

THE CADMIUM STANDARD CELL.

BY GEORGE A. HULETT.

A STANDARD cell with a low temperature coefficient was devised by Mr. Edward Weston in 1891.¹ By substituting cadmium sulphate and cadmium amalgam for the zinc sulphate and zinc of the Clark cell, it was found that the temperature coefficient of the cell was reduced 95 per cent., and when the solid cadmium sulphate was dispensed with and only a solution of cadmium sulphate used in the cell, the temperature coefficient was still less. With a solution saturated at 0° C., Barnes and Lucas found² that the E.M.F. of the cell was constant for all ordinary temperature changes. This latter combination is a valuable laboratory instrument, but is not sufficiently reproducible or constant to serve as a standard of E.M.F.

The Clark cell has a variation of E.M.F. of over a millivolt per degree, and for accurate work requires a very exact control of the temperature for a considerable time. The saturated cadmium cell has only one twentieth of the temperature coefficient of the Clark cell and many other desirable features, so that considerable work has been done in testing its reproducibility and constancy.

A. Dearlove³ found that attention must be given to the cadmium amalgam and concluded that it was best to use a 12.5 per cent. amalgam, made by melting together one part of cadmium and seven parts of mercury. Since then considerable work has been done on cadmium amalgams. Kerp and Boettger⁴ concluded that the solid which separates from cadmium amalgams of over 5 per cent. was a compound represented by the formula Cd_2Hg_7 . However, from the work of Bijl⁵ and Puschin⁶ it appears that between about 5 and 15

¹ U. S. Patent No. 494,824. Applied for April 24, 1891.

² Jour. Phys. Chem., 8, 196, 1904.

³ Electrician, 31, 645, 1893.

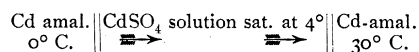
⁴ Zeit. f. Anorg. Chem., 25, 1, 1900.

⁵ Zeit. Phys. Chem., 41, 641, 1900.

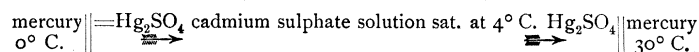
⁶ Zeit. f. Anorg. Chem., 36, 201, 1903.

per cent. of cadmium, the amalgam is a two-phase system, composed of a solid and a liquid phase, and that the solid phase is not a compound, but an isomorphous mixture of cadmium and mercury. The composition of this mixed crystal varies with the temperature, but has a definite composition and E.M.F. for each temperature. The result is that on adding cadmium to mercury, the E.M.F. of the amalgam, towards a cadmium sulphate solution, increases with the increasing per cent. of cadmium until the mixed crystal appears. If the temperature is constant, further additions of cadmium will not effect the E.M.F., but only the relative amounts of the two phases. When the liquid phase disappears a further addition of cadmium will increase the E.M.F. of the system. From Bijl's results this two-phase range is between 10 and 18 per cent. of cadmium at 50°, 5.3 to 15 per cent. at 25° and 4 to 14 per cent. of cadmium at 18°. Jaeger¹ showed that all amalgams in a two-phase range have, for a given temperature, the same E.M.F. almost to the limit of measurement, and it is this property that makes the cadmium amalgam valuable for a standard cell, since little attention need be given to the exact composition of the amalgam, only that it must always remain in the two-phase range for all temperatures at which the cell is used. The 12½ per cent. amalgam first proposed by Dearlove, l. c., satisfies these conditions and also has the desired solidity.

It will be concluded from the above that there must be a temperature coefficient for the E.M.F. of the junction : Cd-amal. || cadmium sulphate solution. To test this the following combination was set up :



This showed a thermoelectromotive force of .00917 V. in the direction of the arrow, also the following combination :



showed the same .00917 V. and in both cases the cold metal was the anode. Therefore both legs of the cadmium cell have a decided temperature coefficient, but when the directions of the electromotive forces at the two electrodes are considered, it will be seen that the

¹ Wied. Ann., 65, 106, 1898.

two temperature effects are oppositely directed as far as the total E.M.F. of the cell is concerned, and it is merely a coincidence that the E.M.F. of the cadmium cell is so little affected by temperature changes.

