

# THE PHYSICAL REVIEW

## EQUILIBRIA IN STANDARD CELLS.

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THE two combinations which have shown the greatest reproducibility and constancy are the Clark cell and the Weston or cadmium cell and these cells are very similar in construction :

Zinc amalgam	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{Hg}_2\text{SO}_4$	$\text{H}_2\text{O}$	mercury
Cadmium amalgam	$\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$	$\text{Hg}_2\text{SO}_4$	$\text{H}_2\text{O}$	mercury

Many other combinations have been suggested and tried but have been found wanting in constancy or reproducibility. It has been the universal experience that a metal in the solid state gives an inconstant potential against a solution even of its own salt and, while the cause of this is not fully understood, the fact has restricted the choice of materials to liquid electrodes for standard cells, thus mercury forms one electrode and a liquid amalgam the other. For this amalgam it is desirable that the base metal be well toward the positive end of the electrochemical series and hence far removed from mercury, and that it have a fair solubility in mercury. Gouy<sup>1</sup> gives as the percentage solubility of metals in mercury: Cadmium 4, zinc 1.8, lead 1.3, bismuth 1.2, tin .6, gold .13, and distinctly less for other metals. It is further desirable that the base metal exist in only one state of oxidation and that its salts be well defined. In these requirements zinc and cadmium are distinctly superior to all other metals and it is improbable that other metals will be found to be of service in standard cells. Furthermore the depolarizer must have a certain solubility since mercury shows a constant potential

<sup>1</sup>J. de Physique, 4, 320.

only in electrolytes which contain definite amounts of mercury in solution and experience has shown that this solubility must not be too small, as in the case of the calomel cell, or too great as in the case of the Daniell cell where the depolarizer, copper sulphate, is quite soluble.

Since mercury is the cathode the depolarizer must be a mercurous salt with a solubility of a few parts in a thousand and there are very few available salts of mercury answering to these requirements; mercurous sulphate is distinctly the best, although mercurous chlorate deserves to be considered. It is also to be noted that the acid radical of the base metal must be the same as that of the depolarizer and if mercurous sulphate is used as depolarizer, zinc or cadmium sulphate must be used in the construction of the cell. There are then excellent reasons for devoting attention to the Clark and cadmium cells rather than seeking for other combinations.

*The Cathode Systems.*—The potential difference between an amalgam and an electrolyte varies with the concentration of the metal in the amalgam and so this concentration must be fixed and reproducible for any given temperature. This requirement is attained by utilizing a saturated solution of the metal with an excess of the solid so that at each temperature the proper concentration is automatically produced whether the electrode has lost or gained metal from the electrolyte or in other ways. In the Clark cell this two-phase system is made up of zinc and a saturated amalgam, while in the cadmium cell the solid phase in the amalgam is an isomorphous mixture of mercury and cadmium which has a definite composition for each temperature as well as the liquid amalgam in equilibrium with it. The liquid phase of this cadmium amalgam at 25° has been carefully analyzed and found to contain 5.903 g. of cadmium to 100 g. of mercury and it is probably one of the most accurately reproducible concentrations known. In some experiments on the E.M.F. of cadmium amalgams observations were made on two amalgams containing 10 per cent. and 7 per cent. of cadmium; these formed two-phase systems with different amounts of the solid, and were used as electrodes in a cadmium sulphate solution. The system was made free from oxygen and hermetically sealed in a glass cell; the observations extended over a period of six months, and

although the system was subjected to wide variations of temperature whenever it was brought to 25°, equilibrium was soon established and there never was an E.M.F. between the amalgams greater than .0000012 volt; it was generally less than this, but if this difference was all due to differences in the concentration of cadmium in the two liquid phases it indicated differences of only seven parts in a million. In order that this two-phase amalgam may give a definite potential difference, it is necessary that it be in contact with a solution which contains a cadmium salt of definite concentration, and here again use is made of the property of a saturated solution with an excess of the solid salt. Crystallized cadmium sulphate,  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$ , is a particularly well-defined salt and gives a concentration of 3.363 mols in a liter at 25°, the density of this solution is 1.6176.

Since the anode is made up of two metals, cadmium and mercury, it is essential for equilibrium that the electrolyte contain in solution salts of both metals and that there be a definite ratio between the concentrations of these salts, depending on the relative concentration of the metals in the electrode and upon their relative solution pressures or positions in the electrochemical series. The most thoroughly investigated case of this kind is the equilibrium between mercury, silver and a solution of their nitrates.<sup>1</sup> It was shown that silver did not completely remove mercury from solution and that mercury, when brought into contact with a silver nitrate solution, did go into solution and reduce an equivalent amount of silver. From whichever side approached there resulted a definite equilibrium with both silver and mercury in the metal phase and in the solution, the equilibrium was represented by the following relation proposed by Nernst<sup>2</sup>  $\sqrt[n_1]{P_1/p_1} = \sqrt[n_2]{P_2/p_2}$ , where  $P_1$ ,  $P_2$  represent the solution pressures of the two metals and  $p_1$ ,  $p_2$  the osmotic pressures of the ions of these metals in the electrolyte;  $n_1$  and  $n_2$  represent their respective valencies. It was further pointed out by Reinders that in case the metals formed a solution (liquid or solid) that  $P_1$  and  $P_2$  would vary with their respective concentrations in the metal phase and the equation was correspondingly modified.

<sup>1</sup> Ogg, Zeit. Phys. Chem., 27, 285. Reinders, Zeit. Phys. Chem., 54, 609.

<sup>2</sup> Zeit. Phys. Chem., 22, 537.

It must be concluded therefore that cadmium will not completely remove mercury from solution and that if mercury is brought into contact with a cadmium sulphate solution, some of the mercury will go into solution and force out an equivalent amount of cadmium. Reinders<sup>1</sup> suggested that this state of affairs existed in the standard cells, but due to the wide difference between cadmium and mercury in the electrochemical series, the equilibrium concentration of mercury in the anode leg must be very small. Observations on the cells themselves tend to confirm this point since the anode shows its correct potential difference soon after a cell is constructed, later mercurous sulphate diffuses over from the cathode and then there is a certain concentration of mercury about the amalgam, but the arrival of the dissolved mercury at the anode is not accompanied by a change in E.M.F., so it would seem that the equilibrium concentration of mercury about the anode was already present before the mercury diffused over from the cathode, having been furnished by the interaction of the amalgam and the solution. Some results on the E.M.F. of dilute amalgams, which will soon be published, give more direct evidence of this relation and indicate that the mercury concentration is very small. It is to be remembered, however, that it is not the absolute but the relative concentrations which are of importance in determining electromotive forces.

The anode of a standard cell may then be made up of an electrode in two phases, the liquid amalgam has an exceedingly exact and reproducible concentration for each temperature and when this equilibrium is established the solid phase has of course the same potential as the liquid phase and does not show the irregularities exhibited by a solid metal electrode. The electrolyte about this electrode is saturated with cadmium sulphate and an excess of the crystals insures a definite concentration of cadmium in the electrolyte for each temperature while the interaction of the amalgam and this solution furnishes an equally definite mercury concentration in the liquid surrounding the electrode. The anode system is thus seen to be made up of five phases: solid and liquid amalgam, solution, solid salt of the base metal, and vapor. The components are therefore: mercury, base metal, water and acid radical and thus for each temperature they form a non-variant system.

<sup>1</sup>Zeit. Phys. Chem., 42, 232.

