$$\begin{aligned}GeH_3I + HI &= GeH_2I_2 + H_2\\ GeH_2I_2 + HI &= GeHI_2 + H_2\\ GeHI_3 &= GeI_2 + HI\end{aligned}$$

The formation of germanium di-iodide was established by first pumping off the hydrogen, monogermane and hydrogen iodide from the reaction bulb and then adding an excess of hydriodic acid to the yellow residue in the bulb. This dissolved the substance and the filtered solution deposited, on cooling, yellow, feathery crystals[6] of GeI_2. Some GeI_4 was also present, this being formed by the dissociation of some of the di-iodide

$$2\,GeI_2 = GeI_4 + Ge$$

The end-products of the reaction between monogermane and hydrogen iodide therefore appear to be germanium di-iodide, hydrogen and some germanium tetra-iodide.

Summary

This article deals with the preparation and properties of monochloromonogermane, dichloromonogermane, monobromomonogermane and dibromomonogermane. Evidence was obtained that indicated the formation of the corresponding iodo compounds which, however, could not be isolated because of their instability.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY]

POLARIZATION IN STANDARD CELLS

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Introduction

Experimental studies of the effects of withdrawing current from standard cells[1] have shown these cells to be subject to a considerable degree of polarization, even at relatively low currents. It has also appeared that the polarization is roughly proportional to the strength of current, and that the cells recover quite satisfactorily following polarization, provided it has not been too prolonged. The passage of a current in the reverse direction through the cells also causes polarization, which, from the published results, appears to be somewhat more severe and of longer duration than that produced by discharging.[1e,f]

In all of the work mentioned above the cell has been considered as a

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[1] (a) Rayleigh and Sidgwick, *Trans. Roy. Soc. London*, **175A**, 411 (1884); (b) Threlfall and Pollock, *Phil. Mag.*, **28**, 353 (1889); (c) Skinner, *ibid.*, **38**, 271 (1894); (d) Wulf, *Sitzb. Akad. Wiss. Wien*, Abt. IIa, **106**, 562 (1897); (e) Barnett, *Phys. Rev.*, **18**, 104 (1904); (f) Smith, *Trans. Roy. Soc. London*, **207A**, 393 (1908); (g) Wold, *Phys. Rev.*, **28**, 132 (1909); (h) Hackett and Feely, *Sci. Proc. Roy. Dublin Soc.*, **15**, 279 (1918).

single unit and the results refer to the total polarization. This is, of course, the sum of the polarizations of the individual electrodes, quantities which may be widely different. Jaeger, in a theoretical treatment of the polarization of such cells,[2] deals with the cases of the individual electrodes and mentions some experimental work done by Lindeck in which measurements were made of these separate effects. That a more complete report of Lindeck's work does not appear to have been published is regrettable, inasmuch as the results of the one experiment mentioned by Jaeger are in direct contradiction to those which are here presented. No other work on these single effects in standard cells has been found in the literature.

This paper presents the results of a study of the polarization of the individual limbs of the saturated, unsaturated and acid cadmium cells, and of the zinc cell at very low currents. Both the effects of discharging and of charging the cells are studied, and the results are interpreted in terms of the processes which take place at the separate electrodes during and after the passage of the current. No attempt is made to apply a theoretical treatment, such as that proposed by Jaeger, to the results, since the factors entering into such a treatment (ionic mobilities, rates of diffusion, and rates of solution and of crystallization of the salts present) are too uncertain to admit of accurate use.

General Experimental Methods

Preparation of Materials.—Mercury was purified by treatment with nitric acid followed by distillation under diminished air pressure.[3]

Cadmium amalgam (10%) was prepared by dissolving the weighed amount of Kahlbaum's purest, electrolytically prepared, stick cadmium in mercury on a steam-bath. Zinc amalgam (7%) was prepared in a similar manner.

Cadmium sulfate and zinc sulfate were recrystallized from solutions of the purest salts obtainable commercially.

The mercurous sulfate was prepared electrolytically in a 1:6 sulfuric acid solution (1.15 density), using a current density of 1 ampere per square decimeter of anode surface, according to the methods of Wolff[4] and Hulett.[5] The product varied from a fairly dark gray, finely divided material containing much mercury, to a pure white, somewhat coarser substance, according to the efficiency with which the anode surface of electrolyte was renewed by stirring during the preparation. The white material, the average grain size of which was about 25 microns, gave the most normal values when placed in cells and was used in most of the cells made in this work. A gray product having an average grain size of about 10 microns gave nearly identical cell values and was also employed in some of the work.

The saturated cadmium sulfate and zinc sulfate solutions were prepared by shaking an excess of the purified crystals with conductivity water in a thermostat at 25.0°. For unsaturated cells the electrolyte was prepared by dissolving the amount of the crystalline cadmium sulfate required to give a 43.06% solution (on the basis of the

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[2] Jaeger, *Ann. Physik*, [4] **14**, 726 (1904).

[3] Hulett and Minchin, *Phys. Rev.*, **21**, 388 (1905).

[4] Wolff, *Trans. Am. Electrochem. Soc.*, **5**, 49 (1904).

[5] Carhart and Hulett, *ibid.*, **5**, 59 (1904).

anhydrous salt) in conductivity water in a stoppered bottle. Cells containing such a solution have a temperature coefficient of approximately zero.[6] The electrolyte for the acid cells was prepared by saturating a 0.1 *M* solution of sulfuric acid with cadmium sulfate.

