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COMPOUND FORMATION AND SOLUBILITY IN SYSTEMS OF THE TYPE SULFURIC ACID: METAL SULFATE.

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The present investigation completes the study of the freezing-point curves of neutral metal sulfates in 100% sulfuric acid, already covered in part in a recent paper by Kendall and Landon.¹ As explained in an earlier article,² the work constitutes the first stage of a broad attack upon the important problems of salt hydration and ionization in aqueous solutions, being undertaken in the hope that the discovery of general rules governing systems of the type: $RX:HX$ may make possible the subsequent formulation of analogous rules for systems of the more complex type $RX:HOH$.

Kendall and Landon established the fact that extensive compound formation occurs in solutions of the sulfates of potassium, sodium, lithium and ammonium in 100% sulfuric acid, several distinct acid sulfates being isolated in each case and their compositions determined either from their maxima on the freezing-point curve or by direct analysis. No systematic examination of the sulfates of other metals with pure sulfuric acid has hitherto been undertaken, although a number of acid sulfates are reported in the literature.³ In almost all cases, such compounds have been derived by treating the neutral sulfate with concentrated (not 100%) acid, under various conditions of concentration and temperature. Measurements of the solubility of barium, calcium and zinc sulfates in the pure acid at 25° have been made by Bergius,⁴ but the results obtained are altogether erroneous, as will appear below.

In the present work, the freezing-point method previously described⁵ has been utilized to investigate compound formation and solubility relationships for the sulfates of barium, calcium, magnesium, aluminum, zinc, iron (ferrous and ferric), nickel, lead, copper, mercury (-ous and -ic) and silver with 100% sulfuric acid. In most cases the solubilities of the

¹ Kendall and Landon, *THIS JOURNAL*, **42**, 2131 (1920).

² Kendall, Booge and Andrews, *ibid.*, **39**, 2322 (1917).

³ References to previous work will be given later, under each particular system examined. Many hydrated acid sulfates and several compounds containing two different sulfates and sulfuric acid have also been described (see Roozeboom, "Heterogene Gleichgewichte," [1] **3**, 190 (1911); also Etard, *Compt. rend.*, **86**, 1399 (1878); **87**, 602 (1878)); these are not considered in this investigation, which is limited to two-component systems.

⁴ Bergius, *Z. physik. Chem.*, **72**, 354 (1910). The remarks of Bergius regarding the relative solubilities of other sulfates in sulfuric acid are also without foundation, equilibrium never being attained in the experiments performed.

⁵ Kendall, *THIS JOURNAL*, **36**, 1225 (1914).

sulfates in the pure acid, even at the highest temperatures available,¹ were not very large, so that the curves could be followed through a short concentration range only. This behavior is altogether different from that of the sulfates of the alkali metals, since these exhibit considerable solubility in sulfuric acid even at ordinary temperatures and give curves which can readily be carried beyond 50 mol. % acid. Here the system $\text{Ag}_2\text{SO}_4:\text{H}_2\text{SO}_4$ was the only one which could be investigated through such an extended concentration interval. The curve for this system, indeed, closely resembles that obtained in the case of sodium.

Experimental.

The particular precautions necessary for the preparation and preservation of pure sulfuric acid have been described in previous papers.² The acid employed throughout this work possessed a freezing point above 10.4° , *i. e.*, within error limits of the freezing point for the 100% acid as given by Hantzsch.³ The metal sulfates used were, in general, *c. p.* samples of reliable character, a trace of moisture constituting the only significant impurity. This was removed by heating to constant weight; only in a few instances was special purification necessary.

The experimental procedure was essentially as described by Kendall and Landon, the work at the lower temperatures being carried out in a modified Beckmann apparatus and the work at the higher temperatures in sealed bulbs.⁴ Unfortunately only a comparatively small number of points could be determined by the more accurate freezing-point tube method, since most of the sulfates used dissolved extremely slowly in the pure acid. In order to obtain a saturated solution within a reasonable period, it was necessary to heat the mixture to a temperature well above its saturation point,⁵ and solutions containing a large excess of acid cannot be kept at temperatures much above 100° for any length of time, except in sealed bulbs, owing to gradual decomposition of the acid. Sealed bulbs were accordingly employed for the majority of the determinations, solution being effected fairly rapidly, in most cases, by heating to 200° .

The solutions thus obtained exhibited a high degree of supercooling, and it was often exceedingly difficult to induce crystallization even at temperatures 100° below the true freezing point (*e. g.*, in a bath of carbon-dioxide snow and acetone), the mixture merely setting to a "glass." Crystallization was found to occur most easily when such a "glass" was

¹ The limitation of the temperature range in certain systems is discussed later.

