

THE SOLUBILITY OF BARIUM SULPHATE IN SULPHURIC ACID

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The high solubility of barium sulphate in absolute sulphuric acid and its marked decrease on addition of water presents a real anomaly when considered from the point of view of modern theories of strong electrolytes whilst realising that the dielectric constant of absolute sulphuric acid is of the same order as that of water. A search of the literature for reliable data on the system revealed a complete lack of concordance among the results of many investigators, not only in the solubility of the salt in the pure acid but more particularly in the solid phases in equilibrium with aqueous sulphuric acid solutions.

Kendall and Davidson² attempted to isolate the solid phase by freezing it from solution and drying between porous plates. They find an analysis corresponding to $\text{BaSO}_4 \cdot 3\text{H}_2\text{SO}_4$. Barter³ attempted to analyse the wet solids and the saturated solutions deducing the composition of the solid by graphical extrapolation, obtaining two compounds $3\text{BaSO}_4 \cdot 8\text{SO}_3 \cdot 7\text{H}_2\text{O}$, stable from 85.5 to 93 percent sulphuric acid and $4\text{BaO} \cdot 5\text{SO}_3 \cdot 6\text{H}_2\text{O}$ stable in high concentrations. The latter stable at high concentrations of acid having an excess of water, whilst the former stable at lower concentrations, an excess of SO_3 is almost beyond credence. The difficulty no doubt lies in the handling of so viscous and hygroscopic a system where experience shows that exposure to the atmosphere even for a very short period renders an analysis worthless.

An attempt was made therefore to determine the true solubility relationships between BaSO_4 , H_2SO_4 and H_2O with as reasonable a degree of accuracy as such a system would permit.

Experimental

Preparation of Materials.

1. *Sulphuric Acid.* Absolute sulphuric acid was prepared by two different methods which gave consistent results. In the first method a pure nitrogen and arsenic free acid was redistilled at a pressure of 1-2 mms. of mercury yielding about a 95 percent acid. To bring this up to absolute acid, purified fuming sulphuric acid was distilled into it until its concentration was correct as determined by specific gravity methods. Careful volumetric analyses were then made. In the second method a slightly fuming sulphuric acid prepared from redistilled acid and sulphur trioxide, was brought down to absolute by addition of water. The change in resistance of the acid at constant temperature, was meanwhile measured. According to Lichty⁴ the

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² J. Am. Chem. Soc., **43**, 979 (1921).

³ Trans. Roy. Soc. Canada, **7**, 208 (1913).

⁴ J. Phys. Chem., **11**, 238 (1907); J. Am. Chem. Soc., **30**, 1834 (1908).

resistance of absolute acid is a maximum. Subsequent analyses showed the acid to be 100 percent within 0.05 percent.

2. *Barium Sulphate.* Barium chloride recrystallised three times was used to precipitate barium sulphate from pure sulphuric acid. The possible impurities could then be only barium chloride, hydrogen chloride or sulphuric acid. Of these the two latter seem to be strongly adsorbed since after washing continuously with hot water until the wash water showed no acidity to methyl orange, upon roasting, copious fumes of hydrogen chloride and sulphur trioxide were evolved. To remove the first two the sulphate was redissolved in absolute sulphuric acid and maintained at about 200°C. for not less than half an hour. The supernatant liquid was drawn off and cooled, no crystallisation taking place. When cold, this solution was poured into a very large volume of cold distilled water yielding barium sulphate with no other possible impurity than sulphuric acid. Since the decomposition of BaSO_4 only becomes apparent above 900°C., the sulphuric acid, admixed or adsorbed, was removed by roasting at about 600°C. for from 18 to 24 hours. Different preparations yielded samples of different particle size. Some fine-grained samples were obtained by pulverising in an agate mortar and required nine days to settle completely from solution as compared with less than twenty-four hours for the usual samples.

Method of Measurement. The solubility determinations were made on various mixtures of barium sulphate, sulphuric acid and water which had been allowed to come to equilibrium in sealed tubes by rotation for seven days in a thermostat at $25 \pm 0.05^\circ\text{C}$. The ternary complexes were prepared by placing a known weight of the salt in the tube which had two openings: one, a fine capillary as an air vent, the other carrying a constricted tube with a ground joint and stopper, also fitting a Lunge pipette from which the acid-water mixtures could be forced with dry air. The acid solutions were made up by drawing into the pipette a calculated amount of absolute acid and water, each being weighed. The weight of the acid-water mixtures run into the solubility tube having been determined, the capillary and constricted side tubes were sealed off, the whole procedure occurring in an atmosphere of dry air. Three weighed samples of acid were taken at each filling for check determinations by titration of the acid concentration.

Equilibrium being established in the tubes the solutions were allowed to settle for twenty-four hours, the supernatant liquid being then drawn into a Lunge pipette for analysis. The titration of the acid in the saturated solution was made using carbonate-free sodium hydroxide with methyl orange as indicator. The titration had to be performed in the presence of solid barium sulphate thrown down by dilution with water. The end-points were matched with a color standard adjusted for opacity by addition of about the average amount of suspended barium sulphate. Weighed samples were drawn from the pipette for titration and also for the gravimetric analyses of the sulphate. Check determinations were made for every measurement.

Experimental Results and Discussion

The results obtained by the above method are given in detail in Table I.

TABLE I

Initial Complex			Saturated Solution			Conc.	Solid
H ₂ SO ₄	H ₂ O	BaSO ₄	H ₂ SO ₄	H ₂ O	BaSO ₄	H ₂ SO ₄	Phase
A							
82.92	—	17.08	84.11	—	15.89	100.00	—
—	—	—	—	—	15.77	99.81	—
74.87	0.14	24.99	84.05	0.21	15.74	99.75	67.33
83.85	0.16	15.99	84.22	0.17	15.61	99.80	—
—	—	—	—	—	15.68	99.70	—
—	—	—	—	—	15.22	99.61	—
—	—	—	—	—	14.79	99.45	—
62.92	0.21	36.87	84.84	0.46	14.70	99.47	—
—	—	—	—	—	13.84	99.07	—
69.78	0.52	29.71	85.27	0.90	13.83	99.95	—
78.94	0.57	20.49	85.49	0.89	13.62	98.97	68.86
62.87	0.61	36.52	85.80	0.95	13.25	98.91	—
84.00	1.12	14.88	85.57	1.26	13.17	98.65	—
73.94	0.60	25.47	86.00	1.21	12.79	98.61	62.09
77.99	1.16	20.84	86.06	1.65	12.29	98.12	58.86
84.10	1.60	14.29	86.54	1.78	11.68	97.99	62.38
80.37	1.60	18.03	87.22	1.83	10.95	97.80	32.70
81.23	2.63	16.15	88.45	3.02	8.53	96.70	32.55
85.06	3.47	11.47	88.86	3.63	7.05	96.08	—
60.55	1.89	37.56	89.13	3.58	7.29	96.14	28.60
73.26	2.84	23.90	89.28	3.86	6.86	95.85	28.68
—	—	—	89.68	4.53	5.79	95.19	—
75.28	3.97	20.75	90.40	4.97	4.63	94.79	15.24
B							
78.07	3.67	18.26	90.57	5.33	4.10	94.44	50.43
—	—	—	90.58	6.91	2.51	92.91	—
77.69	5.42	16.89	90.75	7.27	1.97	92.58	39.37
69.46	9.07	21.47	87.45	12.06	0.486	87.96	14.87
69.40	9.12	21.49	85.90	13.87	0.230	86.10	37.70
68.10	9.10	22.80	85.50	14.29	0.210	85.63	37.60
73.25	11.26	15.49	84.93	14.87	0.203	85.08	36.80
—	—	—	—	—	0.058	83.62	—
68.98	13.80	17.23	83.21	16.74	0.050	83.25	2.21

The values in the above table are expressed in percent by weight. The concentration of sulphuric acid is expressed as the ratio of sulphuric acid to sulphuric acid plus water in the saturated solution. Fig. 1 shows the solubility of barium sulphate plotted against the concentration of sulphuric acid in the saturated solution.

In the last column in Table I the percentage of sulphuric acid in the solid phase was obtained by a mathematical extrapolation of the tie-line joining the composition of the initial complex with that of the saturated solution which it yields. To this end it was assumed that the solid phase extracts no water from the solution phase, sulphuric acid alone being possibly removed. The assumption appears to be justifiable in the concentration range studied, where the acid actually possesses a sulphur trioxide vapor pressure. The theoretical percentages of sulphuric acid in possible compounds of the formulae $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$, $\text{BaSO}_4 \cdot 4\text{H}_2\text{SO}_4$, and $\text{BaSO}_4 \cdot 5\text{H}_2\text{SO}_4$ are 29.67, 62.72 and 67.79

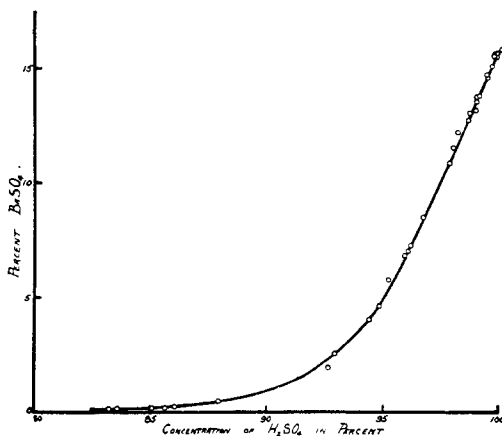


FIG. 1

respectively. An examination of the data would at first sight suggest that all these compounds are present in the solid phase at certain acid concentration but a reference to Fig. 1 shows no apparent transitions as evidenced by a change in direction of the solubility curve. We are led therefore to consider in more detail the accuracy of the data and more particularly the reliability of the extrapolation.

It is obvious that since the quantity of water both in the initial complex and in the saturated solution is in all cases much less than the quantity of sulphuric acid that the greatest error involved in the extrapolation will be due to an error in these two values for the water. At the higher concentrations of acid this error naturally will be less than at lower acid concentrations and we might expect a greater reliability of the extrapolation under the former conditions. In fact, a complete analysis of the probable error, which need not be detailed here, shows that for acid around 88 percent of the saturated solution the probable error in the extrapolated percentage of acid in the solid phase is of the order of four percent, whereas at 85 percent acid with now only 0.3 to 0.4 percent water the error may be as high as forty percent, despite the previously mentioned care in all volumetric and gravimetric determinations.

In part A of Table I there are four values of the percentage of sulphuric acid in the solid phase in the neighborhood of 30, namely 32.70, 32.55, 28.60 and 28.68 or a mean of 30.6 which might be compared with the 29.67 percent calculated on the basis of $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$ suggesting a compound of this type as the solid phase. Values below this for example the 15.24 percent quoted might correspond to a mixture of BaSO_4 and $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$. The values above 30 percent as the analysis shows are unreliable and no conclusion can justifiably be drawn concerning compounds with excess sulphuric acid despite the apparent agreement between the extrapolated values and those above mentioned for $\text{BaSO}_4 \cdot 4\text{H}_2\text{SO}_4$ and $\text{BaSO}_4 \cdot 5\text{H}_2\text{SO}_4$. If therefore the compound $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$ should exist a transition from the unsolvated salt should appear in the solubility curve. From the data this would be expected at around 88 percent sulphuric acid which reference to Fig. 1 will show to be on the flat portion of the curve where a break would be very difficult to realise. Its apparent absence cannot be judged then as indicating the non-existence of the compound.

In order therefore to settle definitely the existence of this compound and to determine the exact invariant area in the three-component diagram it was decided to follow the change in a property of the system as the concentration of one of the components was gradually increased. According to the phase rule such a system undergoing a transition of solid phases is invariant and any property of the system will remain constant throughout this process. The limits of constancy of the property then becomes the limits of the invariant area. The property chosen for study was the conductance and the component to be successively increased was water, the determinations of Lichty having shown that as small an amount of water as 0.01 percent gave a measurable change in the conductance of sulphuric acid in the region around absolute acid.

The cell used in these measurements consisted of a pyrex tube carrying electrodes of heavy platinum foil about one square centimeter area and about 40 cms. apart, dimensions chosen to give a conveniently measurable resistance range. Experience showed that for a sharp null point a heavily platinised surface was necessary. The opening in the cell, for the purpose of introducing the various components, carried a wide tube giving free space to allow mixing during tumbling in the thermostat. This tube was closed with a ground-glass stopper and as further protection against water leakage during immersion the whole was covered by a cap ground to fit the outside of the tube.

The resistance of the cell was measured using the usual Wheatstone bridge arrangement, a specially constructed vacuum tube Hartley type oscillator producing a smooth 1000 cycle note being used as source of current. The oscillator was located some ten feet away from the cell and carefully shielded and grounded to minimise extraneous capacity effects. The reliability of the measurements may be illustrated by a comparison of the specific conductivity of absolute sulphuric acid found namely 1045×10^{-6} ohms⁻¹ with that found by Lichty, 1040×10^{-6} as the mean of several samples.

The procedure consisted in introducing absolute sulphuric acid, using all the precautions against water absorption mentioned previously, into the weighed conductivity cell and reweighing to show the amount. The conductivity at 25°C was then measured to check the acid concentration. After drying and reweighing, the requisite amount of barium sulphate was added and the whole reweighed. The cap was then secured in place with a rubber jacket and the whole cell rotated in the thermostat until successive conductivity readings gave the same result indicating the establishment of equilibrium, a process requiring not more than 18 hours. The tube was then

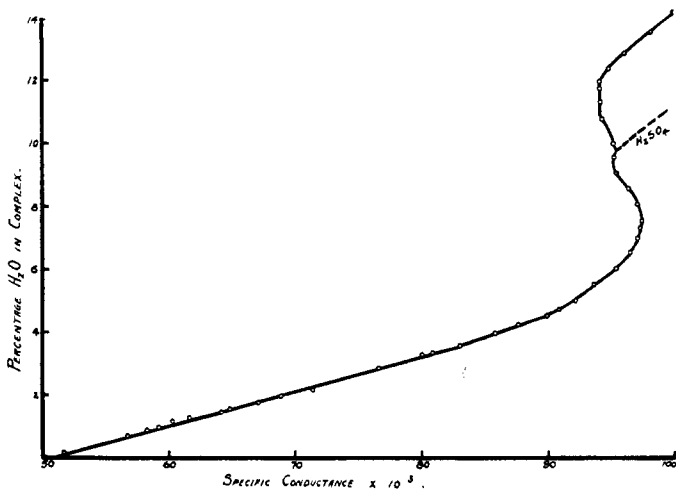


FIG. 2

again dried and reweighed as a check against water absorption, between 0.25 and 0.5 gram conductivity water introduced and the whole reweighed and returned to the thermostat, a process repeated at about 24 hours intervals throughout the entire range of water concentration desired.

The values of the specific conductance at various water concentrations are given in Table II, and shown graphically in Fig. 2.

A second cell was also used with a slightly different initial complex which unfortunately developed a leak before the run was completed. The data obtained however checked the above figures when due allowance was made for the slight difference in amount of the solid phase present. The general shape of the curve is in agreement with that for sulphuric acid alone, which has been accounted for by the existence of hydrates. The S in the curve occurs at 84.80 percent acid which would correspond to $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The constancy of the starred values in the Table would indicate an invariance of the system at this point only, since over the remainder of the region covered

TABLE II

Initial Complex		81.54% H ₂ SO ₄ , 18.46% BaSO ₄	
Percent Water	Sp. Cond.	Percent Water	Sp. Cond.
0.000	4889 $\times 10^{-5}$	5.468	9363 $\times 10^{-5}$
0.136	5135	5.992	9535
0.722	5681	6.498	9649
0.897	5831	6.980	9710
0.961	5925	7.280	9725
1.103	6030	7.512	9731
1.241	6161	8.044	9700
1.454	6420	8.528	9645
1.542	6486	9.026	9540
1.777	6719	9.496	9520
1.952	6880	9.988	9520
2.190	7142	10.740	9430
2.806	7663	11.256	9420*
3.328	8081	11.760	9418*
3.584	8300	11.941	9418*
3.982	8585	12.390	9495
4.202	8763	12.834	9608
4.532	8990	13.502	9816
4.698	9092	14.111	10000
4.988	9215		

there is a gradual change in conductance with change in water concentration. This constancy would indicate the presence in the system of another compound besides BaSO₄, probably an acid solvated barium sulphate.

The composition of the initial complex used and the quantities of water added, being known, the composition of the invariant complex may be calculated. An analysis of the invariant solution then would yield sufficient data to locate the invariant area and thus by extrapolation, the composition of the solid phases in equilibrium. Fig. 3 shows the graphical extrapolation.

