

# The Journal of the American Chemical Society

VOL. 53

AUGUST, 1931

No. 8

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

## HYSTERESIS IN THE WESTON STANDARD CELL<sup>1</sup>

BY WARREN C. VOSBURGH AND KELLY L. ELMORE

RECEIVED DECEMBER 6, 1930

PUBLISHED AUGUST 5, 1931

A theory of hysteresis in the Weston standard cell has been proposed by Niederhauser and Hulett<sup>2</sup> based on the formation of a supersaturated solution of mercurous sulfate at the cathode as a result of a decrease in temperature. This involves the assumption that the solubility of mercurous sulfate increases with temperature and that the rate of crystallization from a supersaturated solution is slow while the rate of dissolving in an unsaturated solution is rapid.<sup>3</sup>

Barre<sup>4</sup> found that the solubility of mercurous sulfate increases with the temperature, and it is probable that the solubility in a saturated cadmium sulfate solution would do the same. Calculation on the basis of the Nernst theory indicates that a concentration of mercurous ion 1% in excess of that of a saturated solution would account for an electromotive force about 1 mv. higher than the normal. The increase in solubility observed by Barre for a ten-degree increase in temperature was several times 1%, and so is sufficient to account for many, at least, of the hysteresis data.

Marc<sup>5</sup> showed that the velocities of crystallization of ammonium alum, potassium sulfate and potassium dichromate from their water solutions were slower than the velocities of dissolving under comparable conditions. Furthermore, Marc and Wenk<sup>6</sup> found that the presence of certain salts decreased the velocity of crystallization of potassium sulfate somewhat, and that certain dyes which were strongly adsorbed by the crystals of potassium sulfate greatly retarded the crystallization. In some cases no crystallization at all was observed during a period of six hours after seeding the super-

<sup>1</sup> Thesis presented by Kelly L. Elmore in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

<sup>2</sup> Niederhauser and Hulett, *THIS JOURNAL*, 51, 2349 (1929).

<sup>3</sup> Hysteresis is observed with decreasing temperature, but usually not when the temperature increases.

<sup>4</sup> Barre, *Ann. chim. phys.*, [8] 24, 202 (1911).

<sup>5</sup> Marc, *Z. physik. Chem.*, 67, 493 (1909).

<sup>6</sup> Marc and Wenk, *ibid.*, 68, 104 (1910).

saturated solution. On the other hand, the dyes had little or no effect on the rate of dissolving of the crystals.

The results of Marc and Wenk support the supersaturation theory of hysteresis, which now seems preferable to that proposed by Vosburgh<sup>7</sup> based on a lag in the attainment of equilibrium between mercuric and mercurous ions and mercury.

A somewhat different mechanism than the one proposed by Niederhauser and Hulett is suggested by Marc's work. The rate of crystallization of the various salts from their supersaturated solutions as observed by Marc was rapid as compared with the change in electromotive force of many Weston cells after a decrease in temperature. However, in the light of the results of Marc and Wenk, adsorbed impurities on the surface of the mercurous sulfate might well account for the hysteresis phenomena, their effect being to retard crystallization.

The experiments described below were suggested by the theory of Niederhauser and Hulett and were undertaken with the object of obtaining more data on hysteresis.

### Materials

**Water.**—For the preparation of other materials, water redistilled from alkaline permanganate was used. For the solutions used in the cells this water was again redistilled in a silica still.

**Mercury.**—Commercial redistilled mercury was passed several times through a column of mercurous nitrate solution and redistilled in a current of air.

**Cadmium Amalgam.**—By electrolysis with a cadmium sulfate electrolyte cadmium was transferred from c. p. sticks to mercury which had been washed with mercurous nitrate solution. It was again transferred to purified mercury by electrolysis, using the same electrolyte, forming a 12% amalgam to which was added enough mercury to give a 10% amalgam.

**Cadmium Sulfate.**—Material of c. p. grade was dissolved and the solution treated with basic cadmium sulfate to precipitate impurities. The cadmium sulfate was then recrystallized twice by slow evaporation at room temperature.

Basic cadmium sulfate<sup>8</sup> was prepared from the normal salt by precipitation with ammonium hydroxide. It was washed free from ammonium salts by decantation, with the help of a small centrifuge.

