SOME EXPERIMENTS ON THE POLARIZATION AND
RECOVERY OF CADMIUM CELLS.

BY S. J. BARNETT.

ALL the elements used in these experiments were set up in small H-form vessels by me, following the methods of the Reichsanstalt with unimportant¹ deviations. The cells designated as Nos. 1, 2, and 3 were mounted about the middle of last November, and their e.m.f.s were first compared some ten days later. Their maximum difference was then about 1 part in 10,000, and in recent comparisons (except after severe treatment, described below) they have not differed by more than a few parts in 100,000. Nearly the same degree of excellence, tested either by agreement among themselves or by agreement with the cells of the first group, was attained within a few days after their mounting by Nos. 4, 5, and 6, which were set up on April 13, and Nos. 7, 8, and 9, which were set up on April 16. The mercury used in all the cells was from the same stock, while the other constituents were from different stocks for the cells of the first groups and those set up later. The paste in Nos. 4, 5, and 6 contained no free mercury. The volume of paste in No. 5 and in No. 6 was much greater than in any of the other cells (accounting for their high resistances).

The resistances of the cells were measured by a variety of methods, the only one wholly satisfactory being that of the bridge and secohmmeter with alternating currents. The resistances of Nos. 1, 2, 3, 4, 5, 6, 7, and 9, which will be denoted by $B_1, B_2, \dots, B_9$, determined by this method on May 12 at $22^\circ.3$ C. were $B_1 = 361, B_2 = 401, B_3 = 342, B_4 = 408, B_5 = 571, B_6 = 587, B_7 = 351, B_9 = 421$, all in ohms. The resistance at the same temperature of No. 8, obtained by a different method but reduced to correspond with the above values by comparison with other cells whose resistances were determined by both methods, was about 435 ohms.

¹ At least for the purposes of these experiments.

The temperature coefficient of the resistance of the cells at 20° C. was found to be -0.029 . The resistances given above, properly corrected for temperature, were used in calculating the recovery curves given below.

The current through a cell during polarization was read on a Weston millivoltmeter of 5 ohms resistance.

The e.m.f.s of polarization during recovery experiments were determined by the differential method of direct deflections, which offered the advantages of great rapidity and sensitiveness. Two cells, one with normal e.m.f., the other polarized, were connected in series with a galvanometer and a box resistance of 100,000 ohms

Fig. 1.

and the deflection read. The cells were then opposed to one another in the same circuit, the box resistance plugged out, and the deflection again read. If E_1 and E_2 denote the e.m.f.s of the two cells, B_1 and B_2 their resistances, G the resistance of the galvanometer, and $D +$ and $D -$ the deflections (corrected when necessary) with the cells in series and opposition respectively, the ratio of the difference of the e.m.f.s to their sum is

$$\frac{E_1 - E_2}{E_1 + E_2} = \frac{B_1 + B_2 + G}{B_1 + B_2 + G + 100,000} \times \frac{D -}{D +}$$

The method is open to the objection that during the recovery of the cell under test the standard cell is furnishing a current in such a direction as to polarize itself and to hasten the recovery of the other cell. Inasmuch, however, as the current was never greater than about $\frac{1}{1500}$ ampère at its maximum value in the early part of a recovery series, and fell in a few seconds to an excessively small value, the e.m.f. of the standard cell was assumed to remain constant in calculating the recovery curves. The same method was used in comparing the e.m.f.s of the cells from time to time, although it must always give somewhat too close an agreement, and was occasionally roughly checked by a potentiometer. In some of the later experiments, in which the e.m.f. of polarization was very great, the box resistance was left in for both deflections.

The galvanometer was a heavy instrument of the Wiedemann type with a highly damped bell magnet, making it possible to begin observations about 6^s after closing the circuit. The variations of the null point were small and easily allowed for. The resistance of the coils used was about 500 ohms.

The time was recorded with a clock and chronograph or with a watch, according to the demands of speed and convenience. The temperature was read when necessary from a thermometer hanging on the wall.

After a few preliminary experiments more accurate observations began on February 28 with No. 1 as standard and No. 2 under test. No. 2 had been frequently short-circuited before, though never for a great length of time.

About 8^h 20^m $D+$ was 11.5 cm. and $D-$ was inappreciable (0.005 cm. could be detected, though readings were taken in general only to 0.01 cm.). At 8^h 22^m No. 2 was short-circuited through the millivoltmeter and its deflections and the time were read simultaneously for about five minutes. The observations are platted in Curve I. of Fig. 1.

