

The reaction mixture was formed by mixing freshly prepared nitrogen pentoxide with oxygen and ozone, the latter serving to re-oxidize the decomposition products until it was exhausted. In contradiction to the results of Daniels, Wulf and Karrer, the measured excess of ozone did not retard the decomposition of the nitrogen pentoxide for an unduly long period of time—a discordance which can be explained only by further investigation.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

## CONDITIONS AFFECTING THE REPRODUCIBILITY AND CONSTANCY OF WESTON STANDARD CELLS

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Hulett<sup>1</sup> and Smith<sup>2</sup> found that Weston normal cells with electrolytes containing sulfuric acid were more nearly constant than cells made with neutral cadmium sulfate solutions. Previous work at this Laboratory<sup>3</sup> has shown that cells containing acid are reproducible within 0.02 mv., or 0.002%. It has not been shown, however, what concentration of acid in the electrolyte gives the best results and whether or not cells made with acid electrolytes are suitable for use as primary standards of electromotive force.

The effect of very small concentrations of acid on the electromotive force is somewhat in question. Hulett<sup>4</sup> states that while acid in concentrations greater than 0.1 *M* causes a decrease in the electromotive force proportional to the concentration, "the linear function applies only for concentrations greater than 0.1 molar acid, since for very small acid concentrations the e.m.f. curve changes are very great and follow quite different curves. . . ." Obata<sup>5</sup> found that a linear relationship held down to an acid concentration of 0.04 *M*, but he did not report any experiments on cells with lower acidities. If normal mercurous sulfate is the form in equilibrium<sup>6</sup> in the Weston cell there seems to be no reason why the linear relationship found by Obata<sup>5</sup> should not hold in solutions of very small acid concentration. In order to select the acid concentration best adapted for prac-

<sup>1</sup> Hulett (a) *Phys. Rev.*, **27**, 361 (1908); (b) *Trans. Am. Electrochem. Soc.*, **14**, 89 (1908).

<sup>2</sup> Smith, *Electrician*, **75**, 464 (1915).

<sup>3</sup> Vosburgh and Eppley, *THIS JOURNAL*, **46**, 106 (1924).

<sup>4</sup> Ref. 1a, p. 352. Ref. 1b, p. 80.

<sup>5</sup> Obata, *Proc. Phys. Math. Soc. Japan*, **2**, 232 (1920).

<sup>6</sup> Hulett [Ref. 1a, p. 354; Ref. 1b, p. 83; *Phys. Rev.*, **30**, 652 (1910)] has claimed that normal mercurous sulfate is in metastable equilibrium in cadmium sulfate solutions containing less than 0.08 mole of sulfuric acid per liter, but with this Smith [*Trans. Roy. Soc. London*, **207A**, 408 (1908)] does not agree.

tical use, if indeed acid cells are more reliable standards than neutral cells, it was considered necessary that cells with electrolytes of very low acidities be investigated and that the difference in electromotive force between cells made with neutral and acid cadmium sulfate solutions, respectively, be determined.

### Materials and Apparatus

**Mercury.**—Commercial redistilled mercury was passed through a column of mercurous nitrate solution and redistilled in a current of air under low pressure. It was tested by comparison with some twice redistilled mercury by the method of Hulett<sup>7</sup> and found satisfactory within the limits of error of the method.

**Cadmium Amalgam.**—Except as otherwise noted the cadmium amalgam was prepared electrolytically from sticks of commercial c. p. cadmium metal. A weighed amount of purified mercury was placed in a glass crystallizing dish and covered with a solution of recrystallized cadmium sulfate which contained some sulfuric acid. Sticks of cadmium inside coarse alundum thimbles which dipped into the solution were made anodes and the mercury the cathode, and current was passed at a density of 0.3 amp. per sq. dm. When the current had been passed for a sufficient length of time to give an amalgam of more than 12.5% cadmium the amalgam was washed, melted by gentle heat, dried and weighed. The calculated amount of mercury required to bring the proportion of cadmium to 12.5% was then added.

**Cadmium Sulfate.**—A good grade of commercial cadmium sulfate was recrystallized twice by a slow evaporation at room temperature. In preparing the cadmium sulfate solutions water redistilled over alkaline permanganate was used.