**Nitrogen and Oxygen.**—Nitrogen from a tank of the compressed gas was passed through acidified potassium permanganate solution, alkaline pyrogallate solution, alkaline sodium thiosulfate solution, potassium hydroxide solution and then distilled water and a plug of cotton. Oxygen was passed through acidified potassium permanganate solution, potassium hydroxide solution, distilled water and a plug of cotton.

**Mercurous Sulfate.**—For the two similar preparations A and B, 400 g. of thrice recrystallized mercurous nitrate was dissolved in three liters of 0.1 *M* nitric acid solution, and this solution was added drop by drop to four liters of hot 2 *M* sulfuric acid solution. Preparation A was digested for twelve hours with the mother liquor on a hot-plate, and

<sup>7</sup> Vosburgh, *THIS JOURNAL*, 49, 87 (1927).

<sup>8</sup> It is immaterial for present purposes whether this is a basic salt or a mixture of oxide and normal salt.

Preparation B was digested for one hour. Both were washed with 2 *M* sulfuric acid solution and Preparation A was not further treated. Preparation B was digested for another hour with 2 *M* sulfuric acid solution.

The crystals of Preparation A ranged in size from 30 to 2300 $\mu$ , most of them being between 300 and 500 $\mu$ . The crystals of Preparation B ranged from 15 to 1000 $\mu$ , most of them being between 30 and 50 $\mu$ .

Preparation C was made like Preparation B except that the mercurous nitrate solution was added rapidly to the sulfuric acid solution, and it was digested for a total of eight hours, three hours under the mother liquor and five hours under a fresh 2 *M* sulfuric acid solution. The crystal size ranged from 15 to 40 $\mu$ .

Preparation D was like Preparation C except that it was prepared from c. p. mercurous nitrate and ordinary distilled water.

Preparation E was made by the electrolytic method.<sup>9</sup> It was digested for three hours with 2 *M* sulfuric acid solution on a hot-plate. The crystals were about 9 $\mu$  in length.

Preparation F was one made for an earlier investigation by reduction of mercuric sulfate by mercury. The crystals ranged from 20 to 40 $\mu$  in length and the material contained much finely divided mercury.

**Cell Vessels.**—The vessels used were of soft glass with sealed-in platinum wires for connection to the electrodes. They were of the usual H form, the length of the vertical tubes being 11 cm. and that of the cross-arm 3.5 cm. Both had a diameter of 1.5 cm., and the cross-arm was 3.5 cm. from the bottom.

### Preparation of the Cells

The cells were prepared essentially as described previously.<sup>10</sup> For the protection from air the pipet described by Randall and Stone<sup>11</sup> was used.

When it was desired to prepare comparable groups of cells which differed more or less in materials or method of construction, care was taken to use as nearly the same procedure as possible. The method of washing the mercurous sulfate received special attention. In setting up a group of cells protected from air and a comparable group exposed to oxygen, all the cells were constructed from the same materials. Two portions of mercurous sulfate were filtered and washed in the same way, one in an atmosphere of oxygen with an electrolyte saturated with oxygen and the other in an atmosphere of nitrogen with an oxygen-free electrolyte.

In sealing the cells the tops of the tubes were flushed out with nitrogen (or in special cases oxygen) and the nitrogen was kept running into them as long as possible during the sealing process. It is not claimed that all oxygen was kept out by this process, but that its concentration was materially reduced.

In some of the earlier cells a little trouble was experienced with gas collecting above the amalgam. This trouble, at first thought to be caused by reaction of acid with the cadmium, was not confined to acid cells. It was probably caused by air trapped in and around the amalgam. Evacuation

<sup>9</sup> Hulett, *Phys. Rev.*, 32, 262 (1911).

<sup>10</sup> Vosburgh, *THIS JOURNAL*, 47, 1257 (1925).

<sup>11</sup> Randall and Stone, *ibid.*, 51, 1753 (1929).

of the vessel with the amalgam in place and a little electrolyte above it overcame the trouble.<sup>12</sup>

### Electromotive Force Measurements

The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer, the measuring system being properly shielded. The standards were the previously described Cells 353-6 and 496<sup>10,13</sup> to which an electromotive force of 1.01805 v. was assigned. The five cells agreed within 0.01 mv. A cell of larger capacity than the standards was used as the working standard, and a value was assigned it that would lead to the assumed value for the standards when they were measured. The absolute values of the standards were checked by means of two portable cells certified by the Bureau of Standards. The value found for the portable cells on the basis of the assumed values for the standards agreed with the certified value within 0.01 to 0.02 mv. There was evidence of a slight change in the portable cells, perhaps as a result of shipment.

