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MERCUROUS SULPHATE AND THE STANDARD  
CELLS.

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THE question as to the best method of preparing the mercurous sulphate and the depolarizer for standard cells does not yet seem to be satisfactorily settled. Mr. F. E. Smith<sup>1</sup> proposes four methods for trial: (*a*) The electrolytic method; (*b*) by adding drop by drop mercurous nitrate to a strong sulphuric acid solution; (*c*) mercurous sulphate is dissolved in strong sulphuric acid and precipitated by diluting; (*d*) by the action of fuming sulphuric acid on mercury at ordinary temperatures. Mr. Smith invites various workers to construct cells according to his specifications and forward them to the National Physical Laboratory where they may be compared. This should give interesting information as to the reliability of the various methods.

H. v. Steinwehr<sup>2</sup> concludes from a few experiments that the principal if not the only cause of the variation of the E.M.F. of standard cells is traceable to a difference in the size of the particles of the mercurous sulphate used as depolarizer. It is well known that a fine-grained sample of a salt has a greater solubility, and therefore its solution will show a greater E.M.F. than the solution of a coarser-grained sample of the same salt. H. v. Steinwehr concludes from theoretical considerations that variable amounts of the

<sup>1</sup> Electrician, 55, 856, 1905.

<sup>2</sup> Zeit. Instrumentk., 20, 205.

hydrolyzed basic salt in the depolarizer could not be the cause of the variations observed in the E.M.F. of standard cells.

Last fall a number of cells were made which give experimental evidence on these important points. The main object of the work was to determine the effect of varying not only the strength of the sulphuric acid used in making the electrolytic mercurous sulphate, but the effect of varying the current density for a given strength acid. Samples of the sulphate were made by passing an electric current from a mercury anode into sulphuric acid. The concentrations of the acid used were .05 molecular, .5 molecular, molecular and 2.6, 3.7 and 12 times molecular, while the current densities were varied from 0.1 amp. to 5 amp. per 100 cm.<sup>2</sup> mercury anode surface. The details of the method employed in making these various samples will be described below.

Some of the samples were gray and others white. With a low current density the white product appeared while higher current densities gave the gray. The point at which the gray appeared depended also on the strength of the acid used. With 2.6 molar acid the product was gray at a current density of 0.3 amp. and above, while with molecular acid the product was still white with 5 amp. per 100 cm.<sup>2</sup> surface.

The gray preparation seems to give more uniform results than the white and a slightly lower value of the E.M.F. One is inclined to attribute this grayness to finely divided mercury, probably an "anode slime" which appears only at the higher current densities, but a high power microscope did not with certainty confirm this supposition. If the grayness is due to mercury it must be in an exceedingly fine state of division and would be an advantage as it would tend to prevent the formation of mercuric mercury.

Previous experiences have shown me that the comparison of samples in an *H* cell with a common electrolyte is often misleading, therefore the various samples were actually tested in cells in which all the other materials were the same. Further the cells were kept in a large constant temperature oil bath and compared at frequent intervals for several months. The bath contained 100 liters of kerosene oil and was electrically heated and controlled. The temperature was maintained constantly at 25° C. and has very

seldom varied  $.02^{\circ}$  from that temperature. Certificated thermometers were used to determine the temperature.

The cells were placed in wooden racks, and all the anode wires were joined together while the cathode wires passed up through little glass tubes which extended 15 cm. above the racks, ending near the top of the bath, where they were very accessible. The bath now contains 120 cells, some of them over two years old. The comparisons were made by means of a Feussner potentiometer (built by Otto Wolff, Berlin) and a sensitive D'Arsonval galvanometer. The apparatus worked very satisfactorily, a difference of 0.00001 volt caused a deflection of 2 mm. on the scale. The unit chosen for this and the previous work was the international volt, which is based on the Clark cell made according to the old specifications with an assumed value of 1.434 volts at  $15^{\circ}$  C.

The cells here considered are of the usual form and were hermetically sealed. The cadmium sulphate used was carefully recrystallized and only the perfectly clear well-rinsed crystals were used. A large stock of 12.5 per cent. cadmium amalgam was made from pure materials, and the mercury was distilled.<sup>1</sup> The cells were made as nearly alike as possible with the exception of the depolarizers to be tested. Precautions were taken to avoid hydrolysis in removing the acid from the various samples of mercurous sulphate, and attention was given to uniformity in making the pastes.