**Mercurous Sulfate.**—Preparations of mercurous sulfate designated as Nos. 1, 8 and 9 have been described before.<sup>8</sup> No. 1 was prepared electrolytically, No. 8 by reduction of mercuric sulfate by mercury, and No. 9 by reaction of sulfuric acid and mercurous nitrate. All these were well digested at boiling temperature with 2 *M* sulfuric acid solution. No. 8 was given an extra digestion after its use in the previous investigation.<sup>8</sup> No. 11 was an electrolytic preparation similar to No. 1 and No. 12 was another electrolytic preparation that contained very little finely divided mercury.

**Vessels.**—Glass H-vessels of the type described in a previous paper<sup>9</sup> were used.

**Apparatus.**—The potentiometer described by Eppley and Gray<sup>10</sup> was used. The system was shielded in the manner recommended by White.<sup>11</sup>

An oil thermostat operating at  $25 \pm 0.02^\circ$  was used for temperature control.

The cells were mounted on racks holding 10 cells each and when placed in the thermostat were totally immersed in the oil. The leads from the cells were soldered to copper pins embedded in a rubber plate at the top of the rack, and when making measurements connection from the potentiometer leads to the copper pins was made by spring clips.

**Standards.**—Cells 1-5, 7-9 and 11-12, which were described in previous papers,<sup>12</sup> were used as the standards. No. 3 was the working standard and the other nine cells were frequently measured against it. Their average on this basis varied not more than 2 mmv. Corresponding correc-

<sup>7</sup> Hulett, *Phys. Rev.*, **21**, 392 (1905).

<sup>8</sup> Ref. 3, p. 105.

<sup>9</sup> Vosburgh and Eppley, *THIS JOURNAL*, **45**, 2269 (1923).

<sup>10</sup> Eppley and Gray, *J. Optical Soc. Am.*, **6**, 859 (1922).

<sup>11</sup> White, *THIS JOURNAL*, **36**, 2011 (1914).

<sup>12</sup> Ref. 9, p. 2270. See also Ref. 3.

tions were applied to the unknown, thus making the average of the nine cells the standard. The electromotive force<sup>13</sup> of 1.018054 v. at 25° was originally assumed for Cells 1-15, and in the previous work three other cells were used as reference standards. In comparison with the latter, cells 1-15 dropped about 6 mmv. soon after the value was assumed, but remained constant for the next ten months. After this period the three reference cells appeared more variable than Nos. 1-12<sup>14</sup> so the latter were taken as the standards for this investigation. The value of 1.018050 v. was assumed for No. 3, making the average of the others 1.018049 v. These cells were about a year old when this investigation was started. Toward the end of the investigation four more cells were made, duplicates of 1-15, the precautions described below being taken in washing the mercurous sulfate. The good agreement of the electromotive forces, after the aging period, with the assumed electromotive force of the standards argues against any pronounced change in the standards.

TABLE I

## CELLS 353-356, DUPLICATES OF CELLS USED AS STANDARDS

Mercurous sulfate No. 11 was used for Cells 353-354 and mercurous sulfate No. 9 for Cells 355-356

Age, months	1	2	3	4	8
Mean e.m.f., 25°, v.	1.018042	1.018046	1.018046	1.018046	1.018046
Variation from mean, mmv.	±2.5	±2	±2.5	±2	±3

## Preparation of Reproducible and Constant Cells

A number of cells were set up with neutral electrolytes in a manner essentially that described by Wolff and Waters.<sup>15</sup> The mercurous sulfate, No. 1, was washed with methanol to remove the acid and then with the cadmium sulfate solution to be used in the cells. The materials were those used for Cells 1-15. Two lots of cells similarly prepared did not agree, and the initial electromotive forces were 60 to 110 mmv. higher than that of Cells 1-15. This apparently agrees with the results of Hulett.<sup>16</sup> The electromotive forces, however, decreased slowly, as shown for Cells 135, 136 and 142 of Table IIC. The other cells were similar to these. When a more finely divided mercurous sulfate was used cells more nearly constant with lower electromotive forces were obtained, as illustrated by Cells 169-170 of Table IIC.

Similar results were obtained for cells with electrolytes containing sulfuric acid at concentrations of 0.01 mole per liter or less. In this case, however, the initial electromotive forces were not as high as in the case of cells

<sup>13</sup> The electrolytes contained 0.011 mole of sulfuric acid per liter.

<sup>14</sup> Five of the original fifteen cells were destroyed, three for measurements of the acidity and two by the addition of more acid. See Ref. 3.

<sup>15</sup> Wolff and Waters, *Bur. Standards Bull.*, **4**, 29 (1907).

