Samples of propanol were also distilled from lime as in A; 2-propanol was also distilled from metallic calcium; lime was avoided in the treatment of 1,1-dimethylethanol and pentanol.

Carbon tetrachloride and chloroform were stored over calcium chloride for several months, distilled after decantation, refluxed over "Drierite" and fractionated from fresh drierite through the three-meter column: CCl_4, b. p. 76.67°, $n^{25}D$ 1.45754; $CHCl_3$, b. p. (754.6) 60.91°, $n^{25}D$ 1.44345.

Benzene.—Commercial thiophene-free benzene was dried over sodium and fractionated from fresh sodium through the three-meter column: b. p. (760) 80.15°, $n^{25}D$ 1.49658.

Dioxane was stored over potassium hydroxide pellets for several weeks, distilled and dried over potassium carbonate, then decanted and distilled from sodium through the three-meter column: b. p. (760) 101.19°, $n^{25}D$ 1.4022.

Procedure was essentially the same as by Li and Stewart.[6] Solutions were prepared by adding weighed amounts of cyanohydrin and amine to the solvent in calibrated flasks, and diluting to volume after temperature equilibrium was reached. Aliquots were added to excess 0.02 N silver nitrate in 0.25 N nitric acid with vigorous mixing; silver cyanide was filtered off, washing with 0.25 N nitric acid, and the excess silver titrated with thiocyanate, using ferric alum indicator. Practice was required to obtain the correct end-point in some cases due to coagulation of the silver thiocyanate. In some cases the total cyanide content was determined as a check on the composition and procedure. Equilibrium in some cases was approached from solutions composed of weighed or analyzed amounts of acetone, hydrocyanic acid and amine, with good agreement. In rate determinations the amine was first added, then an approximate amount of cyanohydrin, and the latter at zero time obtained by analysis. End-points were accurate to 0.04 cc. and except for very low or very high degrees of dissociation the analyzed concentrations were reproducible to 0.2%. Values of K_I in some solvents could be reproduced to 1%, in others a 3% uncertainty exists.

If a and b are, respectively, the initial amine and cyanohydrin concentrations (moles/liter) and c the equilibrium concentration of titratable cyanide, then in the absence of amine (Equation I)

$$K_I = (c)^2/(b - c)$$

In water solution, in the presence of amine, Equation II is assumed, correcting for Eq. I.

$$K_{II} = \frac{c(c - K_I(b/c - 1))^2}{(a - c + K_I(b/c - 1))(b - c)}$$

Summary

The dissociation of acetone cyanohydrin into acetone and hydrocyanic acid is catalyzed by amines in all solvents; the catalyzed reaction is immeasurably rapid in water and the lower alcohols, measurable in butanol and non-polar solvents and extremely slow in dioxane. The degree of dissociation is increased by amines in water, is totally unaffected in nine different alcohols and in acetone by amine, and is decreased in carbon tetrachloride, benzene, chloroform and dioxane. These results are contrary to the findings of Li and Stewart. The pure solvents, or with a trace only of catalyst, affect the rates and equilibria of dissociation in a manner correlatable with their capacities to form hydrogen bond complexes and to act as proton sources. The simple Lapworth dissociation mechanism may be true only in water solutions. The heats of dissociation in four types of solvent vary from 8400 to 10,400 cal./mole. The results indicate that in alcohols hydrocyanic acid and amines do not react to a measurable extent.

BERKELEY, CALIFORNIA RECEIVED AUGUST 7, 1940

[CONTRIBUTION FROM THE RESEARCH DIVISION OF THE NEW JERSEY ZINC COMPANY (OF PA.)]

Studies of the Ternary Systems $ZnSO_4$–H_2SO_4–H_2O from −5 to 70° and ZnO–SO_3–H_2O at 25°

BY L. C. COPELAND[1] AND O. A. SHORT[1]

Introduction

The phase diagram for the ternary system zinc sulfate–sulfuric acid–water has been the subject of investigation of several authors. Most of the articles, however, have been limited to one or two temperatures and in general show poor agreement. The present paper is an effort to complete the data from −5 to 70° and to show the range of existence of the various hydrates of zinc sulfate. No data were obtained, however, above 60% sulfuric acid except in the case of a few measurements at 25°. Some data obtained for the basic range of the system zinc oxide–sulfur trioxide–water at 25° indicate the formula of basic zinc sulfate at this temperature.