² Kendall and Carpenter, *THIS JOURNAL*, **36**, 2500 (1914).

³ Hantzsch, *Z. physik. Chem.*, **61**, 260 (1907).

⁴ For details regarding method, apparatus, and limits of accuracy the article of Kendall and Landon should be consulted.

⁵ Thus a mixture containing 7 mol. % BaSO_4 had to be maintained at 110° for several hours, with constant stirring, before the salt dissolved completely, although the temperature at which the solution is saturated is only 9° .

allowed to warm up slowly in an ice-salt bath, but sometimes it was necessary to repeat this process a considerable number of times.

Not one of the compounds isolated proved to be of sufficient stability to give a maximum on the freezing-point curve indicative of its composition; it was consequently necessary to determine the formula of each acid salt obtained by direct analysis,¹ wherever this was possible. A great many difficulties² were encountered in carrying out these analyses, and in spite of extra precautions taken to overcome them the results obtained are not, in all cases, as accurate as might be desired, although sufficiently close for the immediate purpose of the experiment, namely the identification of the compounds formed.

The results for the various systems are taken up in order below, the more complex curves being also indicated in the accompanying diagrams.

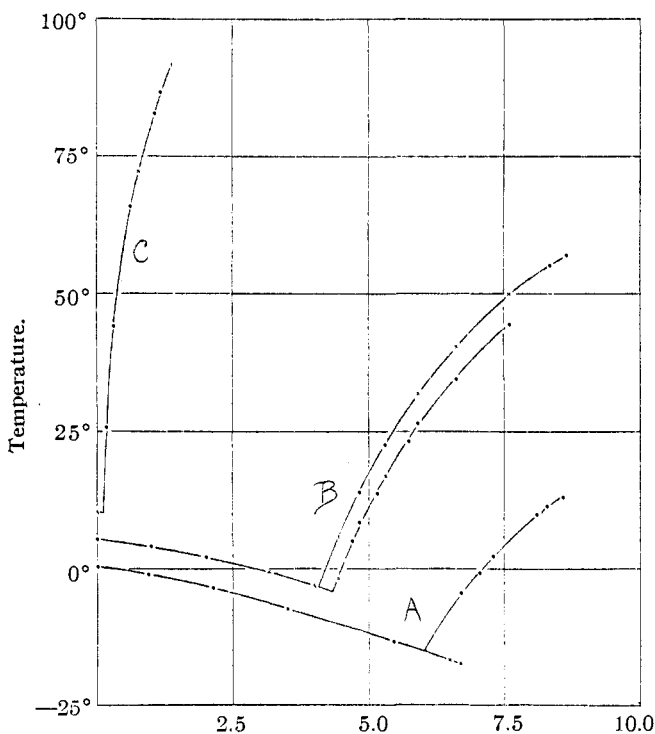


Fig. 1.—Mol. % neutral sulfate.

Curve A, System $\text{BaSO}_4:\text{H}_2\text{SO}_4$, add 10° to temperature scale; Curve B: System $\text{CaSO}_4:\text{H}_2\text{SO}_4$, add 5° to temperature scale; Curve C, System $\text{MgSO}_4:\text{H}_2\text{SO}_4$, temperature scale correct.

¹ See Kendall and Landon, *loc. cit.*, p. 2134.

² In the first place, the amount of solid that could be obtained, even by cooling over the maximum temperature range available, was sometimes very small. In the case of BaSO_4 , MgSO_4 and Hg_2SO_4 , just about enough of the compound for a sufficiently

Compositions are expressed in molecular percentages throughout; T indicates the temperature of *incipient* solidification.

Results.

System BaSO_4 ; H_2SO_4 .—Berzelius¹ has reported the existence of an acid sulfate BaSO_4 , H_2SO_4 . Bergius² measured the solubility of barium sulfate in 100% acid at 25° as 3.23 mol. % (composition of solid phase not stated); this result is, however, far too low.

(a) Solid phase H_2SO_4 .

% BaSO_4	0.0	0.95	2.12	3.50	5.46	6.50	6.70
T	10.4	9.1	6.6	2.8	-3.2	-6.6	-7.3

(b) Solid phase BaSO_4 , 3 H_2SO_4 .

% BaSO_4	6.70	7.05	7.30	8.09	8.28	8.59	8.62
T	5.7	9.3	12.4	20.0	21.5	23.0	^a

^a Did not dissolve completely.