Table I. gives the observations made on these cells, column 1 gives the number of the cell, column 2 the date of construction, column 3 gives the strength of sulphuric acid from which the mercurous sulphate of the depolarizer was made, and column 4 gives for each case the current density employed and is expressed in amperes per 100 cm.<sup>2</sup> mercury anode surface.

Attention is called to the last six cells (A21 to A25 incl.). The depolarizers of these cells were made from acid of *less* than molecular concentration and the values are higher than the others and are irregular, while all the rest of the cells made from molecular sulphuric acid or stronger than molecular, are in good agreement. There is hardly a suggestion of an effect due to dif-

<sup>1</sup> PHYSICAL REVIEW, 21, 388. 1905.

TABLE I.

Cell.	Date.	Source of the $\text{H}_2\text{SO}_4$ Acid	$\text{D}_{100}$	Oct. 26.	Nov. 15.	Nov. 18.	Nov. 22.	Nov. 30.	Dec. 10.	Dec. 17.	Dec. 24.	Jan. 1.
A1	Oct. 21	2.7 molar	0.82 amp.	1.01905	1.01905	1.01906	1.01905	1.01905	1.01904	1.01905	1.01905	1.01905½
A2	"	"	"	04	05½	05	04½	05	05	05	05	05
A3	"	"	"	04	06	05	05½	05½	05	05½	05	05
A4	"	"	"	05	05½	05	05	06½	05½	06	05½	05½
A5	"	"	"	05	05½	05	06	05½	05	05½	05	05
A6	"	"	"	05	05	05	06	05½	05½	06	05	05
A9	Nov. 15	"	0.20 amp.			06	02½	02	03½	03	03	04
A10	"	"	1.5			05	03	04	04	04	04	04
A32	Dec. 15	12 molar	0.25									04
A33	"	4 molar	0.25									04½
A12	Nov. 21	1 molar	1.0				07	07	07	07	07	07
A13	"	"	2.5				06	07	06	05½	06	07
A14	"	"	5.0				04½	07	04	04	04½	05½
A15	"	"	0.2				09	11	08	08½	08½	09
A21	Nov. 27	½ molar	0.2					16	16	18	17½	15½
A21	"	"	1.0					09	08½	08	08	07
A22	"	"	4.0					14	15	14	15	14
A23	"	⅔ molar	0.2					25	22	19	20	22
A24	"	"	0.5					30	26	25	25½	27
A25	"	"	2.5					34	30	29	28	26

TABLE I. — *Continued.*

Cell.	Date.	Source of the Hg <sub>2</sub> SO <sub>4</sub> Acid	0.82 amp. D <sub>100</sub>	Jan. 6.	Jan. 13.	Jan. 20.	Feb. 1.	Feb. 7.	Feb. 20.	Mar. 4.	Mar. 15.	Mar. 31.
A1	Oct. 21	2.7 molar	0.82 amp.	1.01905	1.01905	1.01904	1.01905	1.01905	1.01905	1.01903½	1.01904	1.01905
A2	"	"	"	05	05	04½	05	05	05	03½	04	05
A3	"	"	"	05	05	04½	05	05	05	03½	04	05
A4	"	"	"	05	05	05	05½	05	05	04	04½	05
A5	"	"	"	05	05	05	05	05	05	03½	04	05
A6	"	"	"	05½	06	05	05	05½	05	04	05	06
A9	Nov. 15	"	0.20 amp.	03	03	03	04	04	03½	04	03½	05
A10	"	"	1.5	04½	04½	04	05	05	04½	05	05	06
A32	Dec. 15	12 molar	0.25	03	03	04	04	02	02½	00	02	03
A33	"	4 molar	0.25	04½	04	06	05	05	05	02	04	04
A12	Nov. 21	1 molar	1.0	07½	07½	06½	07½	07½	07½	05	07	08
A13	"	"	2.5	06	06	05	06½	06	06	04	06	07
A14	"	"	5.0	05½	05	03½	05	04½	04½	02	05	06
A15	"	"	0.2	08½	08½	07	08	08½	08	05	07½	08
A20	Nov. 27	½ molar	0.2	15	17	15	18	18	17	15	16	17
A21	"	"	1.0	08	10	07	08	07	07	06	07	08
A22	"	"	4.0	18	19½	14	15	14	14	13	14	15
A23	"	⅓ molar	0.2	21	20	18	20	18	18	17	18	19
A24	"	"	0.5	23	24	23	24	23	23	22	23	24
A25	"	"	2.5	24	23	24	26	25	23	21	20	19½

ferent current densities used in making the mercurous sulphate, but the strength of the acid used certainly does play a rôle as soon as it becomes less than molecular. This is also the strength acid at which the solubility curve (of mercurous sulphate in varying concentrations of sulfuric acid) shows a sharp break.<sup>1</sup> The solubility is .208 grams of the sulphate in a liter of 4 times molecular acid, and increases to a maximum of .550 grams in a liter of molecular acid. Here the curve takes a sharp turn downward, it is .502 gram in .5 molar and .455 gram in .25 molar and .384 gram of mercurous sulphate in a liter of .05 molar sulphuric acid, all at 25° C.

Molecular sulphuric acid then represents a point of discontinuity in the solubility curve and also for the behavior in cells of mercurous sulphate made from various concentrations of the acid. The principal conclusion to be drawn from the standpoint of standard cells is that, in making mercurous sulphate, one may use any strength of sulphuric acid from molecular to concentrated, and any desirable current density. The results obtained with these cells are very favorable for the electrolytic method of preparing the sulphate, for it must be remembered that for each cell a particular sample of paste was made, requiring separate manipulations. They are, therefore, without the advantage of cells made from one uniform batch of paste.

The question of a possible effect of the size particles on the solubility of mercurous sulphate was considered when the method was devised, and it was found that there was not a measurable effect with the electrolytic preparations. Attention was called to this in the necessary precaution of stirring the system, after the current was broken, so that the very finest particles might disappear.<sup>2</sup>

H. v. Steinwehr has lately<sup>3</sup> called attention to this point and claims for it the principle cause of the variations observed in the E.M.F. of cells. Experimental evidence on this point is contained in Table I. The mercurous sulphate used in each cell was microscopically examined and the size of the particles measured. In the case of the

<sup>1</sup> Hulett, *Zeit. Phys. Chem.*, 49, 494, 1904.

<sup>2</sup> Hulett, *Zeit. Phys. Chem.*, 49, 486.

<sup>3</sup> *Zeit. Instrumentk.*, 25, 205. 1905.

first fourteen cells, or all of those samples of sulphate made from molecular or stronger acid, the particles vary over a wide range, from .002 mm. to crystals  $.070 \times .130$  mm. but it will be observed that these cells are all in good agreement.

The samples made from molecular acid were uniformly larger-grained than the other samples. This was to be expected as with this strength acid the sulphate has the maximum solubility. The sample made with .2 amp. was particularly large-grained, and this sample was stirred with the acid and the finest particles decanted until only the very coarsest were left and these were taken for the depolarizer of cell A15. Now it will be seen that the E.M.F. of this cell is not lower but *higher* than the other cells. Furthermore the cells A21 to A25 which have a high value, were constructed with mercurous sulphate made from less than molecular acids, but these samples were decidedly coarser-grained than the samples used in cells A1 to A6. Since finer particles are more soluble, their solution should *increase* the E.M.F. of the cells which are made with the finer-grained depolarizers. Therefore the above results show that the effect of size of particles, in the electrolytic preparations, is not measurable and that whatever deviations there are must have some other explanation.

The microscopic observations made on the samples of electrolytic mercurous sulphate indicated that the higher current densities gave finer-grained but more uniform preparations, and also that the solubility of the sulphate had an effect in the sense that the average size of the particles are smaller in the samples made from the more concentrated acids where the solubility is less. The sample made from 2.6 molecular acid with a current density of 1.5 amp. was carefully examined and found to contain for the most part particles .004 to .008 mm. with few over .010 mm. In all the samples of electrolytic mercurous sulphate examined, comparatively few particles that measured less than .002 mm. were noticed and the failure to find variations in the E.M.F., due to size of particles, with these samples agrees with the work done on the effect of size of particles on the solubility of gypsum and barium sulphate. A measurable increase in the solubility has not been obtained until these powders contained a *large number* of particles of less than .002

mm.<sup>1</sup> Commercial mercurous sulphate is very fine-grained, as has been pointed out by H. v. Steinwehr (*l. c.*), and it is well attention has been called to this question of a possible effect of the size of the particles.

#### THE QUESTION OF HYDROLYSIS.

The complete removal of the acid from the mercurous sulphate before making the paste is important, as sulphuric acid has a very marked effect on the E.M.F. of the cadmium cell, causing a low value. In removing the acid hydrolysis will take place if water or a too dilute acid is used in washing the sulphate. An acid salt is formed and goes into solution while a slightly soluble basic salt remains mixed with the washed salt.<sup>2</sup> The effect that this basic salt has on the E.M.F. of cadmium cells was tested as follows: Some electrolytic mercurous sulphate was washed with absolute alcohol and thoroughly dried. Part of this was completely hydrolyzed by treating it with successive portions of water.<sup>3</sup> The hydrolyzed and normal salt were then mixed in known proportions. Six samples were made containing respectively .1, .5, 1, 5 and 10 per cent. of the basic salt and these were used in cells A35 to A40 (Table II.). It was found that the effect on the E.M.F. of the cells was not constant but varied with the amount of the basic salt present in the depolarizer. The variation, while not uniform, in general increases with the amount of the basic salt.

When the normal salt is shaken with water the hydrolysis goes to the equilibrium point and stops until more water is added. By using definite amounts of salt and water a known amount of the basic salt is left with the solid. Here the effect is even greater as shown by the cells (A44 to A46). In these cells the sulphate of the depolarizer was formed by stirring normal mercurous sulphate with water and mercury until no further change took place and then the amount of the basic salt in the solid depended on the relative amounts of salt and water taken. In this way samples containing 1, 3 and 10 per cent. of basic salt were prepared and used in

<sup>1</sup> Hulett, *Zeit. Phys. Chem.*, 37, 385, 1901.

<sup>2</sup> Gouy, *Compt. rend.*, 130, 1399, 1900; Hulett, *Zeit. Phys. Chem.*, 49, 493.

<sup>3</sup> Gouy, *l. c.*



TABLE II.

Cell.	Date.	Mercurous Sulphate.	Nov. 15.	Nov. 16.	Nov. 22.	Nov. 30.	Dec. 10.	Dec. 17.
A7	Nov. 15.	Kahlbaum's mercurous sulphate.	1.02235	1.02208	1.02001	1.01947	1.01936	1.01935
A11	Nov. 19	Kahlbaum's mercurous sulphate rotated with mercury and 1.4 molar acid.				26	22	23
A29	Dec. 3	Kahlbaum's mercurous sulphate rotated with mercury and 3.7 molar acid.					15	15
A30	Dec. 15	Kahlbaum's mercurous sulphate rotated with mercury and 12.7 molar acid.						20
A26	Nov. 27	(Chemically) mercurous nitrate—sulphuric acid 90°.					22	21½
A27	"	(Chemically) mercurous nitrate—sulphuric acid 20°.					20	20½
A28	"	Mercuric sulphate reduced by mercury.					11	10½
A35	Dec. 21	0.1 per cent. basic mercurous sulphate added.						
A36	"	0.5 per cent. basic mercurous sulphate added.						
A37	"	1.0 per cent. basic mercurous sulphate added.						
A38	"	5.0 per cent. basic mercurous sulphate added.						
A39	"	10 per cent. basic mercurous sulphate added.						
A40	"	50 per cent. basic mercurous sulphate added.						
A44	Jan. 5	Mercurous sulphate stirred with 8 parts of water and mercury 1 per cent. basic.						
A45	"	Mercurous sulphate stirred with 75 parts of water and mercury 3 per cent. basic.						
A46	"	Mercurous sulphate stirred with 25 parts of water and mercury 10 per cent. basic.						

TABLE II.—*Continued.*

Cell.	Date.	Mercurous Sulphate.	Dec. 24.	Jan. 1.	Jan. 6.	Jan. 13.	Jan. 20.	Feb. 1.
A7	Nov. 15	Kahlbaum's mercurous sulphate.	1.01935	1.01935	1.01935	1.01934½	1.01933½	1.01934½
A11	Nov. 19	Kahlbaum's mercurous sulphate rotated with mercury and 1.4 molar acid.	21½	24	23½	24½	20½	23
A29	Dec. 3	Kahlbaum's mercurous sulphate rotated with mercury and 3.7 molar acid.	18	21	17	19	20½	22
A30	Dec. 15	Kahlbaum's mercurous sulphate rotated with mercury and 12.7 molar acid.	18	20	23	21	19	21
A26	Nov. 27	(Chemically) mercurous nitrate—sulphuric acid 90°.	21½	21	22	23	29	18
A27	"	(Chemically) mercurous nitrate—sulphuric acid 20°.	19½	20	20	20	17	17
A28	"	Mercuric sulphate reduced by mercury.	12	14	12	12	10	13
A35	Dec. 21	0.1 per cent. basic mercurous sulphate added.		09	10	11	10	10
A36	"	0.5 per cent. basic mercurous sulphate added.		08	08	09	07	07
A37	"	1.0 per cent. basic mercurous sulphate added.		07	07	07	06	05
A38	"	5.0 per cent. basic mercurous sulphate added.		15	14	15	14	13
A39	"	10 per cent. basic mercurous sulphate added.		21	20	21	19	18
A40	"	50 per cent. basic mercurous sulphate added.		46	44	44	41	41
A44	Jan. 5	Mercurous sulphate stirred with 8 parts of water and mercury 1 per cent. basic.				40	35	36
A45	"	Mercurous sulphate stirred with 25 parts of water and mercury 3 per cent. basic.				27	22	24
A46	"	Mercurous sulphate stirred with 75 parts of water and mercury 10 per cent. basic.				61	56	56

TABLE II.—*Continued.*

Cell.	Date.	Mercurous Sulphate.	Feb. 7.	Feb. 20.	Mar. 4.	Mar. 15.	Mar. 31.
A7	Nov. 15	Kahlbaum's mercurous sulphate.	1.01934	1.01933	1.01931	1.01932	1.01933
A11	Nov. 19	Kahlbaum's mercurous sulphate rotated with mercury and 1.4 molar acid.	18½	20	18	22	24
A29	Dec. 3	Kahlbaum's mercurous sulphate rotated with mercury and 3.7 molar acid.	20	19	17	19	20½
A30	Dec. 15	Kahlbaum's mercurous sulphate rotated with mercury and 12.7 molar acid.	19½	19	16	18	18
A26	Nov. 27	(Chemically) mercurous nitrate—sulphuric acid 90°.	17	20	19	20	22
A27	"	(Chemically) mercurous nitrate—sulphuric acid 20°.	15	—	—	17	18
A28	"	Mercuric sulphate reduced by mercury.	11	11	10½	12	14
A35	Dec. 21	0.1 per cent. basic mercurous sulphate added.	09	08	06	07	08
A36	"	0.5 per cent. basic mercurous sulphate added.	06	06	04	05	06
A37	"	1.0 per cent. basic mercurous sulphate added.	05	04	03	03	04
A38	"	5.0 per cent. basic mercurous sulphate added.	12	11	10	10	11
A39	"	10 per cent. basic mercurous sulphate added.	17	16	15	15	15½
A40	"	50 per cent. basic mercurous sulphate added.	39	35	35	33	33
A44	Jan. 5	Mercurous sulphate stirred with 8 parts of water and mercury 1 per cent. basic.	31	30	28	27	27
A45	"	Mercurous sulphate stirred with 25 parts of water and mercury 3 per cent. basic.	20	20	17	17	17½
A46	"	Mercurous sulphate stirred with 25 parts of water and mercury 10 per cent. basic.	49	46	42	41	41

cells A44, A45, A46. Here the effect on the E.M.F. is very marked, and also variable.