Ternary System $ZnSO_4$–H_2SO_4–H_2O

Experimental Method.—Baker c. p. analyzed chemicals were used throughout the study with no additional puri-

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fication. At temperatures below 15° the samples were thermostated in a crock of water placed in an electric refrigerator, the temperature being controlled to ±0.1° by means of a mercury regulator, relay and heating unit.

TABLE I

TERNARY SYSTEM $ZnSO_4$–H_2SO_4–H_2O

Liquid phase, %		Wet solid phase, %		
$ZnSO_4$	H_2SO_4	$ZnSO_4$	H_2SO_4	
−4.5°C.				
28.8	0.2	..	..	$ZnSO_4 \cdot 7H_2O$
21.8	7.1	49.3	1.8	
18.8	11.3	50.0	2.0	
14.9	16.8	49.8	3.0	
11.1	22.6	49.0	3.8	
8.8	28.2	49.6	4.3	
7.7	34.6	43.6	9.3	
7.3	38.5	49.7	5.8	
8.1 ±0.4	38.9 ±0.3 (av. of 5)			$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot H_2O$
6.2	41.5	61.3	14.1	$ZnSO_4 \cdot H_2O$
3.9	45.1	62.0	14.7	
1.5	51.2	51.9	21.8	
0.9	54.6	53.3	22.4	
0.4	59.1	58.1	21.0	
6°C.				
30.6	0	..	..	$ZnSO_4 \cdot 7H_2O$
26.7	4.8	48.2	1.7	
22.9	9.1	48.2	2.3	
22.5	9.9	45.0	3.7	
17.3	17.8	45.3	5.2	
11.5	31.2	46.8	6.4	
11.6	32.3	43.5	9.5	
11.6	33.8	47.2	7.1	
11.7 ±0.0	34.5 ±0.1 (av. of 3)			$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot H_2O$
10.3	36.1	42.8	21.4	$ZnSO_4 \cdot H_2O$
8.5	38.2	46.4	20.5	
6.0	41.8	46.8	21.3	
1.9	50.2	48.3	23.8	
1.0	53.3	52.9	21.9	
0.2	65.1	..	..	
0.2	66.0	46.1	32.3	
15°C.				
33.5	0.1	..	..	$ZnSO_4 \cdot 7H_2O$
33.4	0.4	..	..	
29.7	4.2	51.8	1.0	
27.6	6.9	50.7	1.4	
21.0	16.7	50.4	2.8	
18.4	21.8	45.2	6.4	
18.1	23.8	48.1	5.2	
18.1	23.8	46.9	6.1	
17.6 ±0.2	28.0 ±0.2 (av. of 10)			$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot H_2O$
17.0	28.6	51.7	15.2	$ZnSO_4 \cdot H_2O$
16.1	29.6	68.6	8.7	
15.7	29.8	68.7	8.5	
15.0	30.5	53.0	14.8	
8.4	38.4	41.9	22.9	
4.6	43.5	51.3	19.7	
0.5	57.5	38.9	32.2	
25°C.				
36.8 ±0.1	0.1 ±0.1 (av. of 2)			$ZnSO_4 \cdot 7H_2O$
29.6	9.8	50.8	2.3	
26.4	16.4	50.0	3.9	
25.6	17.9	55.1	2.6	
25.6	18.2 (single sample)			$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot 6H_2O$
25.1	18.7	53.3	3.6	$ZnSO_4 \cdot 6H_2O$
24.3 ±0.3	20.5 ±0.3 (av. of 7)			$ZnSO_4 \cdot 6H_2O + ZnSO_4 \cdot H_2O$
22.4	22.3	50.4	13.1	$ZnSO_4 \cdot H_2O$
21.6	23.7	45.0	15.5	
20.0	24.9	30.0	21.0	
18.1	27.0	63.4	10.0	
17.6	27.3	47.3	16.7	
13.3	32.8	53.6	15.2	
2.3	49.5	54.1	20.1	
2.2	50.1	55.8	19.9	
0.7	57.9	39.8	33.0	
.9	62.1	45.8	31.2	
.8	68.1	41.2	36.8	
.6	70.8	49.1	32.6	
.8	74.0	44.5	37.8	
.4	74.4	42.4	40.1	
.7	78.2	46.5	38.9	
.1	82.7	38.4	47.4	