Since the unknown electromotive forces were measured in the same manner as the standards and since the electromotive forces differed little from those of the standards, the errors of measurement must have been less than 0.01 mv. in most cases. Although in many standard cell investigations the precision attained is better than 0.01 mv., this was considered sufficient because the objective was to investigate relatively large deviations from constancy rather than to establish conditions for the preparation of cells of the highest quality.

### Experimental Results

The cells were kept in an oil thermostat at  $25 \pm 0.02^\circ$  (fluctuations of temperature were usually not more than  $\pm 0.005^\circ$ ) for some time after their preparation. Subsequently they were kept at room temperature, but put into the thermostat for measurements. In such a case their constancy was tested by at least three measurements made a day or more apart before final results were recorded. Care was taken that a change from room temperature to the thermostat was an increase in temperature rather than a decrease.

The electromotive forces were measured at intervals and the change of electromotive force with time is shown in the tables below. An hysteresis test was made from one to three and a half months after the cells were set up. A second hysteresis test was made later, all the cells being tested at one time. The ages of the cells at the time of the second test varied from three to eight months and are given in the tables. A third test was made four months after the second and a fourth three months after the third.

<sup>12</sup> It was learned later that Dr. Marion Eppley (private communication) had previously discovered the same remedy.

<sup>13</sup> Vosburgh, *THIS JOURNAL*, 49, 85 (1927).

Hysteresis tests were made by transferring the cells to a thermostat at 35°, leaving them there for at least three days, then transferring back to the thermostat at 25° and measuring after one hour and six hours. The hysteresis was measured by the difference between the electromotive force at the time in question and that at 25° previous to the test.

**Acid Cells.**—A number of cells with slightly acid electrolytes were prepared to test the materials and technique and to act as controls for the other cells. The concentration of acid was 0.01 mole per liter. The electromotive forces of these cells over a period of twelve to sixteen months are shown in Table I and the results of four hysteresis tests carried out at different times are given in Table II.

TABLE I  
CELLS WITH ACID ELECTROLYTES

Cells	Hg <sub>2</sub> SO <sub>4</sub>	$E - 1018.00 \text{ mv., } 25^\circ$						
		1 mo.	3	5	7	8-9	11-13	16
531-5 <sup>a</sup>	A	0.05	0.05	0.05	0.05	0.05	0.04	0.04
626-8	B	..	.06	..	.06	..	.08 <sup>b</sup>	
615-7	C	.07	.07	..	..	.06	.08	
605-6	D	.07	.07	.04	..	.06	.06	
607-8	D	.01	.05	.07	..	.05	.05	
632, 634	E	.11	..	.10	..	..	..	

<sup>a</sup> Cell 533 cracked and oil from the thermostat entered. After eight months the electromotive force became variable, and the results are omitted from the average.

<sup>b</sup> Hysteresis caused too high a value for cell 626.

TABLE II  
HYSTERESIS OF ACID CELLS

Cells	Hysteresis I		Age, mo.	Hysteresis II		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.		1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
531-4 <sup>a</sup>	-0.06	-0.06	8	-0.05	-0.06	-0.03	-0.05	-0.02	-0.05
535	....	....	8	+ .04	+ .04	+ .11	+ .06	+ .13	+ .08
626-8 <sup>b</sup>	+ .14	+ .04	3	.20	.08	.39	.20	.52	.30
615-7	.11	.06	4	.15	.07	.19	.10	.23	.12
605-6	.14	.06	5	.15	.06	.17	.07	.17	.08
607-8	.03	.02	5	.04	.02	.05	.03	.05	.02
632, 534	.06	.03	5	.04	.02	....	....		

<sup>a</sup> The hysteresis of Cell 533 (see note *a*, Table I) was omitted from the average. It was much larger than that of the others. <sup>b</sup> Cell 626 showed larger hysteresis and a more rapid increase than the other two.

The effect of impurities on the hysteresis of acid cells was investigated by making cells comparable with certain of those described above except that impurities were introduced. The impurities tried were formaldehyde, urea, material extracted from cork and gelatin. The formaldehyde was suggested by the fact that the coarse mercurous sulfate preparation found by Vosburgh and Eppley<sup>14</sup> to lead to more hysteresis than various finer

<sup>14</sup> Vosburgh and Eppley, THIS JOURNAL, 46, 109 (1924).

preparations was made by reduction of mercuric sulfate by formaldehyde.<sup>15</sup> Urea was tried because it affects the growth of sodium chloride crystals.<sup>16</sup> That material extracted from cork had the effect of increasing hysteresis was shown by Vosburgh and Eppley.<sup>17</sup> The present experiment was a repetition of theirs, except that the cork material was introduced in a different manner.

