6. Without sacrificing accuracy the new method makes possible the use of a much less expensive equipment than is used in the potentiometer method.

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THE FORMATION OF ADDITION COMPOUNDS BETWEEN 100% SULFURIC ACID AND THE NEUTRAL SULFATES OF THE ALKALI METALS.

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An extensive study of the freezing-point curves of various pairs of organic substances[1] and of water solutions of acids and bases[2] has gradually yielded increasing evidence in support of a general rule for compound formation—namely, that "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 the application of this rule to compound formation in aqueous solutions, the complex nature of the question of salt hydration has been briefly treated,[3] and the difficulty of bringing it into line with other work discussed. The proposal was made to attack this question by first investigating the extent of compound formation in systems of the types HX–RX and ROH–RX. If the results of this work should lead to the formulation of any general rules for these cases, then it was suggested that a comparison of these results with those from a study of the systems $HX–H_2O$ and $ROH–H_2O$ might make possible the statement of general rules for the system $RX–H_2O$.

It was in initiation of this broad plan that the present work was undertaken, the type of system investigated being HX–RX. Because of its relatively high freezing point, 100% sulfuric acid was chosen as the acid component. As salts the anhydrous normal sulfates of sodium, potassium, lithium and ammonium were selected.

Previous Work.—The data available on the formation of addition compounds of the neutral sulfates of the alkali metals with sulfuric acid are very incomplete.[4] Most of the results are in the form of isolated observations which have been incidental in the study of other problems,

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[1] Kendall, THIS JOURNAL, **36**, 1222, 1722 (1914); **38**, 1309 (1916); Kendall and Carpenter, *ibid.*, **36**, 2498 (1914); Kendall and Gibbons, *ibid.*, **37**, 149 (1915); Kendall and Booge, *ibid.*, **38**, 1712 (1916).

[2] Kendall, Booge and Andrews, *ibid.*, **39**, 2303 (1917); Kendall and Booge, *ibid.*, **39**, 2323 (1917).

[3] Kendall, Booge and Andrews, *loc. cit.*, p. 2304.

[4] References to previous work will be found later, under each particular system examined.

and apparently in no case has there been a systematic investigation of the question. In the methods of preparation noted for the various acid salts which have been reported, the acid used has been spoken of ordinarily as "concentrated" or as "a hydrate," showing that 100% acid had not been employed. In some cases the properties of the resulting products are given as definitely relating to the anhydrous substance, but this has not been done always, leading one to conclude that the compound may have been a hydrate, and so of no value for comparison in the present problem. Variation in the concentration of the acid, the proportion of the acid to the salt, and the temperature used in the reaction have naturally resulted in the formation of different compounds. Sometimes no melting point is given for the compound claimed, and frequently it is stated as "about" or "above" a certain value. Where more than one determination is available, there is little concordance, as a rule, between the results.

Experimental.

The method employed for this work was essentially the freezing-point method[1] previously used, though the conditions made certain alterations necessary.

The 100% sulfuric acid was prepared as described by Kendall and Carpenter.[2] Most stringent precautions were taken to prevent the acid from absorbing water from the atmosphere at any stage of the work. In spite of all precautions, however, the work was held up frequently for days at a time by unfavorable weather conditions which made it impossible to work with the acid.

The salts used were carefully analyzed sulfates of sodium, potassium, lithium and ammonium. Any impurities present were certainly insufficient in quantity to affect the measurements within the error of the experiment. All salts were dried to constant weight and then kept absolutely free from moisture.

For the lower range of the work—that is, up to 100°—a modified Beckmann apparatus was used. The inner tube, which had no side tube, was 15 cm. long and 3 cm. inside diameter; the outer tube was 17 cm. long with an inside diameter of $4^1/_2$ cm., Pyrex glass having been used for both. A 2-liter Pyrex beaker held the freezing mixture as long as that was needed, and later served as the container for the water-bath. The bath was stirred by a stream of compressed air. Mercury thermometers were used. Up to about 60° one graduated in 0.1° was employed; above 60°, a set of Anschütz short-stem thermometers graduated in 0.2° was substituted. The thermometers were standardized by taking the freezing and boiling points of water, by comparison with a standard thermometer

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[1] This method, as a means of studying compound formation, has been discussed fully in the earlier articles to which reference has been made above.