It was to be expected that the presence of the basic salt on the depolarizer would increase the E.M.F. of the cell since the salt has a slight solubility but it is surprising that there should be such a marked variation when the per cent. of the basic salt was varied. Any mixture of the normal and basic salts such that both are in excess after the solution is saturated should yield a definite solution that is independent of the relative amounts of the two salts. H. v. Steinwehr used this argument to prove that the basic salt could not cause variations in the E.M.F. of cells. But in view of the above facts one must rather conclude that changes are taking place in this system with the possibility of new phases being formed. Further evidence that the cathode leg of the cadmium cell is not a system in equilibrium will be given in another article.

The similar behavior of the samples containing the basic salt (cells A44 to A46) and those made from less than molecular acid (cells A21 to A25) suggests that hydrolysis begins as soon as the acid becomes less than molecular. One might expect a larger amount of basic salt in the sample made from the diluter acids since hydrolysis, if it occurred, would go on until a solution was formed which would prevent further change. Hydrolysis then would be the explanation of the break in the solubility curve at molecular concentration. Further evidence for this view is that an analysis of a sample of the sulphate made from one half molar acid indicated the presence of a basic salt.<sup>2</sup> The behavior in cells of the samples of sulphates made from less than molecular acids makes it difficult to assume the existence of an allotropic modification as explaining the break in the solubility curve. On the other hand Cox<sup>1</sup> concludes from Gouy's results and some of his own observations, that there is only one basic mercurous sulphate and that the basic and normal salts are in equilibrium with .002 molecular acid. It is evident that more work needed on this question of the hydrolysis of mercurous sulphate.

The results here recorded, however, show that one cannot allow the strength of the sulphuric acid, used in making mercurous sul-

<sup>1</sup> Zeit. Anorg. Chem., 40, 178, 1904.

<sup>2</sup> Zeit. Phys. Chem., 49, 496.

phate for standard cells, to become less than molecular. Until further evidence is at hand on the question just considered, it seems best to keep the mercurous sulphate, to be used in standard cells, from coming in contact with sulphuric acid of less than molecular concentration.

Samples of mercurous sulphate from other sources than electrolytic were also used, and the record of these cells will be found in Table II. Cell A7 was made from Kahlbaum's mercurous sulphate. The paste for this cell was washed with water and made according to the old specifications. It had a very high value at first and required about a month at 25° to reach a fairly constant value, and then it was .00030 v. higher than the cells made with electrolytic sulphate. A few experiments were made to test the effect of treating commercial mercurous sulphate with sulphuric acid and mercury. Samples of Kahlbaum's preparation were stirred twelve hours with sulphuric acid and mercury, using different concentrations of acid (from 1.4 to 12 molar). The pastes were made as described later. Cells A11, A29 and A30 are the ones here considered, and while the method of treatment yields a lower value than cell A7, it is not satisfactory. Probably a longer stirring would give a better agreement and nearer the value given by the electrolytic.

For cell A28 the mercurous sulphate was made by reducing mercuric sulphate by stirring it with mercury and sulphuric acid. The method is simple and has the advantage of producing much finely divided mercury. This cell has given satisfactory results and one similarly made two years ago<sup>1</sup> behaved particularly well from the first, this cell, G3, was under observation for eighteen months.

The mercurous sulphate of cells A26 and A27 was made by adding a strong solution of mercurous nitrate to sulphuric acid which was in excess and did not become less than molecular in strength. These cells are distinctly higher than the cells made with electrolytic sulphate, and higher than others I have made with "chemically" prepared sulphate, some of which were very close to the electrolytic, but never as uniform.

<sup>1</sup> Hulett, Zeit. Phys. Chem., 49, 488.

The evidence given by the above-described cells and also the results of the previous work indicate that the electrolytic mercurous sulphate is the most reliable preparation, and that cells made from it are reproducible to 1 or 2 parts in 100,000. It seems well therefore to give a detailed description of the method of preparation based on the results so far obtained.

