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HYSTERESIS IN STANDARD CELLS

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Introduction

The theory has been advanced by Vosburgh[1] that the hysteresis observed when standard cells are subjected to a lowering of temperature is due to an excess of mercuric ions in the electrolyte. He considers that the equilibrium

$$Hg_2^{++} \rightleftharpoons Hg + Hg^{++}$$

which operates at the mercury surface in such cells is displaced to the right when the temperature of a cell is raised. The reverse reaction, which occurs on cooling, is a heterogeneous reaction and would be expected to take place more slowly than the dissociation caused by heating. Until the excess of mercuric ion thus present in a cell after cooling has been removed, the electromotive force is abnormally high.

On the basis of this theory he endeavored to account for earlier observations relating to hysteresis. The fact that cells containing a fine-grained sample of mercurous sulfate show less hysteresis than those containing a coarser material[2] he attributed to the smaller amount of solution in immediate contact with the mercury surface, and the reduced velocity of diffusion of mercuric ions to this surface in cells of the former type, making it possible for the mercury to maintain equilibrium with the solution at all times. The decrease in hysteresis caused by the presence of acid in a cell[2c,3] was considered to be due to a catalytic effect of the acid upon the above reaction. The increase in hysteresis with the age of a cell[3] could not be explained.

The temperature coefficient of the saturated cadmium cell is negative.[2b] A simple hysteresis on cooling the cell would be expected to appear as a low e.m.f., gradually rising toward the equilibrium value. The usual observation, however, is a rapid increase in e.m.f. to a value *above* that predicted by the temperature formula, followed by a slow decrease to equilibrium. The former type of hysteresis has been observed[4,2c] and associated with the use of large crystals of cadmium sulfate in the cells. It is obvious that we are dealing with two distinct effects and must turn to a

[1] Vosburgh, THIS JOURNAL, **49**, 78 (1927).

[2] (a) Von Steinwehr, *Z. Instrumentenk.*, **25**, 205 (1905); (b) Wolff, *Bull. Bur. Standards*, **5**, 309 (1908); (c) Vosburgh and Eppley, THIS JOURNAL, **46**, 104 (1924).

[3] National Physical Lab. Reports, *Electrician*, **71**, 294 (1913).

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

study of the sources of each of these effects if we would understand them more fully.[5]

This paper reports the results of an experimental study of the hysteresis shown by the separate electrodes of the cadmium cell. The results are not in agreement with Vosburgh's theory, and a more satisfactory explanation is presented for the observed facts.

Experimental Methods and Results

Apparatus and Materials.—The "adjustable cells"[6] used in studies of the cathode equilibrium in standard cells were a convenient form of cell for use in studying hysteresis in the separate limbs of cells. The anode and cathode half-cells of which these were made could be subjected separately to any desired temperature change, and tested under the new condition by measuring their potentials in opposition to another half-cell which had been brought to equilibrium previously at the new temperature.

The materials used in the construction of cells were those described in a previous paper.[7] The thermostats were maintained at 25 and 35°, respectively, with an accuracy of ±0.02°. E.m.f.'s were measured by the methods previously described,[7] with reference to standards maintained constantly at 25.00°. The effects of both heating and cooling the separate limbs of the cells were studied.

Hysteresis at the Anode.—Anode half-cells were transferred from the 25° bath to the 35° bath. A cathode half-cell which was kept in the 35° bath was used as a test electrode and the e.m.f's of the cells formed by combining this with the various anodes were measured at frequent intervals. In every case their values became constant within fifteen minutes after the change in temperature, and were in good agreement with the values calculated by use of the Wolff formula. After one hour the anodes were returned to the 25° bath and placed in opposition to cathodes which had been kept in this bath, and against which they had been tested previously. The results of measurements on two anodes, S_1, which contained large crystals of cadmium sulfate (average size about 2 mm.) and S_2, in which finely ground crystals were used, are given in Table I. The values are given as differences in microvolts from their former values at 25°.