[2] Kendall and Carpenter, This Journal, 36, 2500 (1914).

between these 2 temperatures, and by means of fixed points above 100° The standardization was checked at frequent intervals during the work.

At first the introduction of the solids into the tube containing the acid gave considerable trouble because, in their very dry condition, they could not be made into pills and so scattered badly over the thermometer, stirrer and sides of the tube. To overcome this difficulty, a glass-stoppered weighing-bottle with a long delivery tube attached was made and found to be most satisfactory. The length of the delivery tube was sufficient to allow it to reach nearly to the surface of the liquid in the freezing-point tube, and still not so great as to prevent the bottle from standing on the balance pan.

For the range of temperature above 100° the open tube could not be employed to advantage because of the decomposition of the 100% acid. It became necessary, therefore, to enclose the materials in sealed bulbs.[1] Special care was taken in filling and sealing these bulbs to ensure no absorption of water by the acid. The proportions of acid and salt in each mixture were established by direct weighing. The mixture was always melted completely 2 or 3 times and thoroughly shaken before any attempt was made to take freezing-point readings.

The bath used for this higher temperature work varied according to the temperature under investigation. Up to about 190° the bath was conc. sulfuric acid with 25% of ammonium sulfate added to reduce the fuming.[2] From this point up to 230° the bath was a mixture of fused lithium and potassium nitrates (65 mol per cent. of potassium nitrate), while from 230° to 300° a 50 mol per cent. mixture of fused potassium and sodium nitrates was used.[3] Above 300° the bath was of fused zinc chloride.[4] In all cases the bath was stirred by compressed air. The material in the sealed tube was kept thoroughly agitated by energetic rotation during determinations.

At the lower temperatures, it was usually possible to determine the freezing point by reading the temperature to which the thermometer rose after a slight degree of supercooling. In cases where there was persistent supercooling, it was necessary to employ the seeding process.[5] At higher temperatures the point recorded was that at which the last

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[1] See Smith and Eastlack, THIS JOURNAL, 38, 1262 (1916); Kendall and Davidson, *ibid.*, 42, 1142 (1920).

[2] The addition of ammonium sulfate to the hot acid removed the discoloration that had appeared on heating. Afterwards only the slightest darkening was apparent even after prolonged heating. The acid alone is useless for work requiring a transparent bath.

[3] A little conc. nitric acid was added at intervals to the molten mixture to remove the cloudiness that appears after continued heating.

[4] Scudder, THIS JOURNAL, 25, 161–163 (1903).

[5] See Kendall, *ibid.*, 36, 1226 (1914).

crystal disappeared, the temperature being allowed to rise very slowly in a mixture containing only a few minute crystals. A light placed behind the beaker made it possible to determine this point with accuracy. At least 3 readings were taken for each point, the variations obtained being within the following limits:

Limits.	Possible error.
—35° and —10°	0.2 to 0.5°
—10 and 100	0.1 to 0.2
100 and 200	0.2 to 0.5
200 and 300	0.5 to 1.0

In each of the systems investigated, it was possible to carry the work to a temperature of about 300°, at which point the curve was rising very rapidly. In the cases of potassium, sodium and lithium, it was found that, with mixtures containing just a little more salt than the last one used for obtaining a reading, it was impossible to dissolve the material even at the temperature of boiling sulfur. It had been hoped in the beginning of the work that the curve for ammonium sulfate might be carried through to 100% ammonium sulfate, but this proved to be impossible.

When a compound was indicated which was too unstable to give a maximum on its freezing-point curve, it became necessary to perform an analysis to determine its composition. A mixture was made up slightly richer in acid than that corresponding to the upper temperature limit of the curve, and allowed to cool to a temperature just above the lower limit. The solid phase which had separated out in the interval was then filtered off at this temperature by suction, a hot funnel being used when necessary. In order to have as small a surface as possible in the funnel during filtration a perforated plate from a Gooch crucible was fitted into a small glass funnel of the right size to fit into the hot funnel. A layer of asbestos was poured over the plate in such a way as to cover thoroughly any small cracks between it and the sides of the funnel. The compound was freed from excess acid, and wieghed portions of it titrated against standard alkali. This work was done in very cold dry weather when the mositure content of the air was small. In some cases extra protection was given to the material by drawing the air through calcium chloride.