<sup>16</sup> (a) Ref. 4; (b) Hulett, *Phys. Rev.*, **22**, 328 (1906).

made with neutral cadmium sulfate solutions. The results for Cells 157-158 in Table V are typical.

A suggestion as to the cause of the poor results is given by the fact that at the Reichsanstalt<sup>17</sup> and at the Bureau of Standards<sup>18</sup> good results were obtained with cells set up with mercurous sulfate preserved out of contact with the air. The most obvious effect of air would be oxidation, and mercuric ion in cells would be expected to cause abnormally high initial electromotive forces which would decrease as the mercuric ion was reduced by the mercury of the electrode. Oxidation of mercurous sulfate in the presence of neutral or slightly acid solutions would give the slightly soluble basic mercuric sulfate which would not be removed by washing with the cadmium sulfate solution. Therefore, a procedure was devised to allow

washing the mercurous sulfate and introducing it into the cell without contact with the air.

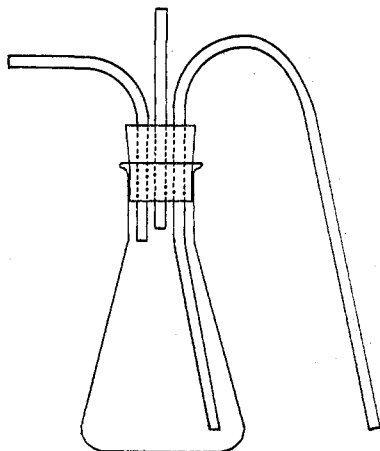


Fig. 1.—Flask used for washing the mercurous sulfate in an atmosphere of nitrogen.

The mercurous sulfate, which had been preserved under an acid solution, was washed first with a 2 *M* sulfuric acid solution in a Gooch crucible to remove any solution containing mercuric ion. Then it was washed in an inert atmosphere by decantation with the solution to be used in the cells. This was accomplished by means of a small Erlenmeyer flask fitted with a rubber stopper through which passed an inlet tube for nitrogen, a short exit tube for the gas, and a siphon tube reaching nearly to the bottom, as shown in Fig. 1. After being washed in the Gooch crucible the mercurous sulfate was put into the flask together with fine cadmium sulfate crystals, covered with cadmium sulfate solution containing acid and nitrogen was passed in for some time. The siphon tube was then adjusted so that its end was just above the mercurous sulfate, and the gas exit tube was closed so that the liquid was forced out through the siphon. About 5 cc. of the solution to be used in the cells was then introduced by means of a pipet which reached through the gas exit tube, and the flask was shaken to get all the solid matter in suspension and wash it completely. After settling, the solution was decanted as before. Tests showed that when washing

<sup>17</sup> Report of the work of the Physikalisch-Technische Reichsanstalt during 1909, *Z. Elektrochem.*, **17**, 34 (1910).

<sup>18</sup> Report to the International Committee on Electrical Units and Standards, Washington, Government Printing Office, 1912, p. 111.

with a neutral solution, five washings removed practically all of the acid, so the mercurous sulfate was always washed at least six times. Two additional washings made no noticeable difference in the cells. The solution, except as otherwise noted, had previously been evacuated to remove dissolved oxygen.

When the mercury and amalgam had been placed in the H-tubes, solution and crystals put in on the amalgam side, and some solution placed above the mercury, the mercurous sulfate was introduced. The siphon tube of the flask was pushed down until its inner end reached nearly to the bottom, and its outer end was put into the mercury leg of the H-tube, usually far enough to extend beneath the surface of the solution above the mercury. Some cadmium sulfate solution was added to the paste. The gas exit tube was then closed and the mercurous sulfate paste expelled from the flask into the H-tube by the nitrogen pressure, the flask being shaken to keep the solids in suspension. The cells were completed by adding cadmium sulfate crystals and sufficient solution, replacing the air in the tubes with nitrogen and hermetically sealing.