At 8^h 27^m the circuit was broken and the cell connected for e.m.f. comparisons (through the galvanometer in opposition to No. 1). Simultaneous galvanometer and time readings were then taken for over ten minutes. From these data and the resistance $B_1 + B_2 + G = 1,375$ ohms, the recovery curve was calculated, and is platted as Curve I. of Fig. 2.

After a few resistance experiments the galvanometer was readjusted and $D + (= 38.1 \text{ cm.})$ and $D - (= 0.20 \text{ cm., } E_1 > E_2 \text{ by } 0.014 \text{ per cent.})$ were observed. At $9^{\text{h}} 32^{\text{m}}$ No. 2 was again short-circuited and a second polarization curve obtained, platted as Curve

Fig. 2.

II., Fig. 1. After ten minutes the circuit was broken and a series of e.m.f. readings begun. The recovery curve calculated from these observations and from the resistance $B_1 + B_2 + G = 1,364$ ohms is platted as Curve II., Fig. 2.

At $10^{\text{h}} 44^{\text{m}}$ the cell was again short-circuited, and at $10^{\text{h}} 31^{\text{m}}$ the circuit was broken and connections made for e.m.f. comparisons. The polarization observations are platted as Curve III., Fig. 1, and the earlier part of the recovery curve (calculated with $B_1 + B_2 + G = 1,353$ ohms) is platted as Curve III., Fig. 2. At $44^{\text{m}} 12^{\text{s}}$ after the circuit was broken E_2 differed from its initial value by less than 0.001 per cent. (The initial deflections before the polarization began were $D + = 38.1 \text{ cm.}$ and $D - = 0.17 \text{ cm.,}$ making $E_1 > E_2$ by 0.012 per cent.)

On April 2 several series of experiments were made upon No. 2. The apparatus was so arranged that all the combinations for the different measurements could be made by simply opening or closing keys, inserting plugs, etc.

At 9^h 36^m No. 2 was short-circuited for 3^m. At 10^h 2^m the process was repeated. At 10^h 39^m connections were made for e.m.f. comparisons. $D +$ was found to be 13.2 cm. and $D -$ to be 0.005 cm. ($E_2 > E_1$). At 10^h 45^m No. 2 was short-circuited through the voltmeter, whose reading fell to 1.7 millivolt at the end of three minutes, when the circuit was broken and the recovery observations began. The galvanometer deflection is platted as a function of the time after breaking the circuit in Curve II., Fig. 4 (the observations being indicated by the circular rings), and the recovery curve is platted in Curve I., Fig. 6. A part of the latter curve is also platted for purposes of comparison in Fig. 2 (Curve IV.). These curves were calculated with $B_1 + B_2 + G = 1,373$ ohms.

The low values to which E_2 fell after polarization in these experiments is evident from the polarization data and the fact that the initial current, calculated from the resistances and the initial e.m.f. of the cell, would exceed $1\frac{1}{5}$ milliampère.

To examine the (possible) variation of resistance during the time of recovery the following experiments were performed. An Edison cell (with e.m.f. 0.88 volt on April 3) was connected to the terminals of a resistance box with 1,010 ohms unplugged, and from traveling plugs connected with the terminals of the 10-ohm coil the current was led through the galvanometer, a reversing key, and the two cadmium cells in opposition. When the key was reversed the current was reversed through the cells, but not through the galvanometer. The deflection was read for both directions of the current through the cells, and the mean deflection at any time was taken as inversely proportional to the resistance $B_1 + B_2 + G$. The initial mean deflection was found to be 3.98 cm. No. 2 was then short-circuited for 3^m, at the end of which the circuit was broken and the cells connected as above with the current from the Edison shunt traversing No. 2 in the normal direction ($-$ to $+$). The galvanometer deflections were then observed as a function of the time after breaking the circuit. The results are platted in Curve I., Fig. 3.

After another short-circuit of 3^m, beginning at 12^h 3^m, a similar set of observations was made, but with the current traversing the cells in the opposite direction (+ to - in No. 2). The results are platted in Curve II., Fig. 3.

At 12^h 16-17^m deflections with the current in both directions through the cells were taken, the mean deflections in two sets being 4.00 cm. and 4.02 cm.