.2	87.0 (single value)			$ZnSO_4 \cdot H_2O + ZnSO_4$
.3	89.0	33.4	59.5	$ZnSO_4$
.2	91.8	34.8	59.2	
.1	94.6	28.2	68.8	$ZnSO_4 \cdot H_2SO_4$
.1	95.5	25.9	71.6	
.1	96.6	27.5	71.0	
35°C.				
39.5 ±0.1	0.2 ±0.1 (av. of 2)			$ZnSO_4 \cdot 7H_2O$
37.3	0.5	..	..	
37.0	3.4	53.0	0.8	
37.0	3.6	53.1	0.8	
36.1	4.9	52.8	1.2	
36.1	5.0	53.2	1.2	
36.1	5.2 (single value)			$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot 6H_2O$
35.7	5.9	55.9	1.2	$ZnSO_4 \cdot 6H_2O$
35.2	6.3	53.0	2.0	
35.3	6.4	54.1	2.0	
34.9	6.5	53.8	2.1	
35.1	6.7	56.3	1.3	
34.7	7.1	54.9	1.7	
33.4	8.6	51.7	2.9	
31.8	11.8	52.5	3.2	
30.4 ±0.1	14.1 ±0.1 (av. of 5)			$ZnSO_4 \cdot 6H_2O + ZnSO_4 \cdot H_2O$
29.4	14.7	56.5	8.2	$ZnSO_4 \cdot H_2O$
28.3	16.0	55.4	8.9	
22.6	22.0	59.4	9.9	
19.1	25.6	51.2	14.1	
14.8	30.6	68.0	9.1	
7.5	39.8	63.7	13.0	
5.8	42.4	65.0	12.7	
2.1	50.1	66.2	13.7	
0.4	60.8	59.8	20.4	
45°C.				
42.0	0.4	55.7	0.6	$ZnSO_4 \cdot 6H_2O$
42.1	0.5	..	..	
40.1	2.4	55.1	1.1	
39.4	3.6	..	..	
39.4	3.8	56.5	1.0	
38.6	4.8	58.3	2.1	
37.5 ±0.4	6.3 ±0.9 (av. of 15)			$ZnSO_4 \cdot 6H_2O + ZnSO_4 \cdot H_2O$
36.4	7.7	60.6	3.3	$ZnSO_4 \cdot H_2O$
36.2	8.5	53.4	3.0	
36.0	8.8	53.7	2.8	
35.8	8.9	57.0	3.3	
34.9	9.3	61.1	4.6	
32.7	10.2	46.2	8.0	
33.9	10.3	64.5	5.2	
32.9	10.7	59.3	5.8	
30.9	12.1	57.6	6.8	
29.7	14.0	57.6	8.0	
29.2	14.4	57.5	8.0	
27.2	16.7	52.3	10.4	
23.5	20.6	54.0	11.3	
23.2	20.8	50.1	12.8	
18.5	26.0	49.2	14.9	
15.4	29.6	48.2	17.0	
6.2	41.8	40.6	24.6	
2.8	48.8	41.4	27.4	
0.8	56.6	43.8	29.3	
0.9	63.9	38.5	36.9	
55°C.				
43.5	0.4	56.3	0.5	$ZnSO_4 \cdot 6H_2O$
43.5	.5	55.2	0.5	
44.1	.5	..	..	
42.1 ±0.2	.8 ±0.1 (av. of 2)			$ZnSO_4 \cdot 6H_2O + ZnSO_4 \cdot H_2O$
41.8	1.8	65.7	0.9	$ZnSO_4 \cdot H_2O$
40.0	3.1	..	..	
39.0	4.6	..	..	
36.5	6.7	..	..	
30.9	11.9	..	..	
21.7	21.4	..	..	
20.8	23.3	54.1	12.5	
12.3	33.6	74.6	7.1	
3.9	46.0	72.3	10.0	
1.1	55.8	71.0	12.4	
0.4	67.9	62.3	21.3	
65°C.				
42.3	0.4	..	..	$ZnSO_4 \cdot H_2O$
42.3	.4	68.2	0.3	
41.8	.4	69.0	.5	
41.6	.4	56.0	.9	
42.3	.5	..	..	
41.6	.7	72.4	.7	
41.2	1.0	70.3	.9	
38.2	3.4	..	..	
36.9	4.8	..	..	
35.6	5.8	70.4	2.8	
34.9	6.2	74.2	2.3	
34.2	7.1	..	..	
33.9	7.1	..	..	
34.3	7.6	..	..	
29.2	12.7	..	..	
27.9	13.4	..	..	
20.9	22.2	..	..	
15.4	29.2	67.8	9.4	
12.5	32.8	..	..	
3.4	48.1	73.3	9.9	
0.7	58.6	..	..	
0.9	59.4	57.8	21.9	
70°C.				
41.1	0.3	..	..	$ZnSO_4 \cdot H_2O$
41.0	0.3	77.9	0	
37.2	3.3	..	..	
36.5	4.9	..	..	
33.5	6.8	..	..	
33.4	7.6	..	..	
27.5	14.5	..	..	
20.7	22.2	..	..	
15.9	29.0	66.9	9.0	
7.4	41.4	63.3	13.3	
1.9	54.4	63.8	16.3	