The above results are also reproduced in Fig. 1. Analyses of the solid phase (b) indicated an acid content of 77.2 ± 0.9 mol. %; in view of the limitations of the method employed³ the formula $\text{BaSO}_4 \cdot 3 \text{H}_2\text{SO}_4$ may safely be assigned to the compound. This acid salt has not previously been reported, although analogous compounds of other metals of the alkaline earths are known. It was impossible to carry the curve further, since all solutions containing more than 7 mol. % BaSO_4 deposit crystals on heating,⁴

accurate analysis (a few tenths of a gram) could be separated out from 50 g. of solution. In the second place, it was very difficult to free the crystals completely from adhering mother liquor without at the same time inducing partial decomposition. The acid sulfates of the alkali metals isolated by Kendall and Landon were sufficiently stable to be freed from liquid by protracted air suction, but here the compounds under examination were found to decompose slowly in dry air, gradually losing SO_3 , so that concordant results could not be obtained. The procedure finally adopted consisted in applying suction only until all supernatant liquid had been drawn off, then transferring the wet crystals as rapidly as possible to a dried porous tile, covering with a second tile and allowing to stand in a desiccator over H_2SO_4 . Most of the excess acid was taken up by the tiles in a few minutes; samples of the crystals remaining were then analyzed by titration against standard alkali. The percentage of acid found, under such circumstances, was always near enough to a point of simple molecular proportions to enable the composition of the solid phase to be satisfactorily fixed, but naturally a little too high in most cases.

¹ Berzelius, *Ann.*, **46**, 250 (1843).

² Bergius, *loc. cit.* The discrepancy is due to the fact that the method employed by Bergius (agitation of the acid with excess sulfate at 25°) would require a period of years for equilibrium to be established, owing to the slow rate of solution at low temperatures.

³ See footnote 2, p. 981.

⁴ This phenomenon has been noted previously for solutions of BaSO_4 in concentrated H_2SO_4 (see Schultz, *Pogg. Ann.*, **133**, 147 (1868); Garside, *Chem. News*, **31**, 245 (1875)). The separation of crystals is probably due to a slight loss of SO_3 from the solvent (equivalent to a slight dilution with H_2O) which occurs on raising the temperature, since even the merest trace of water in sulfuric acid lowers the solubility of BaSO_4 appreciably (compare Bergius, *loc. cit.*, p. 355). In order to reduce to a minimum such evaporation of SO_3 in the present experiments, the air space in the bulbs was made as small as possible, but the more concentrated the solution the lower the temperature at which separation of solid takes place, and more than 8.6 mol. % BaSO_4 could not be brought into solution at any temperature.

which remain undissolved up to the boiling-point of the acid but go into solution very slowly on cooling. The equimolecular compound of Berzelius probably exists beyond the range of this work.¹

System CaSO₄: H₂SO₄.—Three acid sulfates of calcium have been previously recorded; CaSO₄, 3 H₂SO₄;² CaSO₄, H₂SO₄³ and 2 CaSO₄, H₂SO₄.⁴ Bergius determined the solubility of CaSO₄ in 100% acid at 25° as 1.69 mol. % (composition of solid phase not stated), a value again altogether discordant with that here obtained.

(a) Solid phase H₂SO₄

% CaSO ₄	0.0	0.98	1.99	3.17	4.00
T.....	10.4	9.1	7.2	4.7	2.2

(b) Solid phase CaSO₄, 3 H₂SO₄

% CaSO ₄	4.45	4.70	4.84	5.19	5.31	5.74	5.92	6.63
T (unstable modification).....	3.4	10.1	13.5	18.4	22.2	28.4	31.5	39.7
T (stable modification).....			19.1		27.8		36.9	45.4
% CaSO ₄			7.11	7.59	8.34	8.66	9.06	
T (unstable modification).....			45.4	49.4			^a	
T (stable modification).....			51.3	55.1	60.3	62.2	^a	

^a Did not dissolve completely.

The curve for this system also is given in Fig. 1. Analyses of the solid phase (b) gave an acid content of 74.6 ± 0.9 mol. %, evidently corresponding to the compound CaSO₄, 3 H₂SO₄. This exists in two different crystalline modifications, the same form being stable throughout the whole available temperature range.

Solutions containing more than 8 mol. % CaSO₄ deposit crystals on heating,⁵ as in the case of the barium salt. The curve could not, in consequence, be carried further.

System MgSO₄: H₂SO₄.—Two acid sulfates of magnesium have been reported, MgSO₄, 3 H₂SO₄⁶ and MgSO₄, H₂SO₄.⁷ No solubility determinations have been made.

(a) Solid phase MgSO₄, 3 H₂SO₄

% MgSO ₄ ...	0.18	0.32	0.62	0.77	1.07	1.18	1.37	1.53
T.....	25.7	44.2	66.0	72.3	82.8	86.7	91.7	^a

^a Did not dissolve completely.