In preparing the paste, the mercurous sulfate was filtered, with suction, in a Gooch crucible and washed several times with the electrolyte to be used in the cell. About one-third its volume of finely ground crystals (of zinc sulfate or cadmium sulfate as the case might be) was then added and the whole made up to a thin paste with the proper electrolyte.[7]

Cells.—The cells were the customary H-form, the internal diameter of the limbs being 10 mm. and that of the cross-arm somewhat less. Some special forms of cells used in the polarization studies will be described later. All cells were carefully cleaned and the platinum terminals amalgamated before filling. The materials were introduced by means of pipets, after which the cells were hermetically sealed. They were allowed to age for at least a month at constant temperature before use.

Constant-Temperature Bath.—The cells were kept in a constant-temperature bath as described in a previous paper by one of the present authors.[8] A high grade mineral oil[9] was used as a bath liquid. The 25.00° point, at which the bath was maintained, was determined by means of a calibrated platinum resistance thermometer. Under the most favorable conditions the control of temperature could be maintained to ±0.002°.

Reference Standards.—Through the coöperation and kindness of the Bureau of Standards, a series of comparisons was run, during the course of this work, between the cells used as a basis of reference in this Laboratory and the Standards maintained by the Bureau in Washington. The Princeton reference group now consists of 15 cells, all of which are from fourteen to twenty-five years old, and have shown very constant values throughout their history. The mean value of the group has been established to an accuracy of 1 microvolt, on the present basis of the Bureau of Standards.

Measurement of E.m.f.—The electromotive force measurements reported in this work were made with a 5-dial Wolff potentiometer having a resistance of 15,000 ohms and a range from 0.00001 to 1.5 volts. The working current for the potentiometer was obtained from a two-cell standard battery[10] and was controlled by means of a manganin coil resistance box adjustable to 0.1 ohm. As a null instrument a high sensitivity moving coil galvanometer (Leeds and Northrup Co.) was used. The sensitivity of this instrument was such that, with the method of measurement described below, a deflection of 10 mm. or more (on the scale at a distance of one meter) was usually obtained for a change in potentiometer setting of 10 microvolts. This made the estimation of cell voltages to one microvolt relatively easy. For the elimination of parasitic electromotive forces in the circuit, reversing switches were placed in the working

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[6] Vosburgh and Eppley, THIS JOURNAL, **45**, 2268 (1923).

[7] In this and subsequent operations, no attempt was made to prevent access of air to the materials, as suggested by (a) Vosburgh, THIS JOURNAL, **47**, 1258 (1925); and (b) Eppley, *Trans. Am. Electrochem. Soc.*, **53**, 149 (1928). Evidence will be presented in a later paper [THIS JOURNAL, **51**, 2345 (1929)] to show that the high initial values of neutral cells, attributed by them to oxidation of the Hg_2SO_4 of the paste during its preparation, may be partially explained on another basis. Further experiments designed to test more directly the importance of Vosburgh's and Eppley's methods are being conducted in this Laboratory.

[8] Hulett, *Phys. Rev.*, **32**, 257 (1911).

[9] "Marcol" obtained from Stanco Distributors, Inc., New York City.

[10] Hulett, *Phys. Rev.*, **27**, 33 (1908).

battery circuit and the unknown e.m.f. circuit, so that these could be simultaneously reversed and, from the difference in galvanometer deflection obtained, a zero correction applied. The whole measuring outfit, including the baths in which the cells were kept, was carefully shielded against the effects of external e.m.f.'s.[11]

The method of measurement used was the differential method, employed at the Bureau of Standards.[12] Each cell to be measured was placed in opposition to a chosen cell whose e.m.f. had been previously established by a similar comparison with the cells of the reference group, and the difference in e.m.f. between these two cells determined. The potential of the unknown cell could then be calculated. Corrections for parasitic e m.f.'s were made on every reading and with proper care final readings could be duplicated over and over without variation.

Measurement of Internal Resistances of Cells.—The measurement of the internal resistances of the cells, required in this work, presented some difficulty, as it was necessary that the method employed should not cause polarization. A modification of the capacity bridge method of Nernst and Haagn[13] was found most satisfactory. The introduction of a vacuum tube amplifier in the telephone circuit permitted an interchange of the microphone hummer, used as a source of audio frequency current, with the telephones, and the elimination of one condenser. Such a bridge is better balanced than the Nernst–Haagn arrangement. It was found to give a sharp sound minimum and was capable of adjustment well within the 0.5% accuracy required for our work.

To see whether such a measurement was injurious to a cell, potential measurements were made on several cells simultaneously with the resistance measurements. A change of about 10 microvolts could be detected while the resistance measurements were being made but this disappeared immediately upon the removal of the bridge connections. The resistances of most of the cells used were between 300 and 500 ohms.

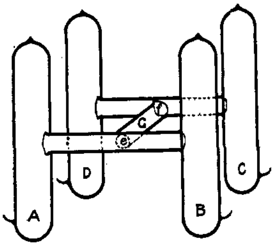

Fig. 1.—Four-legged cell used in polarization studies.

Methods of Study of the Polarization of the Separate Electrodes of Cells.—In order to determine how the polarization was distributed between the separate electrodes of the cell, a special form of cell vessel was devised (Fig. 1). The mid-points of the cross-arms of two H-type cell vessels, AB and CD, were joined by a third cross-arm, G. Limbs A and C were made cadmium amalgam–cadmium sulfate electrodes, while B and D were mercury–mercurous sulfate poles.

When a current was passed through one of the cell combinations thus made, say AB, the other electrodes, C and D, were entirely unaffected and could be used as reference electrodes to test the polarization of the working electrodes. Since A and C were of identical construction, the potential existing between them when the cell was on open circuit was very nearly, or exactly, zero. During the polarization of A, therefore, the potential difference measured from A to C (with a small zero correction if necessary) represented the total change in potential between the point e within the cell and the (external) terminal at A due to the passage of current. This total change in potential, ΔE_{Ta}, is the sum of two quantities, ΔE_{R_a}, which is the e.m.f. required to produce the flow of current through the resistance, R_a, between these two points, and ΔE_{Pa}, which is the polarization of the electrode.

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[11] White, THIS JOURNAL, **36**, 2011 (1914).

[12] Wolff and Waters, *Bull. Bur. Standards*, **4**, 1 (1907).

[13] Nernst and Haagn, *Z. Elektrochem.*, **2**, 493 (1896).

The current flowing through the cell may be obtained by measuring the potential difference, E_x, across a known resistance, R_x, in the external circuit. ΔE_{Ra} may then be calculated from Ohm's Law, and we obtain

$$\Delta E_{Pa} = \Delta E_{Ta} - \Delta E_{Ra} = \Delta E_{Ta} - \frac{E_x}{R_x} \times R_a$$

We may use the subscript, a, in the above equation to designate the amalgam limb of the cell. For the polarization of the mercury limb, ΔE_{Pm}, and of the cell as a whole, ΔE_{Pc}, similar relationships may be derived. The accuracy of the whole method was tested by comparing ΔE_{Pc} with the sum of ΔE_{Pa} and ΔE_{Pm}, each obtained from independent measurements. The agreement was exact at low currents, and never varied by more than 0.5% (due to leakage at the junction e) at the higher currents.

The determination of the resistances of the single limbs of the four-legged cells was accomplished by measuring the resistance across each of the six possible combinations of the four terminals of the cells (Fig. 1). The values thus obtained could be represented as sums of the resistances of the separate limbs of the cells (including in each case the resistance of the connecting cross-arm as far as the junctions e and f, respectively) and the cross-arm, G, connecting the two complete cells. The six equations representing these sums offered solutions for the resistances of the separate limbs. The results of different determinations agreed with each other to better than 0.5%. (There is a slight uncertainty at the junctions e and f, of course.)

In making the potential measurements called for in the above equations, the procedure was as follows. The e.m.f.'s of the two cells, AB and CD (Fig. 1), were first measured by the usual method. The potential differences between the amalgam limbs, A–C, and between the mercury limbs, B–D, were also measured. These latter were always zero or very small initially. The circuit connecting the cell AB across a high resistance[14] so as to discharge it, or in opposition to a larger e.m.f. (2 volts from a lead accumulator) with an appropriate high resistance in series, so as to charge the cell, was now closed. Experience having shown that the potential at the mercury limb was most affected by the passage of the current, special attention was paid to this quantity and readings of the change in it were taken as quickly as possible after closing the circuit and at frequent inter-

[14] The high resistances required to secure the low currents used in this work were specially constructed by the International Resistor Company of Philadelphia, Pa. They consisted of a thin metallic coating on glass wires, insulated and mounted in sealed glass tubes. While these had appreciable temperature coefficients, and were not entirely unaffected by atmospheric conditions, they were much cheaper than coil resistances of the same denominations (0.1 to 10 megohms), and by placing them inside the thermostat they could be kept quite constant in value. Their values were checked from time to time to insure constancy. For all work below 100,000 ohms manganin coil resistances were used.

vals thereafter for at least one-half hour. Between these readings the change in potential at the amalgam limb and the total potentials of the polarized cell and of the unpolarized cell, CD, were also measured. A convenient arrangement of switches facilitated the change from one set of connections to another in making these readings. The unpolarized cell was, as expected, entirely unaffected by the passage of current through the other element. The recovery of the cell after opening the circuit was also observed. A second experiment was not started on a given cell until it had recovered from the effects of the last previous experiment. Inasmuch as the effect of charging was found to be more severe than the effect of discharging the cells, experiments on the polarization due to charging were never run on a given cell until all of the discharge measurements had been made.

A typical set of data from an experiment in which a cell was charged at the rate of 1.7 micro-amperes for thirty minutes is given below.

TYPICAL EXPERIMENTAL DATA

Cell U_3. R_M = 193 ohms. R_A = 192 ohms. R_C = 385 ohms. R_X = 0.583 × 10^6 ohms.

Time, min.	B-D mmv.	A-C mmv.	CD volts	AB volts	E_x, volts[a]
0	− 12	0	1.018080	1.018068	.....
0.5	+650	...	......	......	.....
1.0	700	...	......	......	.....
2.0	764	...	......	......	.....
3.5	...	332	......	......	.....
5.0	862	...	......	......	.....
10.0	916	333	1.018080	......	.....
15.0	940	...	......	......	.....
16.5	...	...	......	1.019356	.....
22.0	...	...	......	......	1.00786
30.0	985	334	......	......	.....

[a] E_x changes as the polarization of AB changes. The percentage change in E_x is negligible, however, in the calculations for which it is used, and in its effect upon the magnitude of polarization of the cell.

From the above data, we calculated $I = 1.729 \times 10^{-6}$ amperes; ΔE_{Rm} = 334 mmv.; ΔE_{Ra} = 332 mmv.; ΔE_{Rc} = 666 mmv.

For the mercury electrode we obtain from the above data the following:

TABLE I

COURSE OF POLARIZATION OF MERCURY ELECTRODE WHILE CHARGING CELL U_3 AT A CURRENT OF 1.7 MICRO-AMPERES

Time, min.	0	0.5	1.0	2.0	5.0	10.0	15.0	30.0
ΔE_{Tm}, mmv.	0	662	712	776	874	928	952	997
ΔE_{Pm}, mmv.	0	328	378	442	540	594	618	663

For the amalgam electrode, on the other hand, ΔE_{Pa} = 0 to 2 mmv. throughout the course of the experiment. The polarization is, therefore, practically entirely in the mercury limb.

The recovery observations (Table II) are given for the mercury limb only, as the recovery of the amalgam limb was practically immediate. Here, of course, the potential measurements represent polarization with no calculation other than a zero correction of 12 mmv.

TABLE II

COURSE OF RECOVERY OF MERCURY ELECTRODE OF CELL U_3 AFTER THIRTY MINUTES' CHARGING AT 1.7 MICRO-AMPERES

Time, min.	0	1	2	5	10	15	30	60	120
B–D, mmv.	...	330	300	250	210	189	147	107	70
ΔE_{Pm}, mmv.	663[a]	342	312	262	222	201	159	119	82

[a] This value is obtained from Table I.

Observations on this cell were discontinued at the end of two hours. A week later the e.m.f. was still about 5 mmv. high.

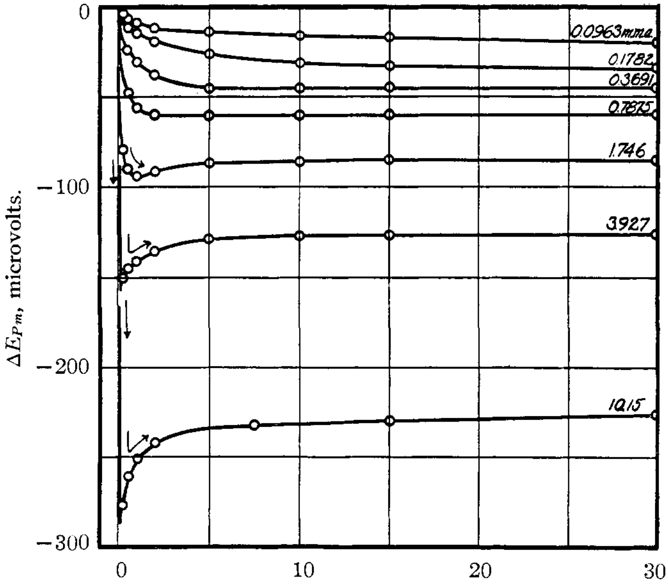

Fig. 2.—Polarization in mercury limb at different discharging currents.

Results

Behavior of Mercury Limb during Discharge.—The course of polarization with time of discharge at the mercury electrode of a cell is shown for different currents in Fig. 2. The true polarizations, ΔE_{Pm}, of the electrode are plotted as ordinates with times as abscissas. The cell from which the data represented by these curves were obtained was a neutral unsaturated cadmium cell. The curves obtained for neutral saturated cadmium cells and zinc cells were entirely anȧlogous to those here shown. The *magnitude* of the polarization at any given current differed from cell to cell, but the *types of curves* obtained as one increased the current were similar to those here shown throughout a number of studies of cells of each type.

It should be noted that at low currents the polarization increases with time, but at a diminishing rate. Although cells were observed at currents of 0.1 micro-ampere for as long as fifty hours, they did not reach a steady state. It is to be assumed, however, that such a state would eventually be reached. As the rate of withdrawal of current is increased, the initial change in potential is more rapid, and a steady state is then reached in a very few minutes. A further increase in the current drawn produces a large initial polarization, followed by a period of apparent recovery, rapid at first and then more gradual. In some cases this recovery reached a maximum, after which the polarization again increased along a curve similar to that obtained at lower currents, while in other cases the recovery continued over a long period of time, apparently approaching a steady state.

Saturated cadmium cells made up with an acid electrolyte differed slightly in behavior from the cells above described. With a given sample of mercurous sulfate, acid cells required a current density nearly ten times as great as neutral cells to produce a polarization of given magnitude. They reached a steady state far more quickly than neutral cells. At 20 mma., for example, an acid cell became constant in e.m.f. in less than thirty seconds after the circuit was closed. The recovery effect, noted above, did not appear in an acid cell until a fifty-fold increase in current density was made.

Behavior of Mercury Limb during Charge.—The course of polarization at the mercury electrode of the same cell during charge is shown in Fig. 3. The effect is, of course, opposite in direction to the effect of discharge. The slopes of the curves are greater at corresponding currents than for the discharge of the same cells, and a steady state is not reached as quickly as on discharge. The recovery tendency, noted in the discharge curves, is less pronounced, and soon gives way to the "normal" polarization effect. The results obtained on charging neutral saturated cadmium cells and zinc cells were strictly analogous to those obtained for the unsaturated cell as given in Fig. 3. For the acid cells the differences in behavior from that of neutral cells noted in the experiments on discharging were found again to hold when the cells were charged.

Polarization over Longer Times.—A saturated cadmium cell was allowed to discharge for eleven days at a rate of 1.75 mma. Figure 4, Curve I, shows that the recovery tendency persisted throughout this time, and that the electrode recovered from an initial polarization of 2600 mmv. to within 300 mmv. of its value on open circuit. When the cirucit was then opened, the cell quickly recovered from the effects of polarization, and in less than nineteen hours the cathode had reached a value 20 mmv. *higher* than it had before the experiment was started. It maintained this value for three days, when the circuit was again closed, giving the curve shown as Curve II in the same figure. It will be noticed that the initial drop is now only 600 mmv., while the recovery seems to approach the same value as before. After sixty-five hours the circuit was opened. Recovery was complete (to the value 20 mmv. above the initial value of the cell) in ninety minutes and the circuit was then closed again. The initial drop was now only 300 mmv. and the curve quickly took up a continuation of Curve II. Eleven days of rest on open circuit followed, and, on again discharging at the same current, an initial polarization of 1400 mmv. was obtained. It is apparent that, although no change in the e.m.f. of the

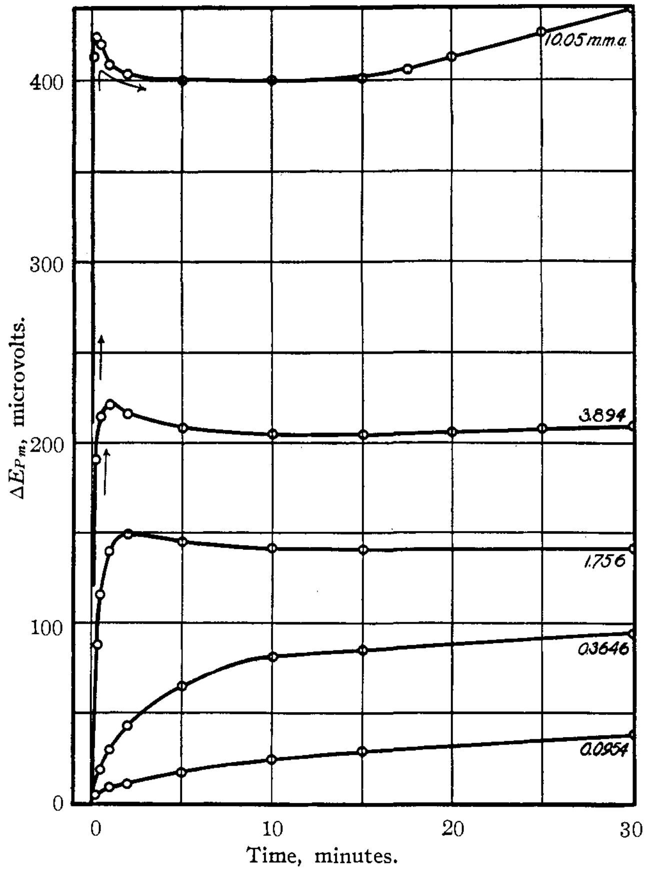

Fig. 3.—Polarization in mercury limb at different charging currents.

electrode took place during these periods of rest on open circuit, some process was going on which caused a decided increase in the *initial* polarization when the cell was later used to deliver current.

Inasmuch as the long time polarization of the cell had produced such a marked change in its behavior at the higher current, the question arose as to how its polarization at a much lower current would now compare with that previously observed for the cell. It was found that the polarization at a current of 0.1 micro-ampere was now 46 mmv., whereas it had formerly amounted to 168 mmv. at the same current.

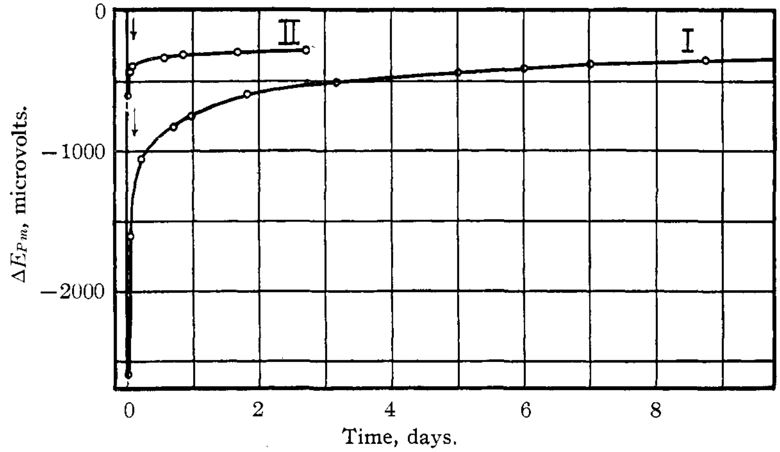

Fig. 4.—Effect of continued discharge at 1.75 micro-amperes upon mercury electrode.

The increase of 20 mmv. in the e.m.f. of the cell above described when allowed to rest after such a long time of polarization is interesting. Some old cells, particularly cells whose e.m.f. had shown a marked decrease, exhibited this effect, the increase in some cases being as great as 100 mmv. It usually disappeared within a few days after the circuit was opened.

Effect of Age of Cells upon their Polarization.—The discharge polarization of a cell was measured at a current of 10 micro-amperes six hours after it had been set up and placed in the bath. The recovery effect observed in older cells was also present in this cell, and its polarization was nearly as great at this time as it was found to be a month later, after the cell had been "aged" somewhat. Several cells built during the early spring of 1927, however, and tested with regard to their polarization in May and June of that year, were found to show an initial polarization nearly 30% higher at a given current when again measured ten months later. The characteristics of the polarization curve are the same, therefore, for new cells as for old ones, but the magnitude of polarization increases somewhat with the age of the cells.

Discharge of a Cell without Solid Depolarizer.—In order to see whether or not the presence of the solid mercurous sulfate had anything to do with the nature of the polarization curve, a cell was made in which the cathode limb contained a saturated solution of mercurous sulfate and cadmium sulfate with no solid salt. This cell was discharged at a rate of 10 mma. The recovery tendency was entirely absent. From an initial value of 313 mmv. the polarization increased in thirty minutes to 6003 mmv. When the circuit was opened the cell recovered to its initial value, though somewhat more slowly than a cell set up with the usual paste.

Internal Resistance of a Cell during Polarization.—The measurements of ΔE_{Tm}, from which the true polarization, ΔE_{Pm}, is obtained, include the ΔE_{Rm} term which is due to the internal resistance of the cell. A change in the internal resistance of the cell during the passage of current might, therefore, account for the recovery effect observed.[15]

To test this point the internal resistance of a cell was measured before and during polarization. The resistance during the passage of current was found to be the same, to within 0.1%, as it had been on open circuit. While these resistance measurements were being made, the polarization of the mercury limb of the cell decreased by an amount which, at the current drawn, would have necessitated a decrease in resistance greater than the total resistance of the cell if due to this cause. A change in the internal resistance of the cell is, therefore, excluded from any explanation of the recovery effect observed during the passage of current.

Recovery of the Mercury Electrode following Polarization.—The general nature of the recovery curve following the discharge of cells has been studied by other workers.[1] For the purpose of comparing the recovery following charge with that following discharge, however, results are here presented (Fig. 5) which show the recovery of the mercury electrode of a cell, (A) after sixty-five hours of discharge at 1.75 mma., and (B) after three and one-half hours' charge at 1.77 mma. The charge curve was the last obtained and the cell had rested for a month immediately beforehand. It is noted that three and one-half hours of charging produced a polarization six times as great as sixty-five hours of discharging at the same current. The recovery was, quite naturally, more rapid after discharge; but, although the effects of discharge disappeared one and one-half hours after the circuit was opened, the polarization following charge persisted for over two weeks. Similar observations were made on a large number of cells. Acid in the cells shortened the time required for recovery, both from discharge and from charge.

[15] Changes in the resistance at the surfaces of the electrodes in certain electrolytic cells during the passage of current have been observed previously: (a) Burgess, *Trans. Am. Electrochem. Soc.*, **7**, 51 (1905); (b) Holler, *Bur. Standards Sci. Papers*, **20**, 153 (1925).

Polarization and Recovery of the Anodes of the Cells.—During the experiments on polarization of the mercury limb of the cell, observations were also made of the polarization of the amalgam limb. These observations showed, in general, that the polarization of the amalgam limb at a given current density was only 1/40 that of the mercury limb, and that the recovery tendency observed during polarization of the mercury limb was not present at these currents in the amalgam limb. The true polarization at these low currents was so small that it was, in many cases, of the same order as the uncertainty in determining ΔE_{Ra}.

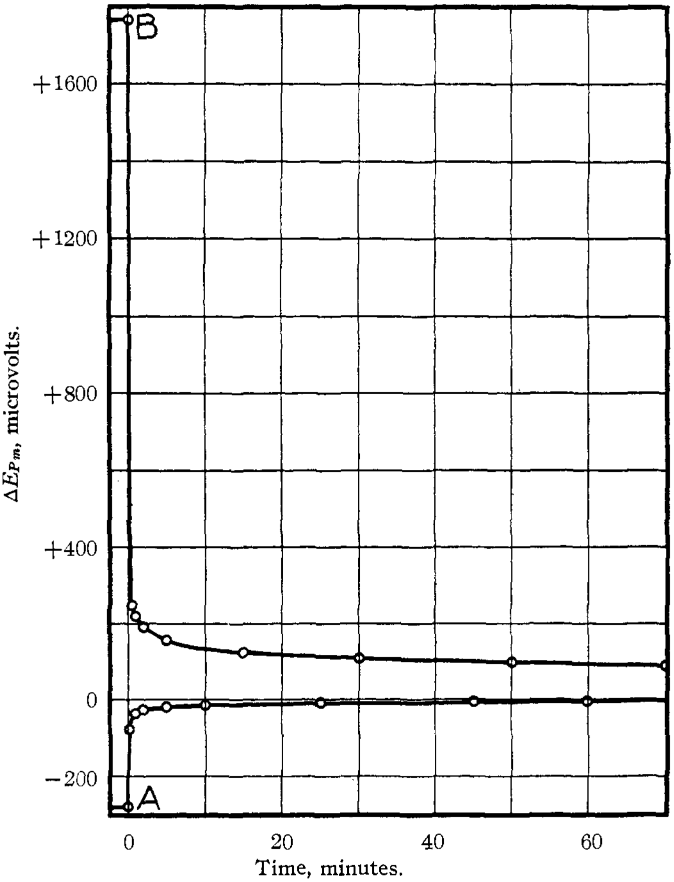

Fig. 5.—Recovery of mercury electrode from polarization: A, after 65 hours' discharging at 1.75 micro-amperes; B, after 35 hours' charging at 1.77 micro-amperes.

In order to compare the effects of charging and of discharging on the amalgam limb, therefore, a current of 15 mma. was passed through two amalgam limbs of a four-legged cell and the polarization and recovery of each limb (one of which had thus been charged and the other discharged) were observed by reference to the unpolarized mercury electrodes. The observations made during polarization are recorded in Table III.

TABLE III

COMPARISON OF EFFECTS OF CHARGE AND DISCHARGE ON AMALGAM LIMB OF A CELL

I = 15 micro-amperes

Time, minutes		0	1	3	5	10	25	75	90
ΔE_{Ta}, mmv.	Discharge	0	−3838	−3841	−3844	−3848	−3856	−3874	−3879
	Charge	0	+4212	+4212	+4212	+4213	+4211	+4210	+4211

It is seen that the polarization of the amalgam electrode during charge is constant throughout at this current, while the polarization of the discharged electrode gradually increases. Calculation of ΔE_{Ra} gives for the discharged limb −3804 mmv. and for the charged limb +4216 mmv. with an uncertainty of 20 mmv. in each case. A calculation of ΔE_{Pa} is seen to be practically meaningless under these conditions.

During recovery on open circuit, however, the potential measurements give us the true polarization of the electrodes directly. The recovery of these limbs is shown in Table IV.

TABLE IV

RECOVERY OF AMALGAM LIMBS OF CELL FOLLOWING THE POLARIZATION SHOWN IN TABLE III

Time, minutes		0	1	5	15	30	75	4 hrs.	8 hrs.
ΔE_{Pa}, mmv.	After discharge	−75[a]	−42	−36	−30	−26	−19	−9	−2
	After charge	?	+ 2	0	0	0	0	0	0

[a] This value is obtained from Table III and is only approximate.