Between 15 and 45° a water thermostat controlled to ±0.05° was used. Above 45° the samples were air thermostated to ±0.5° in an oven provided with a mechanical rotator.

Samples were prepared in 250-cc. ground glass stoppered bottles from $ZnSO_4 \cdot 7H_2O$ crystals, concentrated sulfuric acid and water so that they fell in the appropriate concentration range, allowed to equilibrate in one of the thermostats for from one to four weeks with frequent manual shaking except for those samples above 45° which were agitated mechanically. Some investigators have claimed that this system comes to equilibrium in the course of a few hours, but many of our samples changed visibly over a period of three to four days. At least a week was allowed for equilibration after all apparent change had stopped. In order to be reasonably certain that equilibrium had been obtained, half of the samples in each group were allowed to approach the curve from a supersaturated condition and the other half from an unsaturated condition. If the resulting points fell on a smooth curve, equilibrium was assumed.

Analysis samples were taken from all mixtures below 50° by pipetting about 20 cc. into a weighing bottle. Above 50° the analysis samples were drawn into the weighing bottles through glass tubes that had been warmed to the thermostat temperature. Solid phase samples were obtained by filtering as rapidly as possible on a sintered glass plate and transferring immediately with a hard rubber spatula to weighing bottles.

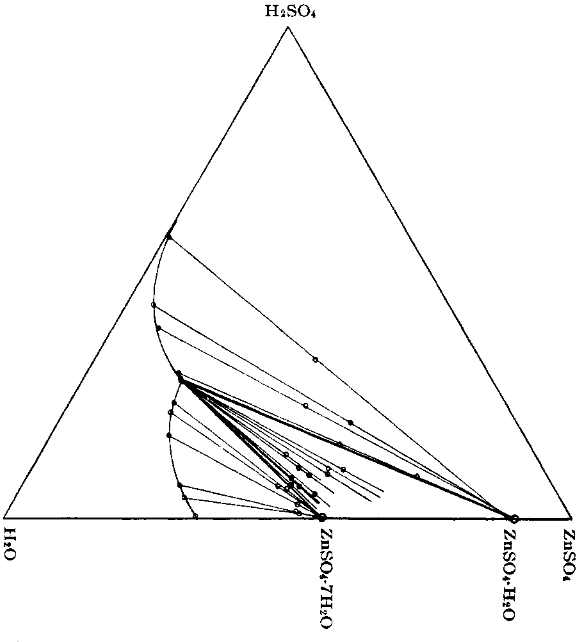

Fig. 1.—Ternary system of $ZnSO_4$-H_2SO_4-H_2O at 15°.

The analysis samples were weighed, diluted to 500 cc. and analyzed for zinc and sulfate. The ferrocyanide titration with ferrous sulfate as internal indicator was used for the zinc analysis and the gravimetric barium sulfate method was used for the sulfate analysis. All samples were analyzed in duplicate and analyses accepted only if the duplicates agreed to within two parts per 1000. However, either due to lack of attaining complete equilibrium or sampling error duplicate mixtures of the same concentration agree to within only two to three parts per 100.