The above results are also shown in Fig. 1.

¹ Solutions containing 8.0–8.6 mol. % BaSO₄ deposited crystals on long standing, which did not redissolve at 25°. The compound BaSO₄, 3 H₂SO₄ must therefore be considered as a metastable phase in this region, but owing to the extremely small amount of crystals separating out and to their exceedingly slow rate of solution at higher temperatures neither the composition of the stable phase nor its solubility curve could be established.

² Schultz, *loc. cit.*, p. 146.

³ Berzelius, *loc. cit.*, p. 249.

⁴ Willoughby, *Trans. Roy. Soc. Canada*, **7**, 211(1913).

⁵ For a description of the changes which occur on heating a solution of CaSO₄ in conc. H₂SO₄, see Garside, *loc. cit.*

⁶ Schiff, *Ann.*, **106**, 115 (1858).

⁷ Schultz, *loc. cit.*, p. 149.

Analyses of the solid phase (*a*) showed an acid content of 74.6 mol. %, agreeing with the formula $\text{MgSO}_4 \cdot 3 \text{H}_2\text{SO}_4$. The solubility of the neutral salt in pure sulfuric acid is very small, not more than 1.4 mol. % being brought into solution even on boiling.

System $\text{Al}_2(\text{SO}_4)_3 : \text{H}_2\text{SO}_4$.—No acid salts have been previously reported, and the extreme insolubility of aluminum sulfate in sulfuric acid renders it highly improbable that any such compounds exist. A mixture containing only 0.017% of aluminum sulfate did not give a clear solution even at the boiling point.

System $\text{ZnSO}_4 : \text{H}_2\text{SO}_4$.—The only previous work on this system is the measurement of the solubility of zinc sulfate in sulfuric acid at 25° by Bergius; the result given, 0.0056 mol. % (composition of solid phase not stated) is, as usual, widely in error.

(*a*) Solid phase $\text{ZnSO}_4 \cdot x \text{H}_2\text{SO}_4$.

% ZnSO_4	0.20	0.32	0.41	0.45
<i>T</i>	28.4	40.1	46.4	49.2

(*b*) Solid phase ZnSO_4 (?)

% ZnSO_4	0.41	0.45	0.52	0.67
<i>T</i>	66.4	78.0	94.8	128.6

The solid phase (*a*) undoubtedly corresponds to an acid salt, the composition of which could not be determined by analysis, as it is stable over too short a concentration range.¹ At 42.5° it undergoes transition, probably to the neutral salt.²

System $\text{FeSO}_4 : \text{H}_2\text{SO}_4$.—Two acid ferrous sulfates have been recorded; $\text{FeSO}_4 \cdot 3 \text{H}_2\text{SO}_4$ and $\text{FeSO}_4 \cdot \text{H}_2\text{SO}_4$.³ No solubility data are available.

The neutral salt used in this work was prepared from a c. p. sample of the heptahydrate by heating to 270° in a current of hydrogen.⁴

(*a*) Solid phase $\text{FeSO}_4 \cdot x \text{H}_2\text{SO}_4$.

% FeSO_4	0.22	0.31	0.40	0.51	0.63
<i>T</i>	30.2	42.3	48.6	57.7	63.8

Here again, from the slope of the curve, the solid phase (*a*) is certainly an acid salt, but on account of the limited concentration range it was impossible to determine its composition. The curve could not be continued to higher concentrations and temperatures, since solutions containing more than 0.5 mol. % of ferrous sulfate became cloudy on heating, probably owing to oxidation by the solvent of ferrous sulfate to ferric sulfate, which is much less soluble.

System $\text{Fe}_2(\text{SO}_4)_3 : \text{H}_2\text{SO}_4$.—No acid ferric sulfates are known. Ferric sulfate is extremely insoluble in 100% sulfuric acid; 0.015 mol. % could not be brought into solution even at the boiling point.

System $\text{NiSO}_4 : \text{H}_2\text{SO}_4$.—No acid sulfates have been reported for this system. The neutral salt is slightly soluble in the pure acid, a clear yellow solution containing 0.25° mol. % being prepared, but only sulfuric acid could be obtained from this as a solid phase on cooling. A mixture containing 0.29 mol. % of nickel sulfate did not give complete solution of the salt even on boiling.

System $\text{PbSO}_4 : \text{H}_2\text{SO}_4$.—No acid lead sulfates are known.⁵ According to solu-

¹ This rendered it impossible to separate out sufficient of the solid for accurate analysis, even from a large bulk of solution.