When an unstable compound was formed beyond the range of the open tube work, no attempt was made to determine the composition of the solid phase because of the obvious change in conditions that would have resulted in any attempt to filter the material. The separation of the crystals in a centrifuge was impracticable owing to the high temperature that it would have been necessary to maintain in the machine.

The addition compounds obtained in every case were well-defined crystals, usually in the form of needles which arranged themselves in star-shaped clusters. In some cases it was possible to confirm change in solid phase directly by observing changes in appearance of the crystallized mass. In the case of the potassium system, the solid in the sealed tubes was clear and transparent as long as the 75% compound was the solid separating. When the eutectic was passed and the 50% compound crystallized out, the solid was white and opaque. In the same way the 2 crystalline modifications of the compound $Na_2SO_4.2H_2SO_4$ could be easily distinguished, the unstable form separating out in long needles, the stable in short plates.

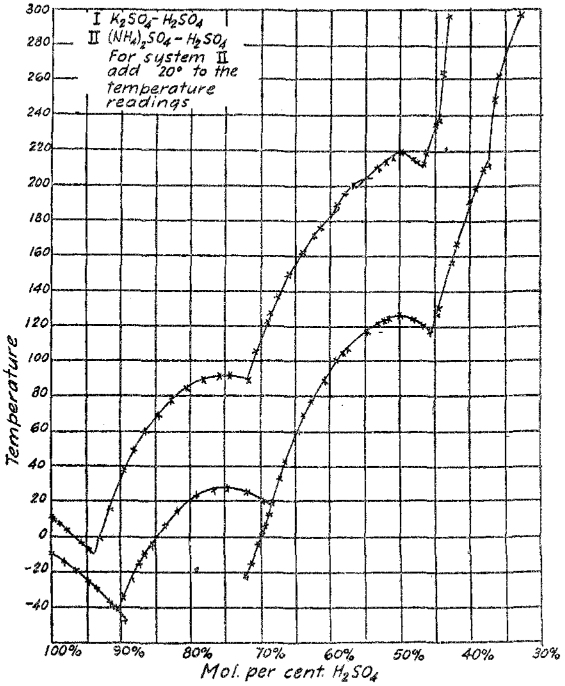

Fig. 1.

Results.

System K_2SO_4-H_2SO_4.—As a consequence of previous work 8 acid potassium sulfates have been claimed — K_2SO_4, $6H_2SO_4$ melting at about 55°;[1] K_2SO_4,$3H_2SO_4$ melting at about 95°;[2] K_2SO_4, H_2SO_4 with recorded melting points of 197°,[3] 200°,[4] 210,[5] and 315.5°;[6] $4K_2SO_4$, $3H_2SO_4$; $5K_2SO_4$, $3H_2SO_4$; $2K_2SO_4$, H_2SO_4 and $3K_2SO_4$, H_2SO_4 all given with no melting points;[7] and $4K_2SO_4$, H_2SO_4 with no melting point.[8]

The freezing point results of the present investigation are tabulated below; their significance is more clearly indicated by the accompanying diagram. Compositions are expressed in molecular percentages throughout.

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[1] Bergius, *Z. physik. Chem.*, **72**, 338–63 (1910); Arzelier, *Compt. rend.*, **147**, 129 (1908) claims that it is impossible to have an acid salt of potassium sulfate with more than 3 molecules of sulfuric acid to one of the salt.

[2] Schultz, *Pogg. Ann.*, **133**, 137 (1868).

[3] Jacquelain, *Ann. phys. chim.*, **70**, 311 (1839).

[4] Mitscherlich, *Pogg. Ann.*, **18**, 152, 173 (1830).

[5] Schultz-Sellack, *Jahresber.*, **24**, 218 (1871).

[6] See Gmelin and Kraut, "Handbuch der Anorg. Chem.," II, **1**, 56.