[5] F. E. Smith, *Phil. Mag.*, **19**, 250 (1910), found an additional type of hysteresis that occurred in the amalgam when it was subjected to sudden temperature changes of 50° or more. He considered this to be due to a slow establishment of equilibrium between the liquid and solid phases of the amalgam. A more detailed theoretical investigation of this case, based upon the theory of solid solutions, was presented by S. W. J. Smith, *Phil. Mag.*, **20**, 206 (1910). In the present work, which deals with manifestations of hysteresis likely to be met in the actual use of cells, we are not concerned with hysteresis of this type.

[6] Hulett, *Phys. Rev.*, **25**, 16 (1907).

[7] Niederhauser and Hulett, THIS JOURNAL, **51**, 2327 (1929).

TABLE I

HYSTERESIS IN ANODE LIMBS OF CELLS AFTER A SUDDEN CHANGE IN TEMPERATURE FROM 35 TO 25°

Time, minutes		10	15	20	25	30	35	40	50	65	85
Diff. from normal value at 25°, mmv.	S_1	−445	−345	−245	−195	−150	−115	−95	−57	−30	−14
	S_2	−2	0	0	0	0	0	0	0	0	0

The effect of large crystals of cadmium sulfate, first described by Wold, is shown by these results.

It was also found that placing a cell in the 35° bath for as short a time as three minutes caused hysteresis nearly as great as that shown above, when the cell was again cooled to 25°.

Hysteresis at the Cathode.—A similar method of study was applied to the cathode limbs of cells. Because of the practically complete absence of hysteresis in the anode limbs of cells containing finely-ground cadmium sulfate crystals, it was also possible to consider that hysteresis in such cells was located entirely in the cathodes. Some typical results are given in Table II, showing the hysteresis in the cathode limbs of cells containing a paste composed of different sized crystals of mercurous sulfate mixed with finely-powdered crystals of cadmium sulfate. The cells had been kept for one hour in the 35° bath and had attained constant values at that temperature, in practical agreement with the Wolff formula, well within that time. The average grain size of the mercurous sulfate used in the cells is indicated in each case.

TABLE II

HYSTERESIS IN CATHODE LIMBS OF CELLS AFTER A SUDDEN CHANGE IN TEMPERATURE FROM 35 TO 25°

Time, hours	Differences in mmv. from normal value at 25°			
	S_5 − 10μ	S_7 − 25μ	X_{53} − 50μ	X_{51} − 150μ[a]
1	+82	+90	+298	+936
5	63	77	197	842
10	55	70	169	774
24	44	58	117	655
48	38	47	79	482
72	35	41	68	333

[a] The large crystals used in cells X_{51} and X_{53} were obtained by recrystallization from a hot acid solution.

The relationship between the size of mercurous sulfate crystals and hysteresis in the cathode limb[2] is confirmed. It is also noted that the disappearance of hysteresis in this limb is very much slower than that in the anode limb.

Here again, placing the cells in the 35° bath for three minutes caused hysteresis, nearly as great as that shown above, when the cells were returned to 25°.

Effect of Temperature Changes on Cathodes Containing No Solid Mercurous Sulfate.—Cathode half-cells were constructed in which the electrolyte was a solution saturated with mercurous sulfate and cadmium sulfate at 25°, but which contained no solid mercurous sulfate.[8]

The effect of temperature changes upon these elements was studied in the manner previously described. There was absolutely no hysteresis observed, either on heating or cooling. They reached constant values at 35° as quickly as temperature equilibrium was attained and showed a similar rapid return to their previous values at 25° when cooled to this temperature. The potential of the cell formed by this element and a normal anode half-cell at 35° was not that predicted for the normal cell by the Wolff formula. The formula predicts a decrease in potential of 563 mmv. on raising the temperature of the cell from 25 to 35°. This cell showed a decrease of 4120 mmv. Obviously the temperature coefficient of such a limb is very much different from one that contains solid salt.