² The upper branch of the curve is rising exceedingly steeply at the last point determined, and there seems to be little likelihood of another break.

³ Kendrick, *J. Phys. Chem.*, **12**, 704 (1908).

⁴ Keppeler and D'Ans, *Z. physik. Chem.*, **62**, 91 (1908).

⁵ Donk (*Chem. Weekblad*, **13**, 92 (1916)), in an investigation of the ternary system $\text{PbSO}_4 : \text{H}_2\text{SO}_4 : \text{H}_2\text{O}$, found no indications of the simple acid salt $\text{PbSO}_4 \cdot \text{H}_2\text{SO}_4$ said to be formed during the evaporation of H_2SO_4 in lead pans. A hydrated acid salt, however, ($\text{PbSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), has been isolated by Schultz (*loc. cit.*, p. 137).

bility measurements by Ditz and Kanhäuser,¹ a saturated solution of lead sulfate in 100% sulfuric acid at ordinary temperatures contains 1.40 mol. % of lead sulfate.

In the present work no solubility curve could be obtained. Solutions containing up to 1.23 mol. % of lead sulfate deposited only sulfuric acid as solid phase on cooling. It was not found possible to bring 1.27 mol. % into solution, even at the boiling point.

System $\text{CuSO}_4: \text{H}_2\text{SO}_4$.—No acid sulfate has been recorded for this system. The neutral salt was found to be only slightly soluble in the anhydrous acid, giving colorless solutions which change to bluish-green when heated to the boiling point. On cooling the color disappears.²

(a) Solid phase CuSO_4 (?).

% CuSO_4	0.10	0.18	0.28	0.52
T.....	37.0	69.0	93.0	^a

^a Did not dissolve completely.

The exceedingly steep curve indicates that the solid phase is most probably the neutral salt; not sufficient crystals, however, could be obtained for analysis.

System $\text{Hg}_2\text{SO}_4: \text{H}_2\text{SO}_4$.—The acid salt $\text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_4$ has been recorded.³ No solubility data are available.

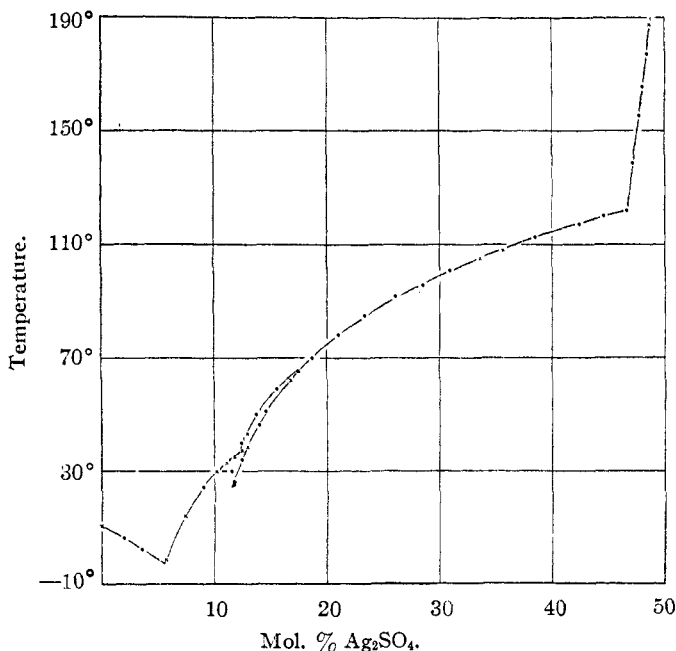


Fig. 2.—System $\text{Ag}_2\text{SO}_4: \text{H}_2\text{SO}_4$.

¹ Ditz and Kanhäuser, *Z. anorg. Chem.*, **98**, 128 (1916).

² The inference may be drawn (cf. Poma, *Gazz. chim. ital.*, **40**, 176 (1910)), that the blue color in aqueous solutions is a property not of Cu^{++} itself, as generally stated, but of hydrated ions. The appearance of the color on heating the pure acid solution may logically be ascribed to loss of SO_3 (equivalent to dilution with H_2O ; see barium sulfate above).

³ Braham, *Chem. News*, **42**, 163 (1880).

(a) Solid phase $\text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_4$.

% Hg_2SO_4	0.68	0.82	1.02	1.18	1.41	1.77	2.17
T.....	20.0	27.0	34.9	40.1	47.7	56.8	63.3

Analyses of the solid phase (a) gave an acid content of 51.9 ± 2.0 mol. %, confirming the salt $\text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_4$ previously reported. The curve could not be continued further, since solutions containing more than 1.7 mol. % of mercurous sulfate rapidly became cloudy on heating, probably due to oxidation, by the solvent, of mercurous sulfate to the much less soluble mercuric sulfate.

