MERCUROUS SULPHATE, CADMIUM SULPHATE AND THE CADMIUM CELL.

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THE previous work[1] on standard cells developed a number of facts which indicated that there was some interaction between the cadmium sulphate solution and the mercurous sulphate of the depolarizer, and now considerable experimental evidence on this question has been obtained. From the standpoint of the electrolytic dissociation theory we might expect mercurous sulphate to be less soluble in a cadmium sulphate solution than in water, since the two salts have a common ion. But the solubility was found to be about five times as great in a saturated cadmium sulphate solution as it was in water, and this fact suggested that the common ion might be ineffective in preventing hydrolysis of the mercurous sulphate. The solubility determinations indicated the presence of about a gram of mercury in a liter of the saturated solution but the solubility varied with the time the system had been rotated. This mercurous sulphate, which had been rotated with the cadmium sulphate solution and mercury, gave abnormal results when used as the depolarizer of cells. The attempt to form mercurous sulphate directly in the cadmium sulphate solution by the electrolytic method also gave an abnormal product. These results were only to be understood after more information had been gained about the conditions of equilibrium of the system (mercurous sulphate, mercury, cadmium sulphate and solution). Accordingly an apparatus was devised by which it was possible to rotate this system at a constant temperature and at any desired speed. By means of an adjustable anode of cadmium amalgam, cadmium sulphate and solution, it was possible to determine any change in the E.M.F. between the mercury and the solution of the rotated system, and thus it was possible to follow the changes of concentration of mercury in the solution.

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[1] Zeit. Phys. Chem., 49, 483, 1904. PHYS. REV., 22, 321 (and 23, 166).

On rotating the cathode system of the cadmium cell, it was found that the E.M.F. increased steadily for over two weeks and was only fairly constant on continued rotation. The experiment was repeated three times with fresh materials and, while the results varied somewhat, the maximum increase was about .00140 V. After the system had been rotated for thirty days it was allowed to rest but the E.M.F. did not remain constant, it decreased 0.00007 V. the first six hours, 0.00013 in twenty-four hours and then more slowly as time passed. The system was therefore not in equilibrium.

The mercurous sulphate from this rotated system was used as the depolarizer of two cadmium cells. For cell A49 the mercurous sulphate was first brought into a Gooch crucible and washed with a little fresh cadmium sulphate solution, while for cell A50 the depolarizer direct from the rotated tube was used. These cells were set up June 11, 1906, and have since been maintained at 25°. The basis of all E.M.F. values given in this article are Clark cells with electrolytic mercurous sulphate as depolarizer. Their value as determined by absolute measurements is 1.42040 V. at 25°.

Cell.	June 12.	June 14.	June 17.	June 23.	June 26.	July 7.
A49	1.01863	1.01875	1.01868	1.01856	1.01855	1.01847
A50	64	64	64	60	55	47

Cell.	August 14.	October 22.	December 19.	January 3.	February 26.
A49	1.01839	1.01827	1.01823	1.01817	1.01814
A50	38	29	26	20	15

The high preliminary value of these cells and the subsequent decrease is characteristic of cells which contain basic mercurous sulphate in the depolarizer. The cells showed no tendency to stop at the normal value, 1.01840. The results show that the rotated system did not come to equilibrium even when rotated at constant temperature for a month, and unless the changes were due to the dissolved air or to some mechanical change in the materials of the system, they clearly indicate that slow chemical changes were taking place. It seemed possible that the oxygen of the air, dissolved in the cadmium sulphate solution, might have oxidized the mercurous sulphate to the more soluble mercuric compound and, if the rate of this oxidation was more rapid than the subsequent rate of reduction by the mercury, the observed results could be readily explained. This possibility had been considered[1] and reasons given for rejecting it, but in view of the importance of the results obtained by rotating the cathode systems of standard cells, it has seemed advisable to further test the possibility of an effect due to the dissolved air. The test was carried out with apparatus similar to that used in the previous experiment. An adjustable cell (Fig. 1) was constructed from the materials which were to be tested in the rotating tubes. This cell was kept at 25° and, although the anode leg was frequently removed to test other systems, the cell has not varied over .00001 V. from its value of 1.01838 V. The rotating tubes are represented by Fig. 2.

