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THE CONSTRUCTION OF STANDARD CELLS AND A CONSTANT TEMPERATURE BATH.

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FOR exact electrical measurements a known electromotive force is indispensable and at present we rely on standard cells. From our knowledge of the source of the energy of a voltaic cell we might expect that any combination made up of two metallic electrodes surrounded by solutions of their respective salts would give a reproducible electromotive force which would be a function of the temperature only, but experience shows that this is not the case even when the two electrolytes are not allowed to mix by diffusion. The difficulty seems to be in the inhomogeneity of the surface of a solid metal, since solid metallic surfaces give variable potentials even against solutions of their own salts while metals in the liquid state do show the desired constancy and reproducibility.

The two combinations which have most nearly answered the requirements of a standard are the Clark cell—mercury, mercurous sulphate, zinc sulphate, zinc amalgam—and the Weston standard cell which is the same as the Clark cell except that the zinc is replaced by cadmium throughout. In these cells the cathodes are liquid mercury and each anode amalgam is made up of two phases, a liquid amalgam and a solid amalgam. The composition of the liquid amalgam, which determines the potential of the electrode, depends on its temperature only, while the composition of the electrode as a whole may vary over a considerable range. All these electrodes function as liquids.

In the Clark cell the zinc amalgam is surrounded by a saturated solution of zinc sulphate with an excess of the solid ($ZnSO_4 7H_2O$) which furnishes a definite concentration of zinc ions in the electrolyte for each temperature. Since the electrode is made up of two metals, mercury as well as zinc, the electrolyte in equilibrium with it must also contain some mercury ions. The relation between the zinc and mercury ions in the electrolyte is expressed by the Nernst equation

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}},$$

where P_1 and p_1 refer to the solution pressure of zinc and osmotic pressure of the zinc ions and these letters with the subscript (2) refer to these magnitudes of mercury, while n_1 and n_2 represent the valences of the metals. In our case the concentration of the mercury ions in the electrolyte (p_2) is exceedingly small but there is evidence that these ions are actually present and that they come from the electrode with an equivalent deposition of zinc in the amalgam.[1] The positive pole or cathode of this cell is mercury surrounded by an electrolyte saturated with both zinc sulphate and mercurous sulphate with an excess of both salts in the crystalline state. Here again the mercury will not remain pure mercury but gains a small amount of zinc from the electrolyte, sufficient to satisfy the equilibrium conditions of the equation. The zinc sulphate has a concentration of 3.36 molecular weights to a liter and the mercurous sulphate one of only .00168 or a .056 per cent. solution while the concentration of the zinc in the mercury electrode is something of the order of 10^{-10}.

The cathode and anode legs of these cells represent two different systems each of which comes to equilibrium at a given temperature, but the cell as a whole is not a system in equilibrium and cannot be as long as it shows an E.M.F. The dissolved mercurous sulphate in the cathode leg slowly diffuses over to the anode amalgam where it is at once reduced to the equilibrium concentration which was already present before it arrived. This is the function of the excess of zinc in the anode, but since the concentration of the mercury in

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[1] Crenshaw, Jour. Phys. Chem., 14, 158.

the cathode leg is small and the electrolyte a very viscous solution, the diffusion of mercury to the anode is a slow process and the life of the cell is very great. These same relations obtain in the Weston standard cell where the zinc is replaced by the cadmium and it would seem that these two combinations were ideal from the standpoint of constancy and reproducibility. The one drawback seems to be in the mercury salt. It is a characteristic of mercury salts to hydrolyze, that is, to interact with water and form a basic salt and acid, and mercurous sulphate is not an exception to this rule.[1] Sulphuric acid and sulphate solutions prevent or decrease this hydrolysis, and the hydrolysis of mercurous sulphate in a zinc sulphate solution has not been detected but it is surely present in a cadmium sulphate solution. Such a reaction need not detract from the value of the cell for equilibrium is established as soon as the basic salt and a definite acid concentration are present and then the potential is again a function of the temperature only. In the Clark cell the reaction has not been detected but in the Weston standard cell the hydrolysis takes place, although it is a very slow change which does not come to equilibrium.[2] However this change is generally small as well as slow and the cell has other qualities which make it valuable.

Materials.—Any amount of work may be done in purifying the materials used in constructing standard cells, but only a few foreign substances (in traces) measurably affect the E.M.F. of these standards and for our purpose it seems best to go only so far as to insure the desired reproducibility since the simpler the operations are the greater will be the agreement between the cells constructed at different times and by different investigators.

Mercury.—Pure redistilled mercury may be obtained from reliable dealers and it answers every purpose. In lieu of this, ordinary mercury is chemically purified and then distilled.[3]

Mercurous Sulphate.—The depolarizer is chiefly responsible for variations in the reproducibility and constancy of standard cells and the preparation of the mercurous sulphate and the making

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[1] Zeit. Phys. Chem., 49, 493.

[2] PHYS. REV., 30, 648.

[3] PHYS. REV., 21, 388.

of the paste is still the most difficult and important part of the construction of these standards. In 1884 Lord Rayleigh called attention to this difficulty and the point was emphasized by Kahle[1] and later by Jaeger and Lindeck,[2] but the first explanation of the changes which caused the trouble was offered by Carhart and Hulett.[3] Evidence was given to show that the irregularities in the standard cells were due to the presence of a basic mercurous sulphate which had been formed in preparing the mercurous sulphate or in making the paste. It was also shown[4] that mercurous sulphate is stable in a sulphuric acid solution when the concentration of the acid is molecular (98 grams H_2SO_4 to a liter) or greater, but when the acid strength drops below this value the mercurous sulphate begins to hydrolyze with the formation of a difficultly soluble basic salt—$Hg_2(OH)_2 . Hg_2SO_2$. After this information was obtained it was found possible to suggest conditions for preparing the mercurous sulphate and making the paste so as to exclude the basic salt and the cells made under these conditions did not require the usual aging but showed a constant value at once and were in exceptionally good agreement.[5] There are a number of methods for preparing mercurous sulphate and in such a way that it is possible to maintain the concentration of the sulphuric acid of molecular strength (or greater), at the point where the mercurous sulphate is forming and under such conditions only the normal mercurous sulphate appears. All such preparations give essentially the same value to standard cells.[6]

It is easy to prepare mercurous sulphate chemically and with sufficient sulphuric acid present to prevent hydrolysis, but there is the inclusion and isomorphism of nitric acid, nitrates or other substances to be considered and while the depolarizer made by these chemical methods does, with the proper precautions, give correct values to the standard cells, it is our experience that the electrolytic mercurous sulphate gives on the whole the most uniform and reproducible values.

[1] Wied. Ann., 51, 225.

[2] Zeit. Instk., 21, 33.

[3] Trans. Amer. Electrochem. Soc., 5, 63.

[4] Zeit. Phys. Chem., 49, 483.

[5] Trans. Amer. Electrochem. Soc., 5, 71.

[6] F. E. Smith, Phil. Trans., 207 A, 395.

The electrolytic method[1] has the distinct advantage that only mercury and moderately dilute sulphuric acid are used and the only foreign substance to be looked after is sulphuric acid which may be effectively removed as indicated below. We use an acid having a density of 1.15, made by pouring one volume of concentrated (density 1.84) sulphuric acid into six volumes of water. When this acid is electrolyzed between a mercury anode and a platinum cathode, mercurous sulphate is formed and goes into solution at the anode, but when the acid is saturated (.2 grm. Hg_2SO_4 to the liter) the solid mercurous sulphate appears and covers the anode. At the cathode, hydrogen is liberated and a little mercury but the efficiency is very great, forming about 9 grams of the salt per ampere hour. If the mercurous sulphate is allowed to collect on the anode to any great extent, a secondary reaction may take place but this is to be avoided and a stirrer has been employed to keep the mercurous sulphate in suspension in the electrolyte while the current was passing,[2] but only a limited amount of mercurous sulphate could be formed at a time. Lately we have improved the method by using an inner dish to hold the mercury and so arranged that the mercurous sulphate passed over the rim of the inner dish and collected in the space between it and the outer dish. The accompanying sketch, Fig. 1, shows the arrangement. A large deep crystallizing dish was nearly filled with the acid and in this was placed a somewhat smaller and very much lower crystallizing dish. Mercury was poured into the inner dish to a depth of about one centimeter and electrical connection was made through a stiff platinum wire fused into the end of a glass tube so that 4 or 5 cm. of the wire extended out into the mercury. The glass tube was bent to fit into the inner dish and over the edge of the outer dish as indicated in the figure. A short spiral of platinum wire was suspended in the sulphuric acid to serve as cathode, the platinum wires used were 0.5 mm. as a current of over two amperes was generally used with the mercury anode surface of 175 cm. (The inner dish has a diameter of 15 cm.) A motor-driven stirrer was

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[1] Carhart and Hulett, Trans. Amer. Electrochem. Soc., V., 59. F. A. Wolff, Trans. Amer. Electrochem. Soc., V., 56, and M. Coste et M. Etaix, Bull. de la Soc. des Electriciens, 2 Serie, VIII., 1908.

[2] Trans. Amer. Electrochem. Soc., V., 63. PHYS. REV., 22, 334.

used and was made from a glass rod which was bent at a right angle and so arranged that the *L* part of the stirrer passed over and near to the surface of the mercury. This stirrer was held in a brass tube *bb* which also carried the pulley *p*. This brass tube turned in bronze bearings in the tube *hh* which was firmly held by clamps (not shown). It was found to be important to have the stirrer well made so that it worked smoothly and with certainty.

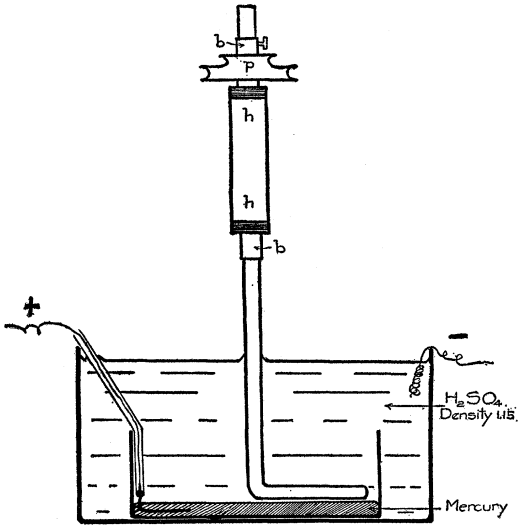

Fig. 1.

After the stirrer was running uniformly at a rate of some 200 revolutions per minute, the current was turned on. With fresh acid a skin formed on the surface of the mercury but by breaking and making the current several times or until the acid became saturated with the mercurous sulphate and the solid sulphate appeared throughout the acid, then there was no further trouble. The position of the stirrer was such that it did not unduly agitate the mercury. The mercurous sulphate formed was carried up by the rotating liquid and settled in the space between the two dishes and much more readily when the rotation of the liquid outside of the inner dish was retarded. This was easily accomplished by inserting glass plates edgewise down into the acid and allowing them to rest on the edge of the inner dish. With a current density of from 1 to 2 amperes per 100 cm.^{2} of mercury anode surface the product obtained was gray, due to finely divided mercury. The presence of this finely divided mercury is an advantage in checking any tendency to oxidation. Generally 50 or 60 grams were prepared at a run and after the stirrer had been removed and the mercurous sulphate had settled, most of the acid was removed, the contents of the inner dish were poured into the outer dish and all well stirred for some time, then the acid, with the suspended sulphate, was poured into a clean dish and after the sulphate had settled the acid was returned to the mercury, stirred and again decanted and this was repeated until the mercury and mercurous sulphate were separated. The product was transferred to a glass stoppered bottle, covered with a little of the acid and kept in a dark place until needed. Some of the acid, diluted with two volumes of water, was brought into an ordinary washing bottle and the stream blown from this bottle aided materially in transferring the sulphate from one dish to another.

After this apparatus was once perfected and assembled it has been a simple matter to prepare the depolarizer whenever needed. Our experience is that this gray electrolytic mercurous sulphate, prepared as just described, is the most reliable and reproducible depolarizer for standard cells and that the grains are sufficiently large to avoid all effects of surface tension.[1]

The Flowing Anode Method.—Lately we have also used an interesting and very simple method for preparing electrolytic mercurous sulphate. A fine stream of mercury flowing from a funnel into the sulphuric acid is made the anode and no stirring is required. The accompanying sketch, Fig. 2, illustrates the apparatus. An ordinary funnel was used, the stem was warmed in a flame and drawn down to a capillary which was about 10 cm. in length and of such a diameter that 10 c.c. of mercury were delivered in about five minutes. An ordinary liter beaker glass was filled nearly full with the sulphuric acid (density 1.15) and the funnel adjusted so that the tip of the capillary was just under the surface of the acid. A short platinum spiral was hung in the acid

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[1] Phys. Rev., 22, 326–328.

and served as cathode, mercury was poured into the funnel and it ran through the capillary and formed a spray as it entered the acid but when contact was made with the mercury in the funnel and a current of from 2 to 3 amperes passed through this mercury, the electrolyte, and out through the platinum spiral, the spray changed to a cylinder of flowing mercury which extended to the bottom of the beaker and looked like a wire. It was distinctly gray save for a short distance at the top which was bright mercury. M. Coste et M. Etaix[1] have used an alternating current in preparing mercurous sulphate. The flowing electrode method also permits us to use an alternating current and very simply. Two funnels were prepared with the same length of capillary stems and of the same diameter. These funnels dipped into the same beaker of sulphuric acid and the two streams of mercury were used as the electrodes, a 60-cycle alternating current was used and so regulated that there was no arcing between electrode and electrolyte and thus a current of about 5 amperes was used. The efficiency here is as great as with the direct current, about 9 grams of mercurous sulphate per ampere hour. With this flowing anode method the preparation is white, even with large current densities, and the sulphate is easily separated from the mercury by decanting it with the electrolyte. Cells made with these preparations as depolarizers show a slightly higher value than with the gray electrolytic previously described. The alternating current preparation seems to

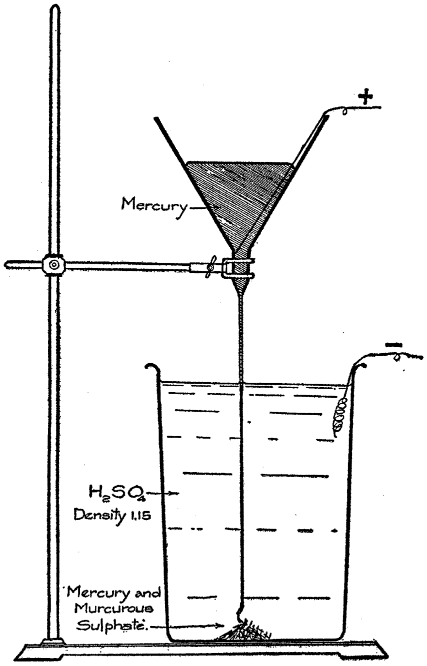

Fig. 2.

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[1] Bull. de la Soc. des Electriciens, 2 Serie, VIII., 1908.

be the better of the two but they have not been tested for a sufficient length of time if we are concerned with the fifth decimal place in the E.M.F. of the cells.

The Paste.—The problem is to prepare a mixture of mercurous sulphate, zinc or cadmium sulphate and saturated solution, but to avoid the presence of sulphuric acid and basic mercurous sulphate. The only impurity in the electrolytic mercurous sulphate is the sulphuric acid in which it is made and preserved but any attempt to remove this acid by washing with water introduces the basic salt. Formerly we used alcohol which was subsequently removed by washing with the saturated zinc or cadmium sulphate solution, but we have found that this preliminary washing with alcohol is not necessary and that really only three washings with the saturated sulphate solution are necessary, when certain precautions are observed. A Gooch crucible, filtering apparatus and good suction were employed. A disk was cut from filter paper and fitted nicely to the bottom of the crucible and then the mercurous sulphate was transferred to the crucible and washed down with the acid. The layer of solid sulphate was about 15 mm. thick and the acid was quite completely removed by suction. By shaking off the drops which formed on the under side of the crucible it was determined when no more of the acid was being removed by suction. The inside of the crucible down to the sulphate was wiped with a bit of filter paper, to remove any drops of acid, and then the sulphate was washed directly with the saturated zinc or cadmium sulphate solution, using one to two cubic centimeters each time and taking care to remove this solution quite completely by suction before a second portion was added. It had been our practice to wash five or six times in this way but some experiments have shown that twc washings gave the same value to the cells as was obtained when the sulphate had been washed five or six times. Now we wash only three times with the saturated zinc or cadmium sulphate solution but with due attention to the details just given. The washed sulphate was quite compact and the top layer with any dust was easily scraped off, then the solid cake was removed by tapping the inverted crucible on a piece of filter paper. A large agate mortar was used in mixing the components of the paste. Zinc or cadmium sulphate crystals, about equal in volume to the mercurous sulphate, were crushed but a few cubic centimeters of the saturated solution were first added to the crystals to prevent partial dehydration by the crushing.[1] After the crystals had been ground to a fine powder, the mercurous sulphate was added and all thoroughly mixed with enough of the saturated solution to make a thin paste and of such a consistency that it readily flowed from a 5-mm. tube. Unless the mercurous sulphate was gray a little mercury was ground up with the crystals and mixed with the paste. In transferring the paste to the cells a thin-walled glass tube 30 cm. long, 5 mm. in diameter was slightly contracted at the lower end and used as a pipette. By gentle suction, and stirring the paste with the end of the pipette, the paste was drawn up into the pipette and easily transferred to the cell and added until it covered the mercury electrode to a depth of about 15 mm. In all the operations of preparing the depolarizer and making the paste, direct sunlight or undue exposure to light was avoided. Excessive exposure to light darkens mercurous sulphate and the product then gives a higher value to the E.M.F. of the standard cells.

Zinc Sulphate. — $ZnSO_47H_2O$ is one of our more soluble salts. The solubility increases rapidly with the temperature and at 39° the solid phase changes to the hexahydrate which is to be avoided in making the Clark cells. E. Cohen gives the following relation between solubility and temperature; $L_t = 41.80 + .522t + .00496t^2$. From this we find that 100 c.c. of water dissolves:

At	$ZnSO_4$. Grams.	$ZnSO_47H_2O$. Grams.
0°	41.80	110.6
0°	41.80	110.6
15°	50.78	154.9
20°	54.22	167.6
25°	57.92	188.5
30°	60.92	207.3
39°	70.66	275.3

Zinc blend, from which this salt is obtained, generally contains cadmium and manganese and often lead and tin. The salt is

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[1] W. F. Hildebrand, J. Amer. Chem. Soc., 30, 1120.

isomorphous with the other vitriols—iron, magnesium, cobalt‘ nickel and copper, but none of these metals, in the small amount usually found present in zinc sulphate, seems to affect the E.M.F. of the Clark cells. Sulphuric acid is to be excluded as .027 per cent. of this acid in the electrolyte of the cell reduces the E.M.F. measurably.[1] Zinc sulphate, as obtained in the trade, generally contains less than the theoretical amount of water of crystallization due to efflorescence, so it is best to recrystallize the salt and at room temperature in order to insure the heptahydrate. Starting with "chemically pure" zinc sulphate we made a saturated solution at room temperature, the solution showed a density of 1.45 and was brought into a flask with a handful of granulated zinc, warmed to 50° and frequently shaken for an hour or so in order to remove less positive metals than zinc and also any excess of acid. The solution was now filtered until perfectly clear. It was then poured into a large crystallizing dish, but not over a centimeter in depth. The dish was placed where the temperature was fairly constant and covered with filter paper. Due to the shallowness of the solution the crystals formed on the bottom of the dish and in a day or so a good crop of perfectly clear crystals one to two centimeters long were obtained. If a crust began to form on the solution or around the edges, a few drops of water were carefully run on to correct the difficulty and with little attention only clear well formed crystals were obtained. The solution was poured off and the crystals brought onto sheets of filter paper to absorb the excess of solution and then they were preserved in a well stoppered bottle to prevent efflorescence. A saturated solution is easily made from these crystals; the preceding table will indicate the amounts to use.

Zinc Amalgam.—Zinc is one of the more soluble metals. With an excess of zinc we have, for each temperature, a liquid amalgam of definite composition and in equilibrium with a solid phase which is pure zinc.

At 0° the liquid amalgam contains 1.35 per cent. of zinc.
15° " " " " 1.74 " " "
20° " " " " 1.99 " " "
25° " " " " 2.18 " " "
39° " " " " 2.85 " " "

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[1] Phys. Rev., 27, 352.

For our purpose it is seen that a 3 per cent. amalgam would serve every purpose since for the range of the Clark cell, such an amalgam is always two phase, but a 3 per cent. amalgam is rather too liquid while the 10 per cent. amalgam commonly used is too hard. We have found a 7 per cent. amalgam to be plastic at ordinary temperatures and most satisfactory. There seems to be no difference between the potentials of amalgams made from "chemically pure" zinc and mercury and amalgams made from the most highly purified metals so the "chemically pure" materials serve every purpose. Zinc dissolves but slowly in mercury and the amalgam oxidizes readily when hot but we have had no trouble with this amalgam since using the following method: A 2.5 cm. hole was cut in a piece of asbestos cardboard and an ordinary porcelain crucible was pushed into this hole so that it was about half way through, the board was placed on a tripod and the crucible was charged with about 7 grams of chemically pure zinc (weighed to .010 gram) and then thirteen times the weight of mercury was added. A small adjustable bunsen flame was placed under the crucible and the contents heated, but without stirring, until the zinc had all dissolved. This takes a temperature near to the boiling point of mercury and the crucible was covered with a little watch glass. The flame was now pushed a few centimeters to one side and when the crucible cooled down to about 100° the amalgam was readily transferred to the cells with a pipette. The pipette was made from a thin-walled glass tube 5 or 6 mm. in diameter with the tip drawn down in the flame to about 3 mm. The amalgam as prepared had only a slight coat, which was readily brushed to one side and the clean amalgam was sucked up into the pipette and transferred to the (warmed) anode leg of the cell without getting it on the sides of the glass. The amalgam was generally run in to a depth of about 10 mm. It soon cooled and solidified and then was ready for the zinc sulphate crystals and the saturated solution.

Cadmium Sulphate. — $CdSO_4 8/3H_2O$ is a very soluble salt but is peculiar in that the *rate* of solution is exceptionally slow so that considerable attention is needed to prepare a saturated solution. The solubility changes only slightly with the temperature and the 8/3 hydrate is stable up to 74° where it changes to the monohydrate.

100 c.c. of water dissolve the following amounts at the indicated temperatures:

At	$CdSO_4$.	$CdSO_4 8/3 H_2O$.
0°	75.5	112.5
15°	76.1	113.4
25°	76.8	114.7
40°	78.5	117.9
74°	78.6	133.8

Cadmium sulphate does not seem to be isomorphous with any known salt and consequently is obtained in a sufficiently pure state in the trade but one may obtain such beautiful crystals that it is worth while to recrystallize the salt. We dissolve a kilogram of the salt in a liter of water, using a mechanical stirrer, and filter the liquid into large crystallizing dishes. The depth of the liquid in the dishes is generally about one centimeter and the dishes are placed where the temperature is quite constant and covered with filterpaper. As the solution slowly evaporates perfect crystals appear on the bottom of the dish and most of them are water clear but some are cloudy, due to minute liquid inclusions. We have not found the cells made with the cloudy crystals to differ in E.M.F. from those made with the perfectly clear crystals; the cloudy crystals may of course be redissolved and recrystallized. Attention is to be given to the preparation of a saturated solution of cadmium sulphate on account of the slow rate of solution of these crystals; 100 c.c. of the saturated solution requires 75 c.c. of water and 86 grams of the crystals but a considerable excess of the crystals are to be used and stirred over night with a motor-driven stirrer.

Cadmium Amalgam. — Cadmium is the most soluble metal in mercury; the saturated amalgam contains the following percentages of cadmium:

At	Per Cent. Cadmium.
0°	2.5
15°	4.4
25°	5.6
35°	7.1

With an excess of cadmium the solid phase is not cadmium but an isomorphous mixture of cadmium and mercury.[1] The composition

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[1] Bijl, Zeit. Phys. Chem., 41, 641.

of this solid phase also varies with the temperature but within certain limits the potential of this amalgam is definite and reproducible for a given temperature. In view of the great solubility of cadmium at ordinary temperatures it does not seem well to use less than 8 per cent. of cadmium in the amalgam. 12½ per cent. has been commonly used but Cohen and Krypt[1] have shown this amalgam to be unreliable below 14° and there is a question as to whether the solid phase of these amalgams are homogeneous and in equilibrium with the liquid phase when the amalgam is cooled from a higher to a lower temperature.[2] The question of equilibrium in this amalgam evidently needs further investigation; it is a much more complicated system than is the zinc amalgam.

We have used for some time a 10 per cent. amalgam for our cells and make it quite accurately and uniformly as follows: 99.00 grams of mercury were placed in a little crystallizing dish, 5 or 6 cm. in diameter, and 25.00 grams of the clear cadmium sulphate crystals (43.82 per cent. Cd) were placed on this mercury and then about 50 c.c. of distilled water was carefully added and made acid with a drop of sulphuric acid. A flat platinum spiral was so adjusted that the spiral was just beneath the surface of the water and contact was made with the mercury which was cathode. When 2 or 3 amperes were used the cadmium was deposited in the mercury about as fast as the sulphate dissolved, then when the crystals had all disappeared the current was increased to 4 or 5 amperes for half an hour. This insured a complete deposition of the cadmium and also liberated enough heat to melt the amalgam. The acid was finally removed by a pipette or syphon and at the same time distilled water was run in. This washing continued until the current dropped to zero. The amalgam may be left under water with the "current on" as long as one pleases as there is no possibility of loss or oxidation as long as the amalgam is cathode. When needed the amalgam was easily melted by removing the water and adding hot water and the hot water was finally removed quite completely by a pipette and then the liquid amalgam transferred

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[1] Zeit. Phys. Chem., 65, 359.

[2] F. E. Smith, Phil. Mag., 19, 250. S. W. J. Smith, Phil. Mag., 20, 206. G. A. Hulett, Trans. Amer. Electrochochem. Soc., 15, 438.

to the cells as described under "zinc amalgams." These quantities suffice for 5 or 6 cells in all cases.

We have prepared cadmium sulphate and cadmium of the highest degree of purity,[1] also zinc sulphate and zinc[2] and constructed cells with these materials but the E.M.F. of these cells did not differ from the cells made with materials prepared as described above and this result is the one we would expect when we consider the factors controlling the potentials at the anodes and cathodes of these standard cells. For example a trace of iron sulphate could not affect the zinc amalgam nor measurably decrease the solubility of the zinc sulphate crystals, and the potential here depends on the ratio of the concentrations of the zinc in the amalgam to that in the electrolyte, nor would a trace of iron affect the mercury of the cathode or the solubility of mercurous sulphate. On the other hand a trace of basic mercurous sulphate would directly increase the concentration of the mercury at the cathode and since this concentration is small, the effect on the E.M.F. would be relatively large. Sulphuric acid also directly and measurably affects the concentration of the mercury in the catholyte and so the greatest attention was given to these points.

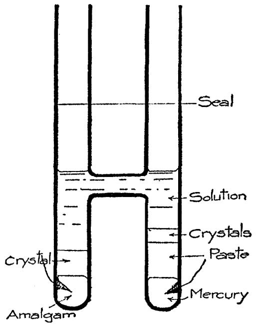

Fig. 3.

The Glass Parts.—The "H" cell proposed by Lord Rayleigh has proved to be the most practical form of cell. It is easily filled and allows the contents of each electrode to rapidly take up the temperature of the bath. We use thin-walled tubing about 10 mm. in diameter made into the form indicated in Fig. 3. The .2 mm. platinum wire leads are sealed through the glass so that all but the tip end is covered with a sheath of glass. The wire is first sealed in so that the end is only just through the glass and then, while the glass is still soft, the wire is pushed in about 5 mm. and covers itself with a sheath of glass leaving only the tip exposed. Wires sealed in this way give uniform contact with the mercury

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[1] Jour. Amer. Chem. Soc., 30, 1808, 10.

[2] Jour. Phys. Chem., 14, 161–164.

or amalgams and are less liable to cause subsequent cracking of the glass especially when a fine wire is used.

The amalgam and mercury are introduced by a 5-mm. thin-walled pipette made of tubing some 30 cm. long with the lower end drawn down in the flame to about 3 mm. A good piece of rubber tubing attached to the upper end of this pipette makes it more convenient to manipulate. This pipette is also used for introducing the paste. The mercury, amalgam and paste are each from 10 to 15 mm. in depth. A few crystals are placed on top of the paste and on the amalgam a layer of crystals not over 10 mm. in depth. Only a small amount of the crystals are necessary for either the Clark or Weston cell, while a large excess may grow together and cause trouble. The cell is filled to the top of the cross tube with the saturated solution and then the glass parts are sealed off 2 or 3 cm. above the liquid by using two small blast flames which impinge on opposite sides of the point to be sealed. The part to be sealed is gently warmed at first to prevent cracking and after sealing, by properly heating a bit lower down, the expanding gas inside the cell will cause the seal to round out perfectly. The cells are arranged in supports and provided with lead wires so that they may be readily compared when in a bath.

The difficulties we have encountered with these cells are, the tendency of the glass parts to crack which is most pronounced in the amalgam leg of the Clark cells, and the fact that the contents of the cell are not accessible. This difficulty was recognized by Lord Rayleigh in recommending the cork seal.[1] It is often desirable to get at the contents of a cell to loosen a crust which has formed or to find a poor contact and while the glass seal may be broken it is seldom possible to reseal it without ruining the cell. The trouble with the cork seal has been that the cork was generally in contact with the liquid and so leaked sooner or later. We have used for some time a form of cell which avoids these difficulties; the glass part is the simplest possible (Fig. 4). Thin-walled tubes, 20 cm. long and 12 mm. in diameter, are closed at one end and blown out

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[1] Phil. Trans., 176, 42, 1886. Cells were first hermetically sealed by Wright, Phil. Mag., 16, 25, 1883.

at the side about 5 cm. above the closed end. Two of these tubes are joined directly together giving the advantages of the test-tube form. No platinum wires are fused into this part of the cell. These cells are closed by corks which are 15 cm. above the liquid of the cell and are never wet and do not need to be covered with wax. These corks carry the long narrow tubes which inclose the contact wires and these may be removed and replaced at any time. This long form of cell is found to have many advantages in handling in the bath; several may be bound together in a very compact form and the contents of these cells most readily take on the bath temperature while the insulation is perfect in any kind of a bath liquid.

The details of the contact wire and protecting tubes are also shown in Fig. 4. A piece of tubing 3 mm. in diameter is softened in the flame and drawn down so that the part which is to pass through the contents of the cell is not over 2 mm. in diameter. This narrow part is about 6 cm. long while the total length is about 22 cm. A piece of .1 mm. platinum wire about 10 cm. long is soldered toa 20-cm. piece of silk-covered copper wire (no. 32). This wire is passed into the protecting tube until the platinum wire projects one or two millimeters from the narrow end of the tube and this end is then sealed in the flame. A bit of wax is run into the upper end to hold the wire securely. Six cells are made at one time and all bound together and then the negative or anode wires are twisted together and the exposed ends soldered so that only one contact need be made for the anodes of all six cells. The positive or cathode wires are scraped to remove the covering and then each one is wound about a small piece of millimeter copper wire which is forced into the warmed wax in the top of the tube leaving about a centimeter exposed and here a good contact is easily and rapidly made with a pinch connector. It is well to amalgamate the platinum tip of the contact wire just before it is inserted into

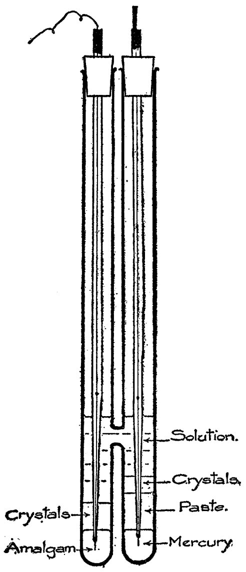

Fig. 4.

the contents of the cell. This is readily done by holding it for a few minutes in boiling mercury (in a test-tube), a suggestion of Mr. J. S. Laird of this laboratory. The numeral of the cell is always etched on the glass part and also written on a little pasteboard disk which is pierced with a small hole and put down over the lead wire and onto the cork so that it is easily read from above when the cell is in the bath. These cells are filled in the same way as the old form but instead of sealing the tops the contact wires with the protecting tubes and corks are inserted.[1]

In the old form of cell a crack was liable to develop at the point where the platinum lead wires passed through the glass. This was most noticeable in the amalgam leg of the Clark cell but would often happen in both legs of either cell. Sometimes the crack was hardly perceptible but sufficient to admit some of the bath oil in time while occasionally it was large enough to allow some of the liquid contents of the cell to escape and thus many cells were rendered worthless. The new form of cell entirely obviates this difficulty. Even if a crack develops where the platinum contact wire is sealed in the protecting tube no damage is done to the cell for this wire and tube is easily removed, repaired and replaced without injury to the cell. It frequently happens that the crystals over the amalgam cake and often a little gas forms between the amalgam and the liquid and crystals, sufficient to break the contact. By removing the contact wire and protecting tube, this gas escapes through the hole left by the tube and is replaced by the saturated solution and then the contact wire may again be inserted, or the crystals may be broken and stirred. This difficulty has been most noticeable in the Clark cells but also happened with some Westons.

The Electromotive Force of Standard Cells.—We have made both Clark and Weston cells at intervals since 1903 and according to the preceding specifications. A dozen Weston cells, made at one time, often agree among themselves to one part in 100,000 but in time the agreement is not so good, in a year or so the variations may be noticeable and when compared with a freshly made set of these cells it has been found that all the older cells have decreased

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[1] Both the (H) and long form of cell have been satisfactorily made for us by Eimer & Amend, New York.

and some of them very noticeably. Clark cells have also been made at intervals during the last seven years and the agreement among themselves of any "set" of these cells is about the same as that of the Westons but the Clark cells made at different times are in better agreement and none of them have shown an E.M.F. decreasing with time such as is noticed in some of the Weston cells. A reason for this difference has been given in previous papers. It seems necessary therefore to make the Weston cells at intervals of about six months and reject those which fall to low values. We make both Clark and Weston cells at such intervals and the cells are all kept in a constant temperature bath which does not vary over .01° from 25.00°. Taken all together these two kind of cells with the aid of a thermostat, give us a standard which is independent of time and is reliable and reproducible to one or two parts in 100,000.

The value in absolute units of this standard of E.M.F. is of course not known to anything like this degree of accuracy but whenever the absolute value is more accurately determined, all work which has been based on this constant may be recalculated if necessary, so we are justified in giving the assumed value to the fifth decimal place.

We have for consideration the following determinations of the E.M.F. of the Clark cell in absolute units:

Rayleigh and Mrs. Sedgwick,	1884	1.4345 at 15°
Kahle,	1896	1.4322 " "
Carhart and Guthe,	1899	1.4333 " "
Ivanoff,	1900	1.4328 " "

The average is 1.4333 as the E.M.F. of the Clark cell at 15°, but these cells were all made in the old way and must have been about .0003 volt too high; allowing for this and calculating to 25° we get 1.42040. In 1906 Guthe,[1] working with standards constructed according to the preceding specifications and with a suitable thermostat, obtained the value 1.4204 for the Clark cell at 25° and 1.0184 for the Weston standard cell. Two determinations were made in 1908 of the value in absolute units of the Weston standard cell.

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[1] Bull. Bureau of Standards, 2, 33, 1906.

Ayerton, Mather and Smith[1] obtained the figure 1.0183 at 17° and Janet, Laport and Jouaust,[2] found the value 1.01885 at 16°. Calculated to 25° these values are 1.01797 and 1.01847 respectively, but the results of these later determinations hardly justify a change in the values which have been used and it may be questioned whether the value in absolute units of our standard of electromotive force is known to better than one part in 2,000, or five parts in the fourth decimal place.

Assuming that the Clark cell is 1.4330 at 15° and using the customary temperature formula we have:

$$E_t = 1.4330 - .00119(t - 15) - .000007(t - 15)^2;$$

the value at 25° is 1.4204. Our cells numbering about 180 are maintained constantly at 25.00° and when we give this value (1.42040) to the Clark cells, the Weston standard cells, or at least those which have not decreased, are found to have the value 1.01840.

The Thermostat.—The E.M.F. of both the Clark and the Weston cells vary with the temperature. The Weston cell has only about one thirtieth of the temperature coefficient of the Clark cell and this was a decided advantage before thermostats were used but for electrical measurements which make any pretense to accuracy, an automatically controlled bath is indispensable for the Weston as well as for the Clark cell so the temperature coefficient is of no consequence. Our thermostat is reliable and constant to .01° and such variations indicate an uncertainty of about 1 in 100,000 in the E.M.F. of the Clark cell or within the variations of the cells themselves. The most reproducible temperature and the one easiest to maintain is 0° C., but the standard cells are very slow to come to their true value at this temperature, due probably to the slow rate of the reactions at low temperatures. The transition point of Glauber's salt is also available and an exceedingly well defined temperature (32.383), but it is not easy to maintain this temperature for the desired length of time. It is our experience that it takes a considerable time at a given temperature for *all* the cells of a set of standards to attain their true value. This can

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[1] Philos. Trans., A, Vol. 207, 34.

[2] Bull. de la Soc. Electriciens, 1908.

be determined by daily observations when the cells are held at a constant temperature; we generally allow a week. It is therefore necessary to have an automatically controlled bath and 25° has been chosen as sufficiently above room temperature to allow of an exact control of the temperature and also moisture may be more readily excluded than at a lower temperature. Our thermostat is an electrically heated and controlled kerosene bath which keeps well within .01° for any length of time. It consists of a tank made from galvanized sheet iron, 50 × 65 cm. and 50 cm. deep which rests in a box on legs. The space between the box and the tank (6 cm.) is packed with excelsior and the top of the tank projects about 2 cm. above the top edge of the box. A cover, 100 × 100 cm., was provided and the center (50 × 65 cm.) cut out so that the top of the tank fits into this place and is flush with the top of the table part when assembled. Plate glass strips of convenient widths cover the tank proper.

About 100 liters of kerosene serve as the bath liquid and has been found to be very clean and easily kept dry by a dish of calcium chloride which is suspended in the upper part of the tank. A motor-driven stirrer was necessary and attention was given to having it well made. The stirrer shaft turns in a bearing which is held by a cross bar near the top of the tank and a second bearing is soldered to the bottom of the tank. This shaft bears a fan wheel which is close to the bottom of the tank with its fans set rather flat so as to force the bath liquid up from the bottom rather than to rotate it. At the top of this stirrer shaft is the pulley wheel, a few centimeters above the top of the bath.

The regulator and heater have received the most attention, the aim has been to get large surfaces well distributed in the bath liquid. Both the regulator and heater are supported by a frame about 10 cm. above the bottom of the tank. This frame was made of brass tubing, 40 × 55 cm., with two cross pieces and is supported by four legs. Fastened to the under side of this frame is the glass part of the regulator (Fig. 5), which contains the toluene and mercury and the expansion or contraction of these liquids makes or breaks a contact of the relay circuit and so controls the heating current. This regulator was made of 15-mm. tubing with walls

½ mm. thick. It is entirely closed save for the outlet through the U tube *a* which is sealed to the under side, extends down and then up ending in the 5 mm. upright tube *b*. The whole system was filled with toluene, except the U tube and the upright *b* which contains mercury. Air bubbles were rigidly excluded from this system. The top of the mercury column in the tube *b* makes contact with a platinum point and this surface is about 5 mm. in diameter, since it was found that a meniscus of this diameter was much better defined than the narrower ones commonly used while with the large volume of toluene well distributed in the bath liquid, the movement of this mercury surface responds rapidly and exactly to the slightest changes of the bath temperature.

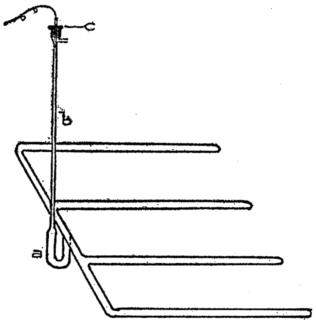

Fig. 5.

Sparking between the mercury and the platinum point causes the mercury to become "dirty," changes the meniscus and thus causes a slow drift of the bath temperature. It is customary to put a condenser in parallel with this contact but we have had much better results by arranging to use a small current of low voltage in the relay circuit and find that our mercury contact surface remains perfect for months at a time and makes and breaks contact with the platinum point at exactly the same temperature. A common 150-ohm telegraph relay was rewound with no. 36 wire so that the resistance of the magnet coils was about 1,000 ohms. The arm which controls the heating circuit was lengthened and adjusted to work very easily and only required .005 ampere in the relay circuit to operate it. This arrangement, without a condenser, has given excellent results.[1] We have had the best success with a very fine platinum point for the contact with the mercury surface. A narrow glass tube was drawn down to a point and a .05-mm. platinum wire sealed in so that only ½ a millimeter projected out beyond the glass point. A small copper lead wire was passed into

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[1] The Weston Electrical Instrument Co. make a relay which operates on a low voltage circuit with a current of only .001 amp. and controls a current of 1 or 2 amps.

the open end of the tube and with a drop of mercury made contact with the platinum wire. This glass tube was fastened into a little 4-mm. brass tube which was threaded and screwed into the metal cap *c*, Fig. 5, and so a very fine adjustment of the bath temperature was possible; rough adjustments were made by adding or removing mercury from the tube *b*.

With the arrangements we have, the heating current is made or broken by a change in the bath liquid of only one or two thousandths of a degree. For constancy, and to avoid oscillations of the bath temperature about the desired point, it was necessary to have the bath well insulated and this was accomplished with the 6 cm. of excelsior packing between the tank and containing box and the plate glass cover. Also it was especially important to have a small amount of heat liberated in the unit of time, and well distributed in the bath liquid. Our heating coils consist of .25 mm. nickel wire wound on 10-mm. glass tubes. These tubes were 50 cm. long and the wire wound on with the aid of a lathe and a little guide which gave a pitch of about one millimeter to the windings. These tubes were shellacked to hold the wire in place and then four of them were fused to other tubes forming the arrangement indicated by Fig. 6. The windings were continued by hand on the new tubes and the ends soldered together so as to make one continuous coil with two free ends soldered to platinum wires which passed through the glass at the joints of the upright tubes. Contact was made with the platinum wires inside the upright tubes. The coils were now thoroughly shellacked. This heater was fastened to the lower part of the frame so that it was held in about the center of the bath liquid. The shellack insulated the wire from the bath liquid and has not been affected in the slightest degree by the kerosene while the heat generated in this coil is at once taken up by the bath liquid. The resistance of our coil is about 120 ohms and is connected with the 110-volt a.-c. lighting circuit, but we also use an external resistance as .4 ampere is sufficient to

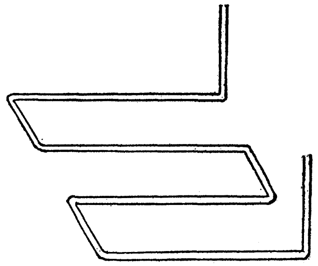

Fig. 6.

control the bath even with very considerable variations of the room temperature. The brass frame which carries the regulator and heater is covered with coarse wire netting so that the glass parts underneath the frame are protected, while the cells, in racks, rest on this netting.

It is not only necessary to have a constant temperature for the standard cells, but it is necessary to know what that temperature is. We use a set of 1/50° calibrated thermometers and they are checked at the ice point and the transition point of Glauber's salt (32.383). Some glass tubes pass horizontally through the side of the tank and box at various distances above the bath liquid and through these tubes the thermometers are read with a telescope. We have also checked our 25.00° temperature with a special 50 ohm resistance thermometer using 0°, 32.383 and 100° as the fixed points. Our known and reliable E.M.F. with a potentiometer, standard resistances, and standard batteries make it possible to determine the resistance of the coil of a resistance thermometer with ease and accuracy.

PRINCETON UNIVERSITY,
October, 1910.