Table IIA shows the electromotive forces over a period of from six to twelve months of a number of cells prepared in this manner. In a few

TABLE II  
EFFECT OF THE PRESENCE OF MERCURIC ION IN CELLS

A. CELLS PREPARED WITH PRECAUTIONS AGAINST OXIDATION OF THE MERCUROUS SULFATE

Cells	Hg <sub>2</sub> SO <sub>4</sub>	Electromotive force minus 1.018000 v., 25°							
		1 week	1 month	2	4	6	8	10	12
		Mmv.	Mmv.	Mmv.	Mmv.	Mmv.	Mmv.	Mmv.	Mmv.
272 <sup>a</sup>	8	74	72	71	69	67	62	63	60
273 <sup>a</sup>	8	72	69	66	63	58	64	51	46
320	11	60	62	62	60	60	58	..	55
321	11	55	60	60	59	60	57	..	53
350	9	47	53	50	47	46			
351	9	64	61	56	52	49			

B. CELLS TO WHICH BASIC MERCURIC SULFATE WAS ADDED<sup>b</sup>

274 <sup>a</sup>	8	154	125	116	111	89	62	49	43
275 <sup>a</sup>	8	180	207	217	209	175	108	36	18
322	11	90	73	67	61	55	52	..	51
323	11	81	73	69	67	67	63	..	68

C. CELLS MADE WITHOUT PROTECTION FROM THE AIR

135	1	115	105	92	68	55	45	47	41
136	1	120	113	105	97	92	89	87	88
142	1	158	134	124	86	48	28	23	21
169	8	...	88	78	78	74	72	72	70
170	8	...	73	78	84	82	84	84	83

<sup>a</sup> The solution was not freed from oxygen in the preparation of these cells.

<sup>b</sup> Cells 274-275 contained about 0.2 g. of basic mercuric sulfate each, and cells 322-323 contained 0.02 g. each.

cases, after two cells had been prepared as described, a small amount of basic mercuric sulfate<sup>19</sup> was mixed with the remaining mercurous sulfate and two additional cells made. The results for some of these are shown in Table IIB, the control cells in each case being those in Table IIA with the next lower numbers. All the cells of Table II were prepared with neutral cadmium sulfate solutions. Most of the results given in this table and also in the others, are the mean of two values obtained on successive days. The two seldom differed by more than 2 mmv.

Table II shows that the most constant and reproducible cells were the ones made with the most precautions against the entrance of mercuric ion. All the cells which showed abnormally high initial values, with subsequent decrease, either were known to contain mercuric ion or were made with mercurous sulfate paste or cadmium sulfate solution not protected from the air. When the mercurous sulfate was not protected from the air in washing, the cells with one exception, showed a decrease quite similar to that of the cells containing basic mercuric sulfate, and it seems not unlikely that mercuric ion is the chief cause of inconstancy or a low degree of reproducibility in the cells of Table II. It is to be expected that the presence of finely divided mercury in the mercurous sulfate would help in bringing about equilibrium between mercuric and mercurous ions, and it has been observed that cells made with gray mercurous sulfate are often more constant than those made with white.<sup>20</sup> Finely divided mercury, however, cannot be depended upon to bring about equilibrium rapidly, as all the cells in Table II except 350 and 351 were made with gray samples of mercurous sulfate.

The reduction of mercuric ion by mercury in a cell must be a slow process. In the cells of Table IIB, for example, the rate of reduction must be slower than the rate of diffusion to the mercury surface, for the mercuric ion influences the electromotive force. If the rate of diffusion were slower than the rate of reduction the electromotive force would not be higher than the normal and would not decrease, unless after a considerable period the accumulation in the vicinity of the mercury surface of the products of the reduction caused a decrease. Therefore, cells made with finely divided mercurous sulfate should be more constant than cells made with coarse mercurous sulfate when precautions against mercuric ion are not taken, which has been observed to be the case.<sup>21</sup>

Further experiments showed what precautions were the most important in protecting from mercuric ion. Six cells were made from the same materials and at the same time. Cells 302-303 were control cells made with all the precautions described above. Cells 303-304 were made similarly,

<sup>19</sup> This was prepared by greatly diluting a mercuric sulfate solution and heating.

<sup>20</sup> (a) Hulett, *Phys. Rev.*, **32**, 263 (1911); (b) Ref. 2.

<sup>21</sup> (a) Steinwehr, *Z. Elektrochem.*, **12**, 579 (1906). (b) Ref. 1 b, p. 87.

except that after the mercurous sulfate paste had been introduced, 0.01 g. of basic mercuric sulfate was dropped in on top of it in each cell. Cells 306-307 were made from a portion of the mercurous sulfate not washed by decantation in an inert atmosphere, but otherwise like the first two. The mercurous sulfate for the six cells was washed in a Gooch crucible twice with 1 *M* sulfuric acid solution and once with a cadmium sulfate solution containing 0.04 mole of sulfuric acid per liter. It was then divided into two portions. The first was used for cells 302-305 after further washing in a nitrogen atmosphere as described above. The second portion was washed thrice in the Gooch crucible with the solution to be used in the cells and made into a paste and put into the cells without protection from the air. The solution used contained 0.002 mole of sulfuric acid per liter.