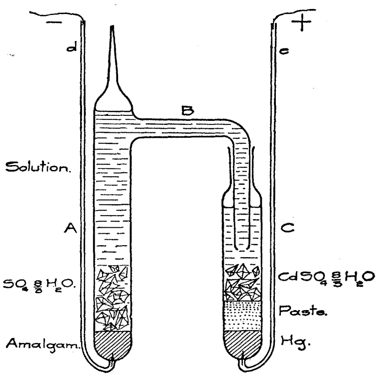

Fig. 1.

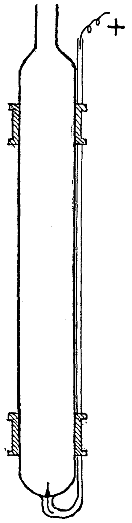

Fig. 2.

the platinum contact wire was sealed through the bottom of the tube, extended 8 mm. up into the tube where it was covered with a thin sheath of glass except for 2 mm. of the end which was exposed and thoroughly amalgamated. A small glass tube was passed over the end of the platinum wire which was outside of the tube, and then sealed to the large glass tube. This little glass tube

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[1] PHYS. REV., 23, 180.

was bent as indicated in the figure and served to protect and insulate the copper lead wire. Contact between the platinum and copper wires was made with a little mercury and the rest of the little tube was filled with wax. The rotating tubes used were 20 mm. in diameter and 200 mm. long, each contained 7 c.cm. of mercury, 4 c.cm. of mercurous sulphate, 4 c.cm. of powdered cadmium sulphate and about 50 c.cm. of the saturated solution. These two systems were alike in all respects except that the air was rigorously excluded from tube No II. while tube No I. contained air and was frequently opened.

These tubes with their contents were rotated about their longer axis in the 25° bath just as described[2] for the first experiments. The temperature of 25° was determined by certified 1/50° thermometers and the large 100 liter thermostat seldom varied .02° from this temperature. Care was exercised to keep the bath covered so as to protect the rotating system from the action of light since the black product, formed by the action of light on mercurous sulphate, increases the mercury concentration of the solution.

The materials used were distilled mercury,[1] recrystallized cadmium sulphate (the clear crystals only were used), and a saturated solution of these crystals. The mercurous sulphate was prepared chemically by adding an acid solution of mercurous nitrate to a 1 to 6 sulphuric acid solution. The sulphuric acid contained mercury and was rapidly stirred while the mercurous nitrate solution was added drop by drop. In the first experiments the gray electrolytic mercurous sulphate was used (l. c.) while here the chemically prepared sample was white, distinctly crystalline and coarse-grained. The preparation was brought onto a Gooch crucible, washed with sulphuric acid ($D=1.15$), with absolute alcohol to remove the acid, and finally with the saturated cadmium sulphate solution. Particular attention was given to these washings, because it had been found that sulphuric acid prevented the changes under consideration. The washed mercurous sulphate was mixed with an equal bulk of powdered cadmium sulphate crystals and brought into the rotating tube No. I., which already contained the mercury and

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[1] Phys. Rev., 23, 177.

[2] Phys. Rev., 21, 387.

saturated solution. This tube was closed with a cork and a rubber cap and was rotated in the bath.

Tube No. II. was first charged with the mercury and powdered cadmium sulphate and then evacuated and filled with pure hydrogen gas. The tube was evacuated and refilled with hydrogen several times in order to make sure that all the air had been removed from the tube and its contents. The saturated cadmium sulphate solution was brought into a vacuum and shaken until the dissolved air had been practically removed. Hydrogen gas was then allowed to bubble through the solution for three days. The mercurous sulphate was washed as before except the final washings were made with the hydrogen saturated solution and care was taken to avoid drawing air through the sulphate. This sulphate was washed into tube No. II. with some of the hydrogen saturated cadmium sulphate solution, a current of hydrogen prevented the entrance of air and after the tube had been nearly filled with the solution it was evacuated and sealed off before the blow pipe. The materials of this tube No. II. may have retained some hydrogen but they were free from oxygen and when the tube was opened, after two weeks' rotation, the vacuum was still in evidence so there could have been no leak.

The tubes were rotated together and at the same rate. After 33 hours, the rotation was stopped, tube No. I. was brought to an upright position and measured with the anode leg of the adjustable cell.

3	minutes after stopping the rotation the E.M.F. was	1.01960
6	" " " " " " " "	51
13	" " " " " " " "	40
45	" " " " " " " "	30
60	" " " " " " " "	29

The rotation was then continued and after 4 days the observations were,

2	minutes after stopping the rotation the E.M.F. was	1.02036
5	" " " " " " " "	17
10	" " " " " " " "	08
20	hours " " " " " " "	1.01986
60	" " " " " " " "	77
6	days " " " " " " "	

The rotation was then continued for 6 days making a total of ten days and tube No. I. was again tested.

