SUMMARY

The inapplicability of the usual forms of gas-metering device to the measurement of small rates of flow is discussed, and the resistance-tube flow meter, developed for this purpose in the Bureau of Mines, is described. The nature of the flow of gas through these resistance tubes is considered from the point of view of flow meter design. Specifications for construction, calibration, and operation are included, and the in-

fluence of temperature and pressure changes discussed.

This work was carried out under the direction of the Bureau of Mines. The writer wishes further to express his deep appreciation of the valuable suggestions of Dr. E. Buckingham, of the U. S. Bureau of Standards.

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ORIGINAL PAPERS

EQUILIBRIUM IN THE SYSTEM $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}^1$

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In considering proposals for the utilization of niter cake, Johnston² has stated that "the best mode of using a solution of niter cake for any particular purpose could be ascertained from the appropriate solubility data; this involves the investigation * * * of four-component systems such as $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--FeSO}_4\text{--H}_2\text{O}$." It is hoped that the present investigation may serve as an aid in that direction.

The problem has been limited to determining the solubility relations, at two temperatures, of the following systems:

- (1) $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$
- (2) $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$
- (3) $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{O}$
- (4) $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$

A knowledge of (1), (2), and (3) is obviously necessary in considering (4). Stated in a different way, the problem has consisted in determining the changes which take place when sulfuric acid, in increasing amounts, is added to the system $\text{Na}_2\text{SO}_4\text{--CuSO}_4\text{--H}_2\text{O}$. Systems containing more than approximately 60 per cent of sulfuric acid in solution were not investigated.

In general, only the solubility of univariant systems was determined and in plotting the results the points which represent them are connected by straight lines to show the composition of the corresponding divariant systems. Actually, these curves are usually somewhat concave. At a given temperature, the univariant systems of three components have two solid phases in equilibrium with a solution of fixed composition and vapor pressure. With four components, there are three solid phases at such points.

METHOD

To determine the univariant points in the three-component systems, a series of crystallization experiments at the given temperature showed approximately the conditions necessary. The solution which deposited one compound near the point where another formed was then treated with an excess of the latter, or in some cases with both, and the solubility of the mixture determined. In all cases, a second result

was obtained by adding further quantities of one or both solids and again shaking, the constancy of the results showing that the univariant point had been reached. When the univariant points in the ternary systems had been fixed, it was usually a simple matter to obtain the corresponding points in the quaternary system by merely adding an excess of the third solid necessary. Here also a duplicate result was obtained after adding further quantities of the solids in equilibrium.

Solubilities were determined at 12° and 25°. For 12° a low temperature thermostat¹ gave excellent service. At 25° the ordinary form of thermostat, heated by gas, was used. The various mixtures were shaken in glass-stoppered bottles, kept tight by dipping the tops in paraffin. Solutions for analysis were removed through small filters of glass wool directly into weighed specimen tubes.

In analyzing solutions containing all four components, copper was determined either electrolytically or, as the amount was always small, by precipitating as sulfide, roasting, and weighing copper oxide. After removing copper, sodium was determined in the filtrate as the sulfate, the excess of sulfuric acid being removed by ignition with ammonium carbonate. Free sulfuric acid was determined directly by titrating with standard sodium hydroxide. Preliminary determinations showed that the small amount of copper sulfate present did not affect the end-point. In a few cases, total sulfate was determined (by precipitating as barium sulfate) instead of weighing sodium sulfate, but the method was abandoned as less accurate than the other. Where only three components were present, the method of analysis could be correspondingly simplified.

(1) SYSTEM, $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$

This system has been investigated previously by D'Ans² at 25° and by Pascal³ through a considerable range of temperature, though the latter expresses his results only in the form of a diagram which contains some obvious inaccuracies. D'Ans gives the solubility conditions for the following salts: $\text{Na}_2\text{SO}_4\text{--}10\text{H}_2\text{O}$, Na_2SO_4 , $\text{Na}_3\text{H}(\text{SO}_4)_2\text{--H}_2\text{O}$, $\text{Na}_3\text{H}(\text{SO}_4)_2$, $\text{NaHSO}_4\text{--H}_2\text{O}$, NaHSO_4 .

