1.909	1.962	2.006

Cell 3 agrees with the storage cells measured by Gladstone and Hibbert,[23] Kendrick,[3] Dolezalek[24] and Vinal and Altrup[4] as well as could be expected. This agreement makes it probable that the lead storage cell is not essentially different from Cell 3 and supports the double sulfate theory of its action.

Activity of Sulfuric Acid

It was suggested above that the apparent decrease in E° for Cell 1 (Table III) for the most concentrated acid solutions might be explained by an error in the value of the activity. It is of interest to calculate the values

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[20] Ref. 2, p. 382.

[21] Originally proposed by Gladstone and Tribe, *Electrician*, **9**, 612 (1882); see also ref. 4, p. 146.

[22] Féry, *Chimie et Industrie*, **17**, 909 (1927).

[23] Gladstone and Hibbert, *J. Inst. Elec. Eng.*, **21**, 425 (1892).

[24] Dolezalek, "Theory of the Lead Accumulator," **1904**, p. 55.

of the activity coefficients from the results for Cell 1 and compare them with the values of Lewis and Randall. This comparison is made in Table VI. Each value for the electromotive force represents the mean value for duplicate cells. The cells in question were all made from the same preparation of lead dioxide with the exception of those with the 1.065 M electrolyte. In this case the lead dioxide was prepared by the same method but at a later time. In the third column of the table the electromotive forces corrected to unit water activity are given. From these the values for the activity coefficient in the fourth column were calculated, the value γ = 0.149 for 1.036 M acid being obtained by graphic interpolation from the data of Lewis and Randall.[16]

There is a fairly large difference between the two sets of activity coefficients in the most dilute solutions and also in the most concentrated. In the former case the activity coefficients based on Cell 1 are of doubtful reliability on account of the lower degree of reproducibility of the cells with the most dilute electrolytes. The activity coefficient for the 3.5 M acid solution, however, should be reliable.

TABLE VI

ACTIVITY COEFFICIENTS OF SULFURIC ACID

H_2SO_4, M	E.m.f., Cell 3, v.	E.m.f., $a_{H_2O} = 1$, v.	γ, Cell 3	γ, L. and R.
0.05355	0.7956	0.7956	0.380	0.390
.1000	.8258	.8258	.302	.313
.1035	.8287	.8287	.303	.309
.2579	.8747	.8745	.220	.222
.5154	.9106	.9101	.175	.176
1.036	.9526	.9516	(.149)	.149
1.065	.9550	.9539	.149	.148
1.964	1.0013	.9990	.145	.146
2.206	1.0121	1.0094	.148	.150
3.499	1.0638	1.0584	.176	.183

Thermochemical Data

From the value E = 0.9526 v. and the temperature coefficients given in Table IV for the cell with the 1.036 M electrolyte, the values for the free energy change, entropy change and heat of reaction for the reaction

$$PbO_2 + 2Hg + 2H_2SO_4\ (1.036\ M) \longrightarrow Hg_2SO_4 + PbSO_4 + 2H_2O$$

are found to be $\Delta F_{25} = -43{,}960$ Cal., $\Delta S_{25} = -2.58$ Cal. and $\Delta H_{25} = -44{,}730$ Cal.

The heat of reaction can be calculated from the following thermochemical data, which have been taken from "International Critical Tables," except as noted: heat of formation of lead dioxide, $\Delta H_{18} = -62{,}600$ Cal.; heat of formation of lead dioxide (Millar[25]), $\Delta H_{25} = -65{,}960$ Cal.; partial heat

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[25] Millar, THIS JOURNAL, **51,** 212 (1929).

of formation of sulfuric acid in 1.036 M sulfuric acid solution,[26] $\Delta H_{25} = -206{,}700$ Cal.; heat of formation of mercurous sulfate, $\Delta H_{18} = -171{,}580$ Cal.; heat of formation of lead sulfate, $\Delta H_{18} = -214{,}600$ Cal.; partial heat of formation of water in 1.036 M sulfuric acid solution, $\Delta H_{25} = -68{,}340$ Cal. Combining these to give the heat of reaction, using the value from "International Critical Tables" for the heat of formation of lead dioxide, gives $\Delta H = -46{,}860$ Cal. Using Millar's value for the heat of formation of lead dioxide, the heat of reaction is $\Delta H = -43{,}500$ Cal.

Summary

1. The conditions necessary for the preparation of reproducible lead dioxide–lead sulfate electrodes have been determined.

2. Cells of the type Hg | Hg_2SO_4, $PbSO_4$, H_2SO_4 (xM) | H_2SO_4 (xM), PbO_2, $PbSO_4$ | (Pt) have been set up and their electromotive forces have been measured over a period of seven to sixteen weeks at 25° and also at 20, 30, 35 and 40°.

3. From the results the following have been calculated: the value of E°_{25}, the electrode potential of the lead dioxide–lead sulfate electrode, the activity coefficients of sulfuric acid at various molalities, the electromotive force of the lead storage cell and the free energy change, the entropy change and the heat of reaction for the reaction $PbO_2 + 2Hg + 2H_2SO_4 \longrightarrow PbSO_4 + Hg_2SO_4 + 2H_2O$. The last compares favorably with the value calculated from thermochemical data.

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THE HEAT OF ADSORPTION OF OXYGEN ON CHARCOAL

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Keyes and Marshall[1] found 72,000 calories per mole for the differential heat of adsorption of oxygen on activated charcoal for initial amounts of gas adsorbed. This heat dropped slowly as the concentration increased to about 0.15×10^{-4} moles per gram of charcoal. As the concentration increased beyond this value the heat of adsorption fell off rapidly to a practically constant value of about 4300 calories per mole.

The course of the curve of differential heat of adsorption against concentration of adsorbed gas at very small concentrations is of considerable theoretical interest, particularly from the point of view of the hypothesis that adjacent carbon atoms may vary greatly in adsorptive character.

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[26] Interpolated with the help of data of Brönsted, *Z. physik. Chem.*, **68**, 702 (1910), for the differential heat solution of sulfuric acid.

[1] Keyes and Marshall, This Journal, **49**, 156 (1927).