Fig. 3.

With the same connections, No. 2 was short-circuited for 3^m, put on open circuit for 1^m, short-circuited again for 1^m, then put on open circuit at 12^h 24^m with the current from the Edison shunt traversing it in the normal direction (- to +). The galvanometer deflection was read as soon as the oscillations of the needle had stopped, then the current was reversed through the cells and the deflection read, then reversed again, etc., times being read simultaneously with deflections. The results are platted in Curves III. and IV., Fig. 3; Curve III. containing the results with the current through No. 2 in the normal direction and Curve IV. the results with the current in the opposite direction.

The mean ordinate of Curves III. and IV., Fig. 3, is platted as a

function of the time after open circuit in Curve I., Fig. 4, the first point, however, being obtained from Curves I. and II., Fig. 3.

The black circles on Curve II., Fig. 4, exhibit the relation between the half difference of the ordinates of Curves III. and IV., Fig. 3, and the time, the first point, however, being obtained from Curves I. and II. of the same figure.

Fig. 4.

The figure (Fig. 4) shows that the resistance of the cells and galvanometer in series did not differ appreciably during the recovery observations from its initial value before short-circuit (deflection 4.01 cm.).

On April 22 observations were made upon cell No. 7, which had not previously been used (except from e.m.f. and resistance comparisons with extremely weak currents). Its initial electromotive force was found to be about 0.002 per cent. greater than that of No. 1.

At 10^h 62^m No. 7 was short-circuited and its polarization curve obtained. The observations are platted in Curve I., Fig. 5.

At 11^h 22^m the circuit was broken and recovery observations began. The results are platted in Fig. 6, Curve III., calculated with $B_1 + B_7 + G = 1,248$ ohms.

No. 7 was short-circuited again at 11^h 59^m, and once more at 12^h 15^m. The two sets of polarization observations are platted in Curves II. and III., Fig. 5.

The occurrence of maxima in some of the polarization curves is not peculiar to No. 7.¹ Such maxima have been observed with No.

¹ Nor is it peculiar to cadmium cells. Nov. 14, 1903.

2 (as in Fig. 1, Curve IV.) and with No. 3, and would doubtless occur with any of the others if short-circuited sufficiently, unless perhaps the resistance of some of the cells is too great. In such cases maxima of the same kind could doubtless be produced by increasing the polarization current with the aid of an additional e.m.f., as in the case of Curve VI., Fig. 1 (see below).

Fig. 5.

On April 25 cell No. 7, whose e.m.f. was then initially about 0.006 per cent. greater than that of No. 1, was short-circuited (without the voltmeter) at 8^h 41^m, and was so left until 12^h 52^m, when the circuit was broken. At 12^h 53^m the e.m.f. of No. 7 was

only 9.7 per cent. of its normal value. Two days later its e.m.f. was less than that of No. 1 by only 0.001 per cent.

On April 25 some experiments were also performed upon Nos. 6 and 9, which had not been previously short-circuited. The initial differences between their e.m.f.s and that of No. 5, with which they were compared throughout the experiments, were 0.002 per cent. and 0.003 per cent.

Fig. 6.

The polarization observations upon No. 9 are platted in Curve I., Fig. 7. Seven and one half minutes after the circuit was broken the e.m.f. had risen to within 0.02 per cent. of its initial value.

Cell No. 6 was short-circuited on the same day at 11^h 48^m and the circuit broken at 11^h 56^m. The polarization observations are

platted in Curve II., Fig. 7. Four minutes after breaking the circuit the e.m.f. had recovered to within 0.03 per cent. of its initial value. At 12^h 0^m No. 6 was again short-circuited. The polarization observations are platted in Curve III., Fig. 7. In 16^m after opening the circuit the e.m.f. had risen to within 0.1 per cent. of its original value.

On the same day (April 25) some experiments were also made upon No. 2, whose e.m.f. was initially 0.0037 per cent. greater than that of No. 1. At 9^h 50^m No. 2 was short-circuited. The polarization observations are platted in Curve IV., Fig. 1. Although the cell had not been short-circuited since April 2, the curve shows all the peculiarities of an experienced cell.

About 4^m later the circuit was broken and recovery observations began. The results (calculated with $B_1 + B_2 + G = 1,378$ ohms) are platted in Curve II., Fig. 6.