The methods of introducing the impurities were the following. For Cells 620 and 622 mercurous sulfate was allowed to stand overnight under an acid solution containing 2 g. of formaldehyde per liter. For Cells 636-638 the mercurous sulfate was untreated, but 0.04 g. of formaldehyde was added to 100 g. of the electrolyte. For Cells 623-625 and 644-646 the electrolyte was shaken with finely divided cork which had been digested previously with two portions of boiling water. In the former group some of the cork was included in the cells also. Cells 639-641 contained 0.1 g. of urea per 100 g. of electrolyte. For Cells 642-643 the electrolyte was heated with gelatin, 0.05 g. of the latter to 100 g. of electrolyte, and approximately half dissolved. The results are shown in Tables III and IV.

TABLE III  
EFFECT OF IMPURITIES ON THE ELECTROMOTIVE FORCE OF ACID CELLS

Cells	Hg <sub>2</sub> SO <sub>4</sub>	Im- purity	$E - 1018.00 \text{ mv., } 25^\circ$				
			1 mo.	3	5	8-9	12
620, 622	B	HCHO	0.05	0.06	..	0.05	0.06
636-8	E	HCHO	.01	..	0.01	.01	..
623-5	B	Cork	..	.11	..	.14	.27
644-6	E	Cork	.08	..	.09	.08	..
639-41	E	Urea	.05	..	.07	.07	..
642-3	E	Gelatin	.19	..	.03	.07	..

TABLE IV  
HYSTERESIS IN CELLS CONTAINING IMPURITIES

Cells <sup>a</sup>	Hysteresis I		Hysteresis II		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
620, 622	0.15	0.07	0.24	0.11	0.33	0.17	0.38	0.20
636-8	.01	.01	.01	.00	.03	.01	..	..
623-5	.38	.19	.62	.35	.75	.45	.76	.44
644-6	.08	.04	.13	.06	.16	.08	..	..
639-41	.03	.02	.05	.03	.09	.03	..	..
642-3	1.09	.82	1.53	1.22	1.91	1.64	..	..

<sup>a</sup> The age at the time of the first hysteresis test was one or two months and at the time of the second test was four or five months.

As far as hysteresis is concerned, formaldehyde seems to have a favorable effect, if any. Cells 620 and 622 differed little from Cells 626-628 (Table II)

<sup>15</sup> Since formaldehyde did not increase hysteresis, the conclusions of Vosburgh and Eppley are not affected by the present work.

<sup>16</sup> Neuhaus, *Z. Krist.*, **68**, 15 (1928), cited in *Chemical Abstracts*, **24**, 9 (1930).

<sup>17</sup> Vosburgh and Eppley, *J. Optical Soc. Am.*, **9**, 70 (1924).

in this respect, while 636-638 showed less hysteresis than Cells 632 and 634 (Table II). With respect to electromotive force, Cells 636-638 were abnormal, though constant, as far as observed.

The material extracted from cork by the solution undoubtedly caused some hysteresis. This is unmistakable in the case of Cells 623-625. The hysteresis of Cells 644-646, however, is not large as compared with many of the other groups, but it is the largest of any of the cells made with Mercurous Sulfate E.

Urea had little or no effect, but there can be no doubt that gelatin had a very pronounced effect.

The behavior of gelatin toward mercurous sulfate was tested qualitatively in another way. If gelatin prevents crystallization from a supersaturated solution, it should interfere with the growth of crystals in the precipitation of mercurous sulfate. Accordingly, mercurous sulfate was precipitated by the addition of mercurous nitrate solution drop by drop to a portion of dilute cadmium sulfate solution containing 0.01 mole of sulfuric acid per liter. Gelatin was dissolved in a second portion of the cadmium sulfate solution (0.025 g. per 100 cc.) and the mercurous nitrate solution added as before. Much more of the mercurous nitrate solution was added before precipitation started in the second case than in the first. Examination of the first mercurous sulfate under the microscope showed that it consisted of clusters of thick needle-like transparent crystals, while the second consisted of much smaller particles of roughly circular cross section.