TABLE III

## PRECAUTIONS NECESSARY TO PROTECT FROM MERCURIC ION

Cells 302-303 were control cells, Cells 304-305 had 0.01 g. each of basic mercuric sulfate above the paste, and Cells 306-307 were prepared from a portion of the mercurous sulfate not washed in an inert atmosphere. Mercurous sulfate 9 was used.

Cells	Electromotive force minus 1.018000 v., 25°						
	1 week Mmv.	1 month Mmv.	2 Mmv.	4 Mmv.	6 Mmv.	8 Mmv.	12 Mmv.
302	58	64	64	64	63	65	64
303	54	59	60	60	59	59	59
304	66	69	69	68	65	68	69
305	30	53	57	59	56	59	52
306	84	90	90	89	85	88	85
307	84	70	79	84	81	82	84

It will be shown (Table IVB) that Cells 302-303 can be duplicated, and therefore they can be considered to have the normal electromotive force. Table III then shows that for results of greatest accuracy the mercurous sulfate must be washed and introduced into the cells out of contact with the air. On the other hand, mercuric ion in the solution above the paste does not appreciably affect the electromotive force. It is necessary that the mercuric salt be mixed with the part of the paste in the vicinity of the mercury for it to have an influence on the electromotive force, during the early life of the cell at least.

**Effect of Acidity of the Electrolyte on the Electromotive Force**

In preparing a series of cells with cadmium sulfate solutions containing various concentrations of sulfuric acid it was found that the procedure described for protecting the mercurous sulfate from the air was necessary when the acid concentration was below 0.01 mole per liter and desirable up to 0.02 mole per liter. Above that point, however, no trouble was experienced in preparing constant cells by the procedure of Wolff and Waters.<sup>15</sup>

Cells made with neutral cadmium sulfate solutions were the hardest to prepare in such a manner that they would be constant. A number were

prepared as described above except that the cadmium sulfate solution was not evacuated. Some of them started with initial values as much as 30 to 40 mmv. too high, but decreased rapidly at first until after a month the cells were in good agreement as compared with cells made without special precautions to exclude mercuric ion and much more nearly constant. They were, however, more variable than cells made with slightly acid electrolytes. The mean electromotive force of 18 cells one month after they were set up was 1.018067 v. After six months it had decreased to 1.018058 v. and after twelve months to 1.018053 v. The average variation from the mean was  $\pm 7$  mmv. Three cells of the 18 decreased less than 5 mmv. between the first and sixth months. The results for these as well as for Cells 320 and 321, which were of the same degree of constancy, are shown in Table IVA.

Although the cells were better than cells made without special precautions against mercuric ion they were distinctly inferior as regards constancy to cells with acid electrolytes, for example, to the standards used in this investigation. Some recent results have indicated that the cells with neutral electrolytes contained some mercuric ion in spite of the precautions, and the lack of constancy can be ascribed to that. The presence of mercuric ion may have been due to insufficient washing of the mercurous sulfate with an acid solution before washing with the neutral cadmium sulfate solution. More care was taken in this respect with Cells 320, 321, 350 and 351 with correspondingly better results. A group of 10 cells, Cells 397-406, prepared more recently using mercurous sulfate 11, showed increasing electromotive forces for the first two months and no variation during the next three months. The average electromotive force at the end of five months was 1.018065 v.

Two sets of cells were made with slightly acid electrolytes by the procedure described above, and the results are shown in Tables IIB and IIC. The cadmium sulfate solutions for the two sets were made by dissolving hydrated cadmium sulfate in 0.0025 *M* and 0.005 *M* sulfuric acid solutions, respectively. According to the data of Hulett<sup>1</sup> the acid concentrations of the finished solutions must have been 0.0019 and 0.0038 mole per liter, respectively. Two cells were rejected for inconstancy, and in these the reason was apparent.<sup>22</sup> Several of the cells made with the more acid solution started with initial values below the normal, and one, Cell 314, was unusually slow in coming to equilibrium.