#### THE PREPARATION OF ELECTROLYTIC MERCUROUS SULPHATE.

The accompanying cut represents the essential parts of the apparatus needed. A battery jar some 15 cm. in diameter and 20 cm. tall is well suited to the purpose. Mercury to the depth of 2 cm. is put into the jar and is covered with sulphuric acid to a depth of

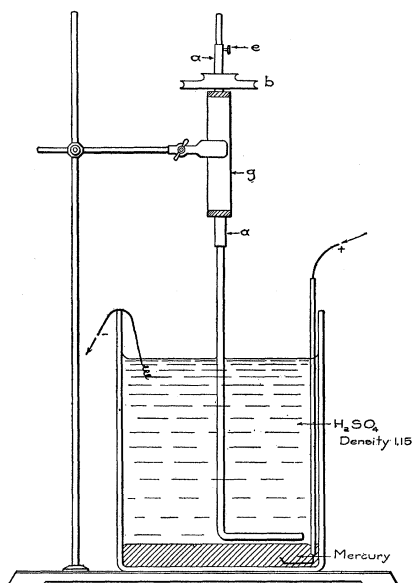


Fig. 1.

15 cm. The strength of the acid used may vary over a considerable range as has been shown. The formation of the sulphate removes an equivalent amount of acid and for several reasons it is best to use 2 or 3 times molecular. If one volume of strong sulphuric acid (1.84 density) is poured into six times its volume of

water, the strength will be about 2.6 molecular. If the acid is made by density it should be about 1.15, and with the two liters used in the jar one may prepare several hundred grams without reducing the strength of the acid to 2 times molecular.

In order to insure contact with the mercury a stiff platinum wire (.8 mm. or over) is sealed into a glass tube with the free end 4 or 5 cm. long. This platinum wire is bent at right angles and extends well out into the mercury when the glass tube is clamped in position. The object of this is to insure contact with the mercury when the solid sulphate collects in the angle of the jar under the mercury. The copper wire from the positive pole of the battery is pushed down inside the glass tube, contact with the platinum wire is insured by running in a little mercury.

A platinum wire suspended in the acid serves as cathode. Here one needs a small surface and large current density in order that much hydrogen and relatively little mercury may be deposited. The solubility of mercurous sulphate in 2.6 molar acid is .4 gram per liter, and with the above arrangement the yield is very good, about 9 grams per ampere-hour.

A motor-driven stirrer is necessary and it is important that the bearings work smoothly. The sketch represents a very simple arrangement. A brass tube (*a*) 8 mm. in diameter is provided with a pulley wheel (*b*). This tube holds the glass stirrer which is made fast by the set screw (*c*), the brass tube turns in the iron bearings which are soldered into the ends of a larger 15 mm. diameter brass tube (*g*). This outer-bearing tube may be clamped in any ordinary clamp. A glass rod that fits the inner brass tube is selected and clamped in the tube. The glass rod extends about 40 cm. below the holder and is bent at right angles. The stirrer is adjusted to the jar so that the *L* part of the stirrer just escapes the mercury when rotating at a rate of about 200 revolutions per minute. Some experience is necessary to adjust the stirrer properly, if the mercury is unduly disturbed much of it will become finely divided and be troublesome.

After all is in order and the stirrer working smoothly, the current is turned on and as soon as the acid is saturated the solid sulphate will appear on the surface of the mercury and form a skin which

does not always break up at once. This difficulty, which happens only when fresh acid and mercury are used, may be avoided by making and breaking the current several times until the solid appears throughout the acid after which no further trouble will be experienced. A current of 2 or 3 amperes may be used and will form some 25 grams an hour. The rapid stirring will keep the mercury surface sufficiently free of the solid until some 50 grams have formed, if more is needed it is best to remove the sulphate and start again, using the same acid and mercury but not allowing the acid to get much below 1.15 in density.

When sufficient mercurous sulphate has formed, the current is broken and the motor stopped. After the solids have settled most of the liquid is decanted (some of it in a wash bottle for assisting in the operations of transferring the solids). The solids and mercury are transferred to a large separatory funnel and the mercury removed. The sulphate finely-divided mercury and about a liter of the liquid are returned to the jar, or run into a large Erlenmeyer flask, and stirred over night. The object of this stirring is to allow the sulphate to become coarse-grained and unless most of the mercury is first removed the sulphate will often collect under it and the action is retarded. After twelve hours' stirring the sulphate settles rapidly and leaves the liquid perfectly clear. The product is still quite gray and is to be kept under the acid from which it was made and protected from the light. It is well to take precautions to protect the sulphate from the light during all the operations.<sup>1</sup>

#### PREPARING THE PASTE.

The results here recorded show that the basic salt, formed by treating mercurous sulphate with water or too dilute acid, effects the E.M.F. of the cell when it is present in the depolarizer. A

<sup>1</sup> The effect of light is to turn the sulphate brown and then black. Just what change takes place does not seem to be known. Two years ago a cell was made up with this blackened sulphate and had a value of 1.02038 (25°) to start with and decreased all the time it was observed (four months). At the same time some cells were made and half of them were protected from the light, by covering with asphalt paint and shellac, but in a year's time there was no distinct difference between the cells. The brown seems to form only on the surface next to the glass and it seems probable that with ordinary usage there is no effect after the cell is made, but the mercurous sulphate should not be exposed to strong light before it is put into the cell.



higher value is obtained than when the normal salt alone is used, and the effect varies irregularly with the amount of this basic salt present in the deplorizer. Until this anomaly is cleared up it seems best to avoid the basic salt all together.

The old method of washing the salt with water gave quite uniform results when the cells were made from a particular sample of sulphate, and with a uniform preparation like the electrolytic mercurous sulphate, the old method of washing might do very well. One point is however to be considered, if water is passed through the sulphate in a filter the top layer only turns yellow, evidently the water becomes saturated with the soluble products of hydrolysis and is no longer capable of effecting the lower layer.<sup>1</sup> This top layer has always been rejected and thus the part taken may have contained very little basic sulphate, but the liquid which could not be entirely removed is distinctly acid.<sup>2</sup> Last year a cadmium cell was made in which the solution was .2 molecular sulphuric acid saturated with cadmium sulphate. This cell has always been low, and has now a value of 1.01845 (25°). Acid seems to have more effect than other impurities and is to be avoided. Jaeger & Wachsmuth.<sup>3</sup>

The problem then is to completely remove the acid and to avoid hydrolyzing the salt. This may be done by washing with alcohol, and then once or twice with cadmium sulphate or zinc sulphate solution, as the case may be. For half a dozen cells, or less, one may use a Gooch crucible and Bunsen filtering flask. A little filter is cut from filter-paper with a large cork borer, and fitted to the crucible. The sulphate is brought into the crucible and the acid removed as completely as possible by suction, then some absolute alcohol is run in so as to wash the sides of the crucible and then drawn through the sulphate by suction. This is repeated five or six times, using only a few c.c. of alcohol each time. The alcohol is removed by washing once or twice with a saturated solution of cadmium or zinc sulphate as the case may be.

The washing with alcohol is much more rapid and in general more effective than with the rather viscous sulphate solutions. If

<sup>1</sup> Zeit. Phys. Chem., 49, 497.

<sup>2</sup> L. c., 497.

<sup>3</sup> Wied. Ann., 59, 586, 1896.

the sulphate is washed only with the alcohol and the paste made without completely removing the alcohol the results are good, but it is best to finally wash once with the saturated sulphate solution to be used in making the paste. In washing larger amounts one may use a small Buchener funnel and filtering flask. For thorough washing it is best not to have the sulphate over 2 cm. deep.

The washed sulphate is mixed with about one fourth its volume of finely-powdered cadmium sulphate or zinc sulphate as the case may be and then the saturated solution is added with stirring until a homogeneous paste is formed. The paste should be of such a consistency that it will just flow from a tube 5 mm. in diameter. The paste may be drawn up into such a tube by slight suction and then easily and neatly introduced into the cell. The addition of mercury is not necessary with the gray electrolytic mercurous sulphate.

In the case of the cadmium cell the paste should be over one centimeter deep in the leg of the cell. A number of cells have been made with less than a centimeter of paste, some only a few mm., and they were very irregular and are now very low. The question of the changes in the cathode leg of the cadmium cell, after it is constructed, will be reported on in a succeeding article.

Dr. M. A. Hunter assisted in constructing the cells and in making the comparisons described in this article, and I take this opportunity to thank him for very valuable aid.

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