Results.—Table I shows the per cent. zinc sulfate and sulfuric acid in the liquid and wet solids as calculated from these analyses. The composition of the solid phase also is shown. The presence of two solid phases in the sample bottles could be observed visually in most cases,

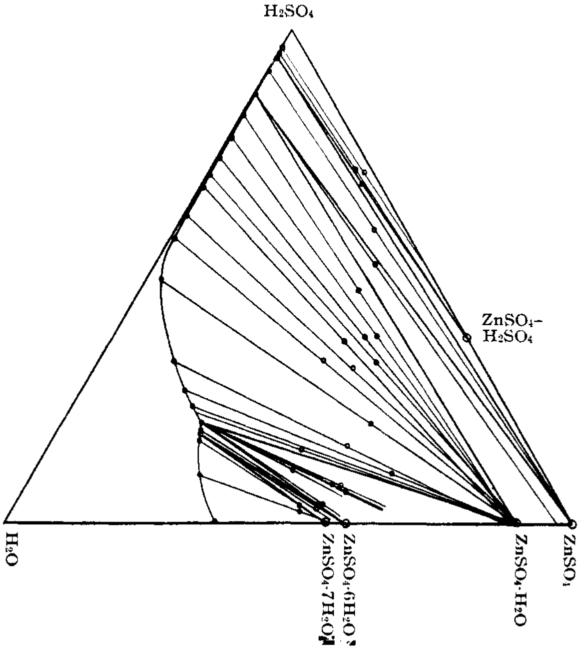

Fig. 2.—Ternary system of $ZnSO_4$-H_2SO_4-H_2O at 25°.

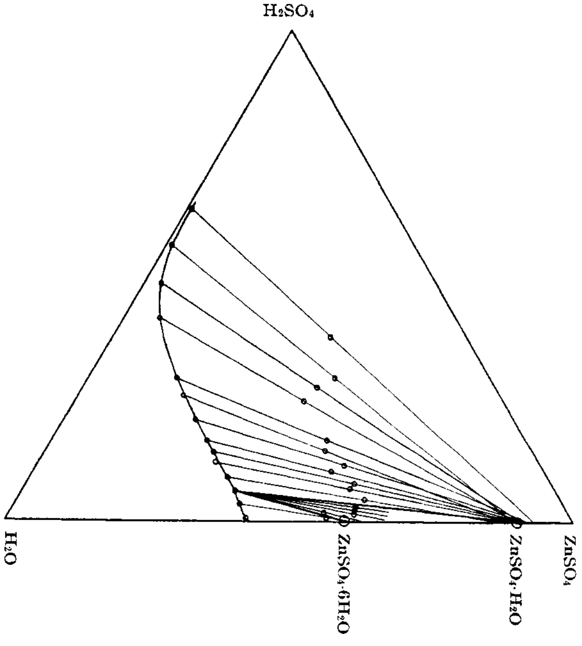

Fig. 3.—Ternary system of $ZnSO_4$-H_2SO_4-H_2O at 45°.

although some difficulty was encountered in distinguishing between $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$. This visual observation was, however, an excellent check on tie line extrapolation. Figures 1, 2, and 3 show typical ternary plots of these data, and Figure 4 is a diagram of a three-dimensional model showing the relations of the system $ZnSO_4$–H_2SO_4–H_2O from −4.5 to 65° and 0–60% sulfuric acid where per cent. water, sulfuric acid and zinc sulfate are plotted along the triagonal altitudes and temperature along the prism axis. Figure 5 is a rectangular projection of this model on 0% sulfuric acid face showing constant % sulfuric acid contours. This latter plot shows the solubility curve for zinc sulfate in water as a function of temperature and shows the difference between the data presented here and found in the "International Critical Tables" and the "Landolt-Börnstein" Tables. Extrapolation of four-phase boundaries on this figure shows that at 21° and 21.5% zinc sulfate and 23.5% sulfuric acid a quintuple point exists where $ZnSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot H_2O$ are in equilibrium with saturated zinc sulfate solution and vapor. Similar extrapolations show that at 39° and 41.2% zinc sulfate an isothermally invariant solution $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$ exists in pure water and at 60° and 44.5 per cent. zinc sulfate the hydrates $ZnSO_4 \cdot 6H_2O$ and $ZnSO_4 \cdot H_2O$ are in equilibrium in pure water.