2 minutes	after stopping the rotation the E.M.F. was	1.02035
8 "	" " " " " " "	18
45 "	" " " " " " "	09
2 hours	" " " " " " "	05
6 "	" " " " " " "	00
Ajustable cell		1.01838

Evidently the system had about reached its maximum value and was nearly .00200 V. higher than the adjustable cell which had been made from the same materials. The increase in E.M.F. was somewhat greater than in the first experiments but the maximum value obtained has no real significance since it is not an equilibrium point; otherwise there would have been no change after the rotation was stopped. The significance of the decreasing E.M.F. will be considered later, here attention may well be called to some features of the experiment. The adjustable cell was compared with the standards before and after each series of measurements on a rotated system and since there was no variation of the adjustable cell greater than .00001 V., it is certain that the anode tester remained constant and that the observed changes were all in the rotated system. Furthermore, after the solids had settled in the rotated tube, some of the clear supernatant solution was removed, and tested on a clean mercury electrode with the adjustable anode and the value 1.02013 V. was observed. We may therefore be quite confident that the large values obtained for the E.M.F. were due solely to an increase in the mercury concentration of the rotated solution.

Tube No. I. had about reached its maximum value but was again rotated and two days later when both tubes had been rotated a total of twelve days, the hermetically sealed tube No. II. was also tested with the anode leg of the adjustable cell.

The agreement between the two tubes is as good as between different measurements on tube No. I., and since the systems were not in equilibrium the agreement in maximum values is better than was to be expected. The decreasing values depend for one thing on diffusion and this rate of decrease varied at different times for the same system as may be seen from the various measurements on tube No. I. The results obtained, therefore, give a decisive answer to the question at issue and we may conclude that the dissolved air plays no rôle in these rotation experiments.

Time from Stopping the Rotation.	Tube No. II. Air Free.	Tube No. I. Air Saturated.	Time from Stopping the Rotation.	Tube No. II. Air Free.	Tube No. I. Air Saturated.
1¼ minutes.	1.02040 V.	1.02060	24 hours.	1.01972	1.020000
2 "	23		2 days.	60	1.01988
5 "	11	50	4 "	46	64
10 "	03	42	7 "	34	40
30 "	1.01997	36	14 "	12	16
60 "	91	33	21 "	00	
3 hours.	86	22	30 "	1.01800	
6 "	81	17			

Since the dissolved oxygen did not cause the changes in the cathode system, there must have been some interaction between the materials of the rotated tubes which increased the mercury concentration of the solution. If this action was hydrolysis, as has been suggested, an explanation of the observed changes would be possible. Assuming that hydrolysis did take place it followed that the presence of sulphuric acid, one of the products of hydrolysis, would minimize or prevent the changes. This conclusion was tested by the following experiment:

A saturated solution of cadmium sulphate was made tenth molecular in respect to sulphuric acid and this acid solution was used in constructing an adjustable cell and in filling a rotating tube. Electrolytic mercurous sulphate was washed with alcohol and with the acid cadmium sulphate solution and was then made to a paste in the usual way. The other materials, apparatus and method were the same as for the preceding experiments. The adjustable cell, due to the presence of acid, was lower than the cadmium cell (1.01825 V. at 25°), but quite as constant. The cathode system in the tube was rotated as previously described at 4 r.p.m. and after twelve hours it was measured with the anode leg of the adjustable cell with results as follows:

3 minutes after stopping the rotation the E.M.F. was...........1.01812 V.
8 " " " " " " " " 22
30 " " " " " " " " 22
60 " " " " " " " " 22
Adjustable cell... 24

After two days rotation the following results were obtained:

2 minutes after stopping the rotation the E.M.F. was	1.01815
5 " " " " " "	20
20 " " " " " "	24
10 hours " " " " "	24
Adjustable cell...	25

The tube was then rotated two weeks:

2 minutes after stopping the rotation the E.M.F. was	1.018200
4 hours " " " " "	21
12 " " " " " "	22
3 days " " " " "	25
4 " " " " " "	23
Adjustable cell...	24

This system — mercurous sulphate, mercury, cadmium sulphate and acid solution of cadmium sulphate — came to equilibrium soon after it was brought together and there was then no further change. The system behaved exactly as did the cathode system of the Clark cell.[1] The effect of the sulphuric acid in eliminating the changes in the rotated system is in agreement with the view that the neutral cadmium sulphate solution hydrolyzed the mercurous sulphate, but this is not by itself a proof of the point.

This experiment, with the previous ones, furnishes more evidence on the question of oxidation by dissolved air. The materials and solution in this last experiment were air saturated and frequently opened to the air but the system came to equilibrium at once with the normal E.M.F. This would hardly have been the case if the dissolved air had been oxidizing the mercurous sulphate. In the rotation experiment with the cathode system of the Clark cell the zinc sulphate solution was air saturated, but did not oxidize the mercurous sulphate because the system showed the normal value and did not change on continued rotation.[2]

It will be seen that the experiment just described also gives some

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[1] Phys. Rev., 23, 181.

[2] The work of J. W. McBain (J. Phys. Chem., 5, 621, 1901) on the oxidation of ferrous solutions by free oxygen, may be mentioned in this connection. The author found that the rate of oxidation of ferrous sulphate by dissolved air was proportional to the square of the concentration of the ferrous sulphate proportional to the concentration of the oxygen, and that sulphuric acid had only a slightly retarding influence on the rate. The rate was unexpectedly slow, it was shown that precautions prescribed in volumetric analysis for preparing a ferrous sulphate solution from iron wire are quite unnecessary, since with air bubbling through the solution only .05 per cent. of ferric iron was formed

evidence on the question of the size of particles changing the solubility of the mercurous sulphate. A fine powder has an abnormally great solubility but the effect has not been observed until the powder contained a large number of particles with diameters less than one or two microns.[1] Previous experiments have shown that mercurous sulphate which settled rapidly in a 1 to 6 sulphuric acid solution was sufficiently coarse-grained to avoid a measurable effect of the size of the particles on the solubility. But the mercurous sulphate might have been ground to a fine powder in the rotating tubes and this would not only have increased the mercury concentration of the solution, but on standing, the finer more soluble crystals would have disappeared and the mercury concentration would then have decreased. The changes in E.M.F. observed on rotating the cathode system of the cadmium cell corresponded with this explanation, but when a little acid was added the system soon came to equilibrium and the slow changes previously observed were entirely lacking. The same kind of mercurous sulphate and rate of rotation were used in both cases so the observed changes in the first experiment cannot be explained as due to finely divided particles or to grinding of the solids since the presence of the acid in the last experiment could not have effected either of these factors.

The electrolytic mercurous sulphate and the same rate of rotation were used in the experiment with the cathode system of the Clark cell, the system came to equilibrium at once with no changes characteristic of the presence of finely divided particles and the same conclusions may be drawn from that experiment. The method of rotating the tubes[2] was devised in order to avoid grinding the solid contents of the system but at the same time it was necessary to insure a thorough mixing of the cathode materials and this was satisfactorily accomplished by the method and apparatus employed.

THE AGING OF STANDARD CELLS.

In the method of constructing cells devised by Clark,[3] Wright and Thompson[4] and Rayleigh,[5] the mercurous sulphate was washed

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[1] Zeit. Phys. Chem., 49, 385, 1901.

[2] PHYS. REV., 23, 177.

[3] Proc. Roy. Soc., 20, 444, 1872.

[4] Phil. Mag., 16, 25, 1833.

[5] Phil. Trans., 175, 411 and 176, 781, 1886.

with water and thus contained the basic salt even if it had not been previously formed in making the mercurous sulphate. Such cells always had a high value (1 to 2 per cent., Rayleigh, l. c., 446) and required a month or two of "aging" before they reached a constant value. On the other hand when the mercurous sulphate was properly prepared and washed so as to exclude the basic salt from the depolarizer,[1] the cells had their constant value at once. Cells have been made with depolarizers which contained known amounts of the basic mercurous sulphate and these cells had a high preliminary value, and then showed the characteristic decrease. Electrolytic mercurous sulphate was shaken with definite amounts of water and an excess of mercury, thus a definite amount of the basic salt was formed and mixed with the undissolved solid. This mixture was made to a paste in the usual way, cell A44 contained one per cent. of the basic salt in the depolarizer, cell A45, three per cent., and cell A46, 10 per cent. while the completely hydrolyzed salt ($2(HgOH).Hg_2SO_4$) was used for cell A41. These cells have been maintained constantly at 25° and their records for over a year are as follows.

Cell.	Jan. 13.	Jan. 26.	Feb. 7.	March 13.	April 13.	May 12.	June 4.
A44	1.01878	1.01871	1.01868	1.01866	1.01865	1.01862	1.01860
A45	64	60	58	55	53	52	47
A46	98	90	86	80	74	69	62
A41	1.01768	760	767	774	776	772	770

Cell.	July 7.	Aug. 14.	Nov. 15.	Dec. 19.	Jan. 3.	Feb. 26.
A44	1.01857	1.01855	1.01853	1.01854	1.01850	1.01849
A45	47	47	45	57	46	46
A46	57	56	44	40	40	44
A41	764	756	747	741	736	732

The cells with one per cent. and three per cent. of basic salt have become fairly constant, while cell A46, with 10 per cent. of basic salt in the depolarizer, had the highest preliminary value and has varied the most while the cell with only the basic salt, A41, shows no sign of becoming constant. The depolarizers of cells A35 to A40[2] were made basic by mixing known amounts of the completely hydrolyzed salt with the normal salt. The effect was not as great

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[1] Phys. Rev., 23, 172.

[2] Phys. Rev., 22, 328.

as in the experiments just described but of the same general character. The higher values and more rapid rate of decrease were found in the case of the cells with the larger per cent. of basic salt, and these cells were liable to go below the normal value.

On rotating the cathode system of the cadmium cell an increase in the E.M.F. was obtained and when the system was allowed to rest the E.M.F. began to decrease, rapidly at first and then at a decreasing rate. The mercurous sulphate which had been rotated thirty days with the cadmium sulphate solution and mercury was used as the depolarizer of cells A49 and A50 (p. 17), and these cells had a high value and then decreased and are now below normal value and still decreasing. The parallelism between all these facts is evident and indicates that a basic mercurous sulphate was formed in the rotation experiments. The fact that a little sulphuric acid prevented the changes in the cathode system is in agreement with this view and on the whole it seems reasonable to conclude that a neutral cadmium sulphate solution interacts with the depolarizer to form a basic mercurous sulphate. Hydrolysis would account for the facts established by the previous experiments, but the basic salt formed by the action of the cadmium sulphate solution is probably different from the one formed by the action of water, otherwise we would expect the cells with variable amounts of the basic salt (due to water) to show more agreement since it would be a case of two solids saturating a solvent and enough of the basic salt to prevent any action of the cadmium sulphate solution. But whatever the nature of the new phase which formed on rotating the cathode system of the cadmium cell, the subsequent decreasing E.M.F. showed that the system had not attained equilibrium.

There evidently were two oppositely directed changes taking place; the one, assumed to be hydrolysis of the mercurous sulphate, increased the mercury concentration of the solution while the other and much slower change was evidently a secondary action of the mercury on the soluble products of hydrolysis. This secondary action occurred only when the basic salt was or had been present and it caused a decrease of the mercury concentration of the solution. Tube No. I. attained the high value of 1.02060 V. and on standing, decreased to 1.01900 V. in three weeks but on examining the supernatant solution it was found to have still retained a high value showing 1.02013 V. against a mercury electrode. This test was made by bringing some of the clear liquid onto a mercury electrode in a little tube like the part (*C*) of Fig. 1 and measuring the E.M.F. with the adjustable anode. When left in contact with the mercury electrode the clear liquid showed a slowly decreasing value and shaking it with the mercury seemed to have very little effect in hastening the action.

First reading	1.02013
6 minutes	00
20 "	1.01998
90 "	89
1 day	68
3 days	51
10 "	49

We may therefore conclude that, both in the cells which contained basic salt and in the rotated systems, there was a slow secondary reaction which took place and that this action *was only at the surface of the mercury*. The rate at which the mercury concentration of the solution above the paste decreased depended on the rate of diffusion of the solution through the paste and thus depended on the mechanical fineness of the solid materials of the cathode system. The hydrolysis, or whatever reaction formed the basic salt, could not have attained equilibrium until the secondary action was completed or had formed a new phase. If this view is correct it is probable that the maximum value was not observed in any of the rotation experiments. In the first experiment with the gray electrolytic mercurous sulphate there was a tendency for the mercury to become divided into fine globules, and thus the mercury surface was much increased and consequently the rate of the secondary reaction. In the experiment with the white chemically prepared mercurous sulphate (p. 19) there was no tendency of the mercury to become finely divided and the maximum value was higher than in the first experiment and attained in less time. Evidently variations in the materials and in the apparatus and method used will give quite different results, but the experiments seem to clearly show that in the cathode leg of the cadmium cell we have a system which is in unstable equilibrium.

The changes that have been observed in the E.M.F. of cadmium cells are of course small compared to those obtained in the rotation experiments. The F series of 10 cells which were made February 15, 1904, showed an agreement among themselves of one part in 100,000 for nearly a year, but now they show variations of 5 parts in 100,000 and are from 10 to 15 parts lower than they were when made. The A series of October 21, 1905, showed the same excellent agreement for nearly a year.

Cell.	Oct. 26.	Dec. 14.	March 4.	June 4.	Oct. 2.	Dec. 19.	March 18.
A1	1.01843	1.01843	1.01843	1.01842	1.01842	1.01841	1.01841
A2	42	43	43	42	46	44	43
A3	42	42	43	42			
A4	43	43	43	42	42	42	42
A5	43	43	43	42	41	40	40½
A6	43	43	43	43	42	42	42

The paste in these (A) cells was about 2 cm. deep and the cells have remained undisturbed in the 25° bath, but are not now in as good agreement as formerly, although they have not shown as great a decrease as was exhibited by the F series.

It is probable that cadmium cells, made with a fine-grained depolarizer of good depth, would show less variations than have been shown by the F and A series, since there would be less chance for diffusion and consequently for the changes indicated in this article. A very fine-grained mercurous sulphate retains the sulphuric acid very tenaciously, and the presence of this acid in the cell also tends to retard the changes. But a standard cell which depends on the mechanical conditions of the solid materials and is in unstable equilibrium must be less reproducible and less constant than cells which are free from these defects. In the experiment in which acid was added to the cathode materials of the cadmium cell it was found that the system soon came to equilibrium, and this has suggested that the cadmium cell should have a definite amount of sulphuric acid. A number of these acid cadmium cells have been constructed and are very constant, but as yet insufficient observations have been made on them to judge of their worth.

At the same time the F and A cells were made, Clark cells were also made and with depolarizers made from the same samples of mercurous sulphate as served for the cadmium cells. These Clark cells are now in good agreement and have the same value as cells made in the last few months from fresh materials. This is in agreement with the results of the rotation experiments on the cathode systems of the Clark and cadmium cells.

The fact that these Clark cells which were made at various times with fresh materials are now in good agreement (± .00002 V.) is proof that they have not changed and that they form a reliable basis of electromotive force. The absolute value of these cells is 1.4204 volts at 25°, as determined by Dr. K. E. Guthe.[1]

The essential points to be observed in constructing these cells have been given.[2] The high temperature coefficient of the Clark cells have made it necessary to have very constant temperature baths. A large copper tank contained 100 liters of kerosene oil and was electrically heated and controlled. A mercury-toluene regulator operated the relay, which in turn controlled the heating current. This regulator consisted of glass tubes joined together in the form of a gridiron so as to be well distributed in the bath. The tubes were filled with toluene, except the outlet, which was filled with mercury. Contact with the relay circuit was made with a very fine platinum wire (.05 mm.), and a condenser was used to prevent sparking. It was found that with the very fine contact wire there was no "fouling" of the mercury and no "drift" of the bath temperature. The heating coils were also in the form of a gridiron, made of glass rods and pianoforte wire, which was wound on the glass rods and then thorougly shellacked. The resistance was 120 ohms and the heating current was only one half ampere (an alternating current was used). The heating surface was large and well distributed in the bath, and only a very small amount of heat was needed, because the bath was well protected with non-conducting materials. The oil was stirred with a motor-driven paddle and there were no differences of temperature in the various parts of the bath that could be detected with a Beckmann thermometer. The temperature was determined by certified 1/50° thermometers, and these thermometers were checked at the transition point of sodium

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[1] Bull. Bur. Standards, 2, 33, 1906.

[2] Phys. Rev., 22, 334–338.

sulphate, 32.383°.[1] An Otto Wolff potentiometer was used in the measurements, and its corrections were known and applied when necessary. The galvanometer gave 2 mm. deflection for .00001 V. In making measurements it was found best to join all the anodes of all the cells together, and particular attention was given to the question of insulation. The measurements given are regarded as correct to the .000005 V.

PRINCETON UNIVERSITY,
March 15, 1907.

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[1] Richards & Wells, Zeit. Phys. Chem., 43, 471, 1903.