It can be seen that while the cells with the lower acid concentration show

<sup>22</sup> Cell 300 after agreeing well with the rest for four months started to decrease, and it was found that the tube had cracked at one seal and oil from the bath had entered. In the construction of Cell 311 some mercurous sulfate got over among the cadmium sulfate crystals in the amalgam leg of the tube. The cell agreed with the others at first but later decreased considerably.



a small decrease, 5 mmv. in eleven months, those with the higher acid concentration show a very slight increase during the eleven months. The beneficial effect of the higher concentration of acid, 0.04 mole per liter, is thus shown.

TABLE IV  
EFFECT OF SMALL AMOUNTS OF ACID IN THE ELECTROLYTE

A. CELLS MADE WITH NEUTRAL CADMIUM SULFATE SOLUTIONS

Cells	Hg <sub>2</sub> SO <sub>4</sub>	Electromotive force minus 1.018000 v., 25°						
		1 month	2	4	6	8	10	12
		Mmv.	Mmv.	Mmv.	Mmv.	Mmv.	Mmv.	Mmv.
279	8	50	46	48	51	50	46	45
283	9	51	51	50	49	47	46	43
295 <sup>a</sup>	9	66	66	65	64	..	51	59
320	11	62	62	60	60	58	..	55
321	11	60	60	59	60	57	..	53
Mean		58	57	56	57	..	..	51
Av. variation		±6	±7	±6	±5	..	..	±6

B. CELLS MADE WITH CADMIUM SULFATE SOLUTIONS CONTAINING 0.002 MOLE OF SULFURIC ACID PER LITER

300-301	8	66	67	65	65 <sup>b</sup>	66 <sup>b</sup>	63 <sup>b</sup>	62 <sup>b</sup>
302-303	9	61	62	62	61	62	62	61
308-309	11	62	62	59	56	56	56	52
310	12	70	68	67	65	63	62	62
Mean		64	64	62	61	61	60	59
Av. variation		±3	±3	±3	±4	±4	±3	±4

C. CELLS MADE WITH CADMIUM SULFATE SOLUTIONS CONTAINING 0.004 MOLE OF SULFURIC ACID PER LITER

312-313	8	61	63	63	63	63	63	64
314-315	9	50 <sup>c</sup>	49 <sup>c</sup>	49 <sup>c</sup>	53	56	57	57
316-317	11	61	63	63	62	62	62	62
318-319	12	55	56	56	57	58	57	58
Mean		57	58	58	59	60	60	60
Av. variation		±6	±6	±7	±6	±3	±3	±4

<sup>a</sup> Carbon dioxide was used instead of nitrogen.

<sup>b</sup> See Ref. 22. These values are for Cell 301.

<sup>c</sup> Cell 314 was unusually slow in coming to equilibrium. Cell 315 had a constant e.m.f. of 1.018060 v.

The cells used as reference standards gave another point in the relationship between electromotive force and acidity. The concentration of acid was 0.011 mole per liter. This electrolyte, as well as that for Cells 353-356 which are described above, was made by saturating a 0.015 *M* sulfuric acid solution with hydrated cadmium sulfate. The average electromotive force of Cells 1, 2, 4, 5, 7-9, 11 and 12 was assumed to be 1.018049 and that of Cells 353-356 found to be 1.018046.

A number of cells were made with electrolytes of still larger acidities. These were all made with mercurous sulfate No. 1, and with the mercury

and amalgam used for Cells 1-15. The cadmium sulfate solutions were prepared by adding acid to portions of a neutral saturated solution. The acid concentrations were determined by titrating portions of the solutions with a standard sodium hydroxide solution, using methyl red as the indicator, this method having been shown to give sufficiently accurate results. After the cells had been observed for a year they were opened and the acid concentrations of the electrolytes were determined. The procedure in setting up the cells did not differ essentially from the procedure in setting up Cells 1-15, no special precautions to avoid oxidation of the mercurous sulfate having been taken. The electromotive forces of these cells over a period of a year and the acid concentrations in the electrolytes are given in Table V.

TABLE V  
ACID CELLS MADE WITHOUT PRECAUTIONS AGAINST MERCURIC ION

Cells	Acidity <sup>a</sup>		Electromotive force minus 1.018000 v., 25°				
	1 Moles/liter	2 Moles/liter	1 month Mmv.	2 Mmv.	4 Mmv.	8 Mmv.	12 Mmv.
157-158	0.012	...	85	89	75	72	68
143-145	.024	0.021	29	43	44	44	43
146-148	.038	.035	15	20	18	15	13
149-151	.052	.048	-38	-23	-22	-20	-16
152-154	.068	.064	-32	-30	-34	-36	-34
155-156	.081	.078	-57	-57	-64	-63	-62

<sup>a</sup> The first values for the acidity were obtained by titrating portions of the solutions with which the cells were set up and the second values by titrating samples of the electrolytes of the cells after thirteen months, a small calculated correction (1 to 2%) being applied for the mercurous sulfate dissolved.