The amalgam may be made by depositing cadmium electrolytically in a weighed amount of mercury. An excess of cadmium is deposited, the amalgam weighed, and then the correct amount of mercury added to make it 12.5 per cent. Very pure cadmium is obtained in this way if recrystallized cadmium sulphate is used for the electrolyte. This method was devised and used for the amalgams of the (*D*) and (*F*) cells of 1903 but it has since been found that a trace of other metals, even zinc, has hardly a measurable effect on the E.M.F. of the cadmium amalgam and that ordinary pure cadmium answers every purpose. The later amalgams have been made by melting together one part of Merck's cadmium with 7 parts of pure mercury, and this was done on a water-bath with the metals covered with a cadmium sulphate solution.

Cadmium sulphate ($\text{CdO}_4\cdot 8/3\text{H}_2\text{O}$) is a well-defined salt and is easily obtained in large monoclinic crystals which do not seem to carry other salts isomorphously mixed.¹ The rate of growth of the crystals is very slow and the clear ones are quite free from inclusions, but in every crop there are many white crystals which grow more rapidly and may have inclusions. It is an easy matter to pick out the clear crystals and, due to their slow rate of solution, they may be thoroughly rinsed with water. In the work so far the cadmium sulphate crystals have been dissolved by grinding them in a mortar with water until a saturated solution was obtained. This solution was treated with a little cadmium carbonate to neutralize any excess of acid which might have been present. The solution was then carefully filtered and placed in a crystallizing dish to a depth of one centimeter, the dish was covered with thin filter-paper to keep out dust and the solution allowed to evaporate until a good crop of crystals formed. Samples of cadmium sulphate from various sources and with known impurities have been used, but it has been found that, after one crystallization and thorough rinsing that there was not a detectable difference in their behavior of the clear crystals in

¹ Retgers, Zeit. f. Phys. Chem., 16, 594, 1895.

cadmium cells. The solution from these crystals is slightly acid as the result of hydrolysis, but the solution of these crystals in distilled water is exceedingly well-defined and reproducible and it has been found unnecessary and undesirable to change it in any way. Kohnstamm and Cohen¹ thought that they had detected a transition point for this salt at 15° C. but the changes on which they based their conclusion have been traced to the 1 to 6 amalgam used.² This strength amalgam is not a two-phase system below 23° and may undergo slow changes.

The mercury used in all this work on standard cells has been distilled under diminished pressure with a current of air passing through with the mercury vapor. This method insures the removal of all oxidizable metals.³

THE DEPOLARIZER.

The most extensive observations on the cadmium cell have been published by Jaeger and Lindeck.⁴ From their results it seemed that the cadmium cell was reproducible to 1 or 2 parts in 10,000 and the authors attributed the observed variations to the fact that the mercurous sulphate used as polarizer was from different sources, just as Lord Rayleigh had previously⁵ traced variations in the Clark cell to differences in the mercurous sulphate.

Commercial mercurous sulphate is usually made from solutions of mercurous nitrate and sodium sulphate. The precipitate is exceedingly finely divided and carries with it traces of the reagents and is acid. Also an insoluble basic salt is formed and, while these impurities are not present in large quantities, they increase the mercury in the solution made from such preparations and give too large a value to the E.M.F. of the cell.

A fine-grained powder is more soluble than a coarser-grained sample of the same salt, and while the fine-grained powder slowly becomes coarser-grained when left in contact with its solution, there is here a possible source of variation, as has been pointed out by

¹ Wied. Ann., 65, 344, 1898.

² Cohen, Zeit. Phys. Chem., 34, 631, 1900, and Jaeger and Lindeck, Zeit. Instk., 21, 33, 1900.

³ PHYS. REV., 21, 387, 1905.

⁴ Zeit. f. Instk., 21, 33, 1901.

⁵ Philos. Trans., 176, 781, 1886.

H. v. Steinwehr.¹ The "Board of Trade" specifications advise the washing of the mercurous sulphate with water, and while this removes some of the impurities, it also hydrolyzes some of the salt. A rather insoluble basic sulphate is left with the salt, while a soluble acid salt goes into solution, and the wash water with the acid salt is not entirely removed even by suction. It will be seen that the materials and methods which have been used in making the paste for cells afford abundant opportunity for variations. Experiments have shown that acids and particularly the basic salt cause irregular variations in the E.M.F. of the standard cells.

