Summary

The actual water-vapor content of saturated compressed gases is larger than is calculated by the usual method in which temperature effects are alone considered and the volume is calculated by means of the laws of a perfect gas. The maximum observed effect in this investigation was with nitrogen at 50° and 1000 atmospheres. In this case the effect of pressure is to increase the water content 4-fold as computed by the usual method, or 2-fold if allowance is made for deviation from the laws of a perfect gas. In every case studied, the amount of water vapor increased with pressure but not in proportion to the increase in density of the gas. In the case cited above, the water-vapor content increased 2-fold while the density increased 516-fold.

The magnitude of the phenomenon depends on the nature of the gas. Under the above conditions a liter of nitrogen will hold 44% more water vapor than the same volume of hydrogen. The amount of water vapor in the 3:1 hydrogen-nitrogen mixture could have been interpolated, using the Leduc rule of additive volumes at constant temperature and pressure, from results obtained with nitrogen and hydrogen.

The application of certain dynamic principles to this phenomenon has been attempted, but as yet quantitative relationships have not been detected between observed and calculated results. Qualitatively, the phenomenon may be correlated, in the absence of an adequate theoretical treatment, by assuming the compressed gas to act as a solvent for water vapor.

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[CONTRIBUTION FROM THE EPPLEY LABORATORY]

THE ELECTRODE EQUILIBRIUM IN THE WESTON STANDARD CELL

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There are some peculiarities in the action of the Weston standard cell which have not been satisfactorily explained. Newly prepared cells sometimes have abnormally high electromotive forces which decrease slowly as time goes on, and sometimes do not stop decreasing at any particular value.[1] Well aged cells are not always constant in electromotive force. Shaw and Reilley[2] found that a number of cells decreased 6 to 8 mmv. a year for ten years. When the contents of the cathode com-

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[1] (a) Hulett, *Trans. Am. Electrochem. Soc.*, **14,** 84 (1908); (b) *Phys. Rev.*, **25,** 16 (1907). (c) Smith, *Trans. Roy. Soc. London*, **207,** 407 (1908). (d) Vosburgh, THIS JOURNAL, **47,** 1257 (1925).

[2] Shaw and Reilley, *Trans. Roy. Soc. Canada*, [iii] **13,** 171 (1919).

partment of a cell are mixed by rotating the vessel, a temporary increase in electromotive force may occur, with a subsequent decrease to the normal value. Hulett[1b] found a large increase, 0.0014 v. to 0.002 v. Under similar conditions Wolff and Waters[3] found a much smaller increase in most cases, less than 0.0001 v. in some of their cells. Finally, Weston cells often show abnormally high electromotive forces after subjection to a decrease in temperature.[4] This is only temporary, the electromotive force decreasing again to its normal value as in the case of the rotated cells. The presence of sulfuric acid in the electrolyte of the cell reduces the magnitude of these phenomena or eliminates them.[5] The use of finely divided mercurous sulfate also tends to prevent the abnormal initial values, leads to greater constancy,[6] and reduces or eliminates the hysteresis.[4b]

Hulett[1a] has explained the high initial values, the decrease and the results of the rotation experiments by assuming that mercurous sulfate is hydrolyzed in solutions which contain less than 0.08 mole of sulfuric acid per liter, that the hydrolysis is very slow and that it is catalyzed by a mercury surface. This leads to the conclusion that the cathode system of the Weston cell is not in equilibrium, but that a constant electromotive force is the result of the establishment of a steady state at the mercury surface.[7] The tendency of acid in the electrolyte to prevent all the above-mentioned phenomena appears to favor the hydrolysis theory.

Against Hulett's theory may be mentioned the fact that only one basic mercurous sulfate is known, and according to Gouy[8] this basic mercurous sulfate is in equilibrium with the normal salt in 0.002 M sulfuric acid solution. It seems unlikely that the presence of cadmium sulfate in the solution should cause the large shift in the equilibrium demanded by Hulett's theory. If a solution saturated with cadmium sulfate and in equilibrium with the normal and basic mercurous sulfates contains sulfuric acid at a concentration of only 0.002 M, Hulett's theory fails. In this case the hydrolysis of only a small amount of mercurous sulfate would be necessary to bring the electrolyte of a Weston cell to the required concentration of acid, and true equilibrium would be possible.

The purpose of this paper is to suggest a more reasonable explanation for the high initial values, the lack of constancy, the abnormal values

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[3] Wolff and Waters, *Bur. Standards Bull.*, **4**, 81 (1907).

