THE ELECTRODE EQUILIBRIUM OF THE STANDARD CELL.

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Some experiments described by Hulett[2] indicating the existence of a state of unstable equilibrium in the Weston cell have, on account of the importance of the subject, led to a further study of the question at the Bureau of Standards.

The equilibrium between cadmium amalgam and cadmium sulphate was first studied. Saturated solutions of the latter were shaken up in air, nitrogen, hydrogen, and *in vacuo* with cadmium amalgam, but in no case did the electromotive force of cells set up with the treated and untreated solutions differ more than 10 microvolts, even though the samples shaken in the presence of air had become cloudy from the formation of an excess of basic cadmium sulphate.

The equilibrium of the system mercury, mercurous sulphate, cadmium sulphate, and of the corresponding system of the Clark cell was then studied in special cells, so constructed that the above materials could be rotated and the effect determined without opening the cell.

This consisted of a tube about 2 cm in diameter and 12 cm long, provided at the lower end with a small bulb into which a platinum wire was sealed. The bulb was connected to the main tube by a narrow neck, so that, with sufficient mercury in the cell, the platinum terminal was not in contact with the solution, even during rotation.

[1] An abstract of this paper was read at the New York meeting of the American Physical Society, December, 1906, Phys. Rev., **24**, 251; 1907.

[2] Phys. Rev., **23**, 166; 1906.

A shorter internal tube about 1 cm in diameter with several lateral openings, sealed in at the other end of the main tube, was charged with amalgam and crystals of cadmium or zinc sulphate, which were held in place by a plug of asbestos. Contact with the amalgam was made by means of a platinum wire, protected from the solution by sealing it into a glass tube, which extended through the upper seal made after the introduction of the above materials.

The mercurous sulphate and cadmium sulphate or zinc sulphate crystals were introduced over the mercury through a side tube by which the cell was exhausted and through which a saturated solution of cadmium or zinc sulphate was subsequently introduced. After filling, the side tube was sealed off, leaving only a small air bubble in the cell, thus practically eliminating any possible influence of air.

The cells were then placed in holders so arranged that one dozen could be simultaneously rotated at any desired speed, with their axes parallel to the axis of rotation and inclined at a small angle to the horizontal, thus insuring a thorough stirring of the paste and mercury with the electrolyte, even at five or six revolutions per minute. The measurements were made in an automatically controlled oil bath at 25°, immediately after stopping the rotation and raising the holder to a vertical position under the oil. Altogether 12 Weston and 5 Clark cells of this type were set up with samples of mercurous sulphate, made not only by the electrolytic method but also by several chemical methods. The mercurous sulphate was washed in a Gooch crucible three times with 1 : 6 sulphuric acid, six times with absolute alcohol, and three times with saturated zinc or cadmium sulphate solution. The data and results are given in the following tables:

TABLE I.

Weston Rotating Cells.

Cell	Date 1906	$CdSO_4$	Cd Amalg.	Mercury	Hg_2SO_4		
					Sample		Method of Preparation
R 1	Oct.13	Purified by Recrystallization.	12½% Kahl. El.Dist.	Distilled at reduced pressure.	b_{13}	gray	Electrolytic (D=5; V=.5)
*R 11	Oct.30	"	"	"	b_{13}	gray	Electrolytic (D=5; V=.5)
†R 12	Oct.30	"	"	"	b_{13}	gray	Electrolytic (D=5; V=.5)
R 3	Oct.13	"	"	"	e_3	gray	By action of HN_2O_3 and H_2SO_4 on Hg
R 5	Oct.16	"	"	"	d_2	gray	From $HgNO_3$ and H_2SO_4
R 6	Oct.16	"	"	"	c	gray	By action of fuming H_2SO_4 on Hg
R 2	Oct.13	"	"	"	a_{12}	white	Electrolytic (D=.25 1:16 H_2SO_4)
‡R 8	Oct.30	"	"	"	a_{12}	white	
R 4	Oct.16	"	"	"	a_9	white	
‡R 10	Oct.30	"	"	"	a_9	white	
R 7	Oct.16	"	"	"	i_2	white	By digestion of Coml. Sample with H_2SO_4
‡R 9	Oct.30	"	"	"	i_2	white	

* Platinum terminal exposed to paste.