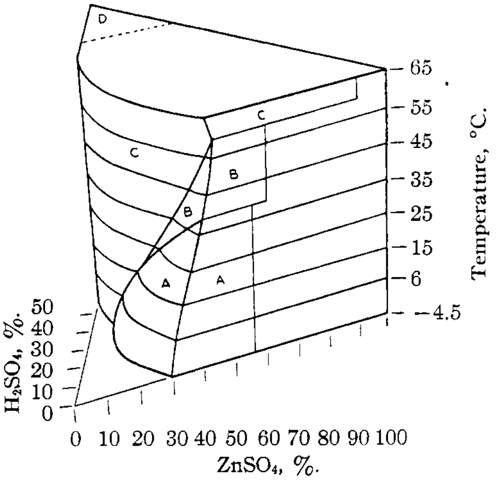

Fig. 4.—The system $ZnSO_4$–H_2SO_4–H_2O from −4.5 to 65°, three-dimensional model; three-phase systems: (A) $ZnSO_4 \cdot 7H_2O$ + solution + vapor, (B) $ZnSO_4 \cdot 6H_2O$ + solution + vapor, (C) $ZnSO_4 \cdot H_2O$ + solution + vapor; unexplored region (D) greater than 60% H_2SO_4.

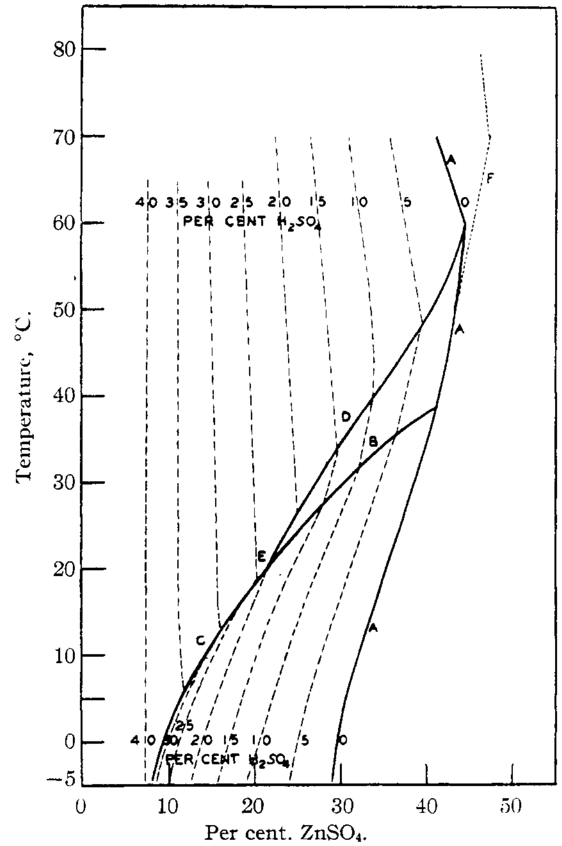

Fig. 5.—Per cent. $ZnSO_4$ *vs.* *T*, °C. at various concentrations of H_2SO_4, constant per cent. H_2SO_4 contours: A, solubility of $ZnSO_4$ in H_2O; B, $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O$; C, $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot H_2O + 6H_2O$; D, $ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5H_2O$; E, $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O = ZnSO_4 \cdot H_2O + 6H_2O$; F, Landolt-Börnstein and "International Critical Tables," solubility of $ZnSO_4$.

At 25° (Fig. 2) some data have been obtained at sulfuric acid concentrations greater than 60%.[2] These data show that at this temperature the anhydrous form of zinc sulfate exists between 87 and 95% sulfuric acid. Above 95% another compound, distinguished from zinc sulfate by X-ray examination of the wet solid, exists. Two tie lines of doubtful accuracy shown on the plot indicate this compound to be $ZnSO_4 \cdot H_2SO_4$.

Decomposition Pressure of Zinc Sulfate Hydrates

Experimental Method.—In order to check the existence of the quintuple point at 21° and the isothermal invariant in pure water at 39° the vapor pressure of saturated water solutions of $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$ and the decomposition pressures of dry hepta- and hexahydrates were measured by the usual static method, tem-

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(2) The authors are indebted to Mr. J. O. Evans, formerly of this organization, for the high acid region of the 25° plot.