[7] Stortenbecker, *Rec. trav. chim.*, **21**, 400–402 (1902).

[8] Mitscherlich, *Pogg. Ann.*, **39**, 198 (1836).

(*a*) Solid phase, H_2SO_4.

% acid	100.00	99.70	98.90	97.63	95.77	94.49
T	10.4	9.5	7.2	3.4	— 3.2	— 7.9

(*b*) Solid phase, $K_2SO_4.3H_2SO_4$.

% acid	93.13	91.66	89.60	88.02	86.47	84.61
T	—0.8	15.4	36.5	48.9	59.1	69.6
% acid	82.79	80.97	78.20	75.95	74.47	71.73
T	77.1	83.3	89.2	91.5	91.6	89.0

(*c*) Solid phase, $K_2SO_4.H_2SO_4$.

% acid	70.71	69.07	68.63	67.51	66.14	64.03	62.44
T	105.4	122.1	126.7	136.7	149.5	162.0	171.5
% acid	61.72	60.78	59.15	58.27	56.69	53.23	52.06
T	176.4	178.3	188.4	195.3	200.2	210.0	213.8
% acid	51.38	49.94	49.64	48.30	47.81	46.86	46.73
T	215.7	218.6	218.2	214.1	213.6	212.3	212.5

(*d*) Solid phase, X?

% acid	46.42	45.48	45.18	44.76
T	219.8	235.9	235.6	237.5

(*e*) Solid phase, Y?

% acid	44.29	43.41	41.53
T	264.3	296.8	300+

It will be seen that no confirmation is given for the compound K_2SO_4, $6H_2SO_4$ claimed by Bergius.[1] The 75% compound gives a well-defined maximum on the freezing-point curve, showing a melting point for the pure substance of 91.5°. At 182° and 202° there are clear evidences of changes in the crystalline habit of the 50% compound. These breaks are in accord with results of Bridgman[2] who, in working on the polymorphism of potassium hydrogen sulfate at high pressures, found 2 not very well defined transition points, one at 180° and the other at 200°. The compound gives a very well defined maximum at 218.6°. Beyond the region of the 50% compound, there is clear evidence of the formation of another compound, which, at 238°, gives a transition point to the next compound richer in potassium sulfate. While it is impossible to put great faith in the composition of Stortenbecker's salts, since there is a decided possibility that they are hydrates,[3] there may be salts of the composition $4K_2SO_4,3H_2SO_4$ and $5K_2SO_4,3H_2SO_4$. Either of these formulas might represent the composition of the substance indicated on the freezing-point curve. Stortenbecker's other salts lie beyond the range of this work.

System $(NH_4)_2SO_4$-H_2SO_4.—Previously there have been only 2 acid

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[1] The work of Bergius was not of the exact nature to justify his statement that this compound was formed.

[2] *Proc. Am. Acad. Sci.*, **52**, 124 (1916).

[3] Stortenbecker himself states in a later article that the compound $3K_2SO_4.H_2SO_4$ previously described should have the formula $3K_2SO_4.H_2SO_4.H_2O$ (*Chem. Zentr.*, **1911**, I, 1405.

salts of ammonium claimed—$(NH_4)_2SO_4.H_2SO_4$, melting at about 146°,[1] and $3(NH_4)_2SO_4.H_2SO_4$ to which no melting point has been given.[2]

The present work gave the following results. (See also Fig. 1).

(*a*) Solid phase, H_2SO_4.

% acid.......	100.00	98.31	96.53	94.61	93.56	91.64	90.59	89.52
T...........	10.4	6.2	1.3	—5.0	—8.5	—16.3	—20.7	—26.7

(*b*) Solid phase, $(NH_4)_2SO_4.3H_2SO_4$.

% acid.......	90.59	89.90	88.52	87.64	86.86	85.67	83.79	81.86
T...........	—20.7	—13.1	—3.9	5.3	10.5	17.6	26.7	35.1
% acid.......	79.33	76.88	74.76	72.12	69.59			
T...........	42.7	46.9	47.9	45.8	39.8			

(*c*) Solid phase, X?