The salt $\text{Na}_3\text{H}(\text{SO}_4)_2\text{--H}_2\text{O}$ forms spontaneously from solutions only very rarely and D'Ans speaks of ob-

¹ This investigation was undertaken at the request of the Division of Chemistry and Chemical Technology of the National Research Council.

² THIS JOURNAL, 10 (1918), 468.

³ Z. physik. Chem., 33 (1900), 749.

² Ber., 39 (1906), 1534; Z. anorg. Chem., 49 (1906), 356; 61 (1909), 91.

³ Compt. rend., 164 (1917), 628.

taining it only by chance, though when it has formed, it can doubtless be obtained afterward by inoculating. In all our experience we have never observed this form. Its solubility relations, as shown by D'Ans, are very nearly those of the anhydrous form, so it affects the diagram but slightly and it is not considered here. It seems unlikely that this form would be met in practice. Our solubility results agree closely with those of D'Ans at 25°. One difference as to the solid phases in strongly acid solution is mentioned later.

The following results were obtained. Percentages here and in all tables following represent the parts in 100 parts of solution. The letters in the last column refer to the corresponding points in the diagrams which are described later.

TEMPERATURE = 12°			
SOLID PHASES	Per cent H ₂ SO ₄	Per cent Na ₂ SO ₄	Corresponding Point in Diagram
Na ₂ SO ₄ ·10H ₂ O.....	None	9.53	A
		9.44	
Na ₂ SO ₄ ·10H ₂ O and Na ₂ H(SO ₄) ₂	16.51	32.96	Q
	16.52	32.90	
Na ₂ H(SO ₄) ₂ and NaHSO ₄ ·H ₂ O.....	27.96	25.38	H
	27.96	25.45	
NaH(SO ₄) ₂ ·H ₂ O (Divariant) ¹	58.79	4.33	G
TEMPERATURE = 25°			
Na ₂ SO ₄ ·10H ₂ O.....	None	21.90 ¹	A
Na ₂ SO ₄ ·10H ₂ O and Na ₂ SO ₄	8.62	33.46	J
	8.62	33.50	
Na ₂ SO ₄ and Na ₂ H(SO ₄) ₂	16.25	35.20	I
	16.29	35.53	
Na ₂ H(SO ₄) ₂ and NaHSO ₄ ·H ₂ O.....	30.59	27.13	H
	30.57	26.91	
NaHSO ₄ ·H ₂ O (Divariant) ²	56.25	6.54	G

¹ Loewel, *Ann. chim. phys.*, [3] 49 (1857), 50.

² This was as far toward the sulfuric end of the diagram as we considered it necessary to go. D'Ans found a univariant point with the solids NaHSO₄·H₂O and NaHSO₄ at about the same concentration at 25°, but at neither 12° nor 25° did we get any indication of the second salt at the concentrations given. The means we had of judging as to the solid present here was that a series of crystallizations carried out in this region all showed the very characteristic crystalline form of the hydrated salt. The solutions contained so much free sulfuric acid that the crystals could not be freed from it properly and analysis could not decide which salt was present. A salt very different in appearance, which was probably NaHSO₄, was obtained in more concentrated solutions but its identity was not determined.

The solubility relations are somewhat simpler at 12° than at 25°, for at the former temperature the anhydrous salt is no longer stable under any conditions, as D'Ans showed originally, and the decahydrate exists in equilibrium with the salt Na₂H(SO₄)₂ at the univariant point.

(2) SYSTEM, CuSO₄-H₂SO₄-H₂O

In this system no acid salt forms, but the presence of sulfuric acid dehydrates the pentahydrate in stages, yielding the trihydrate, monohydrate, and ultimately the anhydrous salt in strong sulfuric acid. A discussion of this behavior will be found in a previous article¹ from which the solubility results at 25° have been taken. Bell and Taber² have also determined the solubility of this system at 25°. Following are the results:

TEMPERATURE = 12°			
SOLID PHASES	Per cent H ₂ SO ₄	Per cent CuSO ₄	Corresponding Point in Diagram
CuSO ₄ ·5H ₂ O.....	None	16.19	D
		16.11	
CuSO ₄ ·5H ₂ O and CuSO ₄ ·3H ₂ O.....	51.63	1.67	E
	51.38	1.61	
CuSO ₄ ·3H ₂ O and CuSO ₄ ·H ₂ O.....	61.56	0.87	F
	61.52	0.75	
TEMPERATURE = 25°			
CuSO ₄ ·5H ₂ O.....	None	18.47	D
CuSO ₄ ·5H ₂ O and CuSO ₄ ·3H ₂ O.....	49.20	2.83	E
CuSO ₄ ·3H ₂ O and CuSO ₄ ·H ₂ O.....	55.72	2.13	F

¹ *J. Am. Chem. Soc.*, 37 (1915), 288.

² *J. Phys. Chem.*, 12 (1908), 171.

(3) SYSTEM, Na₂SO₄-CuSO₄-H₂O

This system has been investigated in some detail by Koppel¹ and his data are given below for 25°. A transition temperature in this system exists at 16.7°, below which only the single salts crystallize, while above it the double salt Na₂SO₄·CuSO₄·2H₂O forms. At 12°, therefore, there is but one univariant system and the two solids present consist of the single salts. At 25° there are two such systems. In one the solid phases consist of double salt and CuSO₄·5H₂O, and in the other, double salt and Na₂SO₄·10H₂O.

TEMPERATURE = 12°			
SOLID PHASES	Per cent Na ₂ SO ₄	Per cent CuSO ₄	Corresponding Point in Diagram
Na ₂ SO ₄ ·10H ₂ O.....	9.53	None	A
	9.54		
Na ₂ SO ₄ ·10H ₂ O and CuSO ₄ ·5H ₂ O.....	10.43	14.69	R
	10.44	14.51	
CuSO ₄ ·5H ₂ O.....	None	16.19	D
		16.11	
TEMPERATURE = 25°			
Na ₂ SO ₄ ·10H ₂ O.....	21.90	None	A
Na ₂ SO ₄ ·10H ₂ O and Na ₂ SO ₄ ·CuSO ₄ ·2H ₂ O.....	21.20	6.28	B
CuSO ₄ ·5H ₂ O and Na ₂ SO ₄ ·CuSO ₄ ·2H ₂ O.....	10.95	16.85	C
CuSO ₄ ·5H ₂ O.....	None	18.47 ¹	D

¹ *J. Am. Chem. Soc.*, 37 (1915), 288.

(4) SYSTEM, Na₂SO₄-CuSO₄-H₂SO₄-H₂O

The general method of obtaining the univariant points in the four-component system has already been mentioned. In most cases there was no special difficulty when once the univariant points in the ternary systems were found. For each univariant point in the latter, there was a corresponding point in the quaternary system, in which the solution was saturated with one more solid phase. For instance, starting with the ternary univariant system containing the solid phases CuSO₄·5H₂O and CuSO₄·3H₂O, a univariant point in the quaternary system could be reached by adding sodium sulfate. As this salt, however, would be converted into the double salt Na₂SO₄·CuSO₄·2H₂O before equilibrium was established, the latter was actually used in the solubility determinations. This double salt was the only one found and exists under a very wide range of conditions. It forms one of the phases in every univariant system containing the four components.

The relations in the system at 12° are unusual in one respect. As already mentioned, the two salts in water do not form a double salt at this temperature, but crystallize separately. With more than 7.4 per cent of sulfuric acid, the double salt forms, and at this concentration of acid there is a univariant system with the three solid phases, CuSO₄·5H₂O, Na₂SO₄·10H₂O, and double salt. The presence of the sulfuric acid causes the double salt to be stable below its transition temperature. The case is comparable with the simpler one of sodium sulfate, in which the anhydrous form may exist in contact with sulfuric acid solutions below its transition temperature into the decahydrate, but I am not aware of any similar case which has been observed with four components.

The solubility data for the univariant systems are given in the following table. The one divariant system included at each temperature shows the limiting value obtained on the curve at the sulfuric acid end.

¹ *Z. phys. Chem.*, 42 (1902), 1.