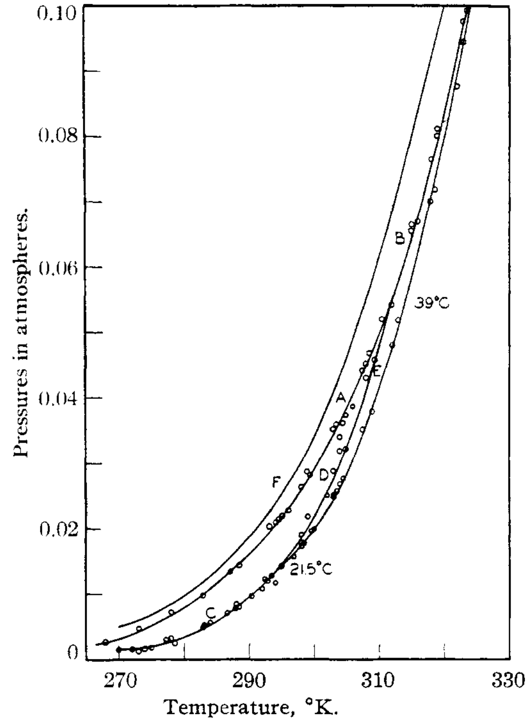

Fig. 6.—Decomposition pressure of zinc sulfate hydrates and vapor pressure of saturated zinc sulfate solutions: A, vapor pressure of solution saturated with $ZnSO_4 \cdot 7H_2O$; B, vapor pressure of solution saturated with $ZnSO_4 \cdot 6H_2O$; C, decomposition pressure $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot H_2O + 6H_2O$; D, decomposition pressure $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O$; E, decomposition pressure $ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5H_2O$; F, vapor pressure of H_2O.

peratures being controlled manually to ±0.2°. Measurements were made only after allowing one-half hour for equilibration after the desired temperature had been reached and equilibrium at each point was approached at any particular temperature by making the measurements at both ascending and descending temperatures.

Results.—Figures 6 and 7 show the data obtained from this study. Figure 6 is a plot of pressure in atmospheres *versus* absolute temperature and shows that at 21.5° the three systems:

$$ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot H_2O + 6H_2O$$
$$ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O$$
$$ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5H_2O$$

all have the same decomposition pressure and at 39° the decomposition pressure of the system

$$ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O$$

is equal to the vapor pressure of saturated solutions of the two hydrates. These data are in excellent agreement with those obtained from ternary systems.

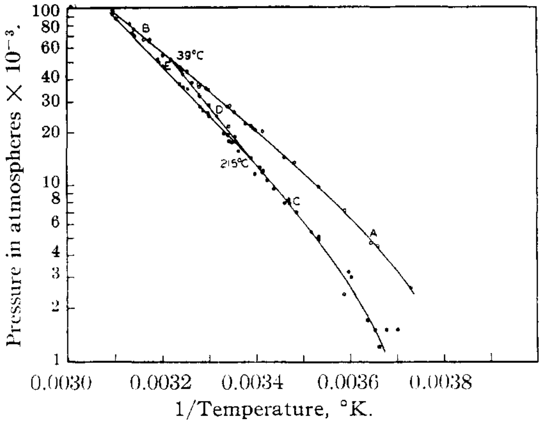

Fig. 7.—Decomposition pressures of zinc sulfate hydrates plotted log P *vs.* $1/T$°K.: A, vapor pressure of solution saturated with $ZnSO_4 \cdot 7H_2O$; B, vapor pressure of solution saturated with $ZnSO_4 \cdot 6H_2O$; C, decomposition pressure $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot H_2O + 6H_2O$; D, decomposition pressure $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O$; E, decomposition pressure $ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5H_2O$.

Heats of reaction were calculated from the slopes of the curve log P *versus* $1/T$°K. and compared with the data from Bichowsky and Rossini's[3] "Thermochemistry of Chemical Substances."

(1) $ZnSO_4 \cdot 6H_2O = ZnSO_4 \cdot H_2O + 5H_2O$ 21.5 to 39° $\Delta H = 66{,}000$ cal.
Bichowsky and Rossini $\Delta H = 63{,}700$
(2) $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot 6H_2O + H_2O$ 21.5 to 50° $\Delta H = 15{,}000$ cal.
Bichowsky and Rossini $\Delta H = 14{,}000$
(3) $ZnSO_4 \cdot 7H_2O = ZnSO_4 \cdot H_2O + 6H_2O$ 12 to 21.5° $\Delta H = 89{,}000$ cal.
Heat of vaporization of solution saturated with $ZnSO_4 \cdot 7H_2O$, 20 to 39° $\Delta H = 10{,}000$ cal.
Heat of vaporization of solution saturated with $ZnSO_4 \cdot 6H_2O$, 39 to 50° $\Delta H = 10{,}000$ cal.

The value of ΔH for equation (3) should equal the sum of that for one and two at 21.5°. However, curve C has a definite curvature even over the narrow temperature limit shown, the slope at 21.5° not being far different from the slope of a line calculated from a ΔH value of 81,000 calories.

Ternary System ZnO–SO_3–H_2O at 25°

Experