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**THE REPRODUCIBILITY OF THE CADMIUM ELECTRODE.**

By FREDERICK H. GETMAN AND VERNETTE L. GIBBONS.

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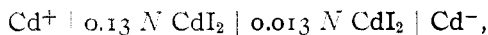
The present work was undertaken to elucidate, if possible, some of the abnormalities observed by Getman<sup>1</sup> in the measurements of the potential of cadmium rods in alcoholic solutions of cadmium iodide. In a study of the reproducibility of the copper electrode, Getman<sup>2</sup> (in a paper read before a recent meeting of the American Electrochemical Society at Niagara Falls) showed that spongy copper, deposited electrolytically upon a loop of platinum wire, gave a constant and reproducible e. m. f. when measured in concentration cells of aqueous solutions of copper sulfate.

<sup>1</sup> *Am. Chem. J.*, **46**, 117 (1911).

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **26**, 67 (1914).

The attempt was first made to study cadmium in the same way. An apparatus was devised similar to the one described by Gibbons and Getman,<sup>1</sup> whereby the two solutions were kept separated from one another except during the time of actual measurement. The measurements were all made at 25°. The temperature was maintained constant to within  $\pm 0.05^\circ$ , in an electrically controlled thermostat. The purest obtainable methyl alcohol was dehydrated over pure lime for a week, then distilled into a dry receiver which was protected from the gases and moisture in the atmosphere by means of a soda-lime tube. The boiling point of this alcohol was  $64.2^\circ$  to  $64.5^\circ$  at 752 mm. of mercury. The solutions were made up by direct weighing of pure cadmium iodide and all volumetric apparatus used was carefully calibrated. The electrodes were either of spongy cadmium deposited on loops of platinum wire with high current density, or freshly cast rods of the purest cadmium obtainable. The Poggendorff compensation method was employed for measuring the electromotive forces of the different cells, and an enclosed type of Lippmann electrometer was the zero instrument.

The e. m. f. of the combination



with methyl alcohol as solvent was much higher when electrolytically deposited electrodes instead of when stick electrodes were used. The greatest value obtained for any pair of stick electrodes was 0.048 volt, after about five hours' standing in the cell, whereas the greatest value obtained for any pair of electrolytically deposited electrodes was 0.1049 volt, after twenty-four hours' standing. No constant values could be obtained, as in every case there seemed to be an increase in e. m. f. with the time, although there was no regularity in this increase. The cell stood in the thermostat for twenty minutes to acquire a uniform temperature, then the solutions were brought into contact with each other and the first measurement was made as quickly as possible.

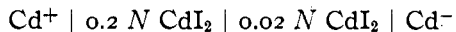
It was thought possible that the greater e. m. f. shown with the electrolytically deposited electrodes might be due to the contact of the finely divided metal with the solution. Therefore, each solution was shaken in a shaking machine for one-half hour in contact with some of the electrolytically deposited metal. The e. m. f. measurements obtained when these solutions were put in the cell were much smaller than before, but quite a deposit of cadmium hydroxide was produced during the shaking. The formation of the hydroxide indicated that the action between the finely divided metal and the methyl alcoholic solution of cadmium iodide was a complex one. It, therefore, seemed inadvisable to consider further the reproducibility of an electrode of cadmium deposited electrolytically with high current density.

<sup>1</sup> THIS JOURNAL, 36, 1645 (1914).

TABLE I.

Stick electrodes.					Electrolytically deposited electrodes.				
Total time.		Diff. in time.		E. M. F. Volts.	Total time.		Diff. in time.		E. M. F. Volts.
Hrs.	Mins.	Hrs.	Mins.		Hrs.	Mins.	Hrs.	Mins.	
0	00	0	00	0.0188	0	00	0	00	0.0181
0	15	0	15	0.0287	0	15	0	15	0.0264
0	30	0	15	0.0310	0	30	0	15	0.0366
0	45	0	15	0.0373	0	45	0	15	0.0477
1	00	0	15	0.0373	1	00	0	15	0.0530
1	45	0	45	0.0369	1	15	0	15	0.0599
2	00	0	15	0.0364	1	30	0	15	0.0623
2	15	0	15	0.0399	3	15	1	45	0.0773
2	30	0	15	0.0381	3	30	0	15	0.0792
2	50	0	20	0.0431	3	45	0	15	0.0792
3	5	0	15	0.0431	4	00	0	15	0.0792
3	35	0	30	0.0468	4	15	0	15	0.0812
4	5	0	30	0.0468	4	35	0	20	0.0814
4	35	0	30	0.0452	5	40	1	5	0.0841
5	15	0	40	0.0482	5	55	0	15	0.0857
5	45	0	30	0.0472	6	10	0	15	0.0867
					6	25	0	15	0.0871
					22	45	16	20	0.1018 <sup>1</sup>
					23	00	0	15	0.1038
					23	15	0	15	0.1036
					23	30	0	15	0.1046
					23	45	0	15	0.1044
					24	5	0	20	0.1049
					24	20	0	15	0.1049
					24	35	0	15	0.1049
					24	40	0	5	0.1034 <sup>2</sup>
					24	55	0	15	0.1046.

A study of the behavior of stick cadmium electrodes in aqueous solutions of cadmium iodide was then undertaken. The following combination was used:



Three pairs of electrodes were so tested and in each case the e. m. f., at first very small, increased with the time. The electrodes did not seem to be coated with white hydroxide, but, on the contrary, the one in the more concentrated solution became gray in color and appeared coated over with a multitude of tiny crystals; and the electrode in the more dilute solution did not so appear. Evidently the cadmium was deposited upon the positive electrode in a different form from that which dissolved from the negative electrode.

To test this assumption the electrodes were each in turn measured against a standard electrode similar to a calomel electrode, only instead of calomel and 0.1 *N* potassium chloride, mercurous sulfate and 0.1 *N*

<sup>1</sup> After standing over night.

<sup>2</sup> After making a fresh boundary between the solutions.

cadmium sulfate were used. The standard electrode in each case proved to be the positive electrode of the combination:

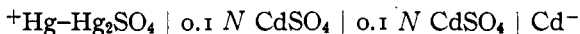


TABLE II.

I <sub>1</sub> .		Diff. in time.		E. M. F. Volts.	I <sub>2</sub> .		Diff. in time.		E. M. F. Volts.
Hrs.	Mins.	Hrs.	Mins.		Hrs.	Mins.	Hrs.	Mins.	
<i>a.</i>									
0	15	0	15	1.1332	0	00	0	00	1.1282
0	35	0	20	1.1324	0	20	0	20	1.1296
1	00	0	25	1.1326	0	40	0	20	1.1302
1	30	0	30	1.1324	1	00	0	20	1.1304
2	00	0	30	1.1325	1	20	0	20	1.1306
					1	40	0	20	1.1310
					2	00	0	20	1.1318
					3	15	1	15	1.1320
					3	55	0	40	1.1325
					4	15	0	20	1.1325
					4	35	0	20	1.1325
<i>b.</i>									
II <sub>1</sub> .		Diff. in time.		E. M. F. Volts.	II <sub>2</sub> .		Diff. in time.		E. M. F. Volts.
Hrs.	Mins.	Hrs.	Mins.		Hrs.	Mins.	Hrs.	Mins.	
0	00	0	00	1.1326	0	00	0	00	1.1272
0	20	0	20	1.1328	0	20	0	20	1.1306
0	40	0	20	1.1328	0	40	0	20	1.1312
1	00	0	20	1.1336	1	00	0	20	1.1317
1	20	0	20	1.1336	1	20	0	20	1.1319
1	40	0	20	1.1336	1	40	0	20	1.1322
18	5	16	25	1.1322	2	00	0	20	1.1323
					3	10	0	20	1.1324
<i>c.</i>									
III <sub>1</sub> .		Diff. in time.		E. M. F. Volts.	III <sub>2</sub> .		Diff. in time.		E. M. F. Volts.
Hrs.	Mins.	Hrs.	Mins.		Hrs.	Mins.	Hrs.	Mins.	
0	00	0	00	1.1344	0	00	0	00	1.1316
0	20	0	20	1.1344	0	20	0	20	1.1316
0	40	0	20	1.1344	0	40	0	20	1.1322
1	00	0	20	1.1346	1	00	0	20	1.1325
2	25	1	25	1.1343	1	20	0	20	1.1326
19	15	16	50	1.1336	1	40	0	20	1.1326
					2	00	0	20	1.1333
					3	10	1	10	1.1328
<i>d.</i>									
A freshly cast electrode was measured against the standard electrode.									
0	00	0	00	1.1231	7	50	1	35	1.1308
0	20	0	20	1.1239	21	50	14	00	1.1308
1	05	0	45	1.1250	22	10	0	20	1.1308
1	30	0	2	1.1254	22	40	0	30	1.1308
1	55	0	25	1.1258	23	10	0	30	1.1309
4	30	2	35	1.1280	24	40	1	30	1.1308
5	55	1	25	1.1292	25	15	0	35	1.1310
6	15	0	20	1.1297	26	15	1	00	1.1310

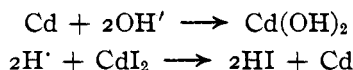
The results are given in Table II. Electrodes which had been used previously as positive electrodes are designated as I<sub>1</sub>, II<sub>1</sub>, etc., while those used previously as negative electrodes are designated as I<sub>2</sub>, II<sub>2</sub>, etc.

Another freshly cast electrode gave, when first placed in the cell, an e. m. f. of 1.1237 volts and after 2 hrs. and 40 min. an e. m. f. of 1.1286 volts. This agrees fairly well with the values for corresponding times given in Table II, *d*.

Table II shows clearly that the electrode upon which the gray crystalline layer had been deposited was the stable one and that the electrodes previously used as negative electrodes gradually assumed the constant value of the gray electrodes. The e. m. f. of the cadmium electrode opposed to the standard electrode is seen to be 1.1324 volts (the average of the final values given in Table II, *a*, *b*, *c* and *d*). The difference between this value and the initial value for the freshly cast electrode amounts to 0.0093 volt.

When a solution of cadmium iodide in contact with a cadmium rod was exposed to the air for some time, it became slightly yellowish and, when it was tested with starch paste, a faint blue color confirmed the suspicion that a trace of iodine had been set free.

It was thought possible that the change in the metal and in the solutions might have been caused by small amounts of hydriodic acid, formed as follows:



If such were the case, the solution should show increased conductance, because of the hydrogen ions present, and a coating of cadmium hydroxide upon the metal should be detected by its solubility in ammonium hydroxide.

To decide the question of the formation of hydriodic acid, a highly polished button of cadmium was etched with nitric acid, thoroughly washed and dried. The conductance of 0.2 *N* aqueous cadmium iodide in contact with this button was measured at 25° at intervals over a period of eleven days. There was no increase in conductance and no change in the color of the solution, but there was a marked change in the appearance of the button. The bright crystalline surface became first dull, then black and at last could be seen to have a beautiful growth of shiny black crystals over its entire surface. At the end of two weeks the button was removed, washed, dried and examined microscopically (see page 969).

The buttons of cadmium which had become gray by standing in cadmium iodide or cadmium sulfate solution were tested with ammonium hydroxide solution, but there was no evidence to the eye or under the microscope, that any of the gray substance had been dissolved. An electrode which had stood for three days in 0.2 *N* cadmium iodide solu-

tion, was washed and treated with ammonium hydroxide. The coating apparently did not dissolve and after thorough washing, the electromotive force measurements showed only slight change. Hence the deposit upon the metal was proven not to be cadmium hydroxide.

Samples of the cadmium iodide solution in contact with cadmium did not, however, show the presence of free iodine when air was excluded, although the buttons and rods became gray. The formation of iodine in the solution may, therefore, have been due to oxidation by the air.

The above experiments seemed to indicate that some, if not all, of the abnormalities observed in the measurements of the concentration cells of metallic cadmium in cadmium salt solutions were, most probably, caused by an allotropic change in the metal and that this change was produced when the metal and the salt solution were in contact with each other.

In 1862, Matthiessen and v. Bose<sup>1</sup> mentioned the fact, that cadmium wires became brittle and easily pulverized, when heated several days at 100°. To hold the wires together it was necessary to coat them with varnish. They did not, however, notice any change in the conductivity of the wires.

Cohen and Helderman<sup>2</sup> have made an extensive investigation of the allotropy of cadmium. Their results are published in three papers and they have shown that cadmium exists in *at least two allotropic modifications and probably more*. One transition point at  $64.9^\circ \pm 0.1^\circ$  has been measured by both pycnometric and dilatometric methods. The former method they consider less reliable, because the density is so easily modified by small amounts of inclusions in the metal. Their study of cadmium amalgams also indicates that there are several modifications of the metal. Cohen and Helderman hold that the electrodes made of cadmium amalgam are in a metastable equilibrium, which may be maintained for years, yet can be changed into stable equilibrium. The explanation given by Cohen for the analogous change from white to gray tin is stated<sup>3</sup> as follows:

“Die Erklärung dieser Wirkung dürfte darauf zurückzuführen sein, dass der grauen Form, welche dann die stabile ist, unterhalb des Umwandlungspunktes eine geringere Lösungstension zukommt als der weissen. Infolge der höheren Lösungstension der letzteren wird diese bestrebt sein, in die stabile Form überzugehen; haben sich einmal Spuren von ihr gebildet, so wirken sie beschleunigend auf die weitere Umwandlung.”