In 1903 the electrolytic method of preparing mercurous sulphate was devised by the author² and independently by Dr. F. A. Wolff, of the Bureau of Standards.³ By this method pure mercurous sulphate, mixed only with dilute sulphuric acid and mercury, was obtained. The acid was removed either by washing with the saturated solution of cadmium sulphate or by using alcohol and ether. Both methods were effective in removing the acid and seemed to prevent hydrolysis. The first cells made with this properly washed electrolytic mercurous sulphate were four (*D*) cells on December 21, 1903, and 10 (*F*) cells on February 15, 1904. These cells agreed among themselves to 1 part in 100,000, assumed their constant value at once but were .00028 V. lower than cells made in the old way with commercial mercurous sulphate.

These cells seemed so much superior to those made according to the old specifications that attention was at once turned to thoroughly testing samples of mercurous sulphate made by the electrolytic method. In brief it was found that it was possible to use a very considerable range of acid strength and current density in making the sulphate. Also that the preparation was sufficiently coarse-grained to entirely avoid any effect due to the size of particles on the solubility, and that it was the most reproducible and reliable preparation for use in standard cells. The details of this work as well as a complete description of the method of preparing electro-

¹ Zeit. f. Instk., 25, 201, 1905.

² Trans. Amer. Electrochem. Soc., 5, 59, 1904; Trans. Internat. Elect. Congress St. Louis, Vol. 2, 109, 1904; Zeit. Phys. Chem., 49, 483, 1904.

³ Trans. Amer. Electrochem. Soc., 5, 49, 1904.

lytic mercurous sulphate and making the paste for cells have already been described.¹

SLOW CHANGES IN THE E.M.F. OF THE CADMIUM CELL.

After the (*D*) and (*F*) cells have been under observation for nearly two years, six cadmium cells, *A*1 to *A*6, were made and the materials and construction were, as nearly as it was possible to make them, a duplication of the (*D*) and (*F*) cells, *but these new cells were .00011 V higher than the older ones*. More cells were made with different samples of electrolytic mercurous sulphate and with variations in the other materials and in the construction, but they all agreed with the new (*A*) cells. Fortunately 10 Clark cells had been made in 1904, and with some of the same electrolytic mercurous sulphate which had served for the depolarizer of the (*F*) cells. These Clarks did not show the usual "ageing" but appeared to have their constant value at once. After two years, however, they appeared to have slightly increased in value (.00011 V.). The cadmium cells had been assumed constant and had been made the basis of all the comparisons. If now the Clarks had been assumed to be constant and taken as the basis, the cadmium cells would, of course, appear to have decreased by this .00011 V. and the difference between the new and the old cadmium cells is then explained by a slow change in the cadmium cell.

More Clark cells (*H*11 to *H*16) were made on July 30, 1905, and on February 25, 1906, cells *H*17 to *H*21 were made, and for depolarizer some of the same sample of electrolytic mercurous sulphate was used as had served for the new (*A*) cells. The following table gives some of the many observations that have been made on these cells. All the cells have been maintained in a large oil-bath since October, 1905. The bath was electrically heated and controlled and the temperature has remained constantly at 25° C. to within $\frac{1}{50}^{\circ}$. For details see this journal, 22, 323, 1906. The basis of all the results given in this paper are the Clark cells, *H*1 to *H*21, which were made on three different dates and are now in good agreement. The value chosen is the one obtained by Dr.

¹ PHYS. REV., 22, 321, 1906.

Guthe for these cells and is 1.42040 V. at 25° C.¹ This gives a calculated value of 1.43300 at 15° but it should be added that these Clark cells were all made with electrolytic mercurous sulphate as depolarizer; the paste was prepared as previously described,² and they are .00030 V. lower than Clark cells made in the old way with commercial mercurous sulphate.