[4] (a) Wolff, *Bur. Standards Bull.*, **5**, 329 (1908). (b) Vosburgh and Eppley, THIS JOURNAL, **46**, 109 (1924).

[5] (a) Ref. 1 a, pp. 80, 89. (b) Smith, *Electrician*, **71**, 294 (1913). (c) Ref. 4 b, p. 110. (d) Ref. 1 d, pp. 1261, 1265.

[6] Ref. 1 a, p. 88.

[7] Hulett, *Phys. Rev.*, **30**, 654 (1910).

[8] (a) Gouy, *Compt. rend.*, **130**, 1400 (1900). The work of Gouy was confirmed at the National Physical Laboratory. (b) *Electrician*, **75**, 463 (1915).

obtained in the rotation experiments, and the hysteresis. It is assumed that the main factor in the cause of these phenomena is the presence of mercuric ion in the cathode system at a concentration in excess of that required for equilibrium. While some of the phenomena are not completely accounted for, the explanation given is useful in formulating the conditions necessary for the setting up of standard cells of the highest quality. It also leads to the important conclusion that the cathode system of the Weston cell, when properly set up, is a stable system and not metastable as Hulett suggested.

High Initial Values

When cells are set up without special precautions to protect the mercurous sulfate from the air during the process[9] the cells are liable to have abnormally high initial electromotive forces. This is illustrated by Table IA which gives the electromotive forces over a considerable period of cells which were selected as typical. Different groups of these cells were made at different times, and it is quite evident that the different groups, although apparently made the same way, did not agree. The electromotive forces of many were considerably higher than the normal at the start and decreased[10] as time went on. However, it has been shown[1d] that great improvement resulted if, in setting up the cells, the mercurous sulfate was washed first with a 2 *M* sulfuric acid solution and then by decantation in an atmosphere of nitrogen or carbon dioxide with the solution to be used in the cells. The object of this precaution was to free the mercurous sulfate paste from mercuric ion and to prevent subsequent oxidation. Care was taken to give as little chance for oxidation as possible while the mercurous sulfate was being transferred to the cell vessels after it was washed.

When this was done the resulting cells could be duplicated with respect to their electromotive forces, after the first month or two. The initial values were much smaller, and the electromotive forces decreased little or none at the start, and in some cases increased. On the other hand, when basic mercuric sulfate[11] was mixed with mercurous sulfate so treated, high initial values resulted in most cases, and the electromotive forces decreased slowly just as in the case of the other cells showing high initial

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[9] See Ref. 1 d, p. 1258.

[10] Some cells which are abnormally high at the start are constant. Such was the case with cells set up by Wolff and Waters [(a) Ref. 3, p. 65] with samples of commercial mercurous sulfate, with cells set up by Vosburgh and Eppley [(b) Ref. 4 b, p. 106] with finely divided mercurous sulfate, and with cells set up by Vosburgh [(c) Ref. 1 d, p. 1266] with alternating-current-electrolytic mercurous sulfate. The expression "high initial values" is taken in this paper to designate the abnormally high values of those new cells which begin immediately to decrease in electromotive force.

[11] Normal mercuric sulfate tends to hydrolyze in contact with solutions containing sulfuric acid at concentrations less than about 3.4 moles per liter, giving the compound $HgSO_4.2HgO$. Cox, *Z. anorg. Chem.*, **40,** 165 (1904).

values. This also is shown in Table I. That the reduction of the mercuric compound is slow under these conditions is shown by the fact that some of the yellow basic mercuric sulfate was observed to be present in cells two years after they were set up. The behavior of the cells containing basic mercuric sulfate, and the fact that exclusion of air while washing mercurous sulfate eliminated the trouble in ordinary cells, indicate that the presence of an excess of mercuric ion[12] is in most cases the cause of high initial values in Weston cells.

The fact that sulfuric acid in the electrolyte, and also in the wash solution, in concentrations of 0.02 mole per liter, or more, prevents the high initial values, even though air is not excluded in washing the mercurous sulfate, remains to be explained. The following is suggested. The solubility of basic mercuric sulfate in neutral solutions is low, but it increases with the acid concentration.[13] Before any solid basic mercuric sulfate is formed, the solution must be saturated with it. The higher the acidity of the solution the longer it would take to saturate the solution and the less chance there would be of depositing the solid mercuric compound during the time required for washing the mercurous sulfate and setting up the cells. Solid basic mercuric sulfate formed during the washing would, of course, be carried into the cell, while that retained by the wash solution would not.

