

POLARIZATION OF CADMIUM CELLS.

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While working on another problem (Phys. Rev. Vol. 16, p. 105) it was noted that the E. M. F. of a cadmium cell was greatly decreased and at times apparently reversed after a considerable quantity of electricity had passed through it.

To investigate the cause of this phenomenon the experiments described below were undertaken. Work of a similar nature has been carried out by F. E. Smith (Phil. Trans. Roy. Soc. Lon., Series A, Vol. 207, p. 393); by S. J. Barnett (Phys. Rev. Vol. 18, p. 104, 1904), and by P. I. Wold (Phys. Rev., Vol. 27, p. 132, 1909). However, in their experiments the time of polarization was comparatively small, the attention of the investigators being directed to the initial polarization or to the rate of recovery. In my work I have attempted to find the cause of this polarization.

Cells were constructed of the H type and according to the accepted formula for cadmium cells. The chemicals used were C. P. chemicals of commerce. With ordinary care a cell could be obtained whose E. M. F. did not differ more than .001 volt from the standard value. Measurements of E. M. F. were made by means of a potentiometer. At times where rapid measurements were desirable and great accuracy was not necessary a voltmeter was used, the readings being corrected for the internal resistance of the cell. Current was measured with a milliammeter and time was measured with a watch. At first it was thought that the polarization was a surface effect, that a relation existed between the area of the surface of the electrode and the quantity of electricity required to polarize a cell to some standard amount. Cells were made with electrodes of various diameters. The current was noted at stated intervals, so that the total quantity could be calculated. This was found to differ in different cells, but it appeared to depend more upon the past history of the cell than upon the electrode surface exposed.

It was found that after a cell has been polarized once and has regained its normal E. M. F. again it required less quantity of electricity to polarize it than it did during the first run. A cell with three legs was

made. Two of the legs were filled with mercury and the third was filled with cadmium amalgam. Connection was made to the amalgam terminal and to one of the mercury terminals and current passed until the cells were polarized. Measurements were made by means of the potentiometer, and it was found that the E. M. F. between the unpolarized mercury terminal and the cadmium terminal was normal, while the polarized mercury terminal gave a very small value, showing the polarization to be at the mercury terminal. Measurements were made between polarized cells and unpolarized cells by connecting the two cells together by means of a siphon filled with cadmium sulphate solution. In every case it was found that the polarized mercury terminal gave low values, while the polarized cadmium terminal gave normal values when connected to unpolarized mercury terminals, never deviating more than could be explained by concentration and temperature effects.

A cell (5) was short circuited for some days and part of the mercury was removed with a pipette, washed and filtered through a pinhole and made the mercury terminal of a new cell (6) from which the mercurous sulphate was omitted. The E. M. F. was measured from time to time and the recovery noted. The following table gives the results.

		E. M. F.	
		(5)	(6)
March	9, 5:15 p. m.	0.1308	0.1290
March	10, 9:00 a. m.1320	.1307
March	10, 3:45 p. m.1363	.1310
March	12, 9:20 a. m.1488	.1339
March	13, 10:15 a. m.1675	.1322
March	14.	1.0222	.1317
March	15.	1.0242	.1335
May	14.	1.0146	.0691
June	8.	1.0177	.0533
August	26.	1.0189	.0637
September	24.	1.0150	.0462

The above table shows that cell (5), which contained mercurous sulphate, recovered its E. M. F. in a few days, while (6) remained polarized for six months. The results show the E. M. F. in March to be greater than the later values. This may be due to the cadmium sulphate solution not being concentrated in the early observations or to some constant error of the potentiometer. The table shows that the polarization is due to

something in the mercury which can not be washed or filtered out. But is removed by mercurous sulphate. The mercury from cell (6) was taken out and placed in a tube and sparked by a large electric machine. Cadmium lines were very distinct in the spectrum. Thus it would seem that polarization is caused by cadmium being deposited in the mercury and that the recovery is due to the removal of the cadmium by the mercurous sulphate.

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