Cell.	Date.	Mar. 18, '04.	Mar. 24, '05.	Aug. 5, '05.	Dec. 14, '05.	Mar. 4, '06.	June 4, '06
D4	Dec. 21, '03.	1.01842	1.01831	1.01928	1.01832	1.01832	1.01830
F1	Feb. 15, '04.	42	31	27	30	32	29
F2	"	42	32	26	31	30	15
F3	"	42	32	28	32	31	34
F4	"	42	31	28	32	32	27
F5	"	42	32	32	31	33	33
F6	"	42	32	27	32	33	32
F7	"	42	32	28	34	32	32
A1	Oct. 21, '05.				1.01843	1.01843	1.01842
A2	"				43	43	42
A3	"				42	43	42½
A4	"				43	43	42½
A5	"				43	43	42½
A6	"				43	43	43
H2	Mar. 15, '04.	1.42040	1.42040	1.42038	1.42038	1.42040	1.42039
H3	"	40	37	38	—	40	39
H4	"	40	38	37	40	43	42
H6	"	39	—	42	37	40	42
H7	"	41	41	44	38	40	40
H8	"	41	40	41	—	40	40½
H11	July 30, '05.				1.42040	1.42041	1.42039
H15	"				41	41	41
H16	"				41	41	42
H17	Feb. 25, '06.					1.42039	1.42041½
H18	"					39	42
H19	"					40	42
H20	"					38	37
H21	"					43	41
C1	Nov. 21, '03.	1.01868	1.01864	1.01858	1.01862	1.01861	1.01860
A7	Nov. 15, '06.				72	70	67

The results given in Table I. from December 14, 1905 on, are the observed values, but the values for March 18, 1904, March 24,

¹ PHYS. REV., 21, 117, 1906.

² PHYS. REV., 22, 334, 1906.

1905, and August 5, 1905, have been recalculated, for the sake of comparison, from the observations which were made at 21° and 18° . These cells all follow the accepted temperature coefficient so closely that the calculated values are reliable, but the conclusive facts are based upon the observations made since October, 1905, when the control of the temperature and the conditions of comparison have been particularly exact.

It is to be observed that the new cadmium cells, *A1* to *A6*, are now .00011 V. higher than the older (*F*) series, and that the values of the (*A*) cells are now very close to the values the (*F*) cells originally had. On the other hand the Clark cells, made on three different dates, are now all in excellent agreement. The depolarizers of the (*F*) cells and the *H1* to *H10* Clarks were all from the same sample, while the sample of mercurous sulphate which was used for the new *A1* to *A6* cells was also used for the Clarks *H17* to *H21*. This indicates that the change observed in the (*D*) and (*F*) cells is not a peculiarity of the electrolytic mercurous sulphate. Further proof that the electrolytic mercurous sulphate is not at fault is at hand in the observations on some cadmium cells which were made in 1903 with commercial mercurous sulphate according to the old specifications. These cells have also changed as indicated by the record of cell *C1* given in Table I. On November 15, 1905, cell *A7* was made with commercial mercurous sulphate and according to the old specifications and it will be seen that this cell is now higher than the older (*C*) cell. All of the cells made with commercial mercurous sulphate and according to the old specifications were very high at first and showed the usual "ageing" for a month before becoming "constant."

In the literature there is some evidence of this "drift" of the cadmium cell, Mr. F. E. Smith¹ describes some cadmium cells which were made in April, 1902, and two years later another cell was made with exactly the same materials, but the new cell was .00007 V. higher than the older ones.

This observed change in the E.M.F. of the cadmium cell is small and slow and from a practical standpoint is of little consequence, but it is not to be overlooked when it comes to a question of a

¹ Electrician, 53, 832, 1904.

standard of electromotive force. The change seems to be more rapid at higher temperatures and especially does the depth of the paste in the leg of the cell play an important rôle. Some cells were made on November 29, 1904, with the paste only 3 or 4 mm. deep, the object was to make a cell with a smaller internal resistance. These cells showed the normal value of 1.01844 V. when first made, but began at once to noticeably decrease. On January 10, 1905, they were 1.01839, April 4, 1905, 1.01811 and by June, 1905, were about 1.0177 V. and were very irregular, only two of these cells were retained and in December, 1905, they were 1.0172 and 1.01815, and now June, 1906, they are 1.0160 and 1.01813 respectively. It is to be noted that the (*F*) cells are no longer in as good agreement as when first constructed. The paste in the (*F*) cells is about 10 mm. deep and it is 20 mm. deep in the *A* cells and in all cells made since these facts appeared. It might be added that the (*A*) cells have not yet shown a decided change but it is probably only a question of time.