It is evident that the equilibria in these anode systems are rapidly established as soon as the temperature is fixed. Of the two anode systems it is probable that they are equally reproducible and constant, the solubility of zinc sulphate crystals changes very greatly with the temperature and there is a tendency for these crystals to "cake" above the amalgam, while the cadmium sulphate crystals have an exceptionally small temperature-solubility coefficient and have not shown this tendency. The tendency of the zinc amalgam to cause the platinum contact wire to crack the glass has been a source of trouble with Clark cells, also the zinc amalgam slowly generates hydrogen from its sulphate solution so it is probable that a zinc sulphate solution has a fair concentration of hydrogen ions while there is no evidence of the liberation of hydrogen in the anode system of the cadmium cell and it is probable from other experiments also that a cadmium sulphate solution is only slightly hydrolyzed, if at all, and so contains practically no hydrogen ions. The cadmium anode is more completely reversible than the zinc anode, for in as far as hydrogen is liberated with the deposition of the metal the change is not reversible, but this does not effect the equilibrium, reproducibility or constancy of the zinc anode system and while the lack of hydrogen ions in the cadmium sulphate solution is an advantage in the anode system of the cadmium cell, it is the cause of a state of unstable equilibrium in the cathode system of this cell as the following results show. In this respect the acid qualities of the zinc sulphate solution constitute a very decided advantage.

Reinders<sup>1</sup> was the first to point out that these cells could not be considered as one system since the electrolyte at the cathode is saturated with mercurous sulphate which continually diffuses over to the anode and is there reduced to a very small concentration by the amalgam. Equilibrium would be established only on the disappearance of the base metal from the anode or the disappearance of the mercurous sulphate as a solid phase, in either case the E.M.F. would become zero or inconstant. This type of cell is made up of two distinct systems which are in electrolytic contact but not in equilibrium with each other, but as the cells are constructed the diffusion from cathode to anode is so slow that the life

<sup>1</sup> Konink. Akad. Wetensch. Amsterdam, Versl. 11, 115.

of the combination is very great. It was further noted by Reinders that, for a constant and reproducible E.M.F., it was essential that both the anode system and the cathode system be nonvariant systems when the temperature was fixed. The Clark cell conforms to these requirements but the results now at hand show that the cathode system of the cadmium cell does not.

*The Cathode Systems.*—The materials used in constructing the cathode system of the cadmium cell are: Mercury, mercurous sulphate, cadmium sulphate and water. An excess of the two sulphates are used and it may be assumed that there results a solution saturated in respect to  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  and  $\text{Hg}_2\text{SO}_4$ , provided that these salts are in their stable forms at the temperatures considered, do not form isomorphous mixtures, double salts or interact chemically. The mercury will not be pure but will contain a small equilibrium concentration of cadmium due to its interaction with the solution. There appears then a potential difference between this electrode and the solution which is a function only of the temperature and if the premises are correct it may be concluded that rotating this system will not affect the potential difference provided the materials are not reduced to such a fine state of subdivision that the effect due to surface tension becomes measurable. But it has been found<sup>1</sup> that there was a very decided change in the potential difference when this cathode system of the cadmium cell was rotated, a slow increase was observed amounting in some cases to two millivolts. The apparatus used in rotating the system gave a thorough mixing of the contents but avoided grinding the solids to a fine powder or reducing the mercury to small globules. Indirect evidence was also obtained to show that the observed change in potential difference was in no way due to surface tension. It seemed possible that the dissolved oxygen had changed some of the mercurous sulphate to the more soluble mercuric form and that the resulting increased mercury concentration caused the increased potential difference. This obvious explanation was rigidly tested<sup>2</sup> but it was found that the absence of oxygen made no difference in the results of the rotation experiment and considerable indirect evidence also pointed to the

<sup>1</sup> PHYS. REV., 23, 176, and 25, 16.

<sup>2</sup> PHYS. REV., 25, 19-24.

same conclusion. The evidence on this point seemed so decisive that it is to be concluded that dissolved oxygen plays no rôle whatever in these systems. If the *rate* of solution of mercurous sulphate was slow the equilibrium point would be slowly approached and only on rotating the system, but it has been frequently noticed that the cell assumes a certain E.M.F. soon after it is constructed and if its value undergoes any change it is to decrease, while an increasing mercury concentration would mean an increasing E.M.F. This fact seems to effectively dispose of the idea of a slow rate of solution of the mercurous sulphate in a cadmium sulphate solution; it shows that, at least the layer next to the mercury electrode, dissolved as much mercury sulphate as it will in a very short time.

There was still the possibility that the mercurous sulphate was hydrolyzed by the cadmium sulphate solution with the formation of a basic salt and an acid solution, a reaction which would proceed until a certain acid concentration was established. This point was tested by adding acid to the system and it was found that it did not then show the slowly increasing potential difference but came to a constant value very soon after the rotation was begun. This was good evidence that mercurous sulphate, conforming to its well known tendency, did hydrolyze in a cadmium sulphate solution. The only evidence for the increase in the mercury concentration was the increase in the potential difference observed in the rotation experiments. This increase of some two millivolts would indicate, according to Nernst logarithmic relation, an increase of some 15 per cent. in the concentration of the mercurous sulphate, assuming that there was a gram of mercurous sulphate in a liter of the solution and it was largely dissociated; but if it was only slightly dissociated in the cadmium sulphate solution, the observed change in potential difference would indicate a much greater increase in the mercury concentration and it therefore seemed possible to detect analytically such changes in concentration if they existed.

The clear solution from the cathode system had a density of 1.6176, contained 760 g. of  $\text{CdSO}_4$  in a liter but only about one gram of mercurous sulphate and considerable difficulty was encountered until a special method of analysis was devised. It was found that an excess of hydrochloric acid entirely prevented the precipita-

tion of CdS by sulphuretted hydrogen but all the mercury was thrown out as a black sulphide. However the difficulty of separating this sulphide of mercury from the viscous liquid was so great that it could not be used for quantitative determinations although it served as a method of detecting traces of mercury in the concentrated cadmium sulphate solution and also to estimate small quantities colorimetrically. Hydrochloric acid was found to precipitate mercury from these solutions as mercurous chloride which Ley and Himbuchen<sup>1</sup> have shown to have a solubility of only .2 mg. in a liter, much less soluble than silver chloride and it was found that the mercurous chloride soon coagulated and filtered nicely. It is known however that these solutions also contain a certain very small concentration of mercuric mercury, since there is always an equilibrium established between the mercurous and mercuric mercury in a solution which is in contact with mercury, but in the case of mercury this equilibrium favors the *-ous* state of oxidation so that probably less than one per cent. of the mercury in solution was in the *-ic* state. In consideration of this point it was deemed best to follow the precipitating reagent, HCl, with a reducing agent and sulphur dioxide was used. These reagents so completely removed the mercury that sulphuretted hydrogen failed to show a trace of mercury in the filtrate. The mercurous chloride was easily collected in a Gooch crucible, washed with water and dried in a vacuum desiccator over calcium chloride.<sup>2</sup> It had been previously shown that this precipitate could be completely dried in this way without loss while it was noticeably volatile at 100° and again it has been found that this is a most satisfactory analysis and an exceedingly exact method of determining mercury.

As soon as it was found possible to determine the mercury quantitatively in these cathode solutions the rotation experiments were repeated and a complete analysis was made of the clear solutions together with the density, conductivity and potential difference against mercury. These determinations have been made also on systems to which known amounts of sulphuric acid were added and from these results the solubility curve of mercurous sulphate as a

<sup>1</sup> Zeit. f. Electrochem., 10, 301.

<sup>2</sup> Zeit. Phys. Chem., 49, 500.



function of the sulphuric acid concentration in this system has been determined and the curve gives definite information about the hydrolysis of mercurous sulphate in a cadmium sulphate solution.

*Materials, Apparatus and Method.*— In the previous experiments<sup>1</sup> it was found that either the electrolytic mercurous sulphate or the chemically prepared salt gave high values in the rotated cathode system of the cadmium cell. The essentials are that the depolarizer be normal mercurous sulphate, that acid be rigidly excluded from the system and that the system be closed during the rotation. For the present work the mercurous sulphate was prepared by adding, drop by drop, a molecular solution of mercurous nitrate to a rapidly stirred sulphuric acid solution. Two liters of this acid, density 1.15, were used in preparing 125 grams of the mercurous sulphate. The stirring was done with a motor and three hours were taken for the precipitation so as to obtain a well crystallized product free of inclusions. The action of light was avoided while with the excess of acid used and metallic mercury in both solutions, the basic salts could not have formed. The product was pure white, distinctly crystalline and easily washed, but as the complete removal of acid was important particular attention was given to this operation. The salt was first thoroughly washed with molecular sulphuric acid, then with absolute alcohol and finally with some of the solution in which it was to be used, this was done in a Gooch crucible with filter disk and strong suction was used after each washing. Cells have been constructed from time to time with this preparation and they have shown the normal value and have remained constant. The cadmium sulphate was recrystallized and only the clear well rinsed crystals used, as this salt is not isomorphous with other sulphates impurities were not feared. The zinc sulphate was more troublesome to obtain in a satisfactory state. Iron, lead and cadmium were removed by the method of Mylius and Fromm.<sup>2</sup> The salt was then recrystallized and the crystals centrifuged (Richards). The mercury used was chemically purified with an acid solution of mercurous nitrate and then distilled under diminished pressure with a current of air passing through with the vapor,<sup>3</sup> a method that insures the removal of such metals as zinc and cadmium.

<sup>1</sup> PHYS. REV., 23, 177, and 25, 19.

<sup>2</sup> Zeit. anorg. Chem., 9, 144.

<sup>3</sup> PHYS. REV., 21, 388.

Conductivity water was used where justified in making the solutions, and when acid was to be added to the system the zinc or cadmium sulphates were dissolved in sulphuric acid of known strength. These acids were all made by dilution from the original molecular sulphuric acid which was made from distilled sulphuric acid and conductivity water, the density of this solution was 1.05948 at 25° and it was found to be 1.012 molar by comparison with a carefully analyzed hydrochloric acid solution.

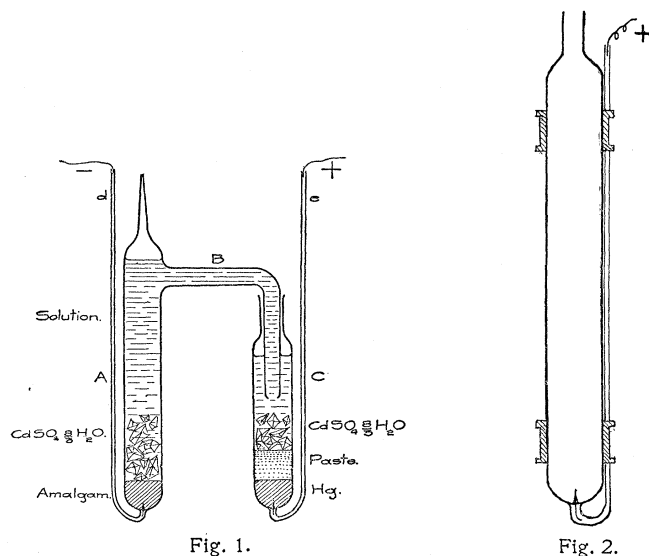


Fig. 1.

Fig. 2.

The systems were brought to equilibrium in tubes 32 mm. in diameter and 150 mm. long, made as shown in Fig. 2. A tube was charged with about 100 g. of mercury, a good excess, then with about 20 g. of the crushed zinc or cadmium sulphate crystals and 25 g. of the properly washed mercurous sulphate crystals. Finally the tube was filled to the neck with the saturated zinc or cadmium sulphate solution. Attention was given to really saturating these solutions at about 25°. The tube was now closed with a cork and a rubber cap was drawn over the cork and neck of the tube to securely close the system. The tube was rotated in the bath in a horizontal position and about the longer axis. It rested in the loops of little belts which extended down from a shaft which

was fixed above the bath and its speed so regulated that the tube rotated at a rate of 10 revolutions per minute. This rate gave a most thorough mixing of the contents of the tube, but was not rapid enough to grind the solid contents to a powder or to cause the mercury to become divided into fine globules. From time to time the tube was brought to an upright position in the bath, the cap and cork were removed and the anode of the adjustable cell *A*, Fig. 1, was brought into contact with the contents of the tube and thus the E.M.F. between the amalgam of this anode and the mercury of the system was determined. Whatever changes in the E.M.F. were observed between successive observations were known to be due to changes in the potential difference of the rotated cathode system because the anode was not rotated, and with its own unrotated cathode *C*, Fig. 1, there was always a check on the constancy of the anode and also a comparison of the rotated and unrotated system since the same materials served for the construction of both of these systems. Each equilibrium tube was rotated until the potential difference of the system became constant and in some cases this required two weeks or more. It is to be noted that during the rotation nothing could enter or leave the system nor at any time since the system was quiet when the anode was adjusted and a diffusion of dissolved mercury out through the narrow tube *B* of the anode tester during the time of making a measurement was not to be considered.<sup>1</sup>

When the system was in equilibrium, as indicated by no further increase in the E.M.F., the tube was allowed to stand quietly in the bath for a day, or until the liquid was perfectly clear, and then it was drawn up into a large pycnometer through a little glass tube. The pycnometer and contents were brought to 25° and the mass of a known volume of the solution was determined. This solution

<sup>1</sup> Attention is called to this point since it will be readily seen that if the anode and cathode systems had been in liquid contact during the rotation that the diffusion of mercurous sulphate to the anode, aided by convection, would have been a maximum, and since the hydrolysis of mercurous sulphate in this system is an exceptionally slow reaction there would have been little increase in the mercury concentration in the cathode system; such methods would not show the real changes that did take place. Neglect to guard against this point may possibly account for the low results obtained in some of the experiments lately made by Drs. F. A. Wolff and C. E. Waters. Bull. Bureau of Standards, Vol. 4, 81.

was transferred, with a little water, to a flask and made acid with sulphuric acid and then the mercury was precipitated with 5 c.c. of strong hydrochloric acid and finally sulphur dioxide was bubbled into the solution to reduce the small amount of mercuric mercury. The  $\text{HgCl}$  coagulated nicely and required only a very thin felt in the Gooch crucible, it was determined as already described (p. 109) and the weight calculated to  $\text{Hg}_2\text{SO}_4$ . The results are regarded as reliable to .1 mg. The clear filtrate was evaporated in a platinum dish, heated to expel the hydrochloric acid and excess of sulphuric acid and, after cooling in a desiccator, weighed. The dish and sulphate was then reheated for an hour at about  $500^\circ$  in an atmosphere containing a little  $\text{SO}_3$  vapor, cooled and reweighed.

Thus for each system the mass of the solution, of the  $\text{CdSO}_4$ , and the mercury as  $\text{HgCl}$  were directly determined while the water was had by difference. In case acid had been added a further calculation was necessary; for example in Experiment No. 1, "cadmium system in molar sulphuric acid," the dissolved  $\text{CdSO}_4 \cdot \frac{8}{3}\text{H}_2\text{O}$  added its water of crystallization to the solution, but the amount was obtained from the weight of the  $\text{CdSO}_4$  and with this allowance the amount of  $\text{H}_2\text{SO}_4$  in the volume of the solution taken was determinable; in this experiment, where molar sulphuric acid had been used, the solution was only .810 molar in respect to sulphuric acid.

The thermostat used in the previous work<sup>1</sup> maintained the temperature to within .02 of  $25^\circ$  throughout the long runs and materially aided in the accuracy of many of the measurements. The temperature was determined by a  $1/50^\circ$  calibrated thermometer which was checked at  $32.383^\circ$ , the transition point of sodium sulphate (Richards and Wells). The two pyknometers used were calibrated from time to time and it was found that the mass of the pyknometer, alone or filled with water, was determinable to less than .5 mg. The volumes were, No. 1 47.7605 and No. 2 49.0856 cm. at  $25^\circ$ . All weighings were made by substitution of calibrated weights and, where justifiable, vacuum corrections were made. The conductivity measurements were made in the usual way, a long narrow Arrhenius form of cell with a capacity factor of 8,040 was used.

<sup>1</sup> PHYS. REV., 25, 19.

In the E.M.F. determinations the same apparatus and precautions were used as in the previous work;<sup>1</sup> it was found quite necessary to thoroughly insulate the lead wires to the rotation tubes and for the adjustable cells since they dipped into the water-bath. This was done by covering them with glass tubes as indicated in Figs. 1 and 2.

*Cathode Systems of the Cadmium Cell.*

*Experiment 1.* — System in 1.012 molar sulphuric acid, rotated 8 days, 25°.

Mass of solution	in	49.0856	c.c.	75.377	g.	Moles in a Liter.
" CdSO <sub>4</sub>	"	49.0856	"	27.384	"	2.6757
" Hg <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.0371	"	.001524
" H <sub>2</sub> O	"	49.0856	"	44.051	"	48.683
" H <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	3.905	"	.810
$D_{25}$ .....		1.53564				E. M. F. .... 1.01678 $V$ .
$\lambda_{25}$ .....		.14423				Adjustable cell ..... 1.01671 "

*Experiment 2.* — System in .506 molar sulphuric acid, rotated 5 days, 25°.

Mass of solution	in	47.7605	c.c.	75.209	g.	Moles in a Liter.
" CdSO <sub>4</sub>	"	47.7605	"	29.989	"	3.0116
" Hg <sub>2</sub> SO <sub>4</sub>	"	47.7605	"	.0442	"	.001867
" H <sub>2</sub> O	"	47.7605	"	43.330	"	50.860
" H <sub>2</sub> SO <sub>4</sub>	"	47.7605	"	1.847	"	.384
$D_{25}$ .....		1.57511				E. M. F. .... 1.01747 $V$ .
$\lambda_{25}$ .....		.07738				Adjustable cell ..... 1.01745 "

*Experiment 3.* — System in .2024 molar sulphuric acid, rotated 6 days, 25°.

Mass of solution	in	47.7605	c.c.	76.433	g.	Moles in a Liter.
" CdSO <sub>4</sub>	"	47.7605	"	32.0905	"	3.2226
" Hg <sub>2</sub> SO <sub>4</sub>	"	47.7605	"	.0478	"	.002017
" H <sub>2</sub> O	"	47.7605	"	43.570	"	50.641
" H <sub>2</sub> SO <sub>4</sub>	"	47.7605	"	.7263	"	.155
$D_{25}$ .....		1.60032				E. M. F. .... 1.01808 $V$ .
$\lambda_{25}$ .....		.05350				Adjustable cell ..... 1.01802 "

*Experiment 4.* — System in .1012 molar sulphuric acid, rotated 10 days, 25°.

<sup>1</sup> PHYS. REV., 25, 29.

Mass of solution	in 47.7605	c.c.	76.836	g.	Moles in a Liter.
" CdSO <sub>4</sub>	" 47.7605	"	32.805	"	3.2944
" Hg <sub>2</sub> SO <sub>4</sub>	" 47.7605	"	.04937	"	.002084
" H <sub>2</sub> O	" 47.7605	"	43.622	"	50.700
" H <sub>2</sub> SO <sub>4</sub>	" 47.7605	"	.360	"	.0769
$D_{25}$ .....	1.60880			E.M.F.....	1.01823 <i>V</i> .
$\lambda_{25}$ .....	.04674			Adjustable cell.....	1.01821 "

*Experiment 5.* — System in .05064 molar sulphuric acid, rotated 7 days, 25°.

Mass of solution	in 47.7605	c.c.	77.032	g.	Moles in a Liter.
" CdSO <sub>4</sub>	" 47.7605	"	33.120	"	3.3260
" Hg <sub>2</sub> SO <sub>4</sub>	" 47.7605	"	.05176	"	.002185
" H <sub>2</sub> O	" 47.7605	"	43.680	"	50.722
" H <sub>2</sub> SO <sub>4</sub>	" 47.7605	"	.180	"	.0384
$D_{25}$ .....	1.61289			E.M.F.....	1.01834
$\lambda_{25}$ .....	.04372			Adjustable cell.....	1.01834

*Experiment 6.* — System in .02024 molar sulphuric acid, rotated 13 days, 25°.

Mass of solution	in 49.0856	c.c.	79.304	g.	Moles in a Liter.
" CdSO <sub>4</sub>	" 49.0856	"	34.262	"	3.348
" Hg <sub>2</sub> SO <sub>4</sub>	" 49.0856	"	.05514	"	.002265
" H <sub>2</sub> O	" 49.0856	"	44.914	"	50.910
" H <sub>2</sub> SO <sub>4</sub>	" 49.0856	"	.0737	"	.0153
$D_{25}$ .....	1.61565			E.M.F.....	1.01847 <i>V</i> .
$\lambda_{25}$ .....	.04180			Adjustable cell.....	1.01835 "

*Experiment 7.* — System without acid added, rotated 21 days, 25°.

Mass of solution	in 47.7605	c.c.	77.251	g.	Moles in a Liter.
" CdSO <sub>4</sub>	" 47.7605	"	33.470	"	3.361
" Hg <sub>2</sub> SO <sub>4</sub>	" 47.7605	"	.0640	"	.002701
" H <sub>2</sub> O	" 47.7605	"	43.717	"	50.800
$D_{25}$ .....	1.61747			E.M.F.....	1.01905 <i>V</i> .
$\lambda_{15}$ .....	.04037			Adjustable cell.....	1.01837 "

*Experiment 8.* — System without acid added, rotated 21 days, 25°.

Mass of solution	in 49.0856	c.c.	79.405	g.	Moles in a Liter.
" CdSO <sub>4</sub>	" 49.0856	"	34.435	"	3.365
" Hg <sub>2</sub> SO <sub>4</sub>	" 49.0856	"	.0726	"	.002980
" H <sub>2</sub> O	" 49.0856	"	44.897	"	50.770
$D_{25}$ .....	1.61771			E.M.F.....	1.01940 <i>V</i> .
$\lambda_{25}$ .....	.04057			Adjustable cell.....	1.01836 "

*Experiment 9.*—System without acid added. Fresh solution was added to the solids of experiment 8, rotated 20 days, 25°.

Mass of solution in	49.0856	c.c.	79.402	g.	Moles in a Liter.
" CdSO <sub>4</sub>	"	49.0856	"	34.417	" 3.363
" Hg <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.0742	" .003047
" H <sub>2</sub> O	"	49.0856	"	44.911	" 50.790
$D_{25}$	1.01765				E.M.F. .... 1.02015 <i>V</i> .
$\lambda_{25}$	.04061				Adjustable cell..... 1.01836 "

*Cathode Systems of the Clark Cells.*

*Experiment 10.*—System with 1.012 molar sulphuric acid, rotated 8 days, 25°.

Mass of solution in	49.0856	c.c.	72.2942	g.	Moles in a Liter.
" ZnSO <sub>4</sub>	"	49.0856	"	24.000	" 3.028
" Hg <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.0296	" .001216
" H <sub>2</sub> O	"	49.0856	"	45.500	" 51.460
" H <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	2.765	" .5744
$D_{25}$	1.47436				E.M.F. .... 1.41588 <i>V</i> .
$\lambda_{25}$	.08588				Adjustable cell..... 1.41595 "

*Experiment 11.*—System with .506 molar sulphuric acid, rotated 3 days, 25°.

Mass of solution in	49.0856	c.c.	72.7524	g.	Moles in a Liter.
" ZnSO <sub>4</sub>	"	49.0856	"	25.355	" 3.1993
" Hg <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.03516	" .001444
" H <sub>2</sub> O	"	49.0856	"	46.032	" 52.060
" H <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	1.330	" .270
$D_{25}$	1.48214				E.M.F. .... 1.41813 <i>V</i> .
$\lambda_{25}$	.06110				Adjustable cell..... 1.41810 "

*Experiment 12.*—System with .1012 molar sulphuric acid, rotated 3 days, 25°.

Mass of solution in	49.0856	"	73.155	g.	Moles in a Liter.
" ZnSO <sub>4</sub>	"	49.0856	"	26.402	" 3.331
" Hg <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.03942	" .001619
" H <sub>2</sub> O	"	49.0856	"	46.455	" 52.537
" H <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.259	" .0537
$D_{25}$	1.49037				E.M.F. .... 1.42016 <i>V</i> .
$\lambda_{25}$	.04500				Adjustable cell..... 1.42015 "

*Experiment 13.*—System without acid added, rotated 5 days, 25°.

Mass of solution in	49.0856	c.c.	73.288	g.	Moles in a Liter.
" ZnSO <sub>4</sub>	"	49.0856	"	26.637	" 3.361
" Hg <sub>2</sub> SO <sub>4</sub>	"	49.0856	"	.04108	" .001687
" H <sub>2</sub> O	"	49.0856	"	46.610	" 52.710
$D_{25}$	1.49308				E.M.F. .... 1.42047 <i>V</i> .
$\lambda_{25}$	.04141				Adjustable cell..... 1.42043 "

In the present state of our knowledge of solutions, solubility results are best expressed as parts or moles to 100 g. of solvent, but in the present case the solvent water was determined by difference and included all the other errors while the volume of the solution analyzed was so accurately known it seemed best to calculate the results to moles in a liter and these data are found in the last column of the tables. The character of the curves obtained were the same whichever way the observations were calculated.

It is well known that acid decreases the E.M.F. of standard cells and this may be seen at once from the tabulated results. On plotting the electromotive forces as a function of the acid concentrations, the curve appeared to be a straight line, and in the case of the Clark cell the most probable curve for the four determinations showed that a change of one millivolt in the E.M.F. of the cell corresponded to a change of .121 mole in a liter of the sulphuric acid. In the case of the cadmium cell the linear function applies only for concentrations greater than .1 molar acid, since for very small acid concentrations the E.M.F. curve changes are very great and follow quite different curves, but for the region of .1 molar sulphuric acid and beyond a change of one millivolt in the E.M.F. of the cell corresponds to a change of .410 mole in the acid concentration of the electrolyte, so sulphuric acid has a much less effect on the E.M.F. of the cadmium cell than in the Clark cell.

On inspecting the tables it is seen that the rotation did not affect the E.M.F. of the Clark cell; in experiment 13 the rotated cathode system of the Clark cell had the same potential difference as did the unrotated cathode system of the adjustable cell. This is also true in experiments 10, 11 and 12 where acid had been added. In the case of the cadmium cell where sufficient acid had been added there was no essential difference between the rotated and unrotated cathode systems, as was found in experiments 1, 2, 3, 4 and 5. But in experiment 6 with only .0153 mole of sulphuric acid to the liter of electrolyte, the rotated system was .00012 volt higher than the unrotated adjustable cell and in experiments 7, 8 and 9 where no acid was added the observed increase in E.M.F. was from .00070 to .00189 volt. These high values did not remain constant when the rotation was stopped but decreased on standing; the first



readings were taken in about one minute after stopping the rotation and then at intervals. On plotting these observations it was possible to get the value at the moment of stopping the rotation. For example in experiment 9 one of the last observations made was as follows :

1 1/2	minutes after stopping the rotation	E. M. F.	1.0200
2 1/2	" " " " "	"	1.01992
6 1/6	" " " " "	"	1.01977
24	" " " " "	"	1.01968

and this indicated 1.02015 as the initial value with an error probably not greater than .00005. That this was the true value was shown by removing some of the clear supernatant liquid and testing it on a clean mercury surface.<sup>1</sup> The reason for the decrease will soon be given.

It was expected that sulphuric acid would decrease the solubility

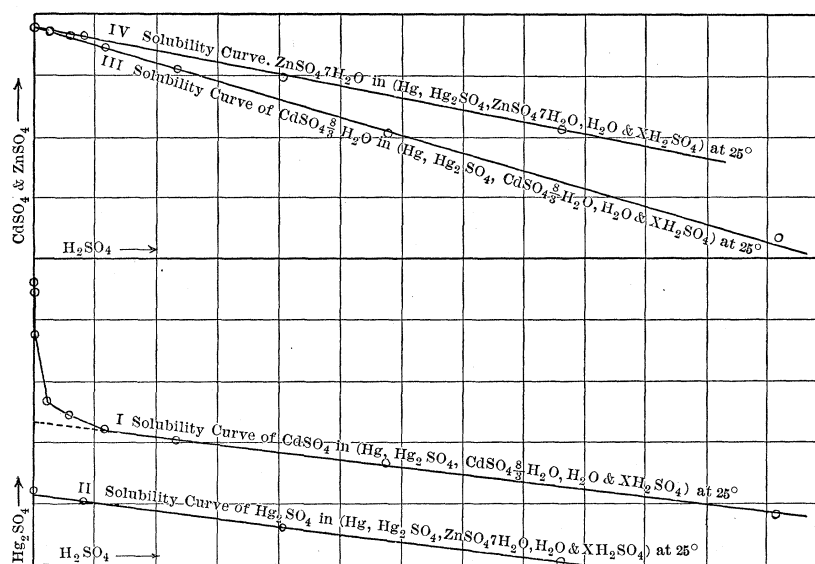


Fig. 3.

of the sulphates in these systems and, for a given temperature, the solubility of the mercurous sulphate and cadmium sulphate (or zinc sulphate) should decrease uniformly with increasing acid concentra-

<sup>1</sup>PHYS. REV., 25, 27.

tion. On plotting the results this was found to be true for all *except the mercurous sulphate in the cathode system of the cadmium-cell*; the results are represented by curve I, Fig. 3. For a concentration of .810 molar sulphuric acid in the system the mercurous sulphate was .001524 mole in a liter and as the acid concentration decreased the mercury concentration increased uniformly until the acid had been reduced to .08 mole in a liter. The results between these values gave a straight line which has been extended to zero concentration of acid. The mercurous sulphate found for the .0384 molar sulphuric acid was distinctly above this line by 4.5 per cent. of its value, while for the concentration of .0153 acid in the system the mercury was 7.3 per cent. too high and for the systems without acid was some 35 per cent. greater than the normal solubility obtained by extrapolating the curve. In short there is a distinct break in the solubility curve of mercurous sulphate in the cathode system of the cadmium cell as soon as the sulphuric acid concentration has been reduced to .08 mole in a liter, and this indicates a change in the nature of the solid mercurous sulphate or that a chemical reaction begins and takes place below this concentration. From the well known behavior of mercury salts there can be no hesitation in concluding that a saturated solution of cadmium sulphate hydrolyzes mercurous sulphate. It is also evident that this change in the solubility curve of mercurous sulphate cannot be due to the cadmium sulphate since the solubility curve of this salt in the system increased uniformly with decreasing acid concentration without a suggestion of discontinuity at .08 mole of sulphuric acid.

When mercurous sulphate comes into a cadmium sulphate solution it begins to dissolve and to hydrolyze and instead of the mercury concentration in the solution becoming constant when the system is saturated in respect to mercurous sulphate, this concentration keeps on increasing as the slow hydrolysis yields basic salt and acid. In time the solution becomes saturated in respect to this basic salt which then appears as a solid phase. But the hydrolysis will not stop until the acid formed by the reaction has reached the equilibrium concentration of .08 mole in a liter. Now the basic salt has a very small solubility, less than the normal salt which is only .00214 mole in a liter, so the acid concentration is

very far from the equilibrium concentration when the basic salt appears as a solid. This state of affairs at once explains the seemingly abnormal behavior of the cells in which mixtures of basic and normal salts were used as depolarizers.<sup>1</sup> It was expected that any mixture of basic and normal salt which contained an excess of both salts, would give a definite concentration of mercury for each temperature and thus a definite reproducible value to the cells. But they did not agree and all showed a decreasing E.M.F. indicating that the cathode systems were not in equilibrium. The explanation that seemed most probable at that time was as follows: Since the basic salt added to the system had been formed by the action of water on mercurous sulphate, it was possibly not the same as that formed in a cadmium sulphate solution and was therefore ineffective in stopping the hydrolysis. Now it appears that the basic salt was quite incapable of stopping the hydrolysis and since the necessary acid concentration was lacking the behavior of these cells is readily understood. Cox<sup>2</sup> concluded that there is but one basic mercurous sulphate and the behavior of these cells may now be brought into harmony with this view. We may then write the reaction as follows:  $2\text{Hg}_2\text{SO}_4 + 2\text{H}_2\text{O} = \text{Hg}_2(\text{OH})_2\text{Hg}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  and it is possible to get some idea of the extent of this hydrolysis in the rotation experiments. In none of these experiments was the maximum mercury concentration, the point of saturation of normal and basic salt, attained so we may conclude that the basic salt formed remained in solution, and the increase in the mercury concentration during the rotation was a measure of the amount of hydrolysis. In experiment 9, the analysis showed .003047 mole of mercurous sulphate in a liter while the normal solubility of mercurous sulphate in a cadmium sulphate solution may be taken to be .00214 mole in a liter, as seen from curve I, Fig. 3. The difference, .0009 mole, represents the amount of hydrolysis and, according to the reaction, a mole of mercurous sulphate gives only .5 mole of sulphuric acid on hydrolyzing so the acid concentration in this system was only .00045 mole of sulphuric acid in a liter, an amount that could readily escape detection by any ordinary means and we see at once why the

<sup>1</sup> PHYS. REV., 22, 328.

<sup>2</sup> Zeit. anorg. Chem., 40, 178.

attempts to find acid in the rotated systems or old cells have failed. Attention is called to the small amount of this hydrolysis in a cadmium sulphate solution, even under the most favorable conditions the reaction had only produced .00045 mole of sulphuric acid in three weeks where .08 was required before equilibrium was established. This 0.009 mole in a liter represents the total change in three weeks in the rotated system, but if the reaction was largely at the mercury surface the rate may have been fairly rapid at that point, and there are good reasons for this assumption.

Lord Rayleigh in 1884 suggested that impurities in the mercurous sulphate used as depolarizer were responsible for observed variations in the E.M.F. of Clark cells and this was later emphasized by Swinburn,<sup>1</sup> while Jaeger and Lindeck<sup>2</sup> came to the same conclusions about the cause of the variations in the E.M.F. of cadmium cells, but there was no suggestion as to the nature of the suspected impurity. Some idea as to the nature of the impurity was first had when precautions were taken to avoid the formation of basic mercurous sulphate in preparing the depolarizer and when the specifications for making the cells were altered so as to avoid hydrolyzing the mercurous sulphate in making the paste. Then it was found that the cells had a much greater reproducibility and especially that the high preliminary values and subsequent decrease in E.M.F., characteristic of cells constructed in the old way, had disappeared. These results pointed to the basic salt and hydrolysis as the disturbing elements. The first cells constructed according to these principles were the four (*D*) cadmium cells made in December, 1903, and described, together with the method of construction, in a paper by Carhart and Hulett read at the Washington meeting of the American Electrochemical Society, April, 1904.<sup>3</sup> In February, 1904, twelve (*F*) cells were made and the agreement among themselves and with the (*D*) cells indicated a reproducibility of one part in 100,000; but in time deviations in the values of these cells were observed and in October, 1905, more cells were made according to the same specifications but they had an E.M.F. about one part in

<sup>1</sup> Brit. Association Report, 1901.

<sup>2</sup> Zeit. Instrk., 21, 33.

<sup>3</sup> See also Trans. Amer. Electrochem. Soc., 5, 59. Trans. International Electrical Congress, St. Louis, Vol. 2, 109-126. Zeit. Phys. Chem., 49, 483.

10,000 greater than the older *D* and *F* cells. Some 120 cadmium cells have been made at intervals during the last five years and they have all been kept together in an oil-bath which has very seldom varied .01° from 25°. Some, like the *D* and *F* cells, showed a slow decrease, others have remained constant and again others have shown a marked and steadily decreasing value and have become so low that they have been rejected as entirely worthless. Considering only the cells which have not been rejected a comparison at the present time shows values ranging from 1.01843 to 1.01827 volts, the older ones being the lowest. Cells have been made at the Bureau of Standards<sup>1</sup> and at the National Physical Laboratory<sup>2</sup> according to the principles just indicated. Some of the cells described by F. E. Smith<sup>3</sup> show unmistakably this decreasing E.M.F. and the author was unable to assign a reason for the observed changes, but noticed discolorations in the paste of some of these "abnormal" cells, a phenomenon which has appeared in some of our cells which have fallen to a very low value.

In interpreting the observed decrease in the E.M.F. of these cadmium cells account must be taken of the conditions in the cell. The viscous solution and fine-grained paste so retard diffusion and convection that concentration differences persist and play a decided rôle. It is the layer of solution immediately next to the mercury electrode and its mercury concentration that determines the potential difference in the cathode leg. That this layer in the cadmium cell is different from the rest of the electrolyte in the cathode leg is shown by the rotation experiments. When the system was rotated the solution became of uniform concentration throughout and the E.M.F. observed immediately on stopping the rotation gave the potential difference between mercury and the solution, but as soon as the "paste" settled down on the mercury the potential difference began to decrease, rapidly at first and then more slowly. The clear supernatant liquid however when brought onto a clean mercury electrode still continued to show the original high potential difference against mercury<sup>4</sup> and thus it was seen that only the mercury concentration in the surface layer had changed.

<sup>1</sup> Bull. Bureau of Standards, 4, 1.

<sup>2</sup> Philos. Trans., A, 207, 400.

<sup>3</sup> L. c., 400.

<sup>4</sup> PHYS. REV., 25, 27.

All of these facts may now be readily interpreted by making a single assumption, namely, that the rate of hydrolysis of mercurous sulphate is accelerated by a plain mercury surface. Basic salt and acid would then form more rapidly in the surface layer than in the rest of the electrolyte and, owing to the difficulty of diffusion from this layer, it would rapidly become saturated and begin to deposit the basic salt and, with the increasing acid concentration in the surface layer, the mercury concentration passed at once into the descending part of curve *I*, Fig. 3.

Thus it is that only decreasing electromotive forces are observed in the cadmium cell. In the rotated system the high values obtained began to decrease as soon as the solids settled down on the mercury and retarded the diffusion of the acid from the surface layer, and this layer came at once into the descending part of the curve. Stirring the paste immediately brought back the high E.M.F. and the true potential between the mercury and the system. When hydrolysis was prevented by the presence of sufficient acid these changes entirely disappeared from the cell and the rotated system and this fact has defeated all attempts to explain the phenomena from the standpoint of oxidation and reduction or as due to surface tension.

The normal solubility of mercurous sulphate in a cadmium sulphate solution was found to be .00214 mole in a liter and no doubt the solution in the paste contains a somewhat greater concentration than this. When saturated with both normal and basic salt the concentration is not far from .004 mole of mercurous mercury in a liter, so it is seen that the surface layer has only a short distance, in quantity, to go to enter the descending part of the curve and the decrease then depends on the amount of the acid generated in the surface layer and the effectiveness of the paste in preventing its diffusion. It is at once seen that diffusion will not cease until the whole system has reached the equilibrium concentration of .08 mole of sulphuric acid in a liter and as this does not take place even under favorable conditions, hydrolysis does not cease and the basic salt continues to form at the expense of the normal salt. This change continues until the normal salt has all disappeared from the vicinity of the electrode and there is the tendency of the surface

layer to approach the very low mercury concentration due to the basic salt, although there is still plenty of normal salt in the paste.

Furthermore there is evidence that the basic salt  $\text{Hg}_2(\text{OH})_2\text{Hg}_2\text{SO}_4$  does not remain intact,<sup>1</sup> but suffers further hydrolysis to mercurous oxide and acid. The mercurous oxide is very unstable and in decomposing furnishes the conditions for the formation of the very insoluble basic mercuric sulphate, a bright yellow compound. The yellow coloration, noted by Smith<sup>2</sup> and confirmed by the appearance of some of our cells which have gone to a very low value, we have taken to indicate the presence of this basic mercuric sulphate. The basic mercurous sulphate is colorless or gray.<sup>3</sup> It is quite within the possibilities that these insoluble basic sulphates separate out as incrustations on the mercurous sulphate and cadmium sulphate crystals in the vicinity of the electrode and in this way decidedly effect equilibrium conditions controlled by these salts. It is true that only a certain per cent. of cadmium cells fall to the very low values, although the number increases with the age of the cells. It is not surprising that the phenomenon does not appear in all cells, no more so than the fact that supersaturated solutions, as near alike as we can make them, do not all crystallize. The cause is possibly the same in both cases, as the basic salt need not appear as a solid phase until the solution is supersaturated in respect to it.

Cell.	Nov. 30.	Dec. 7.	Dec. 12.	Jan. 10.	Feb. 1.	Mar. 1.	Apr. 4.
N 1	1.01842	1.01843	1.01841	1.01839	1.01835	1.01822	1.01776
N 2	44	43	41	45	41	46	830
N 3	44	41	40	40	35	26	797
N <sup>4</sup>	44	42	40	42	39	34	797
N 5	43	41	40	44	41	39	808
N 6	43	42	40	41	41	40	822
N 7	44	41	40	40	38	37	812
N 8	43	45	40	36	32	37	828
N 9	43	40	40	36	31	19	788
N10	43	43	45	45	42	40	823

Some cells made in 1904 now become of interest. In order to make cells with a lower internal resistance a coarse-grained paste

<sup>1</sup> Zeit. Phys. Chem., 49, 491.

<sup>2</sup> Trans. Roy. Soc., A, 207, 407.

<sup>3</sup> Zeit. Phys. Chem., 49, 491.

only 3 or 4 mm. deep was used. The mercurous sulphate was formed electrolytically on a large mercury anode in sulphuric acid and with the low current density used these crystals were several days in forming. Ten of these (*N*) cells were made on November 29, 1904, and their record for the first four months follows: These cells were found to be in excellent agreement after two weeks, but soon began to show irregularities and in four months were so irregular and low that observations were discontinued on all but N9 and N10.

Cell.	1905			1906			
	June 2.	Nov. 12.	Dec. 14.	May 12.	July 7.	Aug. 14.	Oct. 2.
N 9	1.01766	1.01715	1.01722	1.01600	1.01462	1.01364	1.01228
N10	—	1.01815	1.01816	1.01813	1.01813	1.01812	1.01810

It is interesting to notice that the first comparison of these cells soon after they were made showed values, if anything, slightly higher than the "normal" value of the cadmium cell, so it is to be concluded that coarse crystals and a small amount of them in the paste were nevertheless able to saturate the solution in a comparatively short time, but the conditions were very favorable for diffusion to take place and for the changes just outlined to come into play with the results we would now expect. It was the behavior of these cells particularly that suggested that attention was to be given to the depth of the paste in the cadmium cell.<sup>1</sup>

H. V. Steinwehr<sup>2</sup> found, by grinding the mercurous sulphate to a fine powder, that an increased potential was produced against mercury in a cadmium sulphate solution and he at once concluded that all variations of standard cells were due to the size of grains of the depolarizer. V. Steinwehr then prepared a large-grained mercurous sulphate and selected crystals of a uniform size, but the cells were irregular and inconstant and the author attributed their behavior to the little crystals which grew on the larger ones. From the facts now at hand it is to be concluded that surface tension had very little to do with V. Steinwehr's experiments. Not only is the effect of size of particles not to be feared in constructing the cad-

<sup>1</sup> PHYS. REV., 23, 174.

<sup>2</sup> Z. f. Instrumentenk., 25, 205, and Z. Elektrochem., 1906, 578.



mium cell, but it may be concluded that a rather fine-grained paste of good depth would give the most constant results in the cadmium cell. The old way of washing the mercurous sulphate with water made for constancy in this system as the wash water, which was acid, was not entirely removed in making the paste. That such cells do remain constant is shown by the results just published by Professor Carhart<sup>1</sup> on his (*B*) cells which were made in 1903 and have been constant for over four years. Reproducibility could be obtained by preparing the mercurous sulphate in a definite way and with a fine-grained preparation made to a paste in the old way the cadmium cells would not show the changes now encountered. It is questionable whether the new method of construction gives a sufficiently greater reproducibility to the cadmium cell to justify the attempt to exclude the basic salt from the depolarizer. If the basic salt is formed in the cell after it is constructed there is no point to many of the precautions now taken.

Starting with mercury, mercurous sulphate and a cadmium sulphate solution there is little hope of bringing the system to equilibrium as was shown by the rotation experiments and subsequent analyses. The equilibrium might be approached from the other side if we could start with the components of this system: Hg, Hg<sub>2</sub>O, CdSO<sub>4</sub> ·  $\frac{8}{3}$  H<sub>2</sub>O, SO<sub>3</sub> and H<sub>2</sub>O — but the instability of the mercurous oxide excludes this possibility. A knowledge of the equilibrium conditions of this system has suggested still one further possibility: we may start with a sufficiently acid solution of cadmium sulphate to entirely prevent hydrolysis of the mercurous sulphate and then the system rapidly comes to equilibrium—it is then a non-variant system when the temperature is fixed and does not show the changes of the cadmium cell. Some 30 of these “acid” cells have been made during the last three years but the latest results show that the acid concentration was too small but none of them have shown a tendency to decrease. One cell was made in October, 1905, with .2 molar sulphuric acid and has shown a constant value of 1.01792 volts. It has not varied over .00003 volt at any time during the three years; at present its value is 1.01793. The only defect so far noticed in these cells is a tendency of the amalgam to

<sup>1</sup> PHYS. REV., 26, 124.

slowly generate hydrogen, about as much as the zinc amalgam does in the Clark cell. There appears to be no way of keeping the acid concentration automatically fixed but this may not be necessary as the cells show no definite evidence of increasing E.M.F. which would result from decreasing acid concentration. In these acid cells a decrease of .004 mole in a liter of the acid concentration would be needed to increase the E.M.F. .00001 volt. These acid cells deserve further investigation for it is evident that the action of the amalgam on the acid solution is a very slow one and the device of using an acid solution for the unsaturated secondary standards has given most satisfactory results.<sup>1</sup>

The results obtained from the experiments (10, 11, 12 and 13) with the cathode system of the Clark cell are plotted in Fig. 3, curve *II*, and it is seen that there is an entirely different state of affairs in this cell. The mercury concentration in the Clark system to which no acid was added represents a solubility only slightly greater than that indicated by the extrapolated curve from the results with the Clark systems with acid. The results embodied in curves *I* and *II*, Fig. 3, independently confirm the rotation experiments and justify the conclusions that were drawn from those experiments; namely, that a cadmium sulphate solution hydrolyzes mercurous sulphate while a zinc sulphate solution does not. Now hydrolysis is of very common occurrence and need not necessarily affect either the reproducibility or constancy of a cell but in the case of the cadmium cell the hydrolysis establishes a state of unstable equilibrium and so sooner or later, depending upon circumstances, changes appear and it is to be concluded that we are dealing with a non-reversible electrode, a point that has now been pretty thoroughly tested.

*Reversibility of the Cathode Systems.* — In 1905 an attempt was made to make mercurous sulphate electrolytically in a saturated cadmium sulphate solution instead of in sulphuric acid. It was expected that this method would obviate many of the troublesome operations of making the paste and produce a product which would necessarily be in equilibrium with a cadmium sulphate solution. But the cells made up with these preparations as depolarizers had a

<sup>1</sup> PHYS. REV., 27, 33.

high value and did not remain constant but decreased as may be seen from the published results<sup>1</sup> and it may be added that they have since decreased. These results were most puzzling at the time, they showed that with rapid stirring and a low current density the mercurous sulphate formed at a mercury anode in a saturated cadmium sulphate solution was not in equilibrium with the solution and the reaction was not a reversible one while all the experiments with the Clark cell indicate that its cathode system was reversible. An attempt has been made to directly compare the two cells from the standpoint of reversibility. Both Clark and cadmium cells were made without depolarizers, that is, the mercury cathode was covered with coarsely crushed zinc sulphate crystals and the saturated solution, while the anode was of the usual construction. The cadmium cells were made in the same way and were of the same pattern and dimensions. These cells were fastened to a motor-driven shaker so regulated that the mercury of the cathode and the materials above it were in constant and uniform motion, then these cells were all charged with the same current, .020 amp. to a cm.<sup>2</sup> mercury surface. The mercurous sulphate formed soon saturated the solution and then separated as a solid and was mixed with the crystals of zinc or cadmium sulphate. The motion and low current density offered favorable conditions for forming the normal sulphate, after about .100 mg. had formed in each cell, the charging current was broken and the cells placed in the 25° bath. The paste formed in this way was white in color and about 4 mm. deep. Two cadmium cells were made together in series, WN1 and WA; the first was neutral while WA had been made up with .1 molar sulphuric acid. Later WN2, a neutral cadmium cell, was made in the same way, and the two Clark cells, S1 and SH were made up without acid and then the depolarizer formed in the cell as indicated.

The two cadmium cells with neutral solutions, WN1 and WN2, were very high at first and steadily decreased and are still decreasing. There was no suggestion of stopping at the "normal" value of the cadmium cell which is 1.01840 at 25° and this emphasizes the conclusions to be drawn from the rotation experiments, that this value 1.01840 is the value the cells have when put up in a particu-

<sup>1</sup>PHYS. REV., 23, 175.

lar way and is not an equilibrium value. (After the observations of June 6 the pastes in these cells were stirred by shaking the cell and WN2 particularly at once increased but only to subsequently decrease.) The behavior of WA, the cell made with .1 molar sulphuric acid, is quite different; it had a high preliminary value indicating that some basic salt was formed and the E.M.F. decreased but came to a constant value at about 1.01830, which is about the equilibrium value for cells with this amount of acid. The Clark cells, S1 and SH, have been quite constant and the differences between the Clark and cadmium cells is as marked here as in the rotation experiments. These results with the acid cadmium cell and Clark cells suggest that it may be possible to construct these cells and form the depolarizer electrolytically in the cell after they are set up and this would entirely avoid the troublesome manipulations and uncertainties incident to preparing the mercurous sulphate and paste.

Cell.	Date.	Jan. 6.	Jan. 9.	Jan. 20.	Feb. 6.	Feb. 18.	Mar. 5.	Mar. 2.
WN1	Jan. 5	1.01992	1.01974	1.01926	1.01861	1.01827	1.01755	1.01675
WN2	Mar. 12							1.01890
WA	Jan. 5	1.01903	1.01883	1.01873	1.01826	1.01828	1.01828	
S1					1.42082	1.42084	1.02086	1.42080
SH					80	88	89	88

Cell.	Date.	Apr. 8.	May 3.	June 6.	June 30.	July 14.	Aug. 18.
WN1	Jan. 5	1.01190	1.9705	1.9644	.9531	.9255	
WN2	Mar. 12	1.01863	1.01848	1.01770	1.01813	1.01757	1.01611
WA	Jan. 5	1.01821	1.01829	1.01831	1.01851	1.01854	1.01859
S1		1.42080	1.42077	1.42071	1.42080	1.42072	1.42068
SH		87	86	79	79	71	70

*The Clark Cell.*—The Clark cell has been subjected to most searching tests in the investigations on standard cells and it is to be noted that the rotated cathode system showed variations of from .00005 to .00010 volt and that the E.M.F. of the rotated system was always slightly greater than that of the adjustable cell which contained the same materials. The analysis of the liquid of the rotated system showed .837 g. mercurous sulphate in a liter of the solution while the curve II, Fig. 3, gives as the solubility of normal

mercurous sulphate in the cathode system of the Clark cell at  $25^{\circ}$ , .00166 mole or .8234 g. in a liter, a measurably lower value. Also the cells just described, S1 and SH, where the mercurous sulphate was made electrolytically in the cell, are not quite normal as the E.M.F. is noticeably higher than the normal value for  $25^{\circ}$  which is for the Clark cell 1.42040 volts. These deviations are all in the same direction and suggest that a zinc sulphate solution does not entirely prevent a mercurous sulphate from hydrolyzing, but this is probably so slight that equilibrium conditions are established before there is a separation of the basic salt, for the severe tests to which this cell has been subjected lead to the conclusion that this cathode system does come to equilibrium and is essentially reversible. The components of this system may then be taken as mercury, mercurous sulphate, zinc sulphate and water — and at a given temperature it is non-variant. But we cannot take the corresponding substances as components for the cadmium cell cathode system, for, when the hydrolysis is sufficient to produce the basic salt as a solid phase and the acid remains in solution, it diffuses to the anode; then these substances are no longer in stoichiometrical relations in the system, and so the products of hydrolysis must be taken as components and the final product due to the interaction with water in the mercurous oxide, which is unstable and the reaction is not reversible. So there seems little hope of obtaining equilibrium with this system unless acid is added to it, and there probably would not be the possibility of equilibrium in the Clark cell if the basic salt appeared as a solid.

The first Clark cells which were constructed with attention to excluding the basic salt from the depolarizer were the twelve (*H*) cells made on March 15, 1904, and at intervals since then cells have been made according to the same principles. At the present time these cells show no deviations greater than one part in 50,000 and this is the best of evidence that these Clark cells furnish a constant and reproducible basis of electromotive force. Their value has been assumed to be 1.42040 volts at  $25^{\circ}$  and they have been the standard of reference for all previous E.M.F. measurements. The temperature coefficient of the Clark cell is about a millivolt per degree and this was a real objection to the cell before the introduction of thermostats and was the chief reason for the popularity of

the cadmium cell with its much lower temperature coefficient, but for the exact measurements of the present day a thermostat is necessary for any but the Weston secondary cell. The thermostat used for this work is reliable to  $.01^{\circ}$  and such variations indicate an uncertainty of less than one part in 100,000 of the E.M.F. of the Clark cell. The tendency of the glass to crack, where the amalgam contact wire is sealed in, has appeared in the older cells and made it necessary to reject many of them; this and other points in the construction of Clark cells may best be considered in a separate article.

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