**Neutral and Basic Cells.**—Hysteresis in acid cells has been found to increase with decreasing acid concentration.<sup>17,18</sup> If the supersaturation theory of hysteresis is to be applied to this case, a mechanism must be assumed to account for the effect of decreasing acidity on the velocity of crystallization. Such a mechanism might be based on the observation of Gardiner and Hulett<sup>19</sup> that mercurous sulfate becomes covered with a surface layer of basic mercurous sulfate when in contact with a cadmium sulfate solution. How large a concentration of sulfuric acid must be present to prevent such an action is uncertain.

It was thought that some data on the effect of a surface layer of basic mercurous sulfate might be obtained by comparing the hysteresis of groups of cells made with different opportunities for hydrolysis. A number of cells without added acid were made, and some others were made at the same time and of the same materials, but with the inclusion of some basic cadmium sulfate.<sup>8</sup> The basic cadmium sulfate was placed either above the mercurous sulfate, separated from it by a layer of fine crystals of the normal sulfate, or in a similar position on the amalgam side of the cell.

<sup>18</sup> Ref. 10, p. 1265.

<sup>19</sup> Gardiner and Hulett, *Trans. Am. Electrochem. Soc.*, **56**, 121 (1929).

The results are given in Tables V and VI. For convenience, the cells containing no added acid are called neutral cells and those containing basic cadmium sulfate are called basic cells.

TABLE V  
VARIATION OF ELECTROMOTIVE FORCE OF NEUTRAL AND BASIC CELLS

Cells	Hg <sub>2</sub> SO <sub>4</sub>	Basic salt	$E - 1018.00 \text{ mv., } 25^\circ$					
			1 mo.	3	5	8-10	12	16
546-50	A	None	0.06	0.04	0.03	-0.01	-0.03	-0.07
556-60	A	Hg leg	.03	-.01	.00	+.01	.00	.00
561-4	A	Cd leg	.03	.00	.00	.00	-.01	-.01
584-6	B	None	.06	+.05	-.31	-.57	-.81	....
590-4	B	Cd leg	.02	.04	+.03	+.03	+.04	....

The cells containing basic cadmium sulfate were less variable in electromotive force than the neutral cells, and the various groups agreed fairly well with each other. The average variation from the group mean of the individual cells within the groups was about  $\pm 0.01$  mv. It is quite evident that the inclusion of basic cadmium sulfate has in these cases led to better cells than its omission. This recalls the precaution taken by Shaw and Reilley<sup>20</sup> to make the electrolyte in standard cells slightly basic.

It was observed at the end of the twelfth month (the eighth month for Cells 590-4) that the cells containing the basic salt all had a thin layer of gray material above the layer of fine cadmium sulfate crystals which covered the mercurous sulfate. A few contained spots of yellow basic mercurous sulfate in the paste, but no other changes were noticed. In order to learn to what extent basic cadmium sulfate can hydrolyze mercurous sulfate, a nearly saturated cadmium sulfate solution was shaken with a mixture of mercurous sulfate and basic cadmium sulfate. The first result was hydrolysis of the mercurous sulfate to yellow basic mercurous sulfate. On standing in the dark, the mixture turned gray in color, indicating further hydrolysis to oxide. If basic cadmium sulfate can hydrolyze mer-

TABLE VI  
HYSTERESIS OF NEUTRAL AND BASIC CELLS

Cells	Hysteresis I <sup>b</sup>		Hysteresis II <sup>b</sup>		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
546-9 <sup>a</sup>	0.34	0.23	0.52	0.36	0.70	0.39	0.64	0.38
557-9 <sup>a</sup>	.25	.15	.11	.08	.06	.05	.03	.03
561-4 <sup>a</sup>	.12	.07	.04	.01	.03	.01	.03	.00
584-6	1.43	.86	3.48	2.99	2.70	2.17	3.07	2.57
590-4	0.62	.37	0.23	0.12	0.14	0.08	0.11	0.05

<sup>a</sup> In the first two hysteresis tests Cells 547 and 563 and the others indicated were omitted. At the time of the third test these cells agreed with the others as well as could be expected. <sup>b</sup> The age at the time of the first hysteresis test was one and a half to three months, and at the time of the second test five and a half to eight months.

<sup>20</sup> Shaw and Reilley, *Trans. Roy. Soc. Canada* [III], 13, 174 (1919).

curous sulfate to this extent, equilibrium was not attained in the basic cells. The constancy of electromotive force must have been the result of a local equilibrium or a steady state of change.