From the foregoing it is to be concluded that slow changes take place in the cadmium cell and, during the past two years, a number of results have been obtained which indicate that it is the system in the cathode leg of the cell which is not in equilibrium. Mercurous sulphate has been formed electrolytically in a cadmium sulphate solution. The apparatus and method was the same as used for preparing electrolytic mercurous sulphate.¹ The mercury from the anode went into the cadmium sulphate solution and separated as mercurous sulphate while cadmium was deposited at the cathode, the solution remained neutral and was saturated as cadmium sulphate crystals were present. The idea was that this preparation might be used directly in the cell without removing the mother liquor. It was expected that with this method and the rapid stirring that the product obtained would be in equilibrium with the cadmium sulphate solution and the mercury. Two samples were prepared and different current densities were used. The preparations were white and sufficiently coarse-grained to avoid the effect of size of particles on the solubility. One sample was made with a current density of .12 amp. per 100 cm.² mercury anode surface,

¹ PHYS. REV., 22, 334, 1906.

and was used, with some of the solution in which it was made, for the depolarizer of cell *A17*. Some of this same sample was used for cell (*A18*) but its solution was first removed by suction and then it was washed with a fresh cadmium sulphate solution. The second sample was made with a current density of .5 amp. and was used direct in cell *A19*. These cells were made November 23, 1905, and the following results have been obtained :

Cell.	Nov. 30.	Dec. 14.	Jan. 1, 1906.	Feb. 7.	Mar. 4.	Apr. 13.	May 12.	June 4.
<i>A17</i>	1.10878	1.01872	1.01871	1.01870	1.01873	1.01871	1.01869	1.01868
<i>A18</i>	86	78	75	67	65	60	58	55
<i>A19</i>	48	48	47	49	48	49	48	48

It will be seen that the samples made with the different current densities do not agree and that the one made with the larger current density (*A19*) has remained quite constant and is nearest to the *A1* to *A6* cells. The sample which was made with a low-current density was used in cell *A18*, but the solution in which it was made was first removed by suction and then the salt was washed with a fresh cadmium sulphate solution. This cell was high at first and has decreased the most.

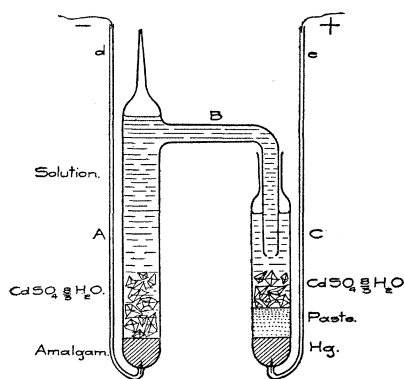
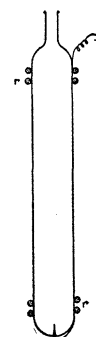
Two years ago an attempt was made to bring mercurous sulphate into equilibrium with a cadmium sulphate solution and mercury. The system—cadmium sulphate, mercurous sulphate, mercury and saturated solution—was rotated at 25° for ten days, and then the mercurous sulphate was brought onto a filter and washed with a fresh solution of cadmium sulphate. With this preparation three cells were made on May 6, 1904, and the following observations, calculated to the present basis and 25°, have been made :

Cell.	May 6.	May 9.	June 13.	July 13.	Aug. 9.	Apr. 14, 1904.	June 3.	July 25.
<i>/6</i>	1.01975	1.01934	1.01900	1.01889	1.01887	1.01817	1.01800	1.01816
<i>/7</i>	77	32	01	88	91	15	1797	1799
<i>/8</i>	63	31	03	93	96	32	1807	1818

The cells had become irregular and had not become constant and it was concluded that the system, which had been rotated ten days, had not reached equilibrium, so the observations on these cells were discontinued. This question was taken up again after the "drift"

in the (*D*) and (*F*) cells has been detected. It was decided to rotate this system in the cathode leg until it should come to equilibrium. When this point is reached there should be no further change in the solution or in the E.M.F. between the system and mercury. It was found most convenient to measure the E.M.F. at frequent intervals as a means of deciding on the absence of further change in the system.