We observe from Tables III and IV that the polarization of the amalgam limb of the saturated cell is greater when it is being discharged than when it is being charged. Similar results were obtained from observations on the anodes of an unsaturated cadmium cell and of a zinc cell.

Discussion of Results

From the foregoing experiments it is seen that:

1. Neutral saturated and unsaturated cadmium cells and zinc cells are very similar in their behavior during the passage of current through them.
2. Most of the polarization in these cells is found in the mercury limbs.
3. At the mercury electrode the effect of charging is the more severe, while at the amalgam electrode discharging the cell causes the greater polarization.
4. A recovery effect, present only in the mercury limb of the cell, appears when the polarization occurs at the higher currents and tends to decrease the polarization of the cell.

5. This effect persists over long periods of time and produces marked changes in the subsequent behavior of the cell during polarization.

6. The magnitude of the initial polarization increases somewhat with the age of a cell.

7. Removal of the solid mercurous sulfate causes the disappearance of the recovery effect.

8. The presence of acid diminishes the magnitude of polarization and prevents the appearance of the recovery effect until greater currents are used than are required for its appearance in neutral cells.

9. No noticeable change in the resistance of a cell is found accompanying polarization.

10. The effects of polarization produced at the mercury electrode by discharging currents disappear more rapidly when the cell is left on open circuit than those of charging, while the converse is found to be the case at the amalgam electrode.

The neutral saturated cadmium cell will be used in the following discussion of the processes which occur during and following the passage ot current through the cell. What is said of it may be applied equally well to the case of the zinc cell, and the additional considerations needed to explain the action of unsaturated and acid cadmium cells will be indicated.

In the mercury limb of the saturated cadmium cell we have a paste composed of crystals of mercurous sulfate and cadmium sulfate, and a saturated solution of these salts lying on a mercury surface. In the solution in contact with the mercury there are Cd^{++} ions, Hg_2^{++} ions, a few Hg^{++} ions, SO_4^{--} ions and the ions of water. When a current is passed through the cell so as to discharge it, positive ions from the solution are discharged into the mercury. We may expect that the ions discharged are principally the mercurous ions. Some cadmium ions are probably discharged, the metal going into solution in the mercury to form a very dilute amalgam. It is doubtful if hydrogen ions are discharged in any appreciable amount. The polarization of the electrode on discharge is due, then, to the removal of mercurous ions and cadmium ions from the solution immediately above the electrode and to the formation of an amalgam in the electrode. These are both concentration polarization effects.

In the solution the migration of positive ions toward the electrode tends to compensate for this type of polarization, as does the process of convection which sets in because of the diminished density of the solution immediately above the mercury surface. Also, cadmium sulfate and mercurous sulfate crystals in this region go into solution to make up the deficiency in concentration. At a given current a steady state would eventually be reached, at which the rate of depolarization due to the above processes would exactly equal the rate of polarization.

When a charging current is passed through the cell, mercury passes from the liquid metallic state into the ionic state in solution. This increases the concentration of mercurous ions in the solution, and results again in concentration polarization in the electrolyte. There is an additional complication in this case, however, because of the possibility of mercurous ions in the vicinity of the electrode being oxidized by the electrolytic action to the mercuric state. The accumulation of mercuric ions in such a neutral sulfate solution would result in the deposition of basic mercuric sulfate in the solid state.[16] There is no change in the composition of the mercury electrode during charging. The depolarizing processes here are those of electrolytic migration and of crystallization of both the mercurous sulfate and basic mercuric sulfate, and we would again expect a steady state to be reached between the polarizing and depolarizing actions.

When the circuit is opened, recovery begins. Diffusion, convection and solution or crystallization of the solid salts present act to restore saturation equilibrium in the electrolyte. Cadmium, which may have been deposited in the mercury during discharge, is removed by electrolytic displacement, and basic mercuric sulfate which was formed during charging redissolves, the mercuric ions being reduced by the mercury and deposited as mercurous sulfate.

The above discussion indicates that the electrolytic actions at the mercury electrode of the standard cell are not strictly reversible, and observed differences between the rates of polarization and recovery of this electrode when the cell is charged from those when it is discharged are easily understood from this point of view.

But this discussion does not indicate any explanation for the recovery effect observed during the polarization of a cell. The simple processes described above can only give a polarization curve which starts at a rapid rate and gradually slows down to a steady state that continues until one of the reacting substances is exhausted. No simple depolarizing process can explain the anomalous nature of the experimental curves, for such processes act only to reëstablish a condition of equilibrium with the polarizing process. They cannot of themselves overbalance the polarizing action.

The recovery effect must be due to an independent change in the rate of one of the polarizing or depolarizing processes. A study of these various effects shows that the rates of most of them are dependent, either directly or indirectly, upon the strength of the current passing and, since this was practically constant, these rates could undergo no such change.

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[16] Smith, ref. 1f, observed the formation of this "green salt" during the charging of a cell, and Wolff, ref. 4, found "a basic salt containing mercuric compounds" formed when the electrolytic preparation of mercurous sulfate was attempted in a neutral solution of cadmium sulfate.

The rates of crystallization and of solution of the mercurous sulfate, however, while dependent upon the degree of unsaturation or supersaturation of the solution, and, therefore, indirectly upon the strength of current, are also a function of the state of the surface of the crystal. The fact that a cell from which the solid paste was omitted did not show the recovery effect lends support to the view that it is to this place we must look for an explanation.