This explanation was tested by two cells in the construction of which the mercurous sulfate was washed with an acid cadmium sulfate solution and introduced into the H-tubes with some of this solution. There was no protection from the air other than the use of the acid solution. After settling, all of the acid solution was decanted, the upper part of the paste and the tube were washed with a neutral solution and the tube was filled with a neutral solution. The electromotive forces over a period of five months, which are given below, showed very little tendency to start high and decrease.[14] They are 10–30 mmv. higher than the electromotive forces of neutral cells prepared with good protection from the air, as shown by comparison with Table IC, below. They do not, however, show the much higher initial values nearly always shown by cells made with a coarse-grained preparation of mercurous sulfate and a neutral electrolyte.

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[12] The high initial values of the cells set up by M. Laporte at the Bureau of Standards in 1910 ["Report to the International Committee on Electrical Units and Standards," Government Printing Office, Washington, **1912**, p. 109] are explainable on this basis. On account of interruptions, the washing, which was done in a Gooch crucible, was extended over several days. Thus, the mercurous sulfate used by M. Laporte must have had much more opportunity to be oxidized than the samples used by the other members of the Committee.

[13] Hoitsema, *Z. physik. Chem.*, **17**, 664 (1895).

[14] The electromotive forces at the start were considerably below the normal and increased to the values given during the first month.

Age of cells, months	1	2.5	5
E.m.f., Cell 474, v.	1.018077	1.018080	1.018079
E.m.f., Cell 475, v.	1.018088	1.018087	1.018081

The fact that these electromotive forces are a little higher than the usual values for neutral cells suggests another possible function of the acid in the electrolyte. This is to increase the velocity of reduction of mercuric ion by the mercury. If the electrolyte of Cells 474–475 had been left acid, the cells probably would have had normal values. Made neutral, the cells show values a little higher than the normal. If the velocity of reduction were increased by the presence of acid there would be a smaller concentration of mercuric ion in the vicinity of the mercury surface in acid cells than in neutral cells, other things being equal. This would account in part for the better results obtained with acid electrolytes.

Constancy

Cells which have high initial values are, of course, not constant in electromotive force for a considerable period following their construction. This can be explained as due to the gradual reduction of mercuric ion. When the excess of mercuric ion in the vicinity of the mercury electrode is exhausted, the cell should have the normal value. However, both Hulett[1a] and Smith[1c] have observed that cells which showed high initial values and which decreased in electromotive force did not always stop decreasing at any particular value. Some of them decreased so much as to be worthless. This is not explainable on the basis of the reduction of mercuric ion without further assumptions.

An examination of some experimental data on the variation in electromotive force of Weston cells will throw some new light on the subject. In Table I are given the electromotive forces, over periods of from four months to two years, of some cells which are typical of a large number. Table IA gives the results for cells prepared without protection from the air, by following approximately the procedure described by Wolff and Waters.[15] Table IB gives the results for some cells prepared with good protection from the air, but with some basic mercuric sulfate added to the mercurous sulfate paste. Table IC gives the results for the most carefully prepared cells that have been made with neutral electrolytes in this Laboratory.

The similarity between the high initial values of the cells made without protection from the air and those of the cells to which basic mercuric sulfate was added has been pointed out above. It is to be noted, in addition, that in both of these groups some of the cells decreased in electromotive force considerably below the much more constant cells of Table IC. With one exception, all of the cells which decreased in electromotive force below

[15] Ref. 3, p. 30.

TABLE I

CONSTANCY OF NORMAL WESTON CELLS

Cells	Concn. of acid, moles/liter	E.m.f. minus 1.018000 v., 25°						
		1 month, mmv.	4, mmv.	8, mmv.	12, mmv.	16, mmv.	20, mmv.	24–25, mmv.
A. CELLS MADE WITHOUT PROTECTION FROM THE AIR								
135	...	105	68	45	41	..	..	31
136	...	113	97	89	88	..	..	75
141	...	141	120	112	104	..	..	91
142	...	134	86	28	21	..	..	15
169	...	88	78	72	70	..	..	69
170	...	73	84	84	83	..	..	79
306	0.002	90	89	88	85	..	87	..
307	.002	70	84	82	84	..	86	..
222	.005	114	87	..	75	..	..	70
223	.005	111	79	..	66	..	..	61
225	.01	82	66	..	59	..	..	57
226	.01	83	65	..	59	..	..	58
237	.01	97	83	..	..	..	..	72
238	.01	87	77	..	..	..	..	67
B. CELLS TO WHICH BASIC MERCURIC SULFATE WAS ADDED[a]								
274	...	125	111	62	43	32	..	−16
275	...	207	209	108	18	00	..	−169
322	...	73	61	52	51	48	49	...
323	...	73	67	63	68	..	52	...
304	0.002	69	68	68	69	..	73	...
305	.002	53	59	59	52	..	51	...
271	.01	257	136	69	52	40	..	32
C. CELLS MADE WITH PROTECTION FROM THE AIR[b]								
320–321	...	61	60	58	54	52	49	..
350–351	...	57	50	..	..	40	..	..
397–406	...	57	66	..	70	..	..	..
450–452	...	71	69	..	..	..	..	..
471–473	...	61	60	..	..	..	..	..

[a] About 0.1 g. of basic mercuric sulfate was mixed with the mercurous sulfate in Cells 271, 274 and 275 and 0.02 g. in Cells 322 and 323. In the construction of Cells 304 and 305 about 0.01 g. of basic mercuric sulfate was placed on top of the mercurous sulfate.

[b] The cells of the various groups agreed well among themselves, in order to save space, average results for groups of 2 to 10 cells are given. Measurements of these cells were not obtained for the full two-year period because the cells were made considerably later than those of Tables IA and IB. Where blank spaces appear in the table, no measurements were made.

1.018050 v. were cells with neutral electrolytes. The cells with slightly acid electrolytes in Table IA all showed a decrease in electromotive force, but in all cases the decrease became very slow after the first year. Up to the second year only one, Cell 271, had gone below the value of similar cells prepared with protection of the mercurous sulfate from the air.[16]

Cells 274–275, in which as much basic mercuric sulfate was present as in Cell 271, but which had neutral electrolytes, decreased further below the normal value than Cell 271. The other cells of Table IB had less basic mercuric sulfate. Cells 322–323 had neutral electrolytes and decreased somewhat, although not much below the normal in 20 months. Cells 304–305 had slightly acid electrolytes, and the basic mercuric sulfate was put on top of the mercurous sulfate instead of being mixed with it. They did not show any appreciable decrease. Evidently, diffusion of the mercuric sulfate was slow and accompanied by diffusion of enough sulfuric acid to prevent abnormal conditions at the electrode.

The mere presence of hydrolyzed mercurous sulfate in a cell is not sufficient to cause an abnormally low electromotive force. Cells 324–325 were made with hydrolyzed mercurous sulfate mixed with the paste, special precautions being taken to exclude mercuric ion. They showed only a little greater decrease in electromotive force than Cells 320–321, which served as control cells, and after 20 months had practically the same electromotive force as these cells.

Age, months	12	16	20
E.m.f., Cells 324–325, v	1.018051	1.018055	1.018050

Evidently a decrease to an abnormally low value, at least during the first two years of the life of a cell, is connected with the reduction of a relatively large amount of mercuric ion in a solution of low hydrogen-ion concentration. Possibly normal mercurous sulfate prepared in an acid solution tends to go over slowly into a more stable state in the presence of a neutral saturated cadmium sulfate solution. This more stable state may be a solid solution. Its formation at any rate seems to be dependent on the maintenance of a low hydrogen-ion concentration. The reduction of mercuric ion in a solution of very low acid concentration seems to be a favorable condition for its formation, while the presence of 0.01 mole or even 0.005 mole of sulfuric acid per liter in the electrolyte seems to prevent it. This explanation is in accord with the slow decrease of some of the most carefully prepared neutral cells set up in this Laboratory. It seems reasonable to ascribe such a slow change to a reaction, or diffusion, in the solid phase rather than in the liquid phase.

[16] In two years, Cell 271 dropped to 1.018032 v. An examination of this cell showed that there was considerable yellowish-green compound in the layer of paste just above the mercury. Smith (Ref. 1 c) made a similar observation in some of his cells which had decreased abnormally. The color of this compound was that of basic nercurous sulfate. If basic mercurous sulfate was present it indicates that the concentration of acid must have been very low in the vicinity of the mercury surface and it is doubtful whether Cell 271 can be considered to be a true acid cell. There was some yellow, basic mercuric sulfate still present in the upper part of the paste of 271 also.

However, regardless of whether or not this explanation is the true one, some facts are apparent from Table I which are useful in outlining the conditions necessary for the construction of cells of the highest degree of constancy. The presence of small concentrations of sulfuric acid in the electrolyte, even when small amounts of mercuric compounds are present, prevents the decrease below the normal and insures constancy after the normal electromotive force is attained. Of a number of cells with electrolytes containing 0.005 to 0.011 mole of sulfuric acid per liter and prepared without any special protection from the air, none has been observed to go below the normal electromotive force in two years.

The results in Table I are based on the assumption that the cells used as reference standards were constant. Some evidence as to the constancy of these cells has been given in a previous paper.[1d] Furthermore, a large number of carefully prepared cells were found to be constant in the previous investigation if Cells 1, 2, 4, 5, 7–9, 11 and 12 were assumed to be constant. These reference standards were made with electrolytes containing 0.011 mole of sulfuric acid per liter.[17] They were compared frequently with three cells made at the National Physical Laboratory[17] which were considerably older. Shortly after the first cells with which this investigation is concerned were made, the three British cells had the average value 1.018012 v. when the average value 1.018049 v. was assigned to the standards. More than two years later, after nearly all of the measurements of this investigation had been made, the British cells had the average value 1.018017 v. Assuming the latter to be the constant value, a decrease of 5 mmv. in the standards is indicated. However, the British cells varied a little among themselves during this period and may have increased a little.

When the standards were 21 months old, while the measurements of the present investigation were being taken, Cells 353–356 were made to duplicate them. The results are given in the earlier paper,[1d] the average value of the new cells after the aging period being 1.018046 v. More than a year later two new groups of cells were made, Cells 492–494 and 495–497, with new preparations of mercurous sulfate. When they were three months old, the average electromotive force of Cells 492–494 was 1.018060 v. and that of Cells 495–497 was 1.018053 v. Even if all of the difference between the standards and the newest cells is ascribed to a decrease in the former, the decrease is not large. It is probable, however, that part of the difference between the standards and the newest cells is due to the difficulty of reproducing cells with different preparations of mercurous sulfate to better than about 10 mmv., or 0.001%. It is to be concluded, therefore, that there was little change in the standards during the investigation.

[17] Vosburgh and Eppley, This Journal, **45**, 2270 (1923).

Rotation Experiments

The results of the experiments of Hulett[18] on partially mixing the contents of the cathode portion of a cell by rotation can be satisfactorily explained otherwise than on the basis of hydrolysis. According to the hydrolysis theory, the high and decreasing electromotive force after the rotation was due to the low but increasing concentration of acid at the mercury surface, and the efforts toward the reëstablishment of a steady state. A better explanation is afforded by assuming that mercuric ion was present in the main body of the solution at a concentration greater than the equilibrium concentration. When the cell was at rest, equilibrium was maintained at the mercury surface by the reduction of mercuric ion as fast as it diffused to the mercury.[19] When the contents were mixed and allowed to come to rest again, an excess of mercuric ion was present in the solution at the mercury surface. This caused the electromotive force to be abnormally high, and the excess had to be reduced before the normal electromotive force was reattained. Thus the high electromotive forces in the rotation experiments are explainable on the same basis as the high initial values, which seems reasonable.

The change in the increase in electromotive force, as rotation was continued over a period of a week or two, is less easily explained. The change was in the direction corresponding to an increase in the amount of mercuric ion in the cell. Perhaps it could have been caused by oxygen in the tube. One cc. of air contains sufficient oxygen to oxidize 0.008 g. of mercurous sulfate to mercuric sulfate, forming the equivalent of about the same weight of basic mercuric sulfate. However, there is so little known about equilibrium conditions in the solution in question, and the rate of attainment of equilibrium, that other factors may be overlooked.

In view of the precautions necessary to prevent high initial values it is not unreasonable to assume the presence of mercuric ion in Hulett's rotation cells. The mercurous sulfate which he used was a pure white preparation. In setting up the cathode systems to be rotated this mercurous sulfate was washed thoroughly with sulfuric acid solution, which may have removed mercuric ion, then with absolute alcohol and finally with the solution to be used in the cells. In the case of a neutral solution this gave a chance for oxidation without the chance for removal of the product. It has been shown[1d] that in the preparation of neutral cells,

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[18] Ref. 1 b, pp. 73–80.

[19] Diffusion was made slow by the thick layer of mercurous sulfate through which the mercuric ion had to pass. That a cell can contain mercuric sulfate and still show the normal electromotive force was made evident by Cells 304–305 mentioned above. Basic mercuric sulfate was dropped in on top of the mercurous sulfate when these cells were set up. After a year, its bright yellow color showed that some of it was still present. The cells varied little more than control cells to which no mercuric sulfate was added and had practically the same electromotive force.

when a coarse preparation of mercurous sulfate is used, it is necessary to wash in an inert atmosphere to prevent high initial values. Also, Hulett's solutions were not freed from oxygen, and a little air must have been present in the tube during the rotation. It is true that in an earlier rotation experiment[20] the solution was freed from oxygen and the *final* washings of the mercurous sulfate were made with this solution. However, no evidence was given that the mercurous sulfate was entirely free from mercuric ion before the final washings. Also, some oxidation may have taken place while the washed mercurous sulfate was being transferred to the tube in which the cathode system was set up.

Wolff and Waters[3] in their rotation experiments arranged the cells in such a way that they were hermetically sealed and contained only a very small bubble of air. They found less change in electromotive force than Hulett did. On continuing the rotation there was a tendency in some of the cells to reach a maximum and then, on further rotation, to decrease and approach the normal. This would be expected on the basis of the above hypothesis. For a time the amount of mercuric compound would increase, as a result of the reaction of oxygen with the mercurous sulfate. The rate of oxidation would decrease as the oxygen supply was exhausted and would finally become less than the rate of reduction. After this the increase in electromotive force after rotation would be less than before and would continue to decrease.

Some of the cells of Wolff and Waters were set up with gray mercurous sulfate, and in these the change was considerably less than in the others. This can be explained as due to a larger rate of reduction caused by the presence of finely divided mercury. Also it is to be recalled that when air is not excluded in setting up cells, gray mercurous sulfate gives the best results. White mercurous sulfate gives higher initial values than the gray, indicating that the latter is less contaminated with mercuric ion as a rule than the former.

Hysteresis

Wolff[4a] noticed that some of his cells showed considerable hysteresis when the temperature was decreased. The cells which showed the most hysteresis were made with coarse-grained, white mercurous sulfate. The same cells had high initial values. At the National Physical Laboratory[21] it was found that cells containing "more than a percentage of acid" did not show any hysteresis and also that hysteresis increased with the age of the cells. Vosburgh and Eppley[4b] showed that the magnitude of the hysteresis was dependent on the grain size of the mercurous sulfate, being much less for fine-grained than for coarse-grained mercurous sulfate, and that the addition of sulfuric acid to cells showing considerable

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[20] Ref. 1 b, p. 19.

[21] National Physical Laboratory, *Electrician*, **71**, 294 (1913).

hysteresis greatly reduced it. Finally, the hysteresis in some portable cells, in which the mercury and mercurous sulfate were held tightly in place by a cork disk, was much greater than that of non-portable cells prepared from similar materials.[22] The hysteresis varied considerably among cells made with the same materials, and these generalizations were based on average results for groups of cells.

When the temperature is raised no hysteresis results. The electromotive forces reach a constant value as soon as the cells are brought to a constant and uniform temperature, but if the temperature be decreased again, an abnormally high electromotive force results. This is not constant, but decreases, rapidly at first, then more slowly, finally becoming constant at the proper value for that temperature. This behavior recalls both the high initial values of cells and the high values in the rotation experiments. It is reasonable to assume that the cause is the same—an excess of mercuric ion at the cathode.

Equilibrium in the system mercury, mercurous ion and mercuric ion can be expected to vary with the temperature, the variable factor being the ratio of mercuric ion to mercurous ion. If this ratio increases with the temperature, the hysteresis can be explained. When the temperature increases, more mercuric ion would be required for equilibrium. Mercuric ion could be formed by precipitation of mercury from mercurous ion; $Hg_2^{++} \longrightarrow Hg^{++} + Hg$. When mercurous chloride is heated with a potassium chloride solution almost to the boiling point it becomes gray, doubtless because of the formation of finely divided mercury. Mercurous sulfate heated with a neutral cadmium sulfate solution shows a similar change in color, but the presence of a small amount of acid prevents it.

When the temperature decreases, the reverse reaction would have to take place, but this is a heterogeneous reaction and observations on the initial values of cells containing basic mercuric sulfate show it to be slow. In consequence there is at the lower temperature a temporary excess of mercuric ion in the cell, which causes an abnormally high electromotive force, just as it would if it had been placed there when the cell was constructed. Therefore, the hysteresis of Weston cells can be explained as due to the slow establishment of equilibrium between mercury, mercurous ion and mercuric ion after a decrease in temperature.

If this explanation is true, the abnormal electromotive force of a cell showing hysteresis should disappear if the cell is heated again to the highest temperature attained before it was cooled to produce the hysteresis. This has already been shown to be the case with portable, unsaturated cells.[23] It was tried with some non-portable saturated cells also, and the results are given in Table II.

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[22] Vosburgh and Eppley, *J. Optical Soc. Am.*, 9, 67 (1924).

[23] Ref. 22, p. 69.

The cells used were cells with neutral electrolytes which were carefully prepared to avoid high initial values. They were brought to equilibrium at 35°, then transferred to a thermostat at 25°, left for one day and the electromotive forces were measured. The differences between these results and the equilibrium values at 25° are given in the fourth column of the table. The cells evidently showed considerable hysteresis. After this measurement the cells were transferred back to the thermostat at 35° and the electromotive forces were measured again a day later with the results given in the fifth column. It is shown that the change to 25° and back again had no effect on the equilibrium at 35° even though the drop in temperature had a large effect at the lower temperature. The same procedure was repeated during the next two days with the same result.

TABLE II

EFFECT OF INCREASE OF TEMPERATURE ON CELLS SHOWING HYSTERESIS

			E.m.f. minus equilibrium e.m.f.			
Cells	E.m.f., 25° equilibrium, v.	E.m.f., 35° equilibrium, v.	1st day, 25°, mmv.	2d, 35°, mmv.	3d, 25°, mmv.	4th, 35°, mmv.
278	1.018067[a]	1.017502	233	1	160	2
279	1.018060[a]	1.017495	232	−1	169	6
280	1.018060[a]	1.017495	369	0	290	5
281	1.018071[a]	1.017506	211	0	169	9
450	1.018074	1.017505	43	1	31	−2
451	1.018064	1.017501	58	0	46	−1
452	1.018068	1.017503	60	3	46	−2

[a] Calculated from the 35° values.

It is not possible to explain in detail the effect of acid in decreasing hysteresis. It may be that the acid increases the rate of reduction of the mercuric ion by mercury. An effect of the acid resulting in a smaller temporary excess of mercuric ion present after a temperature decrease is also possible.

The equilibrium in a solution saturated with cadmium and mercurous sulfates and containing mercuric ion and free sulfuric acid is probably a rather complicated one. Hulett has shown that when the concentration of free acid is low the solubility of mercurous sulfate decreases very rapidly as the concentration of free acid increases. As the acid concentration becomes greater the decrease becomes less and finally constant. It does not seem unreasonable, then, to expect that free acid would alter the equilibrium conditions in such a way that there would be less of a change in mercuric-ion activity as the temperature changed. This would result in less hysteresis than in the case of a neutral solution.

The effect of finely divided mercurous sulfate in reducing hysteresis is caused probably by its reducing the amount of solution in immediate contact with the mercury and reducing the velocity of diffusion to the mercury. If the amount of solution at the mercury surface and the velocity of diffusion are sufficiently small, the mercury can maintain equilibrium in the solution in contact with it at all times. Differences in these two factors in different cells account for the large differences in hysteresis in cells apparently made in the same way.

The increase in hysteresis with the age of the cell cannot be satisfactorily accounted for at present. The attainment of equilibrium in the cathode system must be a slow process. This is in agreement with the fact that some of the best cells do not attain constant electromotive forces until they are one or two months old.

One practical consequence of the above theory is that hysteresis must be regarded as natural in cells with electrolytes of low acid concentration.[24] Standard cells which show considerable hysteresis are not good standards. The hysteresis can be avoided by using finely divided mercurous sulfate. This has the disadvantage of being liable to cause high electromotive forces.[25] Neutral cells have the disadvantage that after temperature decreases, mercuric ion will have to be reduced in a solution of low hydrogen-ion concentration, which, as shown above, seems to be connected with a slow decrease in the electromotive force. Therefore, cells with slightly acid electrolytes are preferable as standards. They show less hysteresis, and the reduction of mercuric ion at the mercury surface should do no harm.

Acid Cells and the Phase Rule

Van Ginneken and Kruyt[26] have defined a standard cell as a cell composed of two parts both of which are invariant systems of the same components, temperature and pressure being constant. The electromotive force of such a cell is not altered by current passing in either direction, or by diffusion and internal action. The Weston normal cell, made with a neutral electrolyte, apparently conforms to this specification, but when sulfuric acid is added to the electrolyte another component is added without an additional phase, and both electrode systems become univariant. Passage of current in this case would either remove water and hydrated cadmium sulfate from the solution, or add them to it, according to the direction of the current. The result would be either an increase or a decrease in the concentration of acid. As the electromotive force varies with the concentration of acid, an acid cell is not a true standard cell.

However, when the concentration of acid is sufficiently small, the acid cell will have, for all practical purposes, the properties of a true standard cell. For example, if the electrolyte contains 0.01 mole of sulfuric acid per liter, a 10% increase in the acid concentration would cause a decrease in the electromotive force of only 2 mmv. To cause a 10% increase in

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[24] Compare **Ref. 22.**

[25] Ref. 4 b, p. 104.

[26] Van Ginneken and Kruyt, *Z. physik. Chem.*, **77**, 758 (1911).

the acid concentration in an ordinary cell nearly all of the mercurous sulfate would have to react with cadmium. Under the usual conditions only a small amount of the mercurous sulfate of a cell is used up in several years, so a variation in the electromotive force due to this cause is not to be feared.

Short-circuiting a cell, and the reaction of cadmium with the mercurous sulfate diffusing to the anode, would tend to increase the acid concentration of the electrolyte. The reaction of hydrogen ion with cadmium, the reduction of basic mercuric sulfate by mercury, and the clean-up of any oxygen in the cell would result in a decrease in the acid concentration. Reaction of cadmium with hydrogen ion is negligible in the most dilute acid solutions, when a sufficiently pure amalgam is used. The amount of acid used by the reduction of basic mercuric sulfate and by the clean-up of oxygen depends on the care with which the cell is constructed, and should be reducible to a very small quantity. The clean-up of oxygen should be very slow even if considerable oxygen is present. Therefore, since a small acid concentration in the electrolyte of a cell will not change appreciably with time, a normal Weston cell with a slightly acid electrolyte can be considered to be practically a true standard cell.

Conclusions

It is to be concluded that the high initial values and the apparently abnormal results of mixing the cathode systems of standard cells are due to the presence of an excess of mercuric ion as an impurity. Lack of constancy may be caused by the presence of mercuric ion, but may also be found in the most carefully prepared cells with neutral electrolytes. Perhaps traces of oxygen, or of mercuric ion, were introduced into these cells, but on the basis of present data it cannot be concluded that the cathode system of a cell with a neutral electrolyte is in stable equilibrium. However, a small acid concentration, about 0.01 mole per liter, or less, will insure constancy, and there is no reason to believe that the cathode system of an acid cell is not in stable equilibrium.

Hysteresis is best explained as due to a shift in the equilibrium between mercurous and mercuric ions and mercury with temperature. With an increase in temperature, mercuric ion is formed, and after a decrease in temperature an excess of mercuric ion is present. This leads to a condition quite similar to that in cells showing high initial values.

It is apparent that Weston cells with slightly acid electrolytes are preferable to cells with neutral electrolytes. Too much acid, however, would lead to reaction of hydrogen ion and cadmium, giving hydrogen which is troublesome. It would also be objectionable on account of making the electrode systems univariant. Evidently there must be an optimum concentration of acid. An acid concentration of about 0.01 mole per liter, about the concentration used in the reference standards, has been found to be satisfactory. It is sufficient to give good reproducibility and constancy, but does not make the electrode systems appreciably univariant or allow an appreciable reaction of hydrogen ion with the cadmium of the amalgam. Non-portable cells made with such an electrolyte and with protection of the mercurous sulfate from the air during construction are very satisfactory.

Summary

1. Abnormally high initial electromotive forces in Weston standard cells and the high values resulting from mixing the contents of the cathode portions of cells can be explained as caused by the presence of an excess of mercuric ion as an impurity.
2. Some cells with electrolytes to which no sulfuric acid was added tend to decrease in electromotive force indefinitely. The presence of mercuric ion in the cell at the start makes this decrease more pronounced. The presence of a small amount of sulfuric acid in the electrolyte prevents a decrease below the normal value. Acid cells are more reliable than neutral cells.
3. Hysteresis is explained as caused by a shift in the equilibrium between mercury, mercurous ion and mercuric ion with temperature. This leaves an excess of mercuric ion in the cell after a decrease in temperature.
4. The presence of sulfuric acid in a cell makes the two electrode systems univariant, with constant pressure and temperature, instead of invariant, as they should be in a true standard cell. However, the acid concentration can be made low enough to make the electrode systems practically invariant without losing the good effects of the acid.
5. While there is a question as to the stability of the cathode system of a Weston cell with a neutral electrolyte, it is probable that the cathode system of an acid cell is in stable equilibrium.
6. An acid concentration of about 0.01 mole per liter in the electrolyte of a Weston cell has been found very satisfactory.

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