The cells were quite constant over a period of a year with the exception of 149-151 which increased slowly in electromotive force and 157-158 which showed a definite decrease. Cells 157-158 were intended as duplicates of Cells 1-5, but did not come to agreement with them. The other cells of this group did not show any initial decrease and a number started with abnormally low values which increased and finally became constant. The largest difference between duplicate cells was 10 mmv. and the average variation from the group mean values when the cells were twelve months old was  $\pm 2$  mmv.

The acidity in all cases showed a decrease. This may have been due to the presence of a small amount of cadmium oxide and basic mercuric sulfate when the cells were set up and the slow reaction of hydrogen ion with cadmium. The difference in acidity is equivalent to only about 6 mmv. in the electromotive force, so is not of great importance. The second acidity values should obviously correspond to the electromotive force values after twelve months.

All of the most reliable results for cells of different acidities are collected in Table VI which, together with Fig. 2 in which the results are plotted,

shows the relation of electromotive force to acidity. The calculated electromotive-force values were obtained by assuming the values 1.018049 v. and 0.011 mole of acid per liter for Cells 1-12 and calculating the others by means of Obata's relation,<sup>5</sup>  $\Delta E = 1710 \Delta M$ , where  $\Delta M$  is the difference in acidity in moles per liter corresponding to  $\Delta E$  mmv. difference in electro-

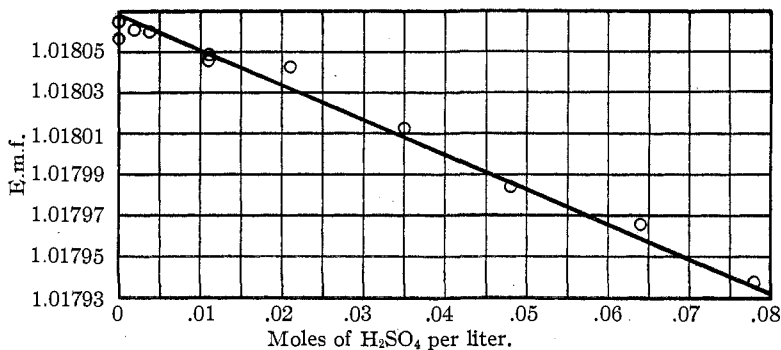


Fig. 2.—Relation between electromotive force and concentration of sulfuric acid in the electrolyte.

motive force. It is shown that there is no large deviation from Obata's relation even at the smallest acidities.

TABLE VI  
RELATION OF ELECTROMOTIVE FORCE TO ACIDITY

Cells	Age Months	Concn. of acid Moles/liter	E.m.f., 25° Obs., v.	E.m.f., 25° Calcd., v.	Difference Mmv.
Selected <sup>a</sup>	6	... <sup>b</sup>	1.018057	1.018068	- 11
397-406	5	...	1.018065	1.018068	- 3
301-310	8	0.0019	1.018061	1.018065	- 4
312-319	8	.0038	1.018060	1.018061	- 1
1-12	20	.011	1.018049	(1.018049)	..
353-356	4	.011	1.018046	1.018049	- 3
143-145	12	.021	1.018043	1.018032	+11
146-148	12	.035	1.018013	1.018008	+ 5
149-151	12	.048	1.017984	1.017986	- 2
152-154	12	.064	1.017966	1.017958	+ 8
155-156	12	.078	1.017938	1.017934	+ 4

<sup>a</sup> Cells, made with a neutral cadmium sulfate solution, which decreased less than 5 mmv. between the first and sixth months, Nos. 279, 283, 295, 320, 321.

<sup>b</sup> Tests with bromophenol blue indicated that the acid concentration in cells made with neutral cadmium sulfate solutions was less than 0.0005 *M*.

### Hysteresis in Acid Cells

A test of the hysteresis with decreasing temperature was made with Cells 143-156 by the procedure previously described.<sup>23</sup> The results agreed with those obtained before in showing that an increase in acid concentration greatly reduced the hysteresis.