A single chloride accumulator (e.m.f. = 2.03 volts) was then arranged to be connected through a key to the terminals of No. 2, with its positive pole to the negative pole of No. 2. The key was closed at 10^h 11^m and opened at 10^h 15^m 9^s. The observations are platted in Curve V., Fig. 1. After open circuit connections were made for e.m.f. comparisons (with 100,000 ohms in the circuit for both arrangements of the cells). At 10^h 22^m and 10^h 38^m the e.m.f. of No. 2 was 7.3 per cent. and 9.4 per cent., respectively, of its initial value.

The same accumulator was then closed in the opposite direction through No. 2 (at 10^h 40^m), and Curve VI., Fig. 1, was obtained. The circuit was broken at 10^h 48^m. Two minutes later the e.m.f. of No. 2, which had increased greatly after 200^s charging, was found to exceed that of No. 1 by only 0.1 per cent., which was reduced in 7^m more to 0.04 per cent.

In the first case (Curve V.) E_2 was reduced almost to zero, and in the second case (Curve VI.) it recovered its normal value within a few seconds. The resistance of the circuit did not alter greatly, if at all, at least in the earlier parts of the experiments.

The accumulator was then again connected to No. 2 (in opposition) and so left for 5^m. Two minutes after breaking the circuit (11^h 3^m 25^s) its e.m.f. was only 0.17 per cent. greater than that of No. 1. At 12^h 44^m the excess was only 0.02 per cent.

At 12^h 46^m No. 2 was short-circuited through the voltmeter. The observations are platted in Curve VII., Fig. 1, which resembles closely the polarization curve of a fresh cell. The approximate coincidence between this curve and a part of Curve VI. is due to the fact that the e.m.f. of the accumulator was almost exactly twice that of the cadmium cell. The e.m.f. of No. 2, on being tested just after breaking the circuit, was found to *exceed* that of No. 1 by 0.06 per cent. — a greater difference than before. Two days later the excess was 0.016 per cent.

Fig. 7.

At 11^h 10^m two accumulators in series (e.m.f. = 4.1 volts) were connected to the terminals of Nos. 4 and 8 in opposition with the current in the normal direction through No. 8, and were so left until 12^h 26^m, when the circuit was broken. At 12^h 31^m the e.m.f. of No. 8 was only 6.9 per cent. of its original value, while that of No. 4 exceeded its initial value by 4.7 per cent. Two days later No. 8 had recovered to within about 0.006 per cent. of its normal e.m.f. and No. 4 to within about 0.09 per cent.

On May 2 at 12^h 52^m a dynamo with an e.m.f. of about 93 volts was connected in series with No. 4 and No. 8 in opposition, the current traversing No. 4 in the normal direction. Ten minutes later the cells had become considerably heated, and the upper part of the mercurous sulphate and adjacent liquid in No. 8 greatly perturbed. The circuit was then broken, and closed again a little later. At the end of about 2^m No. 8 exploded and broke the circuit. The e.m.f. of No. 4 was then tested and found to have fallen to 5.5 per cent. of its original value. On May 2 it had risen

to 6.0 per cent., on May 7 to 9.4 per cent., and on May 12 to within about 0.27 per cent. of its initial value. Shortly after the last comparison the cell was charged for 1^m with a single accumulator (through the millivoltmeter). The e.m.f. was then found to exceed E_1 by 0.3 per cent., the excess rapidly diminishing to 0.15 per cent. On May 15, E_1 exceeded E_4 by 0.04 per cent.¹ (On May 12 the resistances of all the cells had been measured, both by alternating currents and by a charging current from 2 accumulators.)

Also on May 2, about 1^h 10^m, the dynamo was connected in opposition to No. 7 and so left for about 30^s. The e.m.f., on being tested quickly after opening the circuit was found to exceed E_1 by 0.054 per cent., the excess decreasing to 0.04 per cent. by the next morning. On May 7 the e.m.f. of No. 7 was greater than that of No. 1 by 0.024 per cent. and on May 12 by 0.01 per cent. On May 15 the e.m.f. of No. 1 exceeded that of No. 7 by 0.001 per cent.

In most of the experiments here described I have been assisted by one of my students, Mr. C. K. Studley.

STANFORD UNIVERSITY, CALIFORNIA,

May 16, 1903.

¹In a comparison made yesterday E_1 exceeded E_4 by only about 0.004 per cent. Nov. 14, 1903.