† Basic cadmium sulphate added to paste.

‡ Mercurous sulphate rotated with saturated $CdSO_4$ solution 2¾ days before its introduction into the cells.

TABLE II.

Clark Rotating Cells.

Cell	Date 1906	$ZnSO_4$	Zn Amalg.	Mercury	Hg_2SO_4		
					Sample		Method of Preparation
R 2	Nov.5	Purified by Electrolysis	Kahl. I	Distilled at reduced pressure	b_{16}	gray	Electrolytic (D=9.25; V=.75)
*R 3	Nov.5	"	"	"	$_{16}b$	gray	Electrolytic (D=9.25; V=.75)
R 5	Nov.5	"	"	"	a_{12}	white	Electrolytic (D=.25; 1:6 H_2SO_4)
*R 4	Nov.5	"	"	"	a_{12}	white	
R 1	Nov.5	"	"	"	a_9	white	

* Zinc oxide added to paste.

TABLE III.

Weston Rotation Cells.

[Differences in microvolts from mean of reference cells.]

Date	R 1		R 11		R 12		R 3		R 5		R 6	
	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time
		D. H.		D. H.		D. H.		D. H.		D. H.		D. H.
Oct. 18,'06	+72	0	.....	.....	.....	.....	+89	0	+ 83	0	+92	0
" 19	+43	0	.....	.....	.....	.....	+59	0	+ 59	0	+67	0
" 20	+11	0	.....	.....	.....	.....	+24	0	+ 34	0	+39	0
" 22	+29	0	.....	.....	.....	.....	+39	0	+ 54	0	+55	0
" 23	+44	15	.....	.....	.....	.....	+53	15	+ 57	15	+66	15
" 24	+42	18	.....	.....	.....	.....	+57	18	+ 88	18	+43	18
" 25	+45	1 9	.....	.....	.....	.....	+41	1 9	+103	1 9	+41	1 9
" 27	+63	3 1	.....	.....	.....	.....	+64	3 1	+142	3 1	+58	3 1
" 29	+88	5 1	.....	.....	.....	.....	+88	5 1	+149	5 1	+83	5 1
" 31	+61	6 21	− 4	0	−11	0	+69	6 21	+ 93	6 21	+56	6 21
Nov. 5	+73	10 14	+ 55	3 7	+37	3 7	+83	10 14	+ 90	10 14	+65	10 14
" 8	+66	12 17	+ 79	5 11	−17	5 11	+67	12 17	+104	12 17	+46	12 17
" 12	+72	16 12	+ 69	9 0	−31	9 6	+69	16 12	+ 71	16 12	+52	16 12
" 16	+64	20 8	+ 116	12 20	−54	13 2	+70	20 8	+ 50	20 8	+55	20 8
" 19	+59	23 5	+ 139	15 17	−36	15 23	+69	23 5	+ 47	23 5	+54	23 5
" 24	+50	28 4	+ 204	20 16	−26	20 22	+71	28 4	+ 41	28 4	+54	28 4
" 30	+35	28 8	+ 117	20 20	−37	21 2	+35	28 8	+ 29	28 8	+32	28 8
Dec. 5	+31	28 8	+ 93	20 20	−39	21 2	+33	28 8	+ 26	28 8	+30	28 8
" 10	+46	32 1	+ 240	24 13	− 8	24 19	+74	32 1	+ 40	32 1	+54	32 1
" 14	+50	35 16	+ 271	28 4	−25	28 10	+74	35 16	+ 45	35 16	+53	35 16
" 21	.....	.....	+ 348	33 21	−17	34 12	+92	41 18	+ 41	41 18	+38	41 18
Jan. 5,'07	.....	.....	+ 520	46 12	−32	47 3	+67	54 7	+ 41	54 7	+19	54 7
" 10	.....	.....	+ 567	50 6	−27	51 20	+66	59 4	+ 47	59 4	+28	59 4
" 14	.....	.....	+ 427	52 18	−34	54 8	+51	61 16	+ 40	61 16	+13	61 16
" 24	.....	.....	+ 749	61 12	−26	62 16	+66	70 0	+ 46	70 0	+33	70 0
" 30	.....	.....	+ 926	67 2	−36	68 6	+50	75 22	+ 42	75 22	+24	75 22
Feb. 5	.....	.....	+1030	71 10	−36	73 6	+49	80 21	+ 37	80 21	+32	80 21
" 8	.....	.....	+1073	72 21	−35	74 18	+46	82 9	+ 38	82 9	+28	82 9
Mar. 1	.....	.....	.....	.....	−43	93 14	−38	101 5	+ 38	101 5	+35	101 5
" 12	.....	.....	.....	.....	−42	102 14	−29	110 5	+ 32	110 5	+40	110 5
Apr. 5	.....	.....	.....	.....	−41	121 4	− 8	128 19	+ 90	128 19	+51	128 19
" 10	.....	.....	.....	.....	−34	124 10	−10	132 1	+ 94	132 1	+76	132 1
May 25	.....	.....	.....	.....	−38	135 4	− 7	142 19	+127	142 19	+84	142 19
June 4	.....	.....	.....	.....	−34	144 20	− 3	152 11	+135	152 11	+95	152 11
" 7	.....	.....	.....	.....	−37	147 18	+ 2	155 9	+142	155 9	+94	155 9
" 15	.....	.....	.....	.....	−37	155 6	− 3	162 21	+169	162 21	+99	162 21
Aug.15	.....	.....	+ 494	72 21	−40	155 6	− 5	162 21	+ 44	162 21	+43	162 21
Sept.27	.....	.....	+ 571	72 21	−41	155 6	− 6	162 21	+ 38	162 21	+23	162 21