An adjustable cadmium cell was made as represented by Fig. 1, the leg (*A*) contained the cadmium amalgam and the cadmium sulphate of the anode, and it will be seen from the cut that the side tube (*B*) of this leg bends down and passes through the neck of the tube (*C*). This tube (*C*) contained the mercury, paste and cadmium sulphate of the cathode leg of the cell. This cell was used in a water-bath and it was found necessary to attend to the insulation.

Fig. 1. ($\frac{1}{8}$ nat. size.)Fig. 2. ($\frac{1}{8}$ nat. size.)

This was done by sealing on the little tubes (*e*) and (*f*) as indicated in the cut, the contact wires passed up through these tubes and there was then no further trouble on this point. This cell had the value 1.01837 and has remained perfectly constant, although it has many times been taken apart and the anode leg used to test other systems. The cell is now six months old and a new anode leg has lately been made, but it shows exactly the same value as the older ones.

A large tube, 5 × 24 cm. (Fig. 2), contained the materials of the cathode system of the cadmium cell. The neck of this tube was made to admit the side tube (*B*) of the adjustable anode (*A*), Fig. 1,

thus forming a cadmium cell. Contact with the mercury in this large tube was made through a platinum wire which was fused through the closed end of the tube and passed up on the outside. The wire was covered with shellac, a thin strip of cloth was placed over the wire and then it was thoroughly shellaced and finally covered with a coat of collodium (the use of collodium was suggested by Dr. E. H. Loomis and is a very admirable device for protecting anything which is to be in contact with water for any length of time). This large tube contained 140 gr. of mercury, 50 grams of coarse-grained electrolytic mercurous sulphate which had been washed with alcohol and dried, 50 gr. of cadmium sulphate crystals and about 400 c.c. of a saturated solution of cadmium sulphate. In order to bring this system to equilibrium, the neck of the tube was securely closed with a cork and rubber covering, the tube was brought to a horizontal position in the 25° bath and rotated about its longer axis as follows: Above the bath was a shaft which was run at any desired speed by a worm gear, and from this shaft two little belts extend down into the bath. The tube was suspended in the loops of these belts. The belts were kept in place by rubber rings on the shaft and on the tube. In this way it was possible to rotate the tube about its longer axis at any desired speed, the solid contents of the tube were spread out in a long layer and slowly "rolled down hill" as the tube rotated. This method insured a thorough mixing of the contents of the system and was sufficiently gentle to avoid grinding the solids. A fine powder has an abnormal solubility and this error is very considerable when the solubility is small. Also it was found desirable to avoid breaking up the mercury into small globules, because these globules formed larger ones when the rotation was stopped, and this change caused very decided variations in the E.M.F. readings. It was found that by rotating the tube at the rate of one revolution in about six seconds that the mercury generally remained in one globule, and that this rate, with the above method, still insured a perfect mixing of the contents of the tube. From time to time the tube was brought to an upright position in the bath and the E.M.F. measured with the aid of the adjustable anode leg. The large 100 liter thermostat maintained the temperature constantly within $.02^{\circ}$ of 25° C. Since the rotat-

ing would unduly expose the mercurous sulphate to the light, it was decided to avoid this possible source of error by covering the tube with asphalt paint and then with collodium.

The first rotation was for twelve hours, when the system was tested with the anode leg the first reading

3 minutes after stopping the rotation was 1.0190 V.				
9	"	"	"	1.0184
35	"	"	"	1.0178
3 hours	"	"	"	1.0177

The system was now rotated three days and

5 minutes after stopping the rotation the E.M.F. was 1.01938 V.				
20	"	"	"	1.01942
1 hour	"	"	"	1.01941
5	"	"	"	1.01941

The tube was closed and rotated seven and one half days, making a total of eleven days.