<sup>23</sup> Ref. 3, p. 109.

### Abnormal Mercurous Sulfate

In the course of the work described above some preparations of mercurous sulfate were obtained which gave high results in standard cells. A preparation made by slow reduction of mercuric sulfate by formaldehyde gave cells which were about 400 mmv. higher than the normal and were variable. This mercurous sulfate was digested with 2 *M* sulfuric acid solution and mercury at boiling temperature, after which cells made with it were constant and only about 20 mmv. too high. The grain size was very large. Another preparation made by alternating current electrolysis and digested for eight hours with 2 *M* sulfuric acid solution gave cells that were nearly 40 mmv. too high but constant. This has been observed before to be the case with cells made with alternating current mercurous sulfate.<sup>24</sup> Some other preparations were made by direct current electrolysis with a very low current density and a cadmium sulfate solution of low acidity as the electrolyte. These preparations gave high and somewhat variable cells. All of these abnormal preparations were alike in having a light yellowish-brown color. In this they differed from the fine-grained mercurous sulfate No. 4 which also gave high results<sup>3</sup> and which was pure white.

### Conclusions

The results of this investigation show clearly that a small amount of acid in the electrolyte of a Weston normal cell has no harmful effect and does not greatly affect the electromotive force. The linear relation of Obata<sup>5</sup> between acid concentration and electromotive force held, down to the lowest acid concentration tried, and the cells of very low acid concentration were no less constant and reproducible than other acid cells when the mercurous sulfate was protected from air in their construction. The cells made with neutral cadmium sulfate solutions were less constant and less reproducible than the acid cells. This may have been due to greater difficulty in washing mercuric compounds out of the mercurous sulfate and in protecting from the action of air when working with neutral solutions. Doubtless, the presence of mercuric ion is easier to guard against when working with an acid electrolyte. Therefore, in setting up cells for primary standards it would be advantageous to use a cadmium sulfate solution containing a small amount of sulfuric acid, 0.002 to 0.004 mole per liter.

It has been shown that samples of mercurous sulfate prepared by three different methods, namely, the reduction of mercuric sulfate by mercury, direct current electrolysis and the reaction of mercurous nitrate and sulfuric acid, give cells agreeing in electromotive force within 10 mmv. A fourth method, the reduction of mercuric sulfate by formaldehyde at boiling temperature has been shown previously<sup>3</sup> to give mercurous sulfate

<sup>24</sup> Ref. 18, p. 116.

agreeing very well with that prepared electrolytically. In all cases the mercurous sulfate was digested at boiling temperature with 2 *M* sulfuric acid solution for a day or two. It is essential that mercurous sulfate be washed free from mercuric sulfate and that it be protected from contact with air while it is being washed with a cadmium sulfate solution of low acid concentration and also while it is being introduced into the cells. With properly prepared mercurous sulfate and with the necessary precautions in handling it, standard cells constant in electromotive force and reproducible within 10 mmv. or 0.001% can be prepared.

If Weston cells with slightly acid electrolytes are set up as primary standards the assumption for them of the electromotive force assigned to the usual Weston normal cell, namely, 1.01830 international volts at 20°, should give results accurate to well within 0.01%. For practical purposes, there is little difference between the electromotive forces of properly made cells with electrolytes containing either no added acid, or added acid up to concentrations of 0.01 mole per liter.

### Summary

1. Weston normal cells made with neutral or slightly acid cadmium sulfate solutions were the most nearly constant and most reproducible when precautions were taken to remove mercuric ion from the mercurous sulfate and to prevent exposure of the mercurous sulfate to the air during its washing and introduction into the cell.

2. Neglect of such precautions resulted in cells with more or less abnormally high electromotive forces which in most cases decreased as time went on. Similar results were caused by the presence of basic mercuric sulfate when mixed with the mercurous sulfate paste of cells otherwise carefully set up.

3. The electromotive force was a linear function of the concentration of acid in the electrolyte, and the relation found by Obata<sup>5</sup> to hold for acid concentrations from 0.04 to 0.57 mole per liter held, down to an acid concentration of 0.002 mole per liter.

4. The electromotive forces of the most constant cells with neutral electrolytes were about equal to those of the cells with electrolytes containing 0.002 to 0.004 mole of sulfuric acid per liter. Small amounts of acid in the electrolytes of standard cells, therefore, do not have a large effect on the electromotive force, as has been thought to be the case, but do tend to make the cells more reproducible and less liable to vary.