Cells made with Mercurous Sulfate B had more hysteresis than similar cells made with Mercurous Sulfate A, regardless of whether the electrolyte was acid, neutral or basic. It is uncertain what the difference between these two preparations was.<sup>21</sup> It is believed that in the preparation of the neutral and basic cells made with Mercurous Sulfate B, the mercurous sulfate was washed more thoroughly with the neutral electrolyte than in the case of Mercurous Sulfate A. This would lead to a thicker layer of basic salt on the surface.

The basic cells showed less hysteresis than the cells containing no added acid or base. In the basic cells the hysteresis decreased with the age of the cells. Hysteresis in the first group of neutral cells increased with age at first but after a year it was practically constant. In the second group a maximum seems to have been attained, after which there was a decrease to a more or less variable value.

Basic cadmium sulfate was also added to some cells made with an electrolyte containing 0.004 mole of acid per liter. Their behavior and that of some control cells made at the same time are shown in Tables VII and VIII.

TABLE VII  
ELECTROMOTIVE FORCES OF SLIGHTLY ACID AND BASIC CELLS

Cells	Hg <sub>2</sub> SO <sub>4</sub>	Basic salt	$E - 1018.00 \text{ mv., } 25^\circ$					
			1 mo.	3	5	7	12	16
543-5	A	None	0.08	0.07	0.07	0.07	0.07 <sup>a</sup>	<sup>b</sup>
537-9	A	Hg leg	.05	.00	.00	.02	.01	0.00
540-2	A	Cd leg	.03	.03	.03	.02	.00	.00

<sup>a</sup> The agreement of the three cells was not good at this time. <sup>b</sup> Hysteresis interfered with the measurement.

In this case slightly acid cells are compared with basic cells. In electromotive force the basic cells agreed better with the other basic cells shown in Table V than with the acid cells. Any important differences between the acid and basic cells must have been caused by changes which took place after the cells were set up, because acid cells are easy to reproduce. Such changes were doubtless accompanied by a decrease in the acid concentration in the vicinity of the mercurous sulfate—or were the result of it. The hysteresis results for these cells are given in Table VIII. The results for the separate cells are given rather than the average for the groups because of the lack of agreement.

<sup>21</sup> All the digestion of Mercurous Sulfate A was carried out in a solution containing nitric acid, while the last part of the digestion of Mercurous Sulfate B was carried out in sulfuric acid solution. A portion of the latter preparation was given an additional digestion in a sulfuric acid solution containing nitric acid, and two acid cells were made. The hysteresis was very small. Whether or not this was fortuitous was not determined.

TABLE VIII  
 HYSTERESIS OF SLIGHTLY ACID AND BASIC CELLS

Cells <sup>a</sup>	Hysteresis I		Hysteresis II		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
543	..	..	..	..	0.45	0.27	0.70	0.46
544	0.13	0.06	0.26	0.13	.50	.39	.46	.27
545	.10	.06	.18	.10	.31	.16	.31	.15
537	..	..	..	..	- .01	+ .01	- .02	.00
538	.12	.08	.00	.01	.00	.00	- .01	.00
539	.19	.12	.14	.10	+ .07	.06	.04	.04
540	.15	.12	.06	.06	.03	.03	.00	.01
541	.32	.23	.27	.19	.16	.11	.10	.08
542	..	..	..	..	.03	.01	.02	.00

<sup>a</sup> The age of the cells at the time of the first hysteresis test was one and a half months and at the time of the second test eight months.

At the beginning, the acid cells were definitely superior with respect to hysteresis. Their hysteresis increased with age, and by the time of the third hysteresis test, ten months after the first, the basic cells were definitely superior. During the early life, the acid cells agreed among themselves in electromotive force better than the basic cells. At the end of a year, however, the basic cells were superior in this respect. After a year, some of the basic cadmium sulfate was still present, though less than in the basic cells made with a neutral electrolyte.

It is of interest to consider the behavior of some neutral cells made with mercurous sulfate that had been washed with water (Cells 598-600) or a very dilute sodium carbonate solution (Cells 572-4) before the cells were set up, and so presumably hydrolyzed on the surface. In the latter case there was a slight change of color.

 TABLE IX  
 ELECTROMOTIVE FORCE OF CELLS MADE WITH HYDROLYZED MERCUROUS SULFATE

Cells	H <sub>2</sub> SO <sub>4</sub>	$E - \frac{1018.00 \text{ mv.}, 25^\circ}{5}$						
		1 mo.	3	5	7	9-11	15	
572-4	A	-0.01	-0.05	-0.11	-0.14	-0.27	-0.39	
598-600	C	+1.20	+ .97	+ .88	....	+ .80	....	

 TABLE X  
 HYSTERESIS OF CELLS MADE WITH HYDROLYZED MERCUROUS SULFATE

Cells	Hysteresis I <sup>a</sup>		Hysteresis II <sup>b</sup>		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
572-4	0.50	0.40	1.01	0.78	1.89	1.41	2.18	1.65
598-600	.52	.32	0.74	0.55	0.86	0.65	0.89	0.67

<sup>a</sup> The cells were one month old. <sup>b</sup> The cells were seven months old.

Cells 572-4 made with hydrolyzed mercurous sulfate A showed considerably more hysteresis than Cells 546-50 (Table V) made in the usual way. The hysteresis increased with age in both groups made with the hydrolyzed mercurous sulfate.

It seems to be pretty well established<sup>18</sup> that in slightly acid cells the hysteresis increases with decreasing acid concentration. The increase of hysteresis as the quantity of added acid approaches zero must either parallel or be caused by hydrolysis of the mercurous sulfate. The same might be said of the decrease of electromotive force with time. Tables IX and X show that hydrolysis of the mercurous sulfate previous to setting up the cells leads to a still more rapid decrease in electromotive force, or to an initially high and decreasing electromotive force, and to increased hysteresis. However, as shown above, the introduction of basic cadmium sulfate leads to smaller hysteresis than in neutral cells, and the hysteresis in this case decreases with the age of the cells. The difference must have been in the extent of the hydrolysis. As shown above equilibrium could not have been attained in the basic cells and hydrolysis of the mercurous sulfate must have gone on continuously from the time the cells were set up. It is hoped that research now in progress will throw light on why basic cells have so little hysteresis.

**The Effect of Oxygen.**—Conflicting opinions have been expressed as to the effect of the exclusion of oxygen in the preparation of cells. Vosburgh<sup>22</sup> and Eppley<sup>23</sup> considered this precaution necessary, while Gardiner and Hulett<sup>24</sup> considered that it did not help any. Hydrolysis of the mercurous sulfate by washing seems to have been a very important factor in the results of the latter investigators, and its effect may have masked a smaller effect of the oxygen.

If oxygen has any chemical effect, the ultimate result must be to make the cell contents more basic. This could result either from direct union with cadmium or mercury, or the oxidation of mercurous ion to mercuric ion with subsequent reduction by mercury. If this is true, the reported good effect of exclusion of oxygen may have resulted from preventing the neutralization of a small quantity of acid present in the cell. It might be predicted, however, on the basis of the above results and discussion, that in a cell with an electrolyte containing very little free acid, oxygen might have a beneficial effect, making the electrolyte more basic.

Two groups of cells were made with Mercurous Sulfate A, two with Mercurous Sulfate B and two with Mercurous Sulfate F. In each case the two groups were made by as nearly the same procedure as possible except that air was excluded by means of nitrogen in one group and oxygen was used in place of nitrogen in the other. The results are shown in Tables XI and XII.

In the first two groups little effect of oxygen on the constancy is apparent. The oxygen-containing cells were more nearly constant over a period of

<sup>22</sup> Ref. 10, p. 1259.

<sup>23</sup> Eppley, *Trans. Am. Electrochem. Soc.*, **53**, 149 (1928).

<sup>24</sup> Gardiner and Hulett, *ibid.*, **56**, 138 (1929).

TABLE XI  
 EFFECT OF OXYGEN ON CONSTANCY

Cells	Hg <sub>2</sub> SO <sub>4</sub>	Gas	$E - 1018.00 \text{ mv., } 25^\circ$						
			1 mo.	3	5	6-8	9	12	16
546-50	A	N <sub>2</sub>	0.06	....	0.04	-0.01	....	-0.03	-0.07
551-5	A	O <sub>2</sub>	.05	0.01	.00	.00	....	-.05	-.08
584-6	B	N <sub>2</sub>	.06	.05	-.31	....	-0.57	-.81	....
587-9	B	O <sub>2</sub>	.03	-.02	....	-.09	-.22	-.31	....
579-80	F	N <sub>2</sub>	-.04	....	-.56	-.65	-.72	-.73	....
581-3	F	O <sub>2</sub>	+.03	.00	....	-.27	-.22	-.32	....

three or four months, but later decreased to a slightly lower value. On the other hand, the decrease in electromotive force of the nitrogen-containing cells was slower during the first three or four months, and the electromotive force was nearer the normal. In the other four groups there is no question as to the oxygen-containing cells being less variable in the long run, though none of the cells can be called good. Cells 584-6 had an electromotive force nearer the normal for the first three months than the comparable oxygen-containing cells.