It will be observed that the lower limit of the invariant area does not correspond with pure BaSO₄ as the solid phase but gives a solid containing about ten percent acid. This is believed to be due to adsorption which though suspected in earlier work, could not be definitely shown. It is for that reason that the data in Table I were divided into two sections A and B, in the former a coarse grained barium sulphate being used, in the latter an extremely fine grained sample and it was this which was employed in the conductance measurements. The last results in section B of Table I where a somewhat lower acid concentration was used gives an extrapolated solid phase containing 2.21 percent acid indicating clearly a gradual and continuous change in composition of the solid phase below about 85 percent acid, characteristic of adsorption.

Such adsorption would cause a displacement of the invariant area as the diagram shows. The extrapolation of the upper limit of the area gave a solid

phase of 36.80 percent acid. This is to be compared with the other values in section B of Table I namely 39.37, 37.70 and 37.60, values which would appear to correspond most closely with $\text{BaSO}_4 \cdot \frac{3}{2} \text{H}_2\text{SO}_4$. However in section A are found values of 32.70, 32.55, 28.60 and 28.68 percent acid in the solid phase which correspond rather well with 29.60 percent acid in $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$. Realising that the grain size in the latter is much larger than in the former, and hence that the adsorption is probably much less, it must be concluded that the only compound present is probably $\text{BaSO}_4 \cdot \text{H}_2\text{SO}_4$, apparent varia-

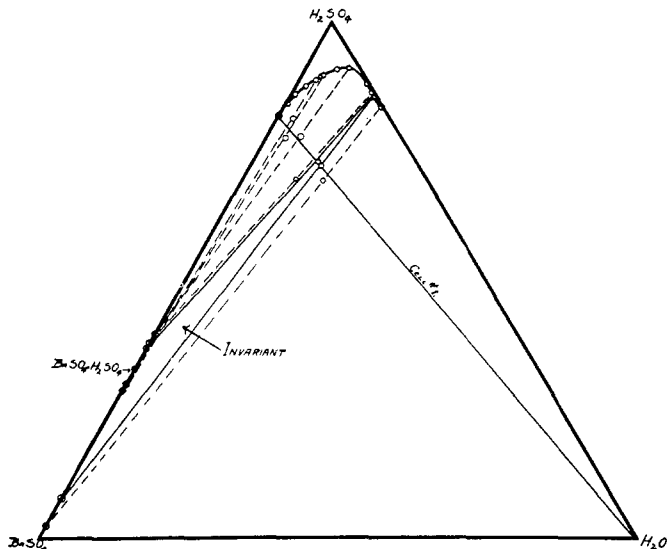


FIG. 3

tions from this being due to adsorption. An analysis of the invariant solution showed it to contain a concentration of sulphuric acid of 85.08 percent. A transition occurs in the system therefore at this point.

In conclusion it may be stated that the system shows a marked metastability. In the early stages of the conductance measurements it was observed that in about two hours the equilibrium had reached almost 95 percent completion but that at least eighteen hours were necessary before constant conductance was attained. Furthermore in the data in section B Table I one sample gave an extrapolated value for the acid content of the solid phase of only 14.87 percent. This sample had been agitated in the thermostat for only eighteen hours. The other values shown were obtained from samples agitated not less than five days and show values in the neighborhood of 38 percent. A distinct change also was to be observed in the state of the solid phase after long agitation, the typical opaque white granules of BaSO_4 yielding finally

well-formed translucent needles. The acid salt therefore would appear to be slow in forming. This metastability together with the complications of adsorption are probably responsible for the lack of a greater concordance than was found in view of the extreme precautions taken throughout the whole work.

Summary

1. The solubility relations for the system $\text{BaSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ at 25°C have been determined over the concentration range 83-100 percent acid. The solubility in absolute acid is 15.89 percent by weight.
2. The system possesses but two solid phases at 25°C BaSO_4 and probably $\text{BaSO}_4\cdot\text{H}_2\text{SO}_4$ with a transition at an acid concentration in the neighborhood of 85 percent.
3. The existence of compound formation as distinct from solid solution and adsorption has been demonstrated by the application of a conductance method which might prove convenient and precise in other similar work.

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