

RESEARCH PAPER RP939

Part of Journal of Research of the National Bureau of Standards, Volume 17,
November 1936

SOLUBILITY OF MERCUROUS SULPHATE IN SULPHURIC- ACID SOLUTIONS

By D. Norman Craig, George W. Vinal, and Francis E. Vinal

ABSTRACT

Although mercurous sulphate has been the subject of many papers, particularly papers relating to its use in standard cells, the information available in the technical literature about its solubility in dilute solutions of sulphuric acid is somewhat conflicting and incomplete. New determinations have been made, therefore, of the solubility of the salt at 28° C and at 0° C. About half of the determinations at each temperature were made on solutions which were brought to saturation from an undersaturated state and the others from an initially supersaturated state. The mercury was determined electrolytically. Each solution was tested after electrolysis for residual mercury. Errors which might arise from the presence of mercuric mercury were shown to be within the limit of experimental error of the determinations. The acid concentration of the solutions ranged from 0.001 to 4 molar. Tables are given for the solubility of the salt in these solutions. The trend of the curves is discussed and comparisons are made with data previously obtained by others.

CONTENTS

I. Introduction	709
II. Experimental procedure	711
1. Materials	711
2. Saturation of solutions	711
3. Determination of mercury	711
4. Determination of sulphuric acid	712
III. Experimental results	712
1. Acid solutions	712
2. "Water" solutions	713
IV. Solubility of mercurous sulphate at regular intervals of sulphuric-acid concentration	716
V. Discussion of results	717
VI. Comparison with previous determinations	719
VII. References	720

I. INTRODUCTION

Although mercurous sulphate has been the subject of many papers, particularly papers relating to its use in standard cells, further study of its properties was deemed to be desirable as part of a larger program of work on standard cell materials and construction. The solubility of mercurous sulphate in water and in dilute solutions of sulphuric acid has been measured by a considerable number of previous experimenters.

Gouy [1]¹ studied the hydrolysis of mercurous sulphate and determined its solubility in water. Cox [2], using Gouy's data and some of his own, concluded that between mercurous sulphate, Hg_2SO_4 , and mercurous oxide, Hg_2O , only one solid phase exists, namely, a basic sulphate. Hager and Hulett's [3] results, as well as those of Gouy, showed that the "equilibrium water" has an acidity equivalent to 0.001 molar sulphuric acid. This is in close agreement with the values obtained in the present work, 0.00108 molar at 28° C and 0.00099 at 0° C. Hager and Hulett, however, argued that a 0.001 molar sulphuric acid solution is not as effective in preventing hydrolysis of the salt as the equilibrium water, which they found to be 0.002 molar in respect of HgHSO_4 .

The solubility of mercurous sulphate in water and in dilute solutions of sulphuric acid was measured by Hulett [4] with precision which merited more recognition than it has received. Results of the present work calculated to 25° C from 28° C are in close agreement with his, assuming that the change in solubility with temperature is linear over this small temperature interval.

Drucker's [5] four determinations, which are the basis of values given in the International Critical Tables (see page 720), are not entirely consistent with Hulett's results. Drucker's data indicated a greater solubility of mercurous sulphate in acid solutions of 0.05 molar than in other solutions immediately above and below this concentration. Hulett, on the other hand, found the solubility to be a minimum for acid solutions in this range.

Some of the earlier determinations lack sufficient data on methods of arriving at saturation equilibrium and others, such as the comprehensive determinations of Smith [7], lack information as to the temperature. There appear to be no systematic data on the effect of temperature on solubility of mercurous sulphate. These and other determinations are discussed in a later section of the paper.

For the present work, an electrolytic method of determining the mercury in solutions which were brought to saturation after prolonged mechanical stirring, was chosen. Each solution was tested after electrolysis for residual mercury.

About half of the determinations were made on solutions which were brought to saturation equilibrium from an undersaturated state, and the others were from an initially supersaturated state. We have not been unmindful of the possibility that small amounts of mercuric mercury might be included in these determinations. However, the precautions which were taken to reduce the mercuric ion to its equilibrium value with the mercurous ion in the presence of free mercury the error produced by the -ic ion is shown by the results to be less than the estimated experimental error of the work.

A series of measurements was made on solutions ranging in acidity from 0.001 to 4 molar at 28° C, which is the temperature at which the primary standard for the volt is maintained, and a similar series of measurements at 0° C.

¹ Numbers in brackets refer to references at end of the paper.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

The mercurous sulphate was part of a gray sample prepared for use in standard cells. It was made electrolytically from new mercury which had been distilled twice under reduced pressure by Hulett's [8] method. The current during electrolysis was equivalent to 2 amp/dm². Other details of the process were essentially the same as those previously described by Wolff and Waters [9]. Since the time of its preparation in 1931 the mercurous sulphate was preserved in the dark under a portion of the acid electrolyte used in its preparation. Although this sample of mercurous sulphate contained an appreciable amount of free mercury, all of the saturated solutions were prepared with the addition of more free mercury.

The sulphuric acid conformed to the requirements recommended by a committee [10] of the American Chemical Society for reagent grade acid.

2. SATURATION OF SOLUTIONS

The saturation of the solutions was accomplished by agitating them mechanically with Pyrex-glass stirrers in 500-ml Pyrex flasks containing free mercury. At 28° C the temperature was controlled to $\pm 0.02^\circ$ C by a water thermostat. At 0° C the temperature was controlled by large dewar flasks containing a mixture of ice and water. The experimental results at both temperatures include values obtained by approaching the saturation equilibrium from a condition of incomplete saturation and from supersaturation.

After agitating the solutions for 72 hours, the stirrers were removed and the flasks were allowed to stand at their respective temperatures until the solutions were clear. This usually required 48 hours. The samples of the supernatant solutions were carefully removed by pressure, the lower end of the delivery tube in each case projecting into the liquid no farther than was required to deliver 100 to 150 ml samples. After each sample was removed it was carefully inspected, and if found to be entirely clear it was then weighed to 0.1 g.

3. DETERMINATION OF MERCURY

The mercury content was determined by electrolytic deposition on platinum-gauze electrodes 3.5 by 3.5 cm. Two pieces of platinum foil, one on either side of the gauze electrode, served as anodes. After electrolyzing the solutions for a period of 40 to 48 hours, the electrolysis was stopped by removing the cathodes, which were then washed promptly and suspended in a desiccator containing P₂O₅ and free mercury. No difficulty was experienced with mercury dropping from the gauze. Repeated weighings indicated that the cathodes reached constant weight after hanging in the desiccator for 3 hours.

The water used in rinsing the cover glasses and the cathodes was caught in the respective beakers containing the electrolyzed solutions. Each solution was then weighed and divided into two portions. One portion was used to test for mercury by H₂S, and the other portion

was titrated to determine the sulphuric acid. It was found that the removal of the mercury was generally complete except in the more concentrated sulphuric acid solutions. Small corrections were therefore necessary in such cases. These corrections were determined with H_2S turbidimetrically by comparison with solutions of the same acid concentration containing known amounts of mercury.

4. DETERMINATION OF SULPHURIC ACID

The sulphuric-acid content of each portion of solution titrated was multiplied by the proper factor to give the total sulphuric-acid content of the electrolyzed sample. The H_2SO_4 equivalent of the mercury was then subtracted from the total sulphuric acid and the weight fraction of the free sulphuric acid in the original solution was calculated. The density of the original solution was then calculated, using the tables in the International Critical Tables. The volume of the original solution and sulphuric-acid molarity could then be calculated, as well as the weight of mercury per 100 ml.

The method for determining sulphuric acid described above was applied to all the solutions. It is referred to in this paper as method *A*. A second method, *B*, was applied to some of the solutions below 0.01 molar acid. This method served as a valuable check on method *A*.

Method *B* consisted in adding 2 ml of a 5-percent KCl solution to a weighed portion of the solution containing the dissolved Hg_2SO_4 . After coagulation of the Hg_2Cl_2 , the sulphuric-acid content of the solution was determined by titration. In the determinations by method *B* no correction was required as indicated for method *A*, in which allowance was made for the formation of sulphuric acid by the electrolytic deposition of the mercury. The agreement between the two methods, as shown in table 3, may be considered to indicate, within experimental error, that the mercury was in solution as mercurous mercury. Additional titrations by both methods of other solutions below 0.01 molar acid led to the same conclusion. No comparisons were made in solutions above 0.01 molar. Hulett [4] reported the ratio of $\text{Hg}(\text{ous})/\text{Hg}(\text{ic})$ to be 200:1 in sulphuric-acid solutions saturated with Hg_2SO_4 . The ratio indicates that 0.5 percent of the mercury is present as mercuric ion. Accordingly, it would be expected that the electrolytic deposition of the mercury would give values slightly greater than those obtained by precipitating the mercury as calomel. The difference, however, is probably smaller than our average experimental error.

III. EXPERIMENTAL RESULTS

1. ACID SOLUTIONS

The weight of mercury in 100 ml of each solution at 28°C , determined directly from the experimental data, is given in table 1 as observed values, together with the acid molarity of the respective solutions. Columns 3, 5, and 6 of this table need not be considered now. They relate to smoothed curves, shown in figure 1, which are discussed on page 716. Corresponding data are given in table 2 for determinations made at 0°C . The direction from which the satura-

tion equilibrium was approached is indicated in these tables by *D* ("down" points) if approached from a supersaturated condition and by *U* ("up" points) if approached from an unsaturated condition.

TABLE 1.—*Experimental data at 28° C and comparison with the smoothed curve, figure 1*

Molarity H ₂ SO ₄	Weight of Hg per 100 ml		Direction	Difference	Difference
	Observed	From curve			
	<i>Gram</i>	<i>Gram</i>		<i>Gram</i>	<i>Percent</i>
0.00107.....	0.0507	0.0504	<i>D</i>	+0.0003	+0.6
0.00109.....	.0501	.0504	<i>U</i>	-.0003	-.6
0.00150.....	.0490	.0493	<i>D</i>	-.0003	-.6
0.00152.....	.0495	.0491	<i>U</i>	+.0004	+1.8
0.00202.....	.0465	.0464	<i>D</i>	+.0001	+1.2
0.00198.....	.0461	.0464	<i>U</i>	-.0003	-.6
0.00304.....	.0424	.0423	<i>D</i>	+.0001	+1.2
0.00307.....	.0420	.0422	<i>U</i>	-.0002	-.5
0.00519.....	.0369	.0371	<i>D</i>	-.0002	-.5
0.00518.....	.0371	.0371	<i>U</i>	.0000	.0
0.01046.....	.0340	.0336	<i>D</i>	+.0004	+1.2
0.01043.....	.0337	.0336	<i>U</i>	+.0001	+1.3
0.02908.....	.0314	.0313	<i>D</i>	+.0001	+1.3
0.02906.....	.0312	.0313	<i>U</i>	-.0001	-.3
0.04854.....	.0318	.0321	<i>D</i>	-.0003	-.9
0.04838.....	.0325	.0321	<i>U</i>	+.0004	+1.2
0.1042.....	.0343	.0346	<i>D</i>	-.0003	-.9
0.1035.....	.0343	.0346	<i>U</i>	-.0003	-.9
0.1583.....	.0360	.0365	<i>D</i>	-.0005	-1.4
0.1576.....	.0375	.0365	<i>U</i>	+.0010	+2.7
0.4121.....	.0423	.0425	<i>D</i>	-.0003	-.7
0.4102.....	.0427	.0425	<i>U</i>	+.0002	+1.5
0.7185.....	.0460	.0462	<i>D</i>	-.0002	-.4
0.6825.....	.0463	.0460	<i>U</i>	+.0003	+1.7
1.466.....	.0454	.0455	<i>D</i>	-.0001	-.2
1.370.....	.0461	.0460	<i>U</i>	+.0001	+1.2
2.142.....	.0393	.0395	<i>D</i>	-.0002	-.5
2.487.....	.0357	.0357	<i>U</i>	.0000	.0
3.550.....	.0232	.0232	<i>D</i>	.0000	.0
3.560.....	.0234	.0233	<i>U</i>	+.0001	+1.4
Average of "downs".....				±.0002 ₃
Average of "ups".....				±.0002 ₄
Average of all determinations.....				±.0002 ₄	±.6

2. "WATER" SOLUTIONS

The observed weights of mercury per 100 ml of "water" solutions and the molarity of the sulphuric acid resulting from hydrolysis are given in tables 3 and 4 for solutions saturated at 28° C and at 0° C, respectively. In the preparation of these solutions water only was added to the mercurous sulphate; they are therefore referred to as "water" solutions. After removal of the portions for the determinations marked *1D* and *1U* the remaining solutions were again agitated and allowed to clear. The portions removed at this time were designated as *2D* and *2U*. Determinations indicated by primes were made after a second or third addition of water.

TABLE 2.—*Experimental data at 0° C and comparison with the smoothed curve, figure 1*

Molarity H ₂ SO ₄	Weight of Hg per 100 ml		Direction	Difference	Difference
	Observed	From curve			
0.00099	Gram 0.0350	Gram 0.0352	D	Gram -0.0002	Percent -0.6
0.00098	.0354	.0353	U	+0.0001	+0.3
0.00155	.0313	.0311	D	+0.0002	+0.6
0.00157	.0309	.0311	U	-0.0002	-0.6
0.00310	.0257	.0256	D	+0.0001	+0.4
0.00309	.0255	.0256	U	-0.0001	-0.4
0.00520	.0229	.0223	D	+0.0006	+2.7
0.00527	.0215	.0221	U	-0.0006	-2.7
0.01014	.0200	.0197	D	+0.0003	+1.5
0.01036	.0195	.0196	U	-0.0001	-0.5
0.01833	.0182	.0183	D	-0.0001	-0.5
0.01861	.0182	.0183	U	-0.0001	-0.5
0.07223	.0185	.0180	D	+0.0005	+2.8
0.09098	.0176	.0181	U	-0.0005	-2.8
0.2877	.0213	.0211	D	+0.0002	+0.9
0.3380	.0214	.0217	U	-0.0003	-1.4
0.7266	.0248	.0245	D	+0.0003	+1.2
0.7608	.0242	.0246	U	-0.0004	-1.6
0.9816	.0250	.0249	D	+0.0001	+0.4
0.9816	.0247	.0249	U	-0.0002	-0.8
1.383	.0248	.0243	D	+0.0005	+2.1
1.595	.0233	.0237	U	-0.0004	-1.7
2.479	.0179	.0179	D	.0000	.0
2.587	.0173	.0173	U	.0000	.0
4.229	.0068	.0068	D	.0000	.0
4.180	.0067	.0067	U	.0000	.0
Average of "downs".....				±0.0002	-----
Average of "ups".....				±0.0002 ₃	-----
Average of all determinations.....				±0.0002 ₃	±1.0

The sulphuric-acid molarities given in tables 3 and 4 indicate that normal and basic mercurous sulphate may be present as solids at 28° C in equilibrium with sulphuric-acid solutions of 0.00108 molar and at 0° C in solutions of 0.00099 molar. These values indicate that the acid concentration in equilibrium with the normal and basic solid increases with temperature. Hulett [4] reported that a solution formed at 25° C by the addition of water to mercurous sulphate contained 0.00235 mole of mercurous mercury and 0.00225 mole of SO₄ and that repeated additions of water gave the same result. These results indicate that his saturated solution at 25° C contained 0.00107 mole of free sulphuric acid as compared with our value of 0.00108 at 28° C.

The formation of a greenish-yellow color by the addition of water to mercurous sulphate was observed in these experiments. This has been reported by many previous investigators. According to Gouy [1] the greenish-yellow color is due to the formation of basic mercurous sulphate and according to his analysis this has the composition Hg₂OHg₂SO₄H₂O. Hulett [4] reported that his analysis of the completely hydrolyzed material confirmed the composition reported by Gouy, but that his product was grayish white rather than yellow.

TABLE 3.—Solubility, 28° C, of mercurous sulphate added to water

Experiment	Molarity of H ₂ SO ₄ ^a		Weight of Hg per 100 ml	Deviation
	Method A	Method B		
			<i>Gram</i>	<i>Gram</i>
1 D.....	0.00110		0.0503	+0.0001
2 D.....	.00106	0.00106	.0509	+ .0007
1' D.....	.00104		.0512	+ .0010
2' D.....	.00109	.00111	.0506	+ .0004
Average of "downs".....	.00107	.00108	.0507	-----
1 U.....	.00109		.0492	- .0010
2 U.....	.00108	.00107	.0500	- .0002
1' U.....	.00111		.0495	- .0007
2' U.....	.00110	.00110	.0501	- .0001
Average of "ups".....	.00109	.00109	.0497	-----
Average of all determinations.....	.00108	.00108	.0502	±.0005

^a Molarity of acid after saturation with mercurous sulphate.

TABLE 4.—Solubility, 0° C, of mercurous sulphate added to water

Experiment	Molarity ¹ H ₂ SO ₄	Weight of Hg per 100 ml	Deviation
1 D.....	0.00102	0.0348	-0.0004
2 D.....	.00103	.0342	- .0010
1' D.....	.00094	.0360	+ .0008
2' D.....	.00098	.0344	- .0008
1'' D.....	.00099	.0357	+ .0005
Average of "downs".....	.00099	.0350	-----
1 U.....	.00099	.0360	+ .0008
2 U.....	.00099	.0352	- .0000
1' U.....	.00092	.0353	+ .0001
2' U.....	.00100	.0350	- .0002
1'' U.....	.00095	.0362	+ .0010
2'' U.....	.00102	.0347	- .0005
Average of "ups".....	.00098	.0354	-----
Average of all determinations.....	.00099	.0352	±.0006

¹ Molarity of acid after saturation with mercurous sulphate.

Other experimenters have reported the hydrolyzed salt to be yellow or yellowish green. In our own experiments we have found that various samples of mercurous sulphates, including white and gray modifications, all become greenish yellow when treated with successive portions of water. The greenish yellow color appears to be characteristic of the hydrolyzed mercurous salt and distinguishes it from hydrolyzed mercuric sulphate, which is bright yellow. There is, however, some variation in color of partially hydrolyzed mercurous salt dependent on the source of the sample and the extent of the treatment. Our own observations are in accord with those of Gouy.

After many washings the hydrolyzed salt becomes finer and the free mercury initially present in a very finely divided state in gray samples is released and coalesces into a relatively large single drop. The yellowish coloration of hydrolyzed mercurous sulphate cannot be regarded as sufficient evidence of the presence of mercuric salt.

When base was added to hydrolyzed mercury sulphates, further color changes were noted as a result of the formation of oxides. Hydrolyzed mercurous sulphate became a dirty brown or black, while mercuric sulphate became an orange color, due perhaps to a mixture of the red and yellow modifications of mercuric oxide.

IV. SOLUBILITY OF MERCUROUS SULPHATE AT REGULAR INTERVALS OF SULPHURIC-ACID CONCENTRATION

Since the experimental determinations reported in tables 1 and 2 were made at acid concentrations which have no simple relation to each other, all of the data were plotted and the solubility read from the curves at regular intervals. To avoid errors which might result from drawing a single curve, three separate plots on large scales in several sections were made, using the molarity of the acid concentration, the square root of the molarity and the logarithm of the molarity as abscissas. The average solubility was then calculated from the readings made of these three plots. These are considered the best data and they are given in table 5. No value is given for 0.001 molar solution at 28° C because of the formation of the basic salt at 0.00108 molar acid.

TABLE 5.—*Solubility of mercurous sulphate in solutions of sulphuric acid*

H ₂ SO ₄ Molarity at t° C	Weight of Hg per 100 ml		H ₂ SO ₄ Molarity at t° C	Weight of Hg per 100 ml	
	t=28° C	t=0° C		t=28° C	t=0° C
0.001	-----	0.0351	0.100	0.0344	0.0183
.002	0.0463	.0290	.200	.0379	.0198
.003	.0424	.0259	.300	.0403	.0212
.004	.0395	.0239	.400	.0423	.0224
.005	.0373	.0224	.500	.0438	.0233
.006	.0360	.0215	.600	.0451	.0239
.007	.0351	.0208	.700	.0461	.0244
.008	.0346	.0203	.800	.0467	.0247
.009	.0341	.0200	.900	.0470	.0248
.010	.0338	.0197	1.000	.0470	.0249
.020	.0318	.0182	1.500	.0452	.0240
.030	.0313	.0179	2.000	.0409	.0216
.040	.0317	.0178	2.500	.0354	.0179
.050	.0322	.0178	3.000	.0294	.0139
.060	.0327	.0178	3.500	.0238	.0105
.070	.0332	.0179	4.000	-----	.0078
.080	.0337	.0180	-----	-----	-----
.090	.0341	.0181	-----	-----	-----

The smoothed values were then plotted against the logarithms of the respective molarities to obtain the curves shown in figure 1. The individual points, which were plotted for the purpose of drawing these curves are not shown in the figure, but we have plotted the actual experimental determinations to show their deviations from the smoothed data. These deviations afford a means of estimating the accuracy of individual determinations. For each point the deviation in grams from the smoothed curve has been read and tabulated in tables 1 and 2. The average deviations are about 0.0002 g at 28° C and at 0° C. The percentage deviations, however, are larger at 0° C

because the total amount of mercury involved in each of these determinations is smaller than for corresponding determinations at 28° C.

V. DISCUSSION OF RESULTS

The data given in table 5 and in figure 1 show definite maxima and minima for the solubility. Each curve for a specified temperature shows that three different solutions with the same mercury content are possible. At 28° C the curve passes through a maximum at 1

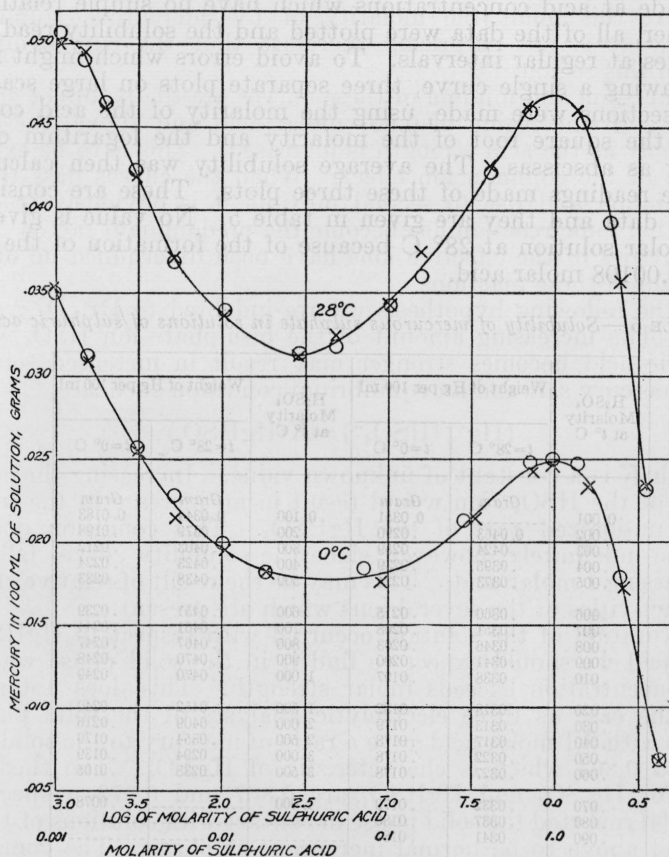


FIGURE 1.—Solubility of mercurous sulphate in sulphuric acid solutions.

Circles represent equilibrium approached from supersaturated solutions and crosses from undersaturated solutions.

molar acid and a minimum at 0.03 molar acid. The 0° C curve also shows a maximum at 1 molar acid and a minimum at 0.04 molar acid.

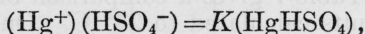
A noteworthy difference between the curves for 28° C and 0° C occurs in the region of the most dilute acid solutions. It is in this region that the molarity of the mercurous sulphate is approximately equal to the molarity of the acid. Below 0.0015 molar acid (log 3.176) a marked change in slope of the curve at 28° C occurs. The

solubility at 0.00108 molar acid ($\log \bar{3}.033$) is much less than would be predicted by an extrapolation of other portions of the curve. At the acid molarity of 0.00108, the molarity of Hg_2SO_4 is 0.00125; that is, the molarity of the mercury salt exceeds that of the acid. It is in this region that the maximum buffer action of any dissolved hydrolyzed mercurous salt would be expected.

A different condition exists in the measurements at 0°C . There is no point on this curve where the molarity of the mercurous sulphate equals the molarity of the acid. The hydrolysis point has shifted toward the weaker acid concentrations and lies below 0.001 molar acid. At this point the molarity of the mercurous sulphate is 0.00087. It is not surprising therefore that the curves differ in shape in this region.

The maxima and minima of these curves are the points of greatest interest. In the region of 0.001 molar acid and above, the curves fall steeply as the acid strength is increased. This is to be expected because of the common ion effect. When the curves pass through their minima and rise to second maxima it is obviously true that some other ionic reaction has become the predominant factor. Until the activities of the effective ions have been determined no one can be certain of these reactions.

For the following hypothesis we are indebted to Dr. D. A. MacInnes. The increasing amount of the bisulphate ion HSO_4^- as the sulphuric acid becomes stronger may result in increased solubility of the mercury salt and an equilibrium condition such as



in which K is a constant of unknown value. Increasing the concentration of the HSO_4^- ion would result in an increase in the solution of the un-ionized part of the HgHSO_4 . This condition does not continue indefinitely, however, since the solubility curves fall again after passing 1 molar acid. This may be the result of relative changes in the activities of the several ions which are present.

If saturation of the solution occurred with respect to HgHSO_4 at molar acid we should expect to find it in the solid phase when the acid concentration exceeds molar strength. This does not appear to be the case as three electrolytic analyses of the solid phase in contact with 3.1 molar acid gave a ratio of mercury to the solid phase equal to 0.804 which is characteristic of Hg_2SO_4 . The theoretical ratios for Hg_2SO_4 and HgHSO_4 are 0.807 and 0.673, respectively. Hulett [4] reported the solid phase in contact with solutions of 1 molar acid and above to be normal mercurous sulphate. The controlling ion beyond molar acid may still be the sulphate, SO_4^{--} . Hulett, however, considers the solid phase in contact with solutions below 1 molar acid to be a mixture of the normal and basic salts. This is not in accord with our observations. Our electrolytic determinations of the ratio of mercury to sulphate in portions of the solid phase removed from contact with the dilute acid solutions, where the tendency to hydrolyze should be greater, gave the results reported in table 6. These results indicate that the solid phase is not a mixture of the two salts, but Hg_2SO_4 alone. Equilibrium conditions would not preclude the possibility of hydrolyzed salt in solution when the acid concentration is above 0.001 molar, but our results indicate that the

hydrolyzed salt can not be present in sufficient amount to cause a change in the solid phase.

Small portions of the solid phase were removed from typical solutions covering acidities from the lowest to the highest concentration. The crystal form of these samples was examined microscopically by Dr. C. P. Saylor, who reported all were of the same crystalline modification.

TABLE 6

Molarity of acid, H ₂ SO ₄	Ratio Hg to SO ₄
0.0013.....	4.15
0.002.....	4.19
0.0025.....	4.12
0.003.....	4.18
Theoretical ratio for Hg ₂ SO ₄	4.18
Theoretical ratio for Hg ₂ OHg ₂ SO ₄ H ₂ O.....	8.36
Theoretical ratio for HgHSO ₄	2.09

VI. COMPARISON WITH PREVIOUS DETERMINATIONS

Hulett's [4] determinations at 25° C. and the present results at 28° C differ so little as to temperature that we have reduced our solubilities by 3/28 of the respective differences between measurements at 28° C. and at 0° C. Such a procedure cannot be justified for large temperature differences. Table 7 gives a comparison of Hulett's results at 25° C. with our results calculated to 25° C. One figure in Hulett's original table, 0.0424, has been changed to 0.0434, as the former is apparently a numerical error. The latter figure, 0.0434, was calculated from his basic data given in column 2 of his table. Table 7 shows agreement between his results and ours within 1 percent, although materials from different sources were used, different methods of determining mercury were employed, and errors of weighing and titrating are included as well as the uncertainty which may be caused by the mercuric ion.

TABLE 7.—Comparison of results with those of Hulett

[NBS results were calculated to 25° C from 28° C]

Molarity H ₂ SO ₄	Weight of Hg per 100 ml		Difference NBS— Hulett
	NBS, 25° C	Hulett, 25° C	
	<i>Gram</i>	<i>Gram</i>	<i>Gram</i>
0.004.....	0.0378	0.0376	+0.0002
0.010.....	.0323	.0321	+ .0002
0.020.....	.0303	.0305	-.0002
0.050.....	.0307	.0307	.0000
0.100.....	.0327	.0325	+ .0002
0.200.....	.0360	.0352	+ .0008
0.250.....	.0371	.0365	+ .0006
0.333.....	.0389	.0392	-.0003
0.500.....	.0416	.0416	.0000
1.000.....	.0446	.0442	+ .0004
1.333.....	.0439	.0434	+ .0005
2.000.....	.0388	.0386	+ .0002
Average.....			±.0003

Summers and Gardner [11] measured the solubility of mercurous sulphate at 100° C, and compared it with other measurements at 25° C. There is an apparent error in the position of their decimal point, however, which makes the scale of ordinates of their figure 1 ten times too much for their 25° C curve. The scale evidently should be 1.0, 2.0, . . . etc. To make a comparison of their measurements with ours it is necessary to convert the molalities given by them to molarities, which is the method we have used for expressing the concentration of acid. Because of the large temperature difference between their work and ours, no simple assumption about the effect of temperature on solubility is warranted. It is evident that the effect of temperature on solubility of mercurous sulphate does not follow a linear relationship.

Drucker's [12] measurements are often quoted and are the basis of values reported in the International Critical Tables [6]. Here, again there is some uncertainty. Drucker reports his acid concentrations as normalities, but the solubilities of Hg_2SO_4 as molarities. Drucker's figures are copied in the Critical Tables, but the concentration of the mercury salt is given in terms of normality instead of molarity, which makes the values reported there one-half as large as Drucker originally reported them. Drucker's determinations of the solubility of mercurous sulphate in water and in 0.1 molar acid agree very closely with our results, but his two other determinations differ by several milligrams.

No comparison with Smith's [7] results can be made since the temperature of his determinations is not known.

A few other determinations have appeared in the literature including those of Wright and Thompson [13], Traube [14], Gouy [1], Wilsmore [15], Cox [2], and Barre [16].

These determinations cover a very limited range. In some cases essential details, such as temperature or methods, are not adequately described. We have not attempted to compare our results with theirs. Of the earlier determinations only Hulett's measurements fulfill all the requirements which we believe are essential.

VII. REFERENCES

- [1] Gouy, *Compt. Rend.* **130**, 1399 (1900).
- [2] Cox, *Z. anorg. Chem.* **40**, 178 (1904).
- [3] Hager and Hulett, *J. Phys. Chem.* **36**, 2095 (1932).
- [4] Hulett, *Trans. Int. Elec. Cong., St. Louis*, **2**, 109 (1904); *Trans. Am. Electrochem. Soc.* **6**, 109 (1904).
- [5] Drucker, *Z. anorg. Chem.* **28**, 361 (1901).
- [6] *Int. Crit. Tables* **4**, 339 (1928).
- [7] Smith, *Glazebrook's Dictionary Applied Physics* **2**, 267 (1922).
- [8] Hulett, *Phys. Rev.* **33**, 307 (1911).
- [9] Wolf and Waters, *Bul. BS* **4**, 18 (1907) S70.
- [10] *Ind. Eng. Chem.* **17**, 756 (1925).
- [11] Summers and Gardner, *Trans. Am. Electrochem. Soc.* **56**, 144 (1929).
- [12] Drucker, *Z. anorg. Chem.* **28**, 362 (1901).
- [13] Wright and Thompson, *Phil. Mag.* **17**, 288 (1884); **19**, 1 (1885).
- [14] Traube, *Z. anorg. Chem.* **8**, 22 (1895).
- [15] Wilsmore, *Z. Phys. Chem.* **35**, 305 (1900).
- [16] Barre, *Ann. chim. phys.* **24**, 203 (1911).

WASHINGTON, August 28, 1936.