interstices or pores containing the atomic hydrogen should change in form would not be surprising since, of course, iron in bulk is altered in dimensions by magnetic influence. Perhaps the shock at the moment of magnetic impulse causes the hydrogen to sink more deeply into the metal. Any more definite attempt to picture the mechanism of the action would be premature. Whatever the final detailed explanation of the effect may be, one cannot help thinking that knowledge of the decrease of the potential of occluded hydrogen in a magnetic field will contribute toward an ultimate interpretation of the nature of magnetism in metals, as well as of the molecular condition and mode of occlusion of hydrogen, and of the "overvoltage" which occlusion produces.

We are indebted to the Carnegie Institution of Washington for some of the apparatus employed.

Summary

The potential of iron in ferrous sulfate is found to be altered only very slightly by the application of a magnetic field. This almost negligible alteration is probably to be traced in part to diffusion in the electrolyte under the magnetic influence. On the other hand, the potential of hydrogen occluded in iron is found to be distinctly lowered, in amount roughly proportional to the intensity of the magnetic field employed. With a given magnetic field the decrease of "overvoltage" is approximately proportional to the "overvoltage" itself, amounting (with the strongest magnet employed) to about 5% of the "overvoltage" value. Many minor details, such as the effect of changing ferrous ion and hydrogen-ion concentration, of the presence of ferric salts, and other pertinent phenomena, are considered.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE EFFECT OF VARIOUS PREPARATIONS OF MERCUROUS SULFATE ON THE ELECTROMOTIVE FORCE AND HYSTERESIS OF WESTON STANDARD CELLS

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Since the solubility of a finely divided substance is dependent on the size of the particles, standard cells set up with mercurous sulfate sufficiently finely divided should have abnormally high electromotive forces.

Steinwehr[1] attempted to show this experimentally, but his results were criticized by Hulett[2] who considered that the effect of the size of the particles was not to be feared

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[1] Steinwehr, *Z. Elektrochem.*, **12**, 578 (1906).

[2] Hulett, *Trans. Am. Electrochem. Soc.*, **14**, 88 (1908); *Phys. Rev.*, **27**, 337 (1908). See also van Ginneken, *Z. physik. Chem.*, **75**, 687 (1911).

and that a fine-grained mercurous sulfate was preferable. Wolff and Waters[3] mentioned the possibility of the fineness of the grains of mercurous sulfate affecting its electromotive properties, but except in cells in which commercial mercurous sulfate[4] was used, found no variations attributable to this cause. Smith[5] found no irregularities due to grain size when the grains were between 3 and 30 μ in diameter. It has been generally considered that special precautions in avoiding too great a degree of dispersion in mercurous sulfate for standard cells are unnecessary.

Standard cells made with an acid electrolyte, on account of their greater reproducibility and constancy,[6] offered a means of obtaining more accurate data on this subject, as well as some information as to the effect of different mercurous sulfate preparations on hysteresis. The results agreed with the conclusions of Steinwehr[1] in showing that some mercurous sulfate samples gave abnormally high electromotive forces in standard cells due to small grain size. Some data were obtained also with regard to the relation of hysteresis in standard cells to the characteristics of the mercurous sulfate.

Materials and Cells

Mercurous sulfate Samples 1, 2 and 3 have been described in a previous communication.[6d] No. 1 was prepared by the electrolytic method and digestion under a sulfuric acid solution for 5 days, No. 2 by reduction of mercuric sulfate by formaldehyde at boiling temperature, and No. 3 by formaldehyde reduction at room temperature. No. 4 was prepared by adding rapidly a 1.1 M solution of mercurous nitrate to a large excess of 6 N sulfuric acid solution. No. 5 was prepared from portions of the solutions used in preparing No. 4, the mercurous nitrate solution being added drop by drop at a very slow rate to the well stirred acid solution at room temperature. Nos. 4 and 5 were washed free from nitric acid by decantation with 2 M sulfuric acid. No. 6 was prepared by reduction of mercuric sulfate by mercury; 217 g. of mercuric oxide was added slowly to 5 liters of 2 M sulfuric acid solution. The resulting mercuric sulfate solution was filtered, 407 g. of mercury was added, and the solution was stirred overnight. A finely divided, gray mercurous sulfate was formed. Nos. 7, 8 and 9 resulted from digesting portions of Nos. 4, 6 and 5, respectively, on a hot plate under a 2 M sulfuric acid solution. No. 10 was an electrolytic preparation similar to No. 1.

The cadmium sulfate solution, crystals, the mercury, and the cadmium amalgam have been described in a previous communication.[6d] The solu-

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[3] Wolff and Waters, *Bur. Standards Bull.*, **4**, 15 (1907).

[4] Wolff [*ibid.*, **5**, 328 (1908)] was inclined to attribute the high values of cells made with commercial mercurous sulfate to impurities.

[5] Smith, *Trans. Roy. Soc. London*, **207A**, 401 (1908).

[6] (a) Ref. 3, p. 99. (b) Smith, *Electrician*, **75**, 463 (1915). (c) Obata, *Proc. Math. Phys. Soc. Japan*, **2**, 232 (1920). (d) Vosburgh and Eppley, THIS JOURNAL, **45**, 2268 (1923).

tion was prepared by dissolving hydrated cadmium sulfate in a 0.03 *N* sulfuric acid solution.

Normal cells were prepared essentially as described by Wolff and Waters,[3] 5 cells being prepared with each of the mercurous sulfate Samples 1, 4, 5, 6, 7 and 8.

Measurements of Grain Size

Samples of the various preparations of mercurous sulfate were examined under a microscope, and the sizes of some of the crystals measured. Nos. 1 and 2 contained crystals of a large number of sizes and shapes, the largest being of the order of 240 μ long by 80 μ wide. No. 3 contained grains as large as 360 μ by 170 μ. The smaller ones were of the order of 31 μ by 18 μ. No. 4 was a uniform, fine-grained preparation, the crystal size being of the order of 3 μ. No. 5 contained no very large crystals, the largest observed being 110 μ in length. There were many small ones of the order of 5 μ in length. No. 6 was composed of small crystals of the order of 5 μ in length together with some larger ones about 70 μ by 50 μ, the surfaces of which were covered with the small 5 μ grains. No. 7, which was obtained by digesting No. 4, was composed of the small grains of No. 4 together with a few larger ones about 18 μ in length. No. 8, resulting from the digestion of No. 6, resembled No. 6 except that the larger crystals were not covered with small ones.

Measurements of Electromotive Force

The electromotive forces of the cells were measured at intervals by means of the potentiometer described by Eppley and Gray.[7] The working standard was checked frequently against 3 reference cells made at least six years previously at the National Physical Laboratory, Teddington, England, and furnished to this Laboratory through the kindness of Dr. F. E. Smith. The reference cells were assigned values such as to make the

TABLE I

ELECTROMOTIVE FORCES OF WESTON NORMAL CELLS MADE WITH VARIOUS PREPARATIONS OF MERCUROUS SULFATE

	Hg_2SO_4		Electromotive forces minus 1.01800 volts. 25°					
Cells	No.	Size μ	1.5 months Mmv.	3 Mmv.	4 Mmv.	5 Mmv.	6 Mmv.	12 Mmv.
1– 5	1	<240	53	51	49	49	...	50
1a–5a	1	<240	58	60	...	...	...	..
6–10	2	<240	54	47	47	47	...	46
11–15	3	30 to 360	55	50	49	52	...	..
66–70	5	5 to 110	55	61	61	63	62	..
91–95	8	5 to 70	58	63	65	65	64	..
86–90	7	3 to 18	89	94	95	95	95	..
71–75	6	5	101	98	98	100	98	..
61–65	4	3	146	143	143	147	147	..

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[7] Eppley and Gray, *J. Optical Soc. Am.*, 6, 859 (1922).

electromotive force of Cells 1–15 when 1 to 2 months old 1.018054 volts.[6d] Table I gives the results of measurements at 25° ± 0.02°. The electromotive forces in each column are the values obtained at the given length of time after the construction of the cells and are averages for groups of 5 cells each. The extreme variation among the members of a group was in only a few cases more than 10 mmv. and in only one group, Cells 61–65, was the variation from the mean greater than 10 mmv.[8] No cells were rejected for inconstancy or disagreement with the others.

The differences between the first six groups of cells and the last three can be explained[9] as due either to differences in free energy of the mercurous sulfate samples, or to the phenomenon called "hydrolysis" by Hulett.[2] That it was not hydrolysis is indicated by the constancy of the cells. Cells in which hydrolysis has taken place have abnormally high values at the start but decrease slowly, often going below the normal value.[10]

The fact that samples of the preparations of fine mercurous sulfate after digestion on a hot plate gave cells with nearer the normal electromotive force supports the conclusion that the abnormal electromotive forces were caused by the small grain size.

For further evidence that the differences in electromotive force were not due to hydrolysis some cells were made in which both electrodes were of mercury and the electrolyte was 2 *N* sulfuric acid solution. An electrolytic mercurous sulfate, No. 10, covered the mercury on one side of all the cells, while various mercurous sulfate preparations were used on the other side, 2 cells being made with each. The electromotive forces were measured by connecting the cells in series with a standard cell of known electromotive force and measuring the sum of the two.[11] Results could be duplicated within about 2 microvolts. Table II gives the results, each value being an average of ten measurements covering a period of a month when the cells were one to two months old. The average variation from the mean values was 1 mmv. The calculated values were obtained by subtracting the electromotive force of Cells 1–5 from those of the other groups.

[8] The e.m.f. of No. 61 was 20 microvolts below that of the others three months after their preparation. Later, this cell came to good agreement with the others.

[9] Impurities cannot account for these differences because the impurities must have been small in quantity, and small amounts of most impurities in standard cells have been found to have practically no effect on the electromotive force. See (a) Ref. 1. (b) Hulett, *Phys. Rev.*, **32**, 259 (1911). (c) Shaw and Reilley, *Trans. Roy. Soc. Canada*, (iii) 13, 171 (1919).

[10] Hulett, *Phys. Rev.*, **25**, 16 (1907). The first four groups of cells of Table II were not measured during the first month. Of the others Nos. 61–65 decreased about 35 microvolts, while all the others were either practically constant or increased during the first 1.5 months.

[11] The range of the potentiometer was limited.

The results are in qualitative agreement with the results for the Weston cells, Table I showing that there are appreciable free-energy differences between some of the samples of mercurous sulfate. If mercurous sulfate 3 were made the standard, quantitative agreement would result for mercurous sulfates 5 and 8 but not for the others. The concentration cells were made about 6 months after the Weston cells and, although changes in free energy of the mercurous sulfate inside the latter are not noticeable, changes may have taken place slowly in the portion of the mercurous sulfate preserved under 2 *M* sulfuric acid solution.

TABLE II

ELECTROMOTIVE FORCES OF MERCUROUS SULFATE CONCENTRATION CELLS

Hg_2SO_4 No.			2	4	5	6	7	8	9	10
E.m.f.	1	Mmv.	−9	50	6	25	23	9	−2	0
	2	Mmv.	−11	53	4	16	22	10	+1	2
E.m.f. calc.[a]		Mmv.	−3	97	12	49	45	14	..	..

[a] Assuming mercurous sulfates 8 and 10 to be equivalent.

Changes in acidity can account for only a small part of the differences between groups. Some of the cells were opened six months to a year after their construction, and the acid concentration in the electrolyte was determined by titration with sodium hydroxide solution, with methyl red as the indicator. The last column in Table III gives the differences in electromotive forces due, according to the relation of Obata,[6c] to the differences in acidity from the calculated. They are negligible in all cases but one, Cell 61, and the difference is negligible for another cell of the same group, Cell 64.

TABLE III

DETERMINATION OF ACIDITY OF ELECTROLYTES

Cell	Vol. of sample Cc.	0.02 *N* NaOH Cc.	Acid obs. *N*	Acid calc. *N*	Diff. in e.m.f. Mmv.
6	3.01	3.20	0.021	0.023	2
10	4.02	4.53	.023	.023	0
13	4.02	4.33	.022	.023	1
61[a]	3.01	1.78	.012	.023	9
64	3.01	3.22	.021	.023	2
66	3.01	3.09	.021	.023	2
71	5.00	5.00	.020	.023	3
86	4.02	4.36	.022	.023	1
91	3.01	3.16	.021	.023	2

[a] Ref. 8.

The small differences between the electromotive forces of the first 6 groups of cells in Table I may be in part due to differences in grain size of the mercurous sulfate. This is probable from the results in Table II. The differences are, however, about of the order of magnitude of differences between cells made with the same materials, as comparison of the first 2 groups shows.[12]

Hysteresis

Wolff[13] found that the majority of cells showing hysteresis were made with large grained, white mercurous sulfate, and that cells could be set up which showed very little hysteresis. For further information on this subject the cells described above were tested for hysteresis. They were transferred to a thermostat at 35° and maintained for 2 to 4 days, usually the latter. Equilibrium was generally attained within one day. They were then transferred to a thermostat at 25° and measured after one hour, five hours and one day. Table IV shows the results, the figures in the column headed "hysteresis" being the difference between the abnormal electromotive force at the given time and the equilibrium value at 25°. The hysteresis in some cases increased slowly with the age of the cells, so only tests made when the cells were six months old are reported in Table II. The hysteresis was found to be fairly reproducible when the same conditions were used in its determination. The variation in hysteresis among cells of the same group was sometimes considerable, as Table V shows.

TABLE IV

HYSTERESIS OF WESTON CELLS WITH DIFFERENT PREPARATIONS OF MERCUROUS SULFATE

	Mercurous sulfate			E.m.f.	Hysteresis		
Cells	No.	Size μ	Color	25° V.	1 hr. Mmv.	5 hr. Mmv.	24 hr. Mmv.
11–15	3	30 to 360	White	1.018050	151	95	48
1–55	1	<240	Gray	1.018050	34	23	10
7–10	2	<240	Gray	1.018047	17	12	5
66–70	5	5 to 110	White	1.018062	6	13	4
86–90	7	3 to 18	White	1.018095	− 51[a]	10	10
91–95	8	5 to 70	Gray	1.018064	− 37[a]	11	10
61–65	4	3	White	1.018147	0	2	2
71–75	6	5	Gray	1.018099	− 9	0	−2

[a] While Cells 86–95 were in the 35° thermostat the temperature went up to 53° one night. They were kept at 35° for four days after this, but the high temperature may have affected the hysteresis somewhat. Earlier tests showed that these two groups exhibited more hysteresis than Cells 61–65 and less than 66–70, and that the hysteresis was practically the same for both.

The hysteresis is different from that observed by Wold,[14] which was due to a lag in solution or precipitation of cadmium sulfate and was in

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[12] This difference may have been partly due to a drift of the standards as the second group was set up 6 months after the first, third and fourth groups. The others were set up after the latter 3 groups and before the former group. The constancy of all the cells in terms of the standards argues against any pronounced change in the latter, however.

[13] Ref. 4, p. 337.

[14] Wold, *Phys. Rev.*, **27**, 329 (1908).

the opposite direction in its effect on the electromotive force of the cells. This type of hysteresis was usually masked by the larger effect in the opposite direction, but appeared in Cells 86–95.

The hysteresis varied greatly with different mercurous sulfate preparations. It was largest in cells made with coarse, white mercurous sulfate and smallest in the cells made with fine, gray mercurous sulfate. Both the size of the particles and the presence of finely divided mercury seemed to affect the hysteresis.

Neutral unsaturated Weston cells show more hysteresis than acid ones.[6d] It is to be expected, therefore, that an increase in acidity would cause a decrease in hysteresis in normal cells. Two cells, Nos. 14 and 15, which showed considerable hysteresis, were opened and 0.3 cc. of 2 *N* sulfuric acid solution was added to each, after which they were resealed. The electromotive forces increased at first, then decreased to a value lower than the previous equilibrium value. The hysteresis, determined as described above, was considerably lower than it had been before, as shown in Table V. In the effect of acid as well as in the slow decrease in electromotive force with time hysteresis resembles the phenomena found by Hulett[2] to result from rotating the cathode system of a cell.

TABLE V

	Hysteresis before adding acid			Hysteresis after adding acid		
Cells	1 hr. Mmv.	5 Mmv.	24 Mmv.	1 hr. Mmv.	5 Mmv.	24 Mmv.
14	193	120	66	21	10	10
15	123	77	41	15	5	8

Temperature Coefficients

The difference between the electromotive forces at 25° and 35°, respectively, was independent of the mercurous sulfate preparation used. The average difference was about 5 mmv. lower than that calculated by Wolff's formula.[4] This is hardly more than the experimental error, as the observed electromotive forces were not as constant at 35° as they were at 25°.

Conclusions

When Weston cells are set up to establish the value of the international volt it is important that the mercurous sulfate be sufficiently large grained.[15] Digestion with a sulfuric acid solution at boiling temperature is a wise precaution, but this cannot be depended upon to correct a very finely divided uniform mercurous sulfate.

Low hysteresis cannot be taken as indicating the reliability of a standard cell in low acid cells. On the contrary, a cell with fairly high hysteresis is the more reliable for use as a primary standard.

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[15] Large grained mercurous sulfate has given irregular results in standard cells. (Refs. 1 and 2.) This source of error is being investigated, and it seems probable that it can be avoided without much trouble.

When it is more important that cells have low hysteresis than that their electromotive forces agree with the established value[16] cells can be made more acid and a fine grained mercurous sulfate used.

Summary

1. Weston standard cells made with finely divided mercurous sulfate had electromotive forces 40 to 100 mmv. higher than cells made with coarser mercurous sulfate.

2. Hysteresis varied greatly with the characteristics of the mercurous sulfate, being largest in the case of a coarse, white mercurous sulfate and practically zero in the case of a fine, gray mercurous sulfate. Both smallness of the particles and the presence of finely divided mercury appeared to influence the prevention of hysteresis.

3. The addition of acid to cells lowered the hysteresis considerably.

NEWPORT, RHODE ISLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE, CALCUTTA]

STUDIES IN DYES WITH MULTIPLE CHROMOPHORES

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A careful examination of the literature on dyes shows that the introduction of an additional chromophore into a dye may have one of the following consequences: (1) the color becomes deeper in some cases; (2) it becomes lighter in some; and (3) it remains practically unaltered in others; at any rate the effect is not perceptible to the naked eye.

In the light of the modern researches of Hartley, Baly, Hewitt, Purvis, Watson and their collaborators regarding the absorption spectra of colored substances, the change of color is intimately associated with the shifting of the absorption bands, and the deepening of color is caused by the shifting of the absorption band (or bands) towards the red end of the spectrum. When, however, the shifting takes place to such an extent that the absorption band (or bands) reaches the infra-red region, the color of the compound attributable to that absorption band or to those bands disappears and a second color termed "the color of the second order"[1] may appear due to another absorption band entering into the visible part of the spectrum from the ultra-violet region. This theory of color of the second order offers a plausible explanation of the apparently anomalous phenomenon of the color of a compound sometimes becoming lighter by the multiplication of chromophores.

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[16] This is the case with unsaturated cells to be used at room temperature, and with any working standards which can be checked occasionally.

[1] Piccard, *Ber.*, **46**, 1843 (1913).