System $\text{Hg}_2\text{SO}_4: \text{H}_2\text{SO}_4$.—No acid salt has been reported. The solubility of the neutral salt in 100% acid is extremely small.

(a) Solid phase HgSO_4 (?).

% HgSO_4	0.023	0.048	0.094
T.....	36.0	77.0	127.0

As in the case of copper, the steepness of the curve suggests the neutral salt.

System $\text{Ag}_2\text{SO}_4: \text{H}_2\text{SO}_4$.—The equimolecular compound $\text{Ag}_2\text{SO}_4, \text{H}_2\text{SO}_4$ has been previously reported.¹ No exact solubility measurements have been made.²

(a) Solid phase H_2SO_4 .

% Ag_2SO_4	0.00	1.73	1.99	3.67
T.....	10.4	7.0	6.1	2.4

(b) Solid phase $\text{Ag}_2\text{SO}_4, 2 \text{H}_2\text{SO}_4$.

% Ag_2SO_4	5.69	7.41	9.03	10.17	11.19	11.80	12.38
T.....	-1.5	13.0	24.5	29.9	33.0	35.3	37.6

(c) Solid phase $\text{Ag}_2\text{SO}_4, \text{H}_2\text{SO}_4$.

% Ag_2SO_4	11.66	11.80	12.38	12.88	13.63	13.88	14.57	
T (α modification).....	40.2	43.1	50.4	
T (β modification).....	25.3	28.5	34.1	38.6	46.1	50.4	
% Ag_2SO_4	14.64	15.62	16.76	17.43	18.71	21.00	23.38	23.96
T (α modification).....	59.3	65.3
T (β modification).....	51.7	62.3	65.3	70.1	78.6	85.1	86.7
% Ag_2SO_4	26.13	28.55	30.94	33.74	35.80	38.57	42.45	
T (β modification).....	92.0	96.0	101.3	105.1	108.0	112.8	117.1	
% Ag_2SO_4	44.69	46.70	47.17					
T (β modification).....	120.0	122.2	122.8					

(d) Solid phase Ag_2SO_4 .

% Ag_2SO_4	47.17	47.22	47.75	48.07	48.44	48.69
T.....	138.9	144.6	165.3	175.8	187.2	197.3

The above results are also reproduced in Fig. 2.

¹ Schultz, *loc. cit.*, p. 144. The color of this salt is not light yellow, as reported by Schultz, but white.

² Bergius (*loc. cit.*) has stated that the solubilities of the sulfates of Cu, Ag, Al and Zn in the pure acid are of the same order; the present work, however, shows that the silver salt is more than 50 times as soluble as that of zinc, more than 100 times as soluble as that of copper, and more than 1000 times as soluble as that of aluminum.

Analyses of the solid phase (*b*) indicated an acid content of 66.4 ± 0.2 mol. %, evidently corresponding to the compound $\text{Ag}_2\text{SO}_4, 2 \text{H}_2\text{SO}_4$ —a salt not before known. Analyses of the solid phase (*c*) showed an acid content of $52.1 \pm 1.2\%$ acid, which agrees within the limits of experimental error with the compound $\text{Ag}_2\text{SO}_4, \text{H}_2\text{SO}_4$, isolated by Schultz. This compound exists in two distinct crystalline modifications: (α) thick prisms, stable below 66° , and (β) fine needles, stable above that temperature. The transition point between $\text{Ag}_2\text{SO}_4, 2 \text{H}_2\text{SO}_4$ and the α form occurs at 36° , between the same salt and the β form at 39° . The β modification of $\text{Ag}_2\text{SO}_4, \text{H}_2\text{SO}_4$ is not stable up to its melting point (which, as indicated by a short extrapolation, would be about 125°), but undergoes transition at 122.5° to a new phase, in all probability the neutral salt.¹

Mention may be made at this point of some anomalous results in this system (occasional deposition of a small amount of crystals from solutions containing between 5 and 24 mol. % Ag_2SO_4 , not soluble except at much higher temperatures) which suggest the metastability of the compounds above described, but which could not be satisfactorily duplicated and were consequently not examined further.

Consideration of Results.