3 minutes after stopping the rotation the E.M.F. was 1.01820 V.				
9	"	"	"	1.01860
30	"	"	"	1.01910
3 hours	"	"	"	1.01971
24	"	"	"	1.01971

The preliminary low values observed here were regarded as due to the mercury being in small globules and as they united to form larger ones the E.M.F. increased to a maximum. That the constant value obtained was reliable is shown by the following test. Some of the clear solution was removed and brought into a tube like the tube (C) of Fig. 1. Some mercury was put in to serve as an electrode and then the solution tested with the anode leg. The value obtained was 1.01983.

The system was now rotated six and one half days, making a total of seventeen and one half days.

3 minutes after stopping the rotation the E.M.F. was 1.01920 V.				
5	"	"	"	85
30	"	"	"	91
1 hour	"	"	"	89
5	"	"	"	90
24	"	"	"	79
72	"	"	"	74

The clear solution was tested as previously described and gave 1.01992 V. Evidently a change begins to take place in the layer next to the mercury as soon as the solids settle down on the electrode and this is possibly the "drift" of the cadmium cell at its maximum rate.

The tube was again closed and rotated for eight and one half days, making a total of 26 days. The following readings were then obtained :

3 minutes after stopping the rotation the E.M.F. was 1.0120 V.				
6	"	"	"	1.0155
18	"	"	"	1.0166
1 hour	"	"	"	1.01910
3	"	"	"	1.01976
7	"	"	"	1.01977
24	"	"	"	1.01973
48	"	"	"	1.01967
170	"	"	"	1.01948

Here the preliminary low value, which has been attributed to changes in the mercury electrode, was more persistent and the maximum value observed was consequently lower. After the tube had stood quietly for a week, the lower end was given a rotary motion in order to break up the mercury into smaller globules but without mixing the entire contents of the tube.

2 minutes after the shaking just mentioned the E.M.F. was 1.0135 V.				
7	"	"	"	1.0161
12	"	"	"	1.0177
45	"	"	"	1.0196
1 hour	"	"	"	1.01985
2	"	"	"	85
6	"	"	"	85

These results indicate that the preliminary low values observed in the preceding experiments were due to the mercury changing from small to large globules, as had been assumed. It was possible to still further test this point as follows. The tube was rotated as before for three and one half days at the rate of one revolution in six seconds and then the rate was decreased to one revolution in seventy seconds and this rate of rotation was continued for one day in order to allow the mercury to collect in one globule. The tube

was then carefully brought to an upright position and the anode leg adjusted.

2 minutes after stopping the rotation the reading was 1.01977 V.

4	"	"	"	"	77
10	"	"	"	"	78
40	"	"	"	"	76
1½	hours	"	"	"	75
5	"	"	"	"	71
9	"	"	"	"	68
24	"	"	"	"	64
48	"	"	"	"	

The clear solution gave 1.01985. It is evident from the preceding experiments that if the system in the cathode leg of the cadmium cell is stirred until no further change takes place that, at 25°, the cell has the value 1.0198 V. or .0014 V. higher than the cadmium cell. If this system, after it has been rotated until no further change takes place, be allowed to rest, the E.M.F. begins to drop but the clear solution, from which the solids have settled, continues to retain its high E.M.F. against a mercury electrode. It seems reasonable to conclude that there is some interaction between the cadmium sulphate solution and the mercurous sulphate which produces an increase in the mercury concentration of the solution, but when the solids settle down on the mercury, another change takes place at the boundary between the mercury and the paste which causes a decrease in the mercury concentration of solution next to the mercury. The possibility, that the oxygen of the air dissolved in the solution produces some mercuric mercury, has been considered. This would explain the results obtained if we assume that the mean rate of oxidation is rapid compared to the subsequent rate of reduction by the mercury. However I have not been able to get experimental proof of this view, while the following results with the cathode system of the Clark cell show that under similar conditions, oxidation by dissolved air does not play a measurable rôle in the case of a zinc sulphate solution. It seems more probable that the interaction between the cadmium sulphate solution and mercurous sulphate is of the nature of an hydrolysis accompanied by the slow formation of a new, slightly soluble solid phase. The evidence for this view will be given when the present experiments are completed.