If a crystal is well developed, as those of the paste must tend to become during long contact with their saturated solution, the removal or deposition of ions at its surface will take place more slowly than if the surface is irregular and imperfect. It is possible that at low currents the degree of unsaturation or of supersaturation of the solution in the vicinity of the mercurous sulfate crystals is such that solution or deposition takes place fairly uniformly over the whole crystal surface, without changing in any marked degree the nature of that surface. The polarization curve at such currents is perfectly normal. At higher currents, however, the degree of unsaturation or of supersaturation is much greater, and the solution or deposition of the ions at the crystal surfaces at the outset may produce a roughened surface which then has a greater rate of solution or crystallization than the original surface. The depolarizing power of such crystals is thus increased and the observed "recovery" takes place. This increase continues until a maximum is reached in the rate of interchange at the crystal surface and we may then have either a steady state in the polarization curve, or, if the other polarizing and depolarizing effects have not yet reached a state of equilibrium, the polarization may again increase until such a state is reached. When the cell is allowed to stand on open circuit, normal saturation equilibrium is first established, at which polarization disappears. The process of rebuilding the crystal face goes on, however, and as this progresses the magnitude of the initial polarization to be found on passing current through the cell is increased. The increase in the magnitude of polarization with the age of a cell would also be accounted for by this gradual building up of more perfect crystal surfaces.

Such changes in the rates of solution and crystallization of the mercurous sulfate do not explain the apparent increase in the equilibrium e.m.f. of the cells on open circuit after discharge. It is possible that this effect, which was observed principally in old cells that had fallen to low values, may be due to the removal, during polarization, of a thin film of basic mercurous sulfate which had been deposited on the crystals and prevented them from showing their normal solubility. Its removal gave the normal salt a chance to dissolve, and the value of the cell was temporarily increased after the circuit was opened. As the cell stood on open circuit, the coating of the basic salt was again formed and the value of the cell decreased.

No entirely satisfactory explanation has been found of the role of acid in decreasing the polarization of cells at a given current and preventing the appearance of the recovery effect at currents at which it appears in neutral cells. It seems that acid greatly accelerates the interchanges at the surface of the crystals, but just how such an effect operates is not clear.

That no difference was observed in the action of the mercury limbs of unsaturated cells from those of saturated cells indicates that the cadmium sulfate crystals mixed into the paste in order to maintain saturation of the solution in the one case do not play an important role in the polarization and depolarization of this limb.

In the amalgam limb of the cell we have a saturated solution of cadmium sulfate, with an excess of crystals, in contact with a two-phase cadmium amalgam. Cadmium ions go into solution from the amalgam during discharge and are deposited in metallic form in the amalgam during charge. The relative changes in cadmium-ion concentration in the electrolyte due to these actions are far smaller than the corresponding changes in mercurous-ion concentration at the other electrode, and it is natural, therefore, that the polarization at the amalgam electrode should be the less severe. Except for the possibility of some mercury from the amalgam passing into the ionic state during discharge, the electrolytic actions here appear to be perfectly reversible. The persistence of polarization following discharge, over the almost immediate recovery following charge, at this electrode, may be due to the presence of such ions in the solution, or to the fact that convection aids in the reëstablishment of saturation equilibrium in the electrolyte in the latter case while in the former we are dependent upon diffusion alone.

Polarization during the Measurement of Cell Potentials.—In the measurement of cell potentials by the deflection method, currents as great as 10^{-8} amperes are occasionally drawn. The smallest current used in the polarization studies above described was 10^{-7} amperes, but a number of cells showed a polarization of 10 microvolts or more at this current. If the linear relationship between current and polarization holds at this current, it appears that some cells must be polarized to the extent of a microvolt or more during measurements that endeavor to determine their values to a single microvolt.

That such polarization does actually occur is indicated by the fact that the sensitivity of the galvanometer to a change of 10 microvolts in the potentiometer setting was always at least 10% lower when cells were being measured than that found when neutral resistances of the same magnitudes were substituted for them. In some cases this loss in galvanometer sensitivity was as great as 80% of its normal value. Such an extreme loss in galvanometer sensitivity is usually attributed to a high internal resistance in the cell. Calculation shows, however, that the resistance of such cells would have to be of the order of 2000 ohms, while their actual resistances were found by measurement to be less than 600 ohms in every case. There is no apparent reason for the high polarization shown by these cells. They were identical in construction, and in many cases had been made at the same time and of the same materials as cells that were less affected by the passage of current.

In actual practice the errors introduced by such polarization are very small and, to a certain extent, cancel one another in the course of a measurement. As a test of their effect a White potentiometer[17] having a range of 10,000 microvolts and adjustable to 1 microvolt was placed beside the Wolff instrument and alternate measurements of a number of cells were taken on the two instruments. In the case of the two cells which had been found to be most subject to polarization, the readings of the two instruments differed by 1 microvolt in the expected direction. In all other cases the agreement was exact. The use of an instrument of the White type is to be recommended, however, when measurements of high accuracy are undertaken.

Summary

The polarization of the separate electrodes of various types of standard cells under the influence of small charging and discharging currents has been studied experimentally, and the results interpreted in terms of the various polarizing and depolarizing actions which operate in the cells during and after a flow of current through them.

An interesting secondary effect of polarization has been found in the mercury limbs of cells, which causes an apparent recovery from polarization to take place during the passage of current. This recovery has been attributed to an increase in the rates of solution and of crystallization at the surfaces of the mercurous sulfate crystals.

It has been shown that cells are subject to polarization at the small currents that flow through them during measurements which undertake to estimate their potentials to microvolts by a deflection method. The actual error introduced because of such polarization is usually negligible.

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[17] (a) White, THIS JOURNAL, **36,** 1868 (1914); (b) Leeds and Northrup Co., Bulletin No. 726, Philadelphia, Pa., 1927.