 TABLE XII  
 HYSTERESIS OF CELLS CONTAINING OXYGEN

Cells	Hysteresis I <sup>c</sup>		Hysteresis II <sup>d</sup>		Hysteresis III		Hysteresis IV	
	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.	1 hr., mv.	6 hr., mv.
546-9 <sup>a</sup>	0.34	0.23	0.52	0.36	0.69	0.39	..	..
551-4 <sup>b</sup>	.43	.31	.89	.69	.31	.17	0.33	0.18
584-6	1.43	.83	3.48	2.32	2.70	2.17	..	..
587-9	1.38	.76	1.56	0.87	1.86	1.10	2.14	1.31
579-80	3.26	2.66	3.47	2.93	3.03	2.33	3.10	2.40
581-3	3.29	2.86	2.31	1.91	1.72	1.24	1.84	1.26

<sup>a</sup> See note *a*, Table VI. <sup>b</sup> Cell 553 was omitted; it agreed with the others in the third and fourth hysteresis tests, as did Cell 555 also. <sup>c</sup> The age of the cells was one to three and a half months. <sup>d</sup> The age of the first two groups was eight months and that of the last four groups was six months.

In the first hysteresis test the presence or absence of oxygen seemed to make no appreciable difference; the groups that were comparable agreed as well as could be expected. In the other hysteresis tests the oxygen-containing cells showed less hysteresis than the others, except in the cells made with Mercurous Sulfate A in the second test. The presence of oxygen, if enough time is allowed, seems to bring about a reduction of hysteresis. The effect of oxygen is in the same direction as the effect of the addition of basic cadmium sulfate, though not as pronounced.

### Discussion

Hysteresis does not in all cases increase with the age of a cell. In some of the acid cells the increase was small, while in some of the basic cells the hysteresis decreased rather than increased. The mechanism of the change

is probably more complicated than that proposed by Niederhauser and Hulett. Instead of an approach toward perfection of the crystal surfaces it seems that adsorption of impurities, or of basic mercurous sulfate, on the surface may be at least a partial explanation.

If the surface is covered with basic mercurous sulfate as a result of hydrolysis, the case is more complicated than when gelatin or a similar material is adsorbed. A layer of basic mercurous sulfate would not necessarily prevent the deposition of mercurous ions from a supersaturated solution, but might make it necessary for these to be deposited as the basic salt rather than the normal salt.

Whether or not protection from oxygen can be considered beneficial depends on the point of view. Slightly acid or neutral cells made with care to avoid appreciable hydrolysis are more likely to give an electromotive force near the normal at the beginning if oxygen is absent. Oxygen in neutral cells seems to cause a more rapid decrease at first, but less variation later. However, the addition of basic cadmium sulfate (or cadmium hydroxide) to the electrolyte helps more in this respect than the addition of oxygen. In a basic cell oxygen should do no harm.

If the action of oxygen in a cell results in the addition of basic material, it follows that its presence in a slightly acid cell is undesirable. Hysteresis increases with a decrease of acidity, and if the added acid should be used up, the electromotive force would be likely to vary. If acid cells are made without protection from the air, enough acid should be added so that after the clean-up of the oxygen present a sufficient excess of acid will still remain. Other sources of basic material, such as cadmium oxide introduced with the amalgam, should be eliminated or taken into account.

### Summary

Gelatin and material extracted from cork increased the hysteresis in acid Weston cells considerably. An explanation based on adsorption is suggested.

Cells with no added acid or basic material (neutral cells) had more hysteresis than cells containing basic cadmium sulfate.

The electromotive forces of cells to which basic cadmium sulfate was added were less variable over a period of several months and more reproducible than those of similar cells with no added basic material (or acid). The electromotive forces of the basic cells were lower than what is considered normal, however, after the first month.

The presence of oxygen caused a decrease of hysteresis in two groups of neutral cells and an increase at first in a third group, with a subsequent decrease. The electromotive forces of most of the cells containing oxygen decreased less than corresponding nitrogen-containing cells.