In order to test the method that has been employed in the preceding experiments and also to confirm many of the conclusions, it was decided to subject the cathode system of the Clark cell to the same processes. An adjustable Clark cell was made similar to the above adjustable cadmium cell. This Clark cell has shown a constant value of 1.42045 V. at 25°. A large rotating tube was charged with mercury, mercurous sulphate (electrolytic washed with alcohol and dried), recrystallized zinc sulphate, and the saturated solution. This system was rotated as previously described and after twelve hours the contents were tested with the adjustable anode of the Clark cell, with the following results :

3 minutes after stopping the rotation the E.M.F. was 1.42052 V.				
45	"	"	"	1.42048
3	hours	"	"	1.42048
6	"	"	"	1.42049

The system was now rotated twenty-four hours and then showed 1.42050 V. and after the solids had settled some of the clear liquid was tested against a mercury electrode with the adjustable anode and the value obtained was 1.42051 V.

The system was now rotated for six days.

3 minutes after stopping the rotation the E.M.F. was 1.42055 V.				
6	hours	"	"	1.42050
27	"	"	"	1.42054

The tube was again closed and rotated for 10 days, making a total of seventeen and one half days, and then gave the value of 1.42052 V. and was constant. This experiment shows that the cathode system of the Clark cell comes to equilibrium in less than twelve hours and remains constant from then on. The slight variations observed may readily be accounted for as due to slight temperature variations to which the E.M.F. of the Clark cell is very sensitive, besides no special precautions were taken to exclude the effect of light, so the test was a very severe one.

These results obtained by rotating the cathode systems of the cadmium and Clark cells seem to confirm in a most decisive manner the validity of the observations of the last two years on the Clark and cadmium cells. The assumption that the "drift" of the E.M.F.

of the cadmium cell is due to changes in the cathode system seems justified, but the possibility that some of the observed decrease in E.M.F. might be at the amalgam of the anode, has not been overlooked. This was tested as follows: some of the old cadmium cells which are now distinctly lower than when they were first observed, were opened and the side tube (*B*) of the anode leg (*A*) of Fig. 1 was brought into contact with the liquid of the cell and the E.M.F. of the cathode leg measured with the new anode as well as with the old. Any difference in the E.M.F. would be due to differences between the old and the new anode.

Cell.	With the Old Anode.	With the New Anode.
<i>F</i> 1	1.01832	1.01829
<i>F</i> 2	1.01830	1.01830
<i>F</i> 4	1.01833	1.01830
<i>C</i> 2	1.01832	1.01827
<i>N</i> 9	1.01616	1.01617

Cell *C*2 was made on November 21, 1903, with commercial mercurous sulphate, and was originally 1.01866. Cell *N*9 was one of the cells made in November, 1904, with only a little paste and is still decreasing. With the new anode the cells are about .00003 V. lower, so the change at the cathode has been even greater than indicated by the direct comparisons of the cells.

The foregoing experiments justify the conclusion that the cathode system of the cadmium cell, as at present constructed, is not a system in equilibrium and that the E.M.F. of the cell decreases with time. The rate of this "drift" depends on a number of factors, but if the paste in the cathode leg is about 2 cm. deep, the change is very slow. The cadmium cell, when properly constructed with electrolytic mercurous sulphate, which has been prepared and washed as previously described, has a value of 1.01843 V. at 25° C. and seems to be reproducible to about 2 parts in 100,000. Cells should be made from time to time to detect the presence and magnitude of the drift. For all ordinary purposes this cell is entirely satisfactory but, if there are no serious errors in the experiments recorded in this article, the cadmium cell as at present constructed can hardly supplant the Clark cell as a primary standard of E.M.F.

The Clark cell made with recrystallized zinc sulphate and elec-

trolytic mercurous sulphate which has been prepared and washed as described in this journal¹ has the value 1.43300 V. at 15° C. as determined by Dr. K. E. Guthe.² This value is also the average of all the best previous determinations of the value of the Clark cell in absolute units. The experiments described in this article have severely tested the Clark cell and with most favorable results. Several improvements and simplifications of this cell have been suggested by the work done are now being tested.

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¹ PHYS. REV., 22, 334, 1906.

² PHYS. REV., 22, 117, 1906.