TABLE III.

Weston Rotation Cells.

[Differences in microvolts from mean of reference cells.]

R2		R8		R4		R10		R7		R9	
Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time
	D. H.		D. H.		D. H.		D. H.		D. H.		D. H.
+148	0	.....	.....	+ 137	0	.....	.....	+ 93	0	.....	.....
+115	0	.....	.....	+ 100	0	.....	.....	+ 49	0	.....	.....
+ 59	0	.....	.....	+ 69	0	.....	.....	+ 10	0	.....	.....
+ 98	0	.....	.....	+ 94	0	.....	.....	.....	0	.....	.....
+103	15	.....	.....	+ 95	15	.....	.....	+ 46	15	.....	.....
+220	18	.....	.....	+ 252	18	.....	.....	+115	18	.....	.....
+275	1 9	.....	.....	+ 354	1 9	.....	.....	+173	1 19	.....	.....
+245	3 1	.....	.....	+ 316	3 1	.....	.....	+168	3 9	.....	.....
+313	5 1	.....	.....	+ 363	5 1	.....	.....	+178	5 9	.....	.....
+321	6 21	− 9	0	+ 441	6 21	+216	0	+111	7 5	+ 76	0
+340	10 14	+515	3 7	+ 440	10 14	+590	3 7	+187	10 22	+295	3 7
+329	12 17	+474	5 11	+ 572	12 17	+556	5 11	+141	13 2	+249	5 11
+292	16 12	+389	9 0	+ 429	16 12	+501	9 0	+ 97	16 0	+186	9 0
+279	20 8	+380	12 20	+ 810	20 8	+440	12 20	+ 90	19 20	+187	12 20
+259	23 5	+414	15 17	+ 754	23 5	+479	15 17	+ 81	22 16	+159	15 17
+237	28 4	+364	20 16	+ 754	28 4	+389	20 16	+ 61	27 16	+104	20 16
+152	28 8	+272	20 20	+ 655	28 8	+265	20 20	+ 57	27 19	+ 93	20 20
+136	28 8	+228	20 20	+ 613	28 8	+234	20 20	+ 52	27 19	+ 85	20 20
+204	32 1	+337	24 13	+ 931	32 1	+336	24 13	+ 69	31 12	+107	24 13
+194	35 16	+336	28 4	+1092	35 16	+314	28 4	+ 68	35 3	+106	28 4
+191	41 18	.....	.....	.....	.....	+248	33 21	+ 74	40 20	+ 95	33 21
+150	54 7	.....	.....	.....	.....	+207	46 12	+ 63	53 12	+ 63	46 12
+147	59 4	.....	.....	.....	.....	+207	50 6	+ 58	57 6	+ 72	50 6
+126	61 16	.....	.....	.....	.....	+195	52 18	+ 70	59 17	+ 53	52 18
+ 56	70	.....	.....	.....	.....	+196	61 12	+ 73	68 12	+ 72	61 12
+110	75 22	.....	.....	.....	.....	+146	67 2	+ 50	74 2	+ 36	67 2
+115	80 21	.....	.....	.....	.....	+135	71 10	+ 44	78 10	+ 38	71 10
+113	82 9	.....	.....	.....	.....	+139	72 21	+ 45	79 21	+ 33	72 21
+118	101 5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+ 60	110 5	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+115	128 19	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+114	132 1	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+113	142 19	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+115	152 11	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+111	155 9	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+135	162 21	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
+ 15	162 21	.....	.....	.....	.....	+ 55	72 21	+ 36	79 21	+ 12	72 21
+ 7	162 21	.....	.....	.....	.....	+ 55	72 21	+ 28	79 21	+ 13	72 21