% acid.......	72.02	71.40	70.38	69.67	69.59	69.13
T...........	—2.6	4.8	16.0	21.4	22.0	26.1

(*d*) Solid phase, $(NH_4)_2SO_4.H_2SO_4$.

% acid.......	68.79	68.37	67.35	66.52	64.94	63.81	62.69	60.87
T...........	32.9	39.4	53.5	63.1	79.8	89.1	97.4	109.5
% acid.......	59.33	58.19	57.53	54.82	53.18	52.40	51.92	50.05
T...........	120.8	124.3	126.4	136.8	141.1	142.6	144.9	146.9
% acid.......	48.16	46.92	45.73					
T...........	144.1	141.7	137.2					

(*e*) Solid phase, $2(NH_4)_2SO_4.H_2SO_4$(?)

% acid.......	44.95	44.57	43.83	42.82	42.02	40.22	39.38
T...........	147.2	151.7	159.3	176.7	187.7	210.2	218.5
% acid.......	38.36	37.62					
T...........	229.2	232.0					

(*f*) Solid phase, Y?

% acid.......	36.55	36.02	32.63
T...........	269.2	281.5	318.0

The data recorded above give distinct evidence of a substance not noted before, the compound $(NH_4)_2SO_4.3H_2SO_4$. This substance is stable at its melting point, having a well-defined maximum at 48°. The 50% compound gives a marked maximum at 146.9°, in close accord with the melting point noted by Smith.[3] It is of interest to note that the melting point given in the literature for the *normal* salt is 140°, a value obtained by Marchand.[4] This apparent contradiction is explained by Smith in objecting to the reference of Hodgkinson and Bellairs to their use of dried and carefully melted ammonium sulfate. Ammonium sulfate itself will not melt, but, on being heated, one equivalent of ammonia is expelled and it is the *acid* salt that melts at about 146°. This, of course, suggests that Marchand heated his material in an open tube which gave an opportunity for escape of ammonia. Bridgman also worked with acid

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[1] Smith, *J. Soc. Chem. Ind.*, **14**, 629 (1895).

[2] Marignac, *Jahresber.*, **10**, 134 (1857); Mitscherlich, *loc. cit.*; van Dorp, *Z. physik. Chem.*, **73**, 284–289 (1910).

[3] *Loc. cit.*

[4] *Pogg. Ann.*, **42**, 556 (1837).

ammonium sulfate and his record shows that his sample was entirely melted at 150°,[1] though no exact melting point was obtained. Below the eutectic between the 75 and 50% compounds there is a branch of the curve showing a metastable modification of unknown composition. Persistent efforts to carry this branch further met with failure. Above the 50% compound, there is a distinct break in the curve, and a slight extrapolation from the curve suggests that the compound formed is $2(NH_4)_2SO_4.H_2SO_4$. The transition point from this substance to the one next richer in ammonium sulfate comes at 234°. The compound containing 3 molecules of ammonium sulfate to one of the acid lies beyond the range of the present work.

System Na_2SO_4-H_2SO_4.—As the result of previous work 6 acid salts of sodium sulfate have been recorded—$Na_2SO_4.8H_2SO_4$ melting at about 40°;[2] $2Na_2SO_4.9H_2SO_4$ for which no melting point is given;[3] $Na_2SO_4.3H_2SO_4$ melting at about 100°;[4] $Na_2SO_4.H_2SO_4$ melting at about 315°;[5] $2Na_2SO_4.H_2SO_4$ and $3Na_2SO_4.H_2SO_4$ with no melting points.[6]

The results of the present work are given below, and also shown more clearly in Fig. 2.

(*a*) Solid phase, H_2SO_4.

% acid	100.00	98.02
T	10.4	4.3

(*b*) Solid phase, $2Na_2SO_4.9H_2SO_4$.

% acid	96.31	95.21	94.16	92.96	91.09	89.62	87.37	84.89
T	10.8	21.2	28.9	36.8	45.4	49.9	55.0	57.4

(*c*) Solid phase, $Na_2SO_4.2H_2SO_4$.