An examination of the freezing-point curves presented in this paper and in the recent article by Kendall and Landon discloses the fact that compound formation between the 100% acid and the neutral salt varies very considerably in extent and stability with different metal sulfates. The most complex compounds of all are those of lithium (*e. g.*, $\text{Li}_2\text{SO}_4, 7\text{H}_2\text{SO}_4$); the most stable are those of potassium and ammonium, which persist right past their melting points. The sodium system still exhibits extensive and complex compound formation, but the acid salts obtained decompose in general just before the melting-point maxima are reached on the curve. Barium and calcium form isolable compounds of the same general type ($\text{RSO}_4, 3\text{H}_2\text{SO}_4$), which are much less stable (losing acid readily on heating or on passing a current of dried air over the crystals) and which can be isolated only over a very limited concentration range. Magnesium gives a similar compound of still more restricted stability. With zinc and iron (ferrous) a single acid salt is shown by the curves in each case, but the available concentration range is too small to permit determinations of its composition to be made. Aluminum, nickel, lead, ferric iron, copper and mercury (ic) all give negative results. Mercurous sulfate, however, forms a very unstable acid salt ($\text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_4$); while silver sulfate, finally, furnishes two compounds with formulas $\text{Ag}_2\text{SO}_4, 2\text{H}_2\text{SO}_4$ and $\text{Ag}_2\text{SO}_4, \text{H}_2\text{SO}_4$ respectively, which resemble the acid salts of sodium in being stable over considerable ranges of temperature and composition and in decomposing just before reaching their true melting points.

These variations in compound formation are (with minor exceptions, which are taken up below) in complete agreement with the general rule

¹ At 200° the curve for this solid phase is still rising very rapidly, and there seems little probability of another break.

stated in preceding papers¹—"the stability of an addition compound increases with the difference in character (*i. e.*, the positive or negative nature of the constituent groups) of its 2 components." In systems of the type here studied, the only variable factor is the difference in the electro-affinity² of the positive radicals. Where this difference is large (*i. e.*, with metals much above hydrogen in the electromotive series, such as potassium, or much below hydrogen, such as silver) compound formation is extensive. As the difference diminishes (*i. e.*, with metals closer to hydrogen, such as zinc or mercury) the stability of the compounds formed also diminishes. Where the difference is very small, finally, (*i. e.*, with metals very near to hydrogen, such as nickel or copper) combination between the components has decreased to such an extent that compounds are no longer isolable.

The two marked exceptions in the series are offered by aluminum and mercuric salts. Aluminum is more electropositive than zinc or ferrous iron (both of which form acid salts) but its sulfate gives no sign of compound formation with sulfuric acid, in fact it is practically insoluble. Similarly mercuric sulfate, although the electrode potential of mercuric mercury is greater than that of mercurous, exhibits no tendency towards compound formation, while mercurous sulfate forms an unstable acid salt. This anomalous behavior is to be referred to a "valence factor" in compound formation, which will be discussed more fully in another paper.³ It will suffice here to note the fact that whenever, in the present work, we compare two metals with approximately the same electrode potentials but of different valence, we find that the sulfate of the metal with the higher valence shows much less extensive acid salt formation. Besides the two examples given above, comparison of the sodium and barium systems is instructive.

Solubility Relationships.

Another regularity which appears in the present work may here be briefly considered. Not only does compound formation between neutral sulfates and sulfuric acid diminish uniformly in extent as we go down the electromotive series from lithium to hydrogen, and then increase again as we proceed to silver, but the solubilities of the salts in sulfuric acid follow a precisely similar course. The alkali sulfates are exceedingly soluble in the pure acid, the sulfates of less electropositive metals are decreasingly soluble, practical insolubility is reached with the sulfates of metals in the neighborhood of hydrogen, silver sulfate is again exceedingly soluble.

¹ Kendall, Booge and Andrews, *THIS JOURNAL*, **39**, 2304 (1917).

² A table of electrode potentials is given on p. 989.

³ The influence of atomic volume upon the complexity of addition compounds will also be considered in a later article.

The following table indicates clearly the quantitative results at a single fixed temperature (25°). The electrode potentials¹ given are mainly taken from the official monographs by Abegg, Auerbach and Luther,² but several minor alterations (due chiefly to the researches of Lewis³ and his collaborators) have been found necessary. The values for barium and calcium are only rough approximations from thermochemical data; the figure for aluminum is taken from a recent article by Heyrovsky.⁴

Metal.	Electrode potential.	Mol. % soly. 25°.	Solid phase.
Li	-3.02	14.28	Li ₂ SO ₄ , 2 H ₂ SO ₄
K	-2.92	9.24	K ₂ SO ₄ , 3 H ₂ SO ₄
Ba	-2.8 (?)	8.85	BaSO ₄ , 3 H ₂ SO ₄
Na	-2.72	5.28	2 Na ₂ SO ₄ , 9 H ₂ SO ₄
Ca	-2.5 (?)	5.16	CaSO ₄ , 3 H ₂ SO ₄
Mg	-1.55	0.18	MgSO ₄ , 3 H ₂ SO ₄
Al	-1.34	<0.01	Al ₂ (SO ₄) ₃
Zn	-0.76	0.17	ZnSO ₄ , x H ₂ SO ₄
Fe (Fe ⁺⁺)	-0.43	0.17	FeSO ₄ , x H ₂ SO ₄
Ni	-0.22	Very small	NiSO ₄
Pb	-0.13	Small	PbSO ₄
Fe (Fe ⁺⁺⁺)	-0.04	<0.01	Fe ₂ (SO ₄) ₃
Cu	+0.35	0.08	CuSO ₄
Hg(Hg ₂ ⁺⁺)	+0.79	0.78	Hg ₂ SO ₄ , H ₂ SO ₄
Ag	+0.80	9.11	Ag ₂ SO ₄ , 2 H ₂ SO ₄
Hg(Hg ⁺⁺)	+0.86	0.02	HgSO ₄

The results as shown are not in all cases strictly comparable,⁵ owing to the diverse character of the solid phases in equilibrium with the saturated solutions at 25°. Nevertheless, the regularity of the decline in solubility for sulfates of metals above hydrogen from lithium to ferric iron and of the subsequent increase for sulfates of metals below hydrogen from copper to silver cannot be mistaken. The "valence" irregularity is again marked in the cases of the aluminum and mercuric salts. Throughout the whole series, compound formation and solubility evidently proceed in parallel.

A detailed discussion of the correlation between solubility and compound formation in solutions in general will be presented in a subsequent communication, where the significance of the above relationships will be more fully treated.

¹ Hypothetical normal potentials, in volts, based upon the normal hydrogen electrode as zero.

² Abegg, Auerbach and Luther, *Abhandl. Deutsch. Bunsen Ges.*, **2**, No. 5, 1911, and No. 8, 1915.

³ Lewis *et al.*, *THIS JOURNAL*, **36**, 804 (1914); **37**, 1990 (1915); **39**, 1912 (1917); Linhart, *ibid.*, **38**, 2356 (1916).

⁴ Heyrovský, *J. Chem. Soc.*, 117, 27 (1920).

⁵ As will be shown later, they must be regarded as *minimum* values in all systems where an acid salt is the stable phase. The neutral salt, under such conditions, will necessarily have a higher solubility.

Summary.

The study of compound formation between sulfuric acid and neutral metal sulfates by the freezing-point method, begun by Kendall and Landon, has here been completed. The results obtained may be summarized¹ as follows.

Salt formula.	Acid compounds isolated.
BaSO ₄	BaSO ₄ , 3 H ₂ SO ₄ (not previously recorded).
CaSO ₄	CaSO ₄ , 3 H ₂ SO ₄ (existent in 2 crystalline modifications).
MgSO ₄	MgSO ₄ , 3 H ₂ SO ₄
ZnSO ₄ } FeSO ₄ } Hg ₂ SO ₄ }	ZnSO ₄ , <i>x</i> H ₂ SO ₄ } FeSO ₄ , <i>x</i> H ₂ SO ₄ } Hg ₂ SO ₄ , H ₂ SO ₄ }
Ag ₂ SO ₄	(a) Ag ₂ SO ₄ , 2 H ₂ SO ₄ (not previously recorded). (b) Ag ₂ SO ₄ , H ₂ SO ₄ (existent in 2 crystalline modifications, with a transition point at 66°).

The neutral sulfates of aluminum, nickel, lead, ferric iron, copper, and mercury (ic) gave no isolable acid salts.

The compounds obtained in this work are considerably less complex and less stable than those given by the sulfates of the alkali metals. If the metals are arranged in the order of the electromotive series, compound formation is seen to be dependent upon the position of the metal with respect to hydrogen. Only those metals much above hydrogen (*e. g.*, lithium, potassium) and those much below hydrogen (*e. g.*, silver) show extensive acid salt formation. As we approach the zero point from either side, the stability of complexes decreases until finally no compounds are isolable. This is in complete agreement with the general rules concerning compound formation formulated in previous papers.

Solubility relationships throughout the series are found to follow a similar course. The alkali sulfates and silver sulfate are extremely soluble in sulfuric acid, the sulfates of metals less pronouncedly positive or negative are much less soluble, the sulfates of metals with electrode potentials near to the zero point are practically insoluble. The significance of the parallelism thus established between compound formation and solubility will be the subject of a subsequent article.

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¹ For a corresponding summary of Kendall and Landon's results see *THIS JOURNAL*, **42**, 2142 (1920).