TABLE IV.

Clark Rotation Cells.

[Differences in microvolts from mean of reference cells.]

Date	R 2		R 3		R 5		R 4		R 1	
	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time	Diff.	Time
		D. H.		D. H.		D. H.		D. H.		D. H.
Nov. 6,'06	−25	0	−120	0	0	0	−140	0	+ 13	0
Nov. 7	−13	22	−130	22	+ 30	22	− 50	22	+ 27	22
Nov. 8	+16	1 22	− 54	1 22	+ 59	1 22	− 26	1 22	+ 49	1 22
Nov. 12	+16	4 16	+ 45	4 16	+100	4 16	+ 25	4 16	+ 90	4 16
Nov. 16	+17	8 13	+ 2	8 13	+ 89	8 13	+ 2	8 13	+ 72	8 13
Nov. 24	+21	16 9	+ 4	16 9	+ 89	16 9	± 0	16 9	+ 81	16 9
Nov. 30	+36	16 12	+ 18	16 12	+ 61	16 12	− 5	16 12	+ 46	16 12
Dec. 5	+22	16 12	− 20	16 12	+ 45	16 12	− 43	16 12	+ 22	16 12
Dec. 10	+22	20 6	+202	20 6	+ 72	20 6	− 34	20 6	+ 22	20 6
Dec. 14	+21	23 20	+273	23 20	+113	23 20	+ 98	23 20	+ 8	23 20
Dec. 21	+26	29 22	+ 22	29 22	+ 34	29 22	+ 20	29 22	− 36	29 22
Jan. 5,'07	.....	.....	−217	42 14	−136	42 14	− 17	42 14	+ 12	42 14
Jan. 10	.....	.....	−243	47 10	−141	47 10	− 3	47 10	+ 7	47 10
Jan. 14	.....	.....	−160	49 22	−199	49 22	− 50	49 22	− 99	49 22
Jan. 24	.....	.....	+ 5	58 7	− 5	58 7	− 47	58 7	+157	58 7
Jan. 30	.....	.....	+ 20	64 4	−159	64 4	− 35	64 4	− 33	64 4
Feb. 5	.....	.....	+ 16	69 4	−155	69 4	− 26	69 4	− 48	69 4
Feb. 8	.....	.....	+ 17	70 16	−145	70 16	− 23	70 16	− 4	70 16
Mar. 1	.....	.....	− 17	89 12	−143	89 12	− 37	89 12	− 97	89 12
Mar. 12	.....	.....	− 20	98 12	−182	98 12	− 60	98 12	−227	98 12
Apr. 5	.....	.....	− 88	117 2	− 68	117 2	− 28	117 2	−108	117 2
Apr. 10	.....	.....	− 91	120 8	− 59	120 8	− 43	120 8	−145	120 8
May 25	.....	.....	.....	.....	− 76	131 2	− 79	131 2	+174	131 2
June 4	.....	.....	.....	.....	− 91	140 18	− 84	140 18	−216	140 18
June 7	.....	.....	− 47	143 16	− 79	143 16	− 62	143 16	.....	.....
June 15	.....	.....	.....	.....	− 86	151 4	− 76	151 4	+ 3	151 4

It will be seen that no initial low values, as observed by Hulett, were obtained. The Weston cells with gray samples of mercurous sulphate show changes which do not exceed 0.01 per cent even after continuing the rotation four months, except in one case in which the platinum terminal was purposely exposed. In this cell the terminal was inadvertently amalgamated, but was treated with aqua regia to remove the mercury before filling. The white samples generally showed considerably larger effects, but not as great as those observed by Hulett. There was also a tendency to reach a maximum value, and then, on further rotation, to approach the normal.

Cell No. 12, in which basic cadmium sulphate[3] was added in excess to the cadmium sulphate solution, gave approximately normal results from the first, although the paste was quite yellow.

Although the Clark cells showed smaller effects than the Weston cells, there seem to be slight differences produced by rotation. Cells 3 and 4, in which an excess of zinc oxide was added to the zinc sulphate solution, showed only a slight difference; but after an interruption of the rotation for several days the paste caked and the results subsequently obtained were irregular. The irregularities of the remaining Clark cells subsequent to December 5 may possibly be due to the cracking of the protecting tube about the platinum wire imbedded in the amalgam. Owing to the construction employed, this can not be determined without destroying the cell.

On December 19, 1906, the Weston cells 1, 4, and 8 were opened and the paste used in setting up cells of the ordinary form. The gray sample from cell No. 1 gave, after two days, practically the same value as in the rotating cell. It has slowly decreased and at present is within 25 microvolts of the normal. The two cells set up with the white samples showed abnormally high values, 600 and 400 microvolts, respectively, both of which steadily decreased until March 25, 1907. On that date they were transferred from the bath in which they had been kept continuously at 25° to another at 20°.

[3] Made by adding sufficient ammonia to a solution of cadmium sulphate to dissolve the precipitate first formed, filtering into a large volume of water, collecting, washing, and gently igniting the precipitate.

While only a very slight hysteresis was observed in the case of our Weston cells, particularly when finely crushed cadmium sulphate crystals were employed in the paste and over the amalgam, the two cells in question showed marked effects of this character. These persisted, with slight changes from day to day, for a long period, indicating either that a surface film was formed on the crystals during rotation or that a large excess of cadmium sulphate was employed in the paste, thus retarding the attainment of saturation equilibrium. A similar effect has been observed in a number of H cells in which the paste contained a large excess of cadmium sulphate crystals.

The results obtained show that not all samples of mercurous sulphate exhibit the behavior observed by Hulett, as gray samples, prepared by different methods, are changed by rotation for months by less than 0.01 per cent.[4] This difference is small enough to be possibly accounted for by attrition during rotation, thus introducing the effect of size of grain, noticed by von Steinwehr.

It does not appear to the authors that the high values shown by some of the rotation cells throw any light upon the decrease below the normal electromotive force observed by Hulett in some cells of the ordinary type. According to him the first reaction which takes place when the cell is set up is a hydrolysis by which the concentration of the mercury ions is increased. Opposing this is a reaction between the mercury and the products of hydrolysis in solution, which reduces the concentration of the mercury ions. The secondary products formed in this reaction would, therefore, be responsible for the decrease observed by him in cells of the ordinary type. As it is evident that this effect can not be due directly to the formation of new mercury compounds in the presence of an excess of mercurous sulphate, since the concentration of the mercury ions would thereby be increased, it must, on this theory, be caused by other products of the reaction.

In the rotation cells the amount of these secondary products would depend upon the duration of the rotation and on the area of the mercury surface exposed to the solution. According to Hulett's

[4] While the samples of mercurous sulphate prepared by Hulett are in practical agreement with our own, as shown by cells set up with exchange samples, his cells differ from those made at the Bureau by about one-third of the above amount.

explanation, the slight effects observed by us with gray samples of mercurous sulphate, which owe their color to the presence of finely divided mercury, would be due, not to decreased hydrolysis, but to the acceleration of the secondary reaction. It would, therefore, follow that such samples should give abnormally low values after stopping the rotation. As in no case was this result obtained, the authors conclude that the effect must be due to some other cause.

In view of the various questions which have arisen in connection with the results described in this paper, it is proposed to continue the investigation.

WASHINGTON, October 4, 1907.