% acid			83.71	82.52	80.79	79.05	76.86
T (unstable modification)			62.9	70.4	79.7	87.0	93.6
T (stable modification)			71.5	78.6	88.5	95.7	102.1

(*d*) Solid phase, $Na_2SO_4.H_2SO_4$.

% acid	74.64	73.63	71.10	70.62	69.57	68.63	66.01	65.72
T	112.5	122.3	136.5	139.8	148.2	148.2	159.0	160.6
% acid	62.73	58.73	56.59	55.88	51.75	49.77		
T	170.0	177.8	180.7	180.9	185.5	185.8		

(*e*) Solid phase, X?

% acid	49.03	48.63	46.04	45.40	44.26	43.28	41.17
T	190.9	194.3	223.3	230.2	243.2	254.2	274.5

As in the case of the potassium system, no confirmation is obtained of the work of Bergius, claiming the compound $Na_2SO_4.8H_2SO_4$. For the

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[1] *Loc. cit.*, pp. 125–126.

[2] Bergius, *loc. cit.*

[3] d'Ans, *Z. anorg. Chem.*, **80**, 236–238 (1913).

[4] Schultz, *loc. cit.*

[5] von Thomson, *Pogg. Ann.*, **6**, 80 (1826).

[6] von Thomson, *ibid.*; Mitscherlich, *Pogg. Ann.*, **39**, 198 (1836); Pascal and Ero, *Bull. soc. chim.*, [4] **25**, 35 (1919).

compound $2Na_2SO_4.9H_2SO_4$ noted by d'Ans there is very distinct evidence,[1] extrapolation from the freezing-point curve indicating that its melting point would be about 60°. It gives transition points to the next compound at 57° and 58°. The compound $Na_2SO_4.3H_2SO_4$ noted by Schultz was not obtained. In its stead, the new compound $Na_2SO_4.2H_2SO_4$ appeared, a substance existing in 2 crystalline modifications.[2] This salt decomposes before its melting point is reached, giving transition points to $Na_2SO_4.H_2SO_4$ at the temperatures of 95° and 109°, respectively, for its 2 modifications. This compound is just barely stable at its melting point, and cannot be separated from a solution containing a greater percentage of sodium sulfate. The melting point of 186° found here is quite out of accordance with the value of 315.5° given in the literature. $2Na_2SO_4.H_2SO_4$ and $3Na_2SO_4.H_2SO_4$, for which no melting points are recorded, lie outside the range of this work. The slope of the upper portion of the curve indicates, however, that com-

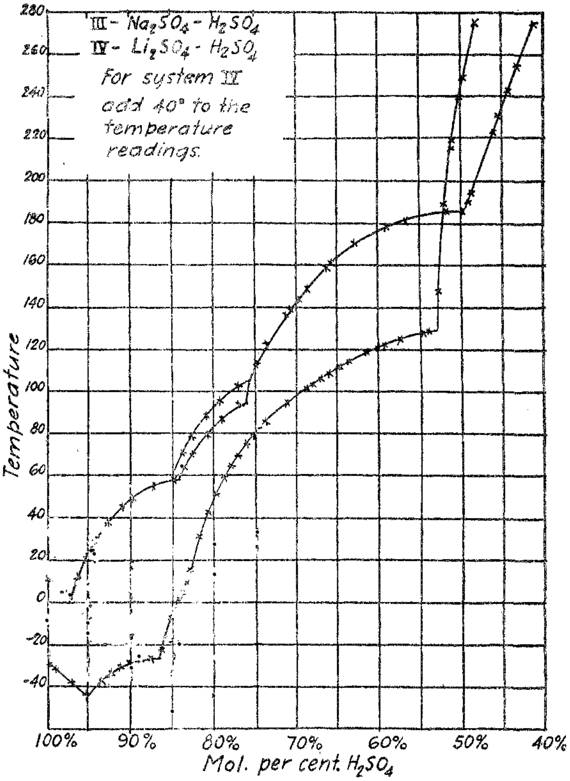

Fig. 2.

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[1] The analytical results, upon which the decision concerning the composition of this substance is based, agree within the limit of error in the acid titration. Computation from these results gave percentage molecular compositions of 81.85%, 81.34%, 81.34%, 81.37% (calculated, 81.81% acid). It was felt in the beginning that it was possible that this percentage corresponded to an 80% compound with some excess acid, but, since persistent filtering did not reduce the proportion of acid and since the substance was in the form of light needle-shaped crystals which did not pack down into a hard mass that opposed the passage of the air through it, there finally seemed to be no reason for not giving the compound the formula $2Na_2SO_4.9H_2SO_4$ previously recorded by d'Ans.

[2] Schultz's compound was very probably this substance, insufficiently freed from excess acid.

pounds of this type would be formed before the melting point of the normal salt could be reached.

System Li_2SO_4-H_2SO_4.—From previous work there are 3 acid salts of lithium sulfate claimed—$Li_2SO_4.7H_2SO_4$ melting at about 12°;[1] $Li_2SO_4.2H_2SO_4$ melting at above 110°;[2] and $Li_2SO_4.H_2SO_4$ melting at 120° according to Lescoeur,[3] and at 160° according to Schultz.[2]

The results of the present work are tabulated below. (See also Fig. 2.)

(*a*) Solid phase, H_2SO_4.

% acid	100.00	99.19	97.15	95.37
T	10.3	8.0	2.0	—3.6

(*b*) Solid phase, $Li_2SO_4.7H_2SO_4$.

% acid	93.58	92.37	91.25	90.27	88.76	87.68	87.50	87.15
T	3.0	6.5	9.7	11.4	12.9	13.1	13.3	13.0
% acid	86.98							
T	13.0							

(*c*) Solid phase, $Li_2SO_4.2H_2SO_4$.

% acid	86.36	85.09	84.69	84.13	83.77	83.42
T	17.9	32.6	36.7	40.9	44.3	48.9

(*d*) Solid phase, $Li_2SO_4.H_2SO_4$.

% acid	82.99	81.61	80.68	79.94	78.84	77.89	76.55	76.08
T	55.3	70.9	82.7	91.2	99.0	105.2	109.3	114.7
% acid	75.27	73.59	71.05	68.72	67.70	66.69	66.03	64.88
T	117.7	125.4	135.8	142.5	144.5	147.1	148.6	152.4
% acid	63.99	61.67	59.89	59.24	57.40	54.90	54.00	
T	155.2	159.4	161.3	161.5	164.7	167.8	168.5	

(*e*) Solid phase, X?

% acid	52.40	51.90	51.45	51.21	50.15	49.52	48.20
T	186.5	229.9	256.0	258.6	279.9	289.0	315.0

The present results confirm in general all the salts previously claimed. The compound containing 7 molecules of sulfuric acid, for which Bergius gives a melting-point of "about 12°," shows a clearly defined maximum at 13.3°. The melting point of 110° for $Li_2SO_4.2H_2SO_4$ recorded by Schultz is in error, since this compound is shown on the freezing-point curve to be unstable at its melting-point and gives a transition point to $Li_2SO_4.H_2SO_4$ at a temperature of 50°. The latter compound is also unstable at its melting-point, but a slight extrapolation from the curve indicates that the value for the melting-point is 170.5°, much higher than any previously given. The stable portion of the curve ends with a transition point at a temperature of 169.7° to a compound with a larger per cent. of lithium sulfate with a maximum beyond the range of the present work. No such compound has as yet been recorded.

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[1] Bergius, *loc. cit.*

[2] Schultz, *loc. cit.*

[3] Lescoeur, *Bull. soc. chim.*, **24**, 516 (1875).

Consideration of Results.

Reference to the diagrams will show at once a strong similarity between the curves for potassium and ammonium salts; the course of compound formation with sodium and lithium sulfates is also much alike. This result is not at all surprising when one remembers the general similarity between the compounds of these respective pairs of radicals. In all cases there is evidence for extensive compound formation, the compounds varying considerably in complexity and stability.

Bergius,[1] in some very rough preliminary work, showed that other sulfates, such as those of barium and strontium, are much less active in forming compounds with sulfuric acid, the majority being, indeed, only very slightly soluble. While Bergius' work is merely qualitative in character, it does indicate clearly that the tendency toward compound formation with sulfuric acid is greatest with the alkali metals here examined.