<sup>1</sup> “Über den Einfluss der Temperatur auf Metalle” 1862.

<sup>2</sup> I. *Proc. K. Akad. Wetenschappen*, 16, 485 (1913); *Verslag. Akad. Wetenschappen*, 22, 420 (1913); Abstract in *J. Chem. Soc.*, 105-106, II, 52 (1914). II. *Proc. K. Akad. Wetenschappen*, 17, 59 (1914); *Verslag. Akad. Wetenschappen*, Utrecht, 22, 1294 (1914). Abstracts in *J. Chem. Soc.*, 105-106, II, 652 (1914) and in *C. A.*, 8, 2514 (1914). III. *Proc. K. Akad. Wetenschappen*, 17, 122 (1914); *Verslag. Akad. Wetenschappen*, 23, 60 (1914); Abstracts in *J. Chem. Soc.*, 105-106, II, 652 (1914) and in *C. A.*, 8, 3389 (1914).

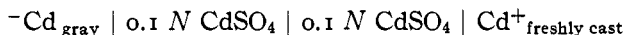
<sup>3</sup> Abegg's *Handbuch der Anorg. Chem.*, 3, 530.

Smits,<sup>1</sup> in a paper entitled "Theory of Allotropy as Applied to Electromotive Equilibria," states that the different allotropic modifications give different kinds of ions and the separated metal may be of a different form from that dissolved. He also assumes that salt solutions have an accelerating influence in bringing about a state of equilibrium.

If the salt solution does have an accelerating effect upon the change taking place in the metal, the action of the iodide should be more marked than that of the sulfate. This was found to be the case, for a rod of cadmium became gray much more quickly in a solution of cadmium iodide than in a solution of cadmium sulfate of the same strength. That the temperature also has an effect upon this change was shown, since at a temperature of about 0° the change was more pronounced in a given period of time than it was at room temperature.

If the abnormalities observed in the cadmium concentration cells are due to a transition from one allotropic modification of the metal to another, there should be an electromotive force developed, when a gray cadmium rod and a polished freshly cast cadmium rod are immersed in a solution of a cadmium salt. This electromotive force should be greater the greater the temperature interval above or below the transition point and should undergo a reversal of sign when this temperature is passed, if no other reaction enters in to cause complications. The electromotive force at 25° in a 0.1 *N* cadmium sulfate solution should equal the difference between the electromotive forces of the two electrodes measured against the standard, *i. e.*, 0.0093 volt, and the gray electrode should be the negative terminal of the cell, because of its lower solution tension (see page 958).

To decide these questions, measurements of the electromotive force of the following combination were made at different temperatures:



The gray rods were the ones that had been measured against the standard electrode and had been shown to have a constant electromotive force. The freshly cast rods were polished with emery cloth, thoroughly washed and dried. In every series of measurements the cell was filled with the solution, corked tightly, placed in the thermostat and allowed to stand for one-half hour. At the higher temperatures the cell was opened occasionally to allow for expansion. The solutions were brought into contact with each other, the electrodes inserted in the cell and the first measurement made as quickly as possible. The results of several series of measurements at a given temperature agreed fairly well. The mean values are given in Table III and plotted in Fig. 1.

<sup>1</sup> *Proc. K. Akad. Wetenschappen*, 16, 699 (1913); Abstract in *J. Chem. Soc.*, 105-106, II, 165 (1914).

TABLE III.

0.1°.					25°.				
(Average of three series).					(Average of two series).				
Total time.		Diff. in time.		E. M. F. Volts.	Total time.		Diff. in time.		E. M. F. Volts.
Hrs.	Mins.	Hrs.	Mins.		Hrs.	Mins.	Hrs.	Mins.	
0	00	0	00	0.0362	0	00	0	00	0.0108
0	20	0	20	0.0294	0	10	0	10	0.0098
0	50	0	30	0.0203	0	20	0	10	0.0096
1	20	0	30	0.0181	0	30	0	10	0.0093
1	45	0	25	0.0170	0	40	0	10	0.0089
2	15	0	30	0.0152	0	55	0	15	0.0086
2	35	0	20	0.0144	1	25	0	30	0.0080
3	5	0	30	0.0140	1	55	0	30	0.0079
3	20	0	15	0.0138	2	25	0	30	0.0076
4	20	1	00	0.0131	3	15	0	50	0.0073
5	20	1	00	0.0126	3	40	0	25	0.0072
6	20	1	00	0.0124	9	30	5	50	0.0055 <sup>1</sup>
7	20	1	00	0.0118 <sup>2</sup>	22	25	12	55	0.0029 <sup>1</sup>
8	20	1	00	0.0109 <sup>2</sup>	23	50	1	25	0.0030 <sup>1</sup>
10	00	1	40	0.0099					
20	00	10	00	0.0058					
21	40	1	40	0.0058 <sup>2</sup>					
25	00	3	20	0.0058					

40°.					79.5°.					No. of Expts.
(Average of three series).					(Average of two series).					
Total time.		Diff. in time.		E. M. F. Volts.	Total time.		Diff. in time.		E. M. F. Volts.	
Hrs.	Mins.	Hrs.	Mins.		Hrs.	Mins.	Hrs.	Mins.		
0	10	0	10	0.0100	0	00	0	00	-0.0030	5
0	25	0	25	0.0095	0	15	0	15	-0.0027	3
0	40	0	15	0.0093	0	50	0	35	-0.0026	3
0	55	0	15	0.0083	1	10	0	20	-0.0022	3
1	10	0	15	0.0072	1	25	0	15	-0.0019	3
1	25	0	15	0.0068	1	50	0	25	-0.0017	3
1	55	0	30	0.0060	2	10	0	20	-0.0011	3
2	25	0	30	0.0053	3	15	1	5	-0.0003	2
2	55	0	30	0.0049	3	50	0	35	+0.0007	2
3	15	0	20	0.0046	4	20	0	30	+0.0013	2
3	45	0	30	0.0043						
4	30	0	45	0.0040						
5	00	0	30	0.0038						
5	30	0	30	0.0036						
17	30	12	00	0.0032						

From Table III and Fig. 1 it is seen (1) that there is a progressive change in the e. m. f. of the concentration cells with the time, each curve tending toward a minimum, (2) that the e. m. f. diminishes with increase of temperature, (3) that at 25°, one-half hour after the electrodes are inserted in the cell, the e. m. f. is 0.0093 volt as calculated on page 957, (4) that the gray electrode is the negative terminal of the cell as was to be expected, and (5) that at 79.5°, a temperature above the transition point (64.9°)

<sup>1</sup> From one series of measurements only.

<sup>2</sup> Interpolated from the curves of the three series.



there is a reversal of the sign of the e. m. f. In the experiments at  $79.5^\circ$  the positive electrode was found to be coated over with white hydroxide of cadmium, which might easily account for the change from a negative

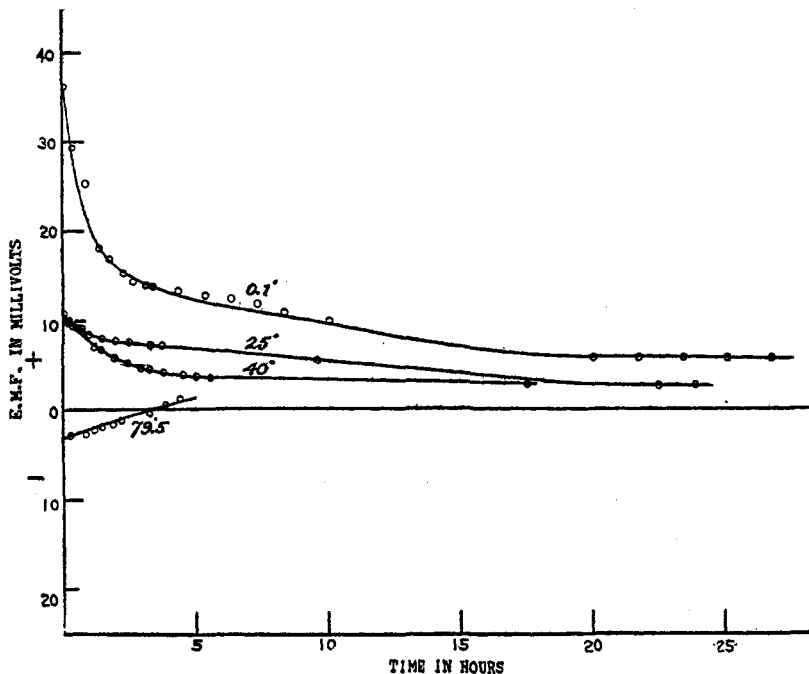


Fig. 1.

to a positive e. m. f. at the close of the series. An attempt was made to carry out a series of measurements of the e. m. f. of the combination at  $98^\circ$ , but the formation of the hydroxide took place so quickly that it was found quite impossible to obtain any reliable values.

Two freshly cast and polished electrodes were then measured against each other in a  $0.1 N$  cadmium sulfate solution. The e. m. f. was appreciable, but fluctuated and the value seemed in some way to depend upon the degree of polishing of the electrode. This behavior might have been expected for the anomalous changes in the potential of cadmium are well known. Thus, Desch<sup>1</sup> makes the following statement: "Cadmium is so sensitive that merely rubbing the surface with emery paper is sufficient to make that specimen the anode when compared with an untreated specimen." The electrodes were washed, dried and left standing over night. They were then polished, washed and dried and placed in fresh  $0.1 N$  cadmium sulfate solution and the e. m. f. of the combination was again determined with the same result as before.

<sup>1</sup> Desch's *Metallography*, p. 287.

The electrodes were then polished and placed in 0.2 *N* cadmium iodide solution and left to stand twenty-two hours in the ice chest, then two hours in the air at about  $-9^{\circ}$ , when the solution solidified. The frozen solution was allowed to melt at room temperature and to stand for two and three-quarters hours before the electrodes were removed, washed and dried. They then appeared grayish and when placed in 0.1 *N* cadmium sulfate solution gave no measurable e. m. f. even after 40 mins. standing. The electrodes were again placed in 0.2 *N* cadmium iodide solution and, after twenty-four hours at room temperature, beautiful metallic crystals were found to be scattered over the gray background. The crystals were examined under the microscope and photographed (see page 966).

Some of the crystals were carefully removed from the electrode with a scalpel. They were found to be very slowly soluble in hydrochloric acid but readily and completely soluble in nitric acid. A few of the crystals were transferred to an evaporating dish, dissolved in a small amount of dilute nitric acid and the solution evaporated to dryness. The residue was dissolved in a small amount of distilled water and analyzed qualitatively. The crystals were found to be pure cadmium.

It seemed advisable to examine the crystalline deposit of cadmium formed upon cadmium or platinum by electrolysis of a cadmium sulfate solution with low current density. The solution employed was made up by diluting 10 cc. of saturated cadmium sulfate solution with 75 cc. of distilled water and 2 drops of dilute sulfuric acid. A current of  $N.D._{100} = 0.15$  amperes (approx.) and at an e. m. f. of 2 volts was passed for about 5 hours. The cathode was either a polished, freshly cast rod of cadmium, or a platinum plate sealed into a glass tube. Three crystalline cadmium rod electrodes and one crystalline cadmium plated platinum electrode were so prepared and the e. m. f. of each measured against the standard electrode. The plated cadmium rods gave constant e. m. f. in each case after about 30 minutes in the cell and remained practically constant for at least 22 hours. The values agreed fairly well and were as follows: (1) 1.1343 volts, (2) 1.1336 volts, (3) 1.1340 volts. The cadmium plated platinum electrode showed greater fluctuations between the limits 1.1333 volts and 1.1348 volts over a period of 23 hours.

From the above it is seen that the e. m. f. of these crystalline electrodes is from 1 to 2 millivolts higher than the e. m. f. (1.1324 volts) of the gray crystalline electrodes formed by immersing the freshly cast rods in a solution of cadmium iodide.

The crystalline deposits were examined under the microscope and the crystal forms were in all cases similar to those shown in Fig. 11.

A gray deposit was formed upon the cadmium rod by electrolysis with high current density and its e. m. f. was measured against the standard

electrode. The measurement showed fluctuations between the limits 1.1341 volts and 1.1364 volts over a period of 24 hours.

The effect of amalgamation of a cadmium electrode was studied by measuring its e. m. f. against the standard electrode. There was much variation in the results, no two electrodes gave even approximately the same results in a given time and the values were in all cases much smaller than the similar measurements of the e. m. f. of the crystalline electrodes.

It seems, therefore, that cadmium electrodes reproducible to within 1 or 2 millivolts, when measured against the standard electrode, may be obtained either by allowing a polished cadmium rod to stand in a cadmium salt solution until it has acquired a uniform gray coating, or by electrolytically depositing crystalline cadmium upon a polished cadmium rod with a low current density. The electromotive behavior of cadmium in alcoholic solution of cadmium salts is now being investigated in this laboratory.

Frequent examination of the electrodes with a pocket lens made it apparent that valuable information as to the nature of the change which occurs when cadmium is immersed in solutions of its salts could be obtained by systematic microscopic observations.

Soon after entering upon the microscopic study of the surfaces of the electrode, it became evident that the cylindrical form of these electrodes was not suited to examination with high power objectives. To overcome this difficulty a cylinder of pure cadmium  $1\frac{1}{2}$  cm. in diameter and about 3 cm. in length was prepared by casting the metal in a suitable mould. The cylinder was then cut into transverse sections about 4 mm. thick and one surface of each of the resulting buttons was polished. The polishing of the buttons was carried out in the following manner: After smoothing both surfaces of the button with a file, it was mounted with sealing wax in a shallow hole cut in a wooden block and then rubbed on blocks covered with emery paper of regularly graded fineness. Care was taken in changing from one paper to the next finer to rub in a direction at right angles to that previously followed, thus gradually reducing the size of the scratches. After a final abrasion with "cuttle-fish bone paper," the button was rubbed on a piece of velveteen with a jewelry polish to which had been added a few drops of xylol. A final brisk rubbing on a dry piece of velveteen developed a mirror-like surface.

After taking a photomicrograph of the surface of one of these buttons (as shown in Fig. 2) it was immersed in 0.2 *N* solution of cadmium iodide and maintained at a temperature of about 5° by placing in the ice chest. After 15 minutes immersion the button was removed from the solution, successively washed in water, alcohol and ether and then re-examined under the microscope. Unmistakable evidence of a distinct change in the character of the surface was obtained. The button was then replaced

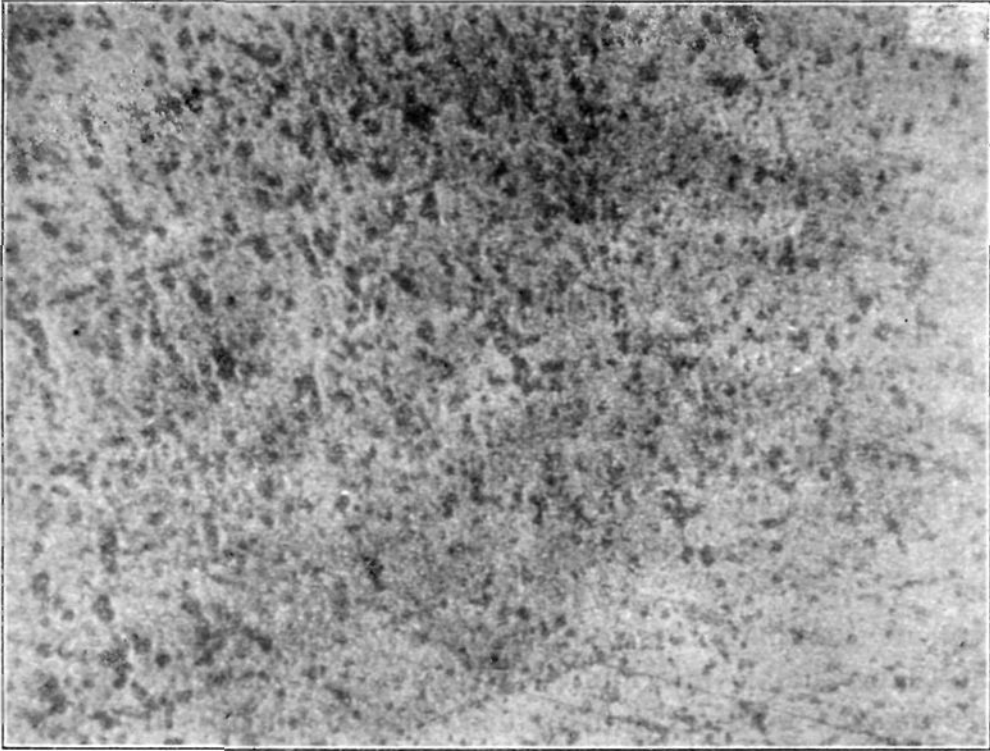


Fig. 2.—Magnification 100.

in the cadmium iodide solution and after 3 hours' immersion was again re-examined microscopically. The small initial nuclei observed after 15 minutes immersion were found to have developed into the well de-

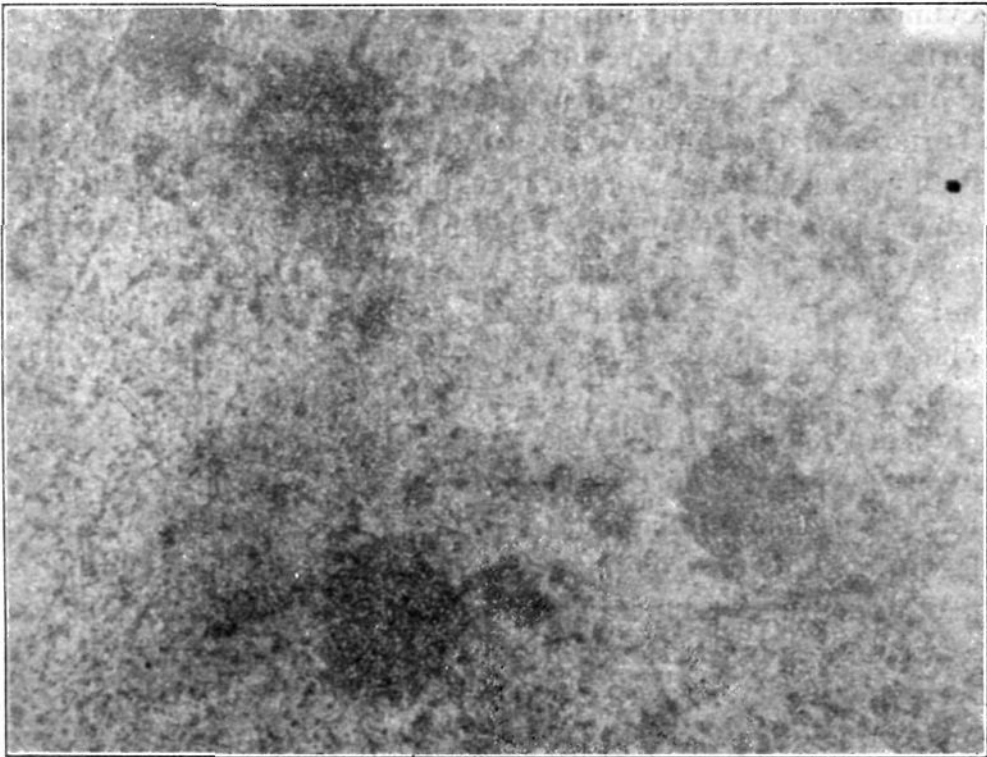


Fig. 3.—Magnification 100.

finer spots shown in Fig. 3. The button was regularly examined at 3 hour intervals, until after 18 hours' immersion the surface had assumed the appearance shown in Fig. 4. In order to determine whether this change

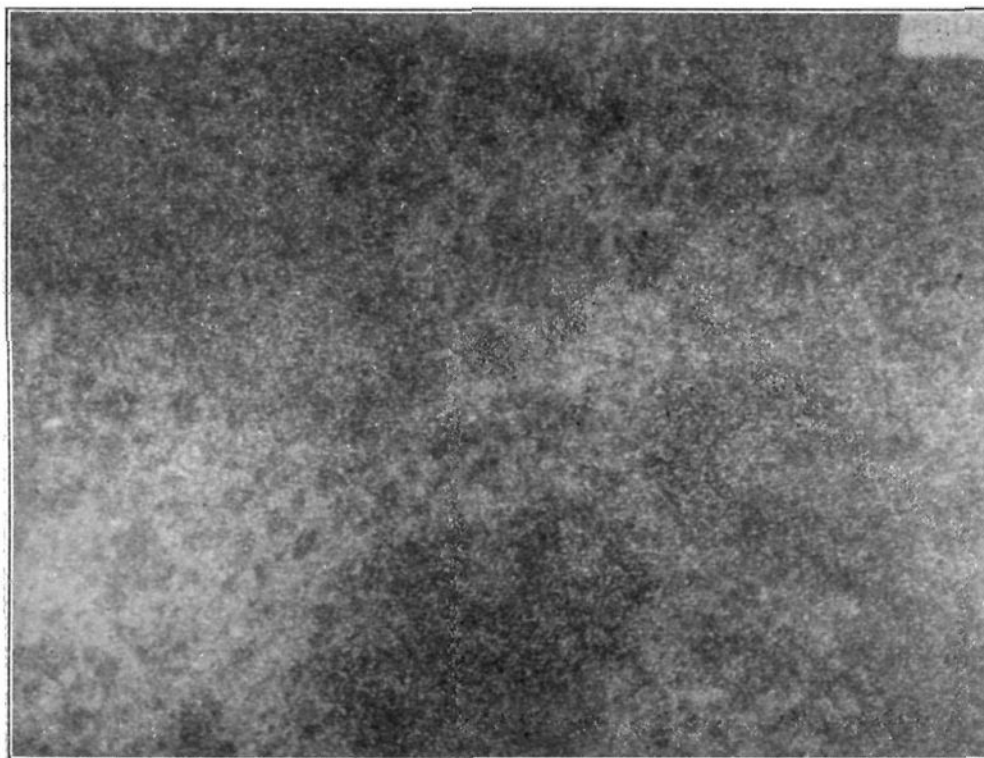


Fig. 4.—Magnification 100.

might be due to a deposition of cadmium hydroxide, the button was immersed for 10 minutes in dilute ammonium hydroxide, and then, after washing with water, alcohol and ether, it was re-examined under the microscope. The appearance of the surface remained unaltered and it was assumed that the deposit was not due to a film of cadmium hydroxide. After two weeks' immersion in 0.2 *N* cadmium iodide solution, the deposit



Fig. 5.—Magnification 200.

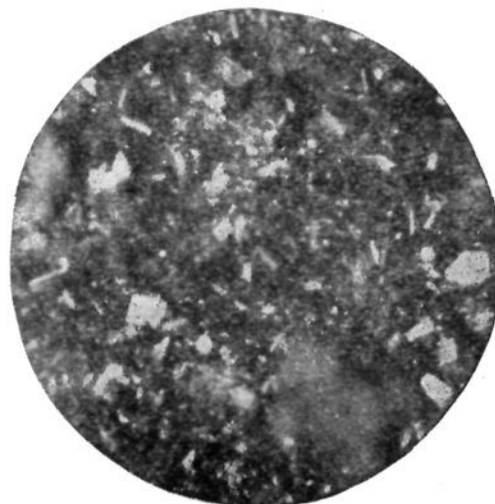


Fig. 6.—Magnification 100.

on the button had assumed a distinctly crystalline appearance as shown in Fig. 5. It has already been mentioned (page 962) that well developed crystals visible to the naked eye appeared on two of the electrodes used in the experimental cell, and it seemed of interest to compare these crystals with those observed on the button shown in the preceding illustration. Accordingly, photomicrographs were made of some typical crystals found on the electrodes as shown in Figs. 6 and 7. It was impossible

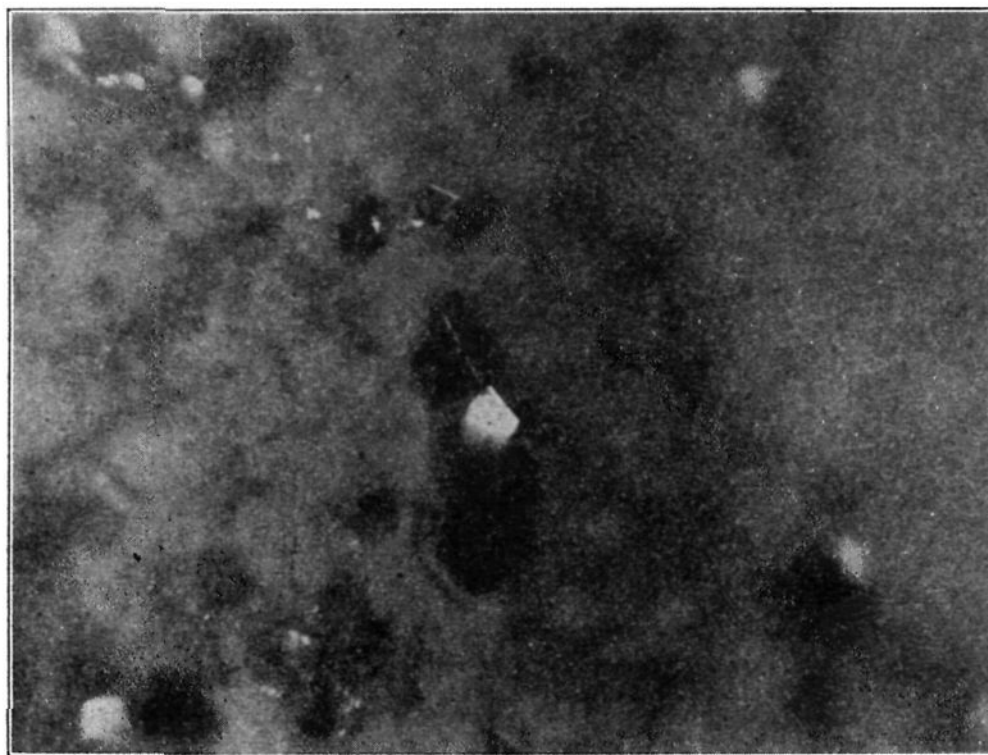


Fig. 7.—Magnification 100.

to bring more than a very limited portion of the field into sharp focus because of the cylindrical form of the electrodes and on account of the thickness of the crystals. However, a careful examination under the microscope in which various portions of the crystals were successively brought into focus, revealed the fact that they belonged to the isometric system, pentagonal dodecahedra and truncated octohedra being the prevailing forms.

Since freshly cast cadmium is known to crystallize in the hexagonal system,<sup>1</sup> the foregoing observations seem to justify the conclusion that prolonged standing in a solution of cadmium iodide involves a change in crystalline form. Furthermore, the change in form being from a system of lower to one of higher symmetry confirms the conclusion drawn from the measurements of electromotive force (page 957) that the freshly cast cadmium electrodes are unstable. In his metallography, Desch<sup>2</sup> (*Loc.*

<sup>1</sup> Gmelin-Kraut's *Handbuch der Anorg. Chem.*, 4, 109.

<sup>2</sup> Desch's *Metallography*, "Text-Books of Physical Chemistry," Longmans, Green & Co.

*cit*) says, "Several metals exist in more than one crystalline modification, in which case the forms stable at high temperatures are of a lower degree of symmetry than those at low temperatures." It has already been pointed out that lowering the temperature favors the formation of a stable cadmium electrode when the metal is immersed in a solution of cadmium iodide.

If the crystalline deposit on the electrode is the stable form of cadmium then it should be possible to inoculate the polished surface of a freshly cast cadmium button with some of these crystals and accelerate the transformation to this modification. In his investigation of the change of white into gray tin, Cohen<sup>1</sup> found that almost complete transformation was effected in 16 days by immersing a specimen of white tin, inoculated with the gray modification, in an alcoholic solution of stannic ammonium chloride. A similar experiment was carried out with a button of cadmium. After making a photomicrograph of the freshly polished surface of the button (Fig. 8) the button was inoculated with several isometric crystals

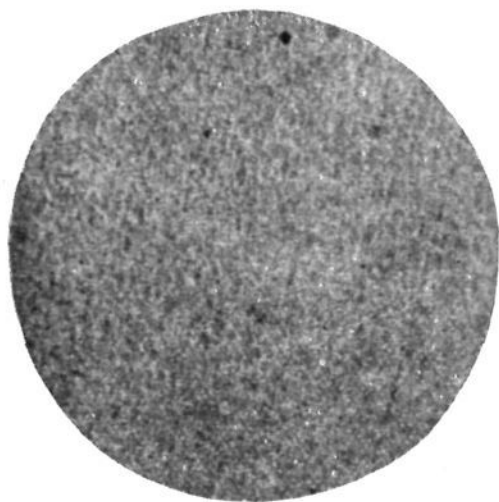


Fig. 8.—Magnification 200.

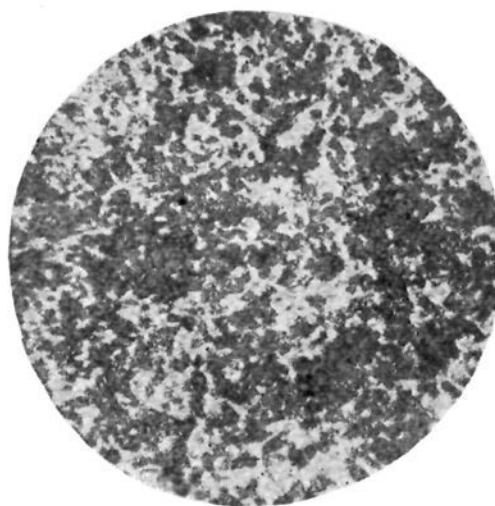


Fig. 9.—Magnification 200.

detached from one of the electrodes and allowed to stand for four weeks in a 0.2 *N* solution of cadmium iodide in ethyl alcohol at about 0°. That a distinct change had occurred is shown in Fig. 9 and that the transformation was more extensive than it would have been had the surface not been inoculated with the stable form of the metal is shown by the photomicrograph (Fig. 10) of an uninoculated polished button treated in exactly the same manner as that shown in Fig. 9. It is evident from this experiment that the transformation from one modification of cadmium to the other is much slower than in the corresponding case of tin.

A microscopic examination of a cadmium electrode upon which cadmium was deposited electrolytically revealed the same general type of crystals as was obtained by prolonged immersion of cadmium rods in a

<sup>1</sup> Abegg's *Handbuch der Anorg. Chem.*, 3, 550.

solution of cadmium iodide, although the potential of the former was about 2 millivolts higher than that of the latter. An experiment was then performed to determine, if possible, whether electrolytically deposited cadmium crystals might not serve as nuclei from which the crystallization would spread to a polished cadmium surface. A polished cadmium

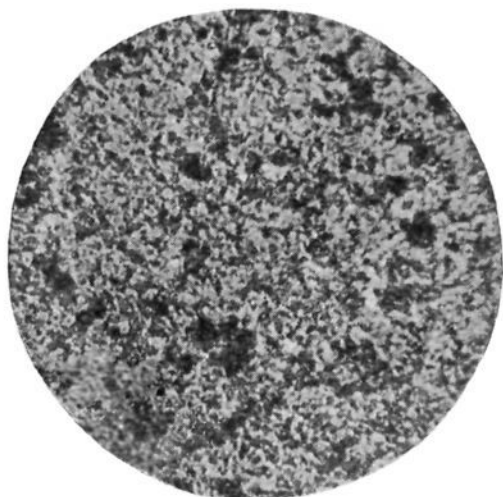


Fig. 10.—Magnification 200.



Fig. 11.—Magnification 100.

button was suspended in a dilute solution of cadmium sulfate acidified with sulfuric acid and one-half of the surface of the button coated with a crystalline deposit of electrolytic cadmium ( $N.D._{100} = 0.15$  amp., 2 volts). A photomicrograph of the deposit revealed the presence of the crystals shown in Fig. 11. The button was then immersed in 0.2  $N$

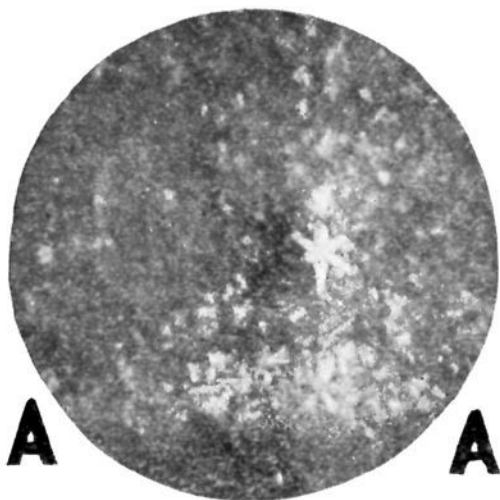


Fig. 12.—Magnification 100.

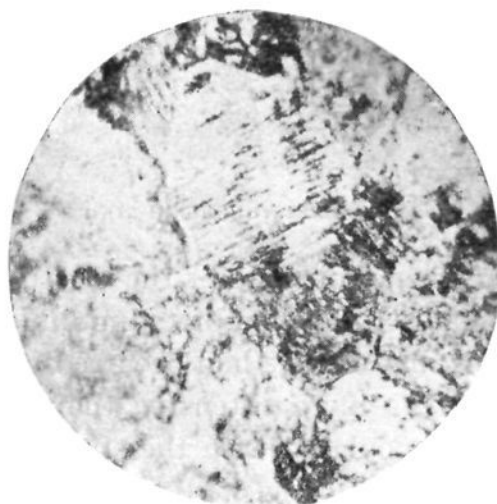


Fig. 13.—Magnification 100.

cadmium iodide solution and allowed to stand for two weeks at room temperature. At the end of this period the electrolytic deposit and the polished half of the button had acquired a dull gray color. The microscopic appearance of the polished half of the button is shown in Fig. 12, the line of demarcation between the polished portions and that upon



which the cadmium was deposited electrolytically being shown at AA. While a marked crystalline growth is apparent upon the polished half of the button, it is doubtful whether this was accelerated by the presence of the electrolytic deposit.

The etched cadmium button used in the conductance experiments (page 957) was examined microscopically before and after immersion in the cadmium iodide solution. The initial appearance of the button is shown in Fig. 13 and that at the end of two weeks in Fig. 14. These shiny, black crystals appear to belong to the isometric system but the cubic form is apparently predominant. A similar black deposit was obtained upon two cadmium rods, in one case the deposit being distinctly nodular. It seems probable that this is another allotropic modification of cadmium.

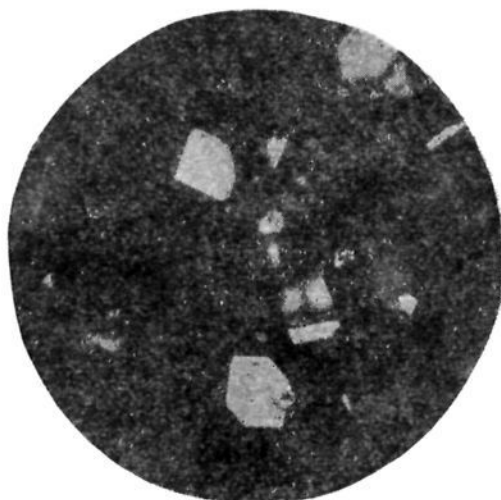


Fig. 14.—Magnification 200.

Newbery<sup>1</sup> considers the dulling or blackening of the surface of metallic electrodes during the passage of a current as due to extremely minute pittings in the metal, as if caused by explosive separation of gas from the interior of the metal. Such, however, was not the case in the present experiments. In every sample of the metal observed under the microscope the change of surface was clearly due to a deposit or growth upon the surface.

The gray form and the bright crystalline forms of cadmium described in this paper have doubtless been obtained by others working on the electrodeposition of cadmium,<sup>2</sup> but, as far as the authors can learn, the black crystalline form has never been obtained nor have the gray and bright crystalline forms been studied microscopically.

### Summary.

1. The measurements of the e. m. f. of concentration cells of methyl alcoholic solutions of cadmium iodide show that neither freshly cast rods of cadmium nor spongy cadmium deposited electrolytically are reproducible.
2. Similarly freshly cast rods of cadmium are shown not to give a reproducible e. m. f. when used as electrodes in aqueous solutions of cadmium iodide.
3. Rods of cadmium which have become gray by standing in cadmium

<sup>1</sup> *J. Chem. Soc.*, 105-106, 2427 (1914).

<sup>2</sup> "Electrodeposition of Cadmium I," Historical Review, by Mathers and Marble, *Trans. Am. Electrochem. Soc.*, 25, 297 (1914).

iodide solution are shown to give a constant e. m. f. when measured against an unpolarizable electrode. Freshly cast rods of cadmium are shown to attain this value with time.

4. The behavior of cadmium electrodes in concentration cells is explained as due to an allotropic change.

5. Crystalline electrolytic deposits of cadmium on cadmium rods or platinum are shown to give a reproducible e. m. f. when measured against an unpolarizable electrode. This e. m. f. is, however, slightly higher than that given by the gray cadmium electrodes. Amalgamated electrodes are not reproducible.

6. Photomicrographs indicate a change in crystalline form and confirm the conclusions drawn from the e. m. f. measurements.

7. Attempts to inoculate the surface of the freshly cast cadmium with the stable modification indicate that the action is extremely slow.

8. Photomicrographs indicate that in all cases the change is due to a deposit upon the surface instead of to a pitting of the surface.

CHEMICAL LABORATORY, BRYN MAWR COLLEGE,  
BRYN MAWR, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## THE ENTROPY OF VAPORIZATION AS A MEANS OF DISTINGUISHING NORMAL LIQUIDS.

By JOEL H. HILDEBRAND.

Received February 23, 1915.

In a series of studies which we are making on the theory of solutions, it has become necessary to distinguish between deviations from Raoult's Law, whose cause may be considered physical, and those due to chemical changes. As has been pointed out in a previous paper,<sup>1</sup> the choice between the alternatives in a given case is possible if we know whether or not the pure liquids are associated. For example, the occurrence of vapor pressures greater than those calculated by Raoult's Law in a mixture of benzene and stannic chloride, is explained by Schulze and Hock<sup>2</sup> on the assumption that the stannic chloride is associated, to a degree depending on the concentration. A great many deviations from Raoult's Law may be explained in this way, as the writer himself has done in the case of a number of amalgams.<sup>3</sup> Such an assumption would be unjustifiable if we were sure that both liquids were themselves normal, that is, unassociated, for the presence of another component must tend to diminish such association rather than to increase it. In fact, in the case of benzene

<sup>1</sup> Ermon D. Eastman and Joel H. Hildebrand. "The Vapor Pressure of Gold, Silver and Bismuth Amalgams," THIS JOURNAL. 36, 2020 (1914).

<sup>2</sup> Z. physik. Chem., 86, 445 (1914).

<sup>3</sup> Trans. Am. Electrochem. Soc. 22, 319, 335 (1912); THIS JOURNAL. 35, 501 (1913); 36, 2020 (1914).