Discussion

F. E. Smith[5] has shown that the temperature coefficient of the anode limb of the saturated cadmium cell is −0.00035 volt per degree, and that of the cathode limb is +0.00031 volt per degree, making the over-all-temperature coefficient of the cell −0.00004 volt per degree, in agreement with the Wolff formula. The hysteresis shown in each limb of the cell corresponds then, to a slow continuous adjustment of that limb to equilibrium at the new temperature, and the anomalous nature of the hysteresis shown by the cell as a whole is due to the more rapid adjustment of the anode limb to the new temperature, leaving the cathode effect predominant.

In the anode limb the size of the cadmium sulfate crystals is found to determine the magnitude of hysteresis. The only function of these crystals is to maintain saturation in the solution. The solubility of cadmium sulfate increases with temperature, and a denser solution is formed at the surfaces of the crystals when the temperature is raised. Convection currents immediately carry this solution downward to the amalgam surface, where a layer of the saturated solution soon forms. Equilibrium at the electrode is thus quickly established. On cooling the cell, cadmium sulfate must crystallize from the solution and it can do this only at the surfaces of the crystals already present. It must reach these surfaces of the crystals already present. It must reach these surfaces by diffusion. In large-crystal cells the distances through which diffusion must take place are greater, and the available surface is less than in cells containing small crystals. The rate at which a state of supersaturation is relieved by crystallization of the excess solute is slower in the former case, and the

[8] The solution was prepared by rotating a saturated solution of cadmium sulfate with solid mercurous sulfate and mercury (ref. 6). Solid cadmium sulfate was added to cells built with this solution so that saturation with respect to this salt would be maintained in the experiments which followed.

longer time required for such cells to reach equilibrium upon lowering the temperature is thus explained.

A similar explanation appears to be the most reasonable one to apply to the cathode limb. The abnormal temperature coefficient shown by a cathode that contained no solid mercurous sulfate indicates that an important role of this substance in the cell is to maintain saturation of the solution at the mercury surface at varying temperatures. The extremely long time taken for the disappearance of hysteresis in this limb in some cases is surprising. The high viscosity of the electrolyte is undoubtedly a factor in preventing a more rapid establishment of equilibrium.[9]

Vosburgh has entirely overlooked the change in solubility of mercurous sulfate with temperature in his consideration of hysteresis. The fact that cells containing no solid mercurous sulfate showed immediate responses to temperature changes is out of accord with this theory, which would predict a maximum of hysteresis in such cells.

The effect of acid in diminishing hysteresis is, from the point of view here presented, the same as its effect in diminishing polarization and accelerating the disappearance of polarization in cells.[7] It appears to increase the rates of crystallization and solution at the crystal surfaces.

The increase in magnitude of hysteresis with the age of cells, which Vosburgh was unable to explain, may be attributed to the same cause as the increase in polarization with the age of cells. We have considered that the surfaces of the crystals become more and more nearly perfect during long contact with their saturated solution. They then show a lower rate of solution or of crystallization than the imperfect crystals first placed in the cells. As the rate of crystallization is thus decreased with age, the hysteresis, which depends upon it, increases.

A study of the effect of temperature upon the solubility of mercurous sulfate in saturated cadmium sulfate solution, and of the mercurous–mercuric ion equilibrium in these solutions in contact with mercury, is now in progress. The results of this work will serve as a final test of the theories advanced to explain hysteresis in cells.

High Initial Values of Cells

Wolff[2b] observed that cells which showed abnormal hysteresis had also shown high initial values, which dropped rapidly during the first month after their construction and finally became nearly normal. He considered that this was because the cells were constructed in a laboratory where the temperature was different from that of the thermostats in which they were subsequently placed. But thermostats are usually maintained, except under

[9] Menzies and Potter, This Journal, **34**, 1452 (1912), have shown that supersaturation may continue over very long periods of time in a viscous solution of H_3AsO_4, even though the solution is being stirred and a large number of nuclei are present to induce crystallization. The present case seems to be analogous to theirs.

special circumstances, at temperatures above room temperature, and we have seen that a change to higher temperatures is not attended by marked hysteresis. Wolff's explanation therefore, does not appear probable.

Vosburgh[10] considered that the high initial values were due to oxidation of the mercurous sulfate during the preparation of the paste and its introduction into the cells, the excess of mercuric salt being only slowly reduced at the mercury surface. He set up cells with great care to prevent access of air to the paste. The records of these cells, as well as those of cells set up without taking such precautions, are given in his papers. The cells made with protection from air are, on the whole, better than those made without such protection, yet some of the latter cells (Nos. 169 and 170) are quite as good as those of the protected group. The cells of the unprotected group which showed the most abnormal values were made from a different sample of mercurous sulfate than those of the protected group. It appears that there are factors other than the possible oxidation of the mercurous sulfate which must be considered in accounting for the high initial values of cells.

The fact noted in the hysteresis experiments that raising the temperature of a cell to 35° for as short a time as three minutes caused hysteresis effects when the cell was again returned to 25° suggested that a very short period of overheating during the construction of cells might cause them to show high initial values. As the temperature of the hand is usually above 30°, such overheating could come from simply holding the cells in the hand. Experimental evidence for this was obtained by warming old cells in the hand for several minutes and then returning them to the 25° bath from which they had been taken. In every case a large increase in e.m.f. was observed, which persisted for several weeks.

New cells were built, therefore, taking great care to avoid warming them above 25° at any time. The laboratory temperature was about 22° and the cells were cooled to 15° just before sealing. For the manipulations in the flame, during the sealing of these cells, they were held by means of a clamp fixed on the cross-arm, and an asbestos guard was used to protect the lower parts of the cells from the heat of the flame. No attempt was made to exclude oxygen from the cells, although the operations connected with the preparation and introduction of the paste were carried on as rapidly as possible.

Table III shows the values of cells made in this way compared with those of cells made by the old methods, in which the lower parts of the cells were supported in the fingers while sealing them. All of these cells were made from the same materials. The mercurous sulfate was a white electrolytic product, the average grain size of which was about 25 microns. Cells 55 and 56 were the first two cells set up in the new way. About a

[10] Vosburgh, This Journal, **47**, 1225 (1925); **49**, 78 (1927).

month later the next four cells, 57–60, were built. Of these four, 57 and 59 were sealed in the new way, while 58 and 60 received the same treatment throughout except for the sealing, which was done in the old way. The values of four other cells, 41–44, which were set up several months earlier and were not measured until they were a day old, are also included for comparison. The values of the cells of each group agreed with each other within a few microvolts, and are averaged in the table.

Table III

Comparison of Cells Built with and without Care to Avoid Heating above 25° during Construction[a]

Age of cells	E.m.f. at 25.00°[b] 55 and 56	57 and 59	58 and 60	41–44
15 minutes	1.018060	1.018036	1.018218	......
30 minutes	1.018068	1.018048	1.018206	......
75 minutes	1.018074	1.018058	1.018188	......
4 hours	1.018076	1.018071	1.018164	......
1 day	......	1.018072	1.018128	1.018121
2 days	1.018069	1.018070	1.018106	......
3 days	......	......	......	1.018099
5 days	....	1.018067	1.018089	......
1 week	1.018070	1.108070	1.018085	1.018084
2 weeks	1.018072	1.018074	1.018084	1.018080
1 month	0.018075	......	......	1.018080
2 months	......	......	......	1.018079

[a] Where blank spaces appear in the above table no readings were taken.

[b] The value of the Weston normal cell at this temperature, according to the Wolff formula, is 1.018074 volts.

The effect of such heating is clearly shown to account for the high initial values of these cells. It is interesting to note that cells made by the new method reached values within a few microvolts of the defined value in less than four hours, and, although they have varied slightly from time to time, they have been very close to that value ever since.

Summary

An experimental study has been made of the adjustment of the individual limbs of standard cells to temperature changes.

A new theory is suggested to explain hysteresis, which is based upon the rate of establishment of saturation equilibrium between the solution and the solid salts present in the cells.

The high values of new cells, which decrease during the first month or so, have been shown to be due, at least in part, to hysteresis which results from overheating them in the course of construction. A method of avoiding this trouble has given excellent results in the construction of cells which reached normal values within a few hours after they were built.

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