This is in exact accordance with the results of previous articles, since according to the rule already stated[2] we would expect the sulfates of the most electropositive metals to form most stable compounds with sulfuric acid. In this acid, in fact, the salts here investigated should give results analagous to those obtained with the corresponding hydroxides in aqueous solution.[3] A systematic study of the remaining metal sulfates in sulfuric acid is now in progress, and it is hoped to obtain, by means of compound formation, solubility and conductivity data in these systems, results which will enable us to establish definitely the general relationships existing between the position of the metal in the electromotive series and compound formation in the first place, and between compound formation and ionization in the second. Extended discussion of the present results will consequently be deferred to the succeeding article of this series.

In conclusion here, the fact may be noted that the freezing-point curves obtained are not without interest in connection with certain industrial problems, such as the utilization of nitre cake, or the treatment of gas liquor.[4]

Summary.

A complete investigation has been made by means of the freezing-point method upon compound formation in systems containing sulfuric acid and the anhydrous neutral sulfates of potassium, ammonium, sodium and lithium from the eutectic point of each system up to a temperature of 300° (approximately).

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[1] *Loc. cit.*

[2] P. 2131.

[3] A sulfate in sulfuric acid being not a salt, but a base.

[4] See, for example, Johnston, *J. Ind. Eng. Chem.*, **10**, 468 (1918); Dawson, *J. Chem. Soc.*, **113**, 675 (1918); Pascal and Ero, *Bull. soc. chim.*, [4] **25**, 35 (1919); Foote, *J. Ind. Eng. Chem.*, **11**, 629 (1919).

The results obtained may be summarized as follows (compounds of undetermined composition being omitted):

Salt formula.	Acid compounds isolated.
K_2SO_4	(*a*) $K_2SO_4.3H_2SO_4$; m. p., 91.5°.
	(*b*) $K_2SO_4.H_2SO_4$; m. p., 218.6°; existent in three modifications, with transition points at 182° and 202°.
$(NH_4)_2SO_4$	(*a*) $(NH_4)_2SO_4.3H_2SO_4$; m. p. 48.0°.
	(*b*) $(NH_4)_2SO_4.H_2SO_4$; m. p. 146.9°.
Na_2SO_4	(*a*) $2Na_2SO_4.9H_2SO_4$; unstable at m. p. (60°, by extrapolation), transition points to the two modifications of (*b*) occurring at 57° and 58°.
	(*b*) $Na_2SO_4.2H_2SO_4$; existent in two modifications both unstable at their m. p., transition to (*c*) occurring at 95° and 109°.
	(*c*) $Na_2SO_4.H_2SO_4$; m. p., 186°.
Li_2SO_4	(*a*) $Li_2SO_4.7H_2SO_4$; m. p., 13.6°.
	(*b*) $Li_2SO_4.2H_2SO_4$; unstable at m. p., transition to (*c*) occurring at 50°.
	(*c*) $Li_2SO_4.H_2SO_4$; unstable at m. p. (170.5°, by extrapolation).

The bearing of the results here obtained upon the general problem of the factors affecting compound formation in solutions has been briefly pointed out, but full discussion is reserved for a later article, in which the compound formation, solubility and ionization relationships of a more complete series of metal sulfates in sulfuric acid will be considered.

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COLLOIDAL ADSORPTION.

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From the work of Stokes, Einstein, von Smoluchowski, The. Svedberg, and others, we have a clear notion of the properties of the unstable colloids when suspended in a fluid; for in their case all the conditions upon which Stokes' law is based seem to be realized. On the other hand, the properties of the gelatinizing and swelling colloids are so much at variance with the requirements for the validity of Stokes' law, that it seems clearly impossible to consider the metallic and the gelatinous colloids in one class, and separate efforts to establish a securely based view-point from which the mechanism of the action of the latter might be considered, does not seem to have hitherto been made.

To make generalizations and general deductions safely, requires a set of accurately determined experimental facts obtained under uniform standard conditions and sufficiently complete so that by coördinating the variations in properties a complete set of descriptive data on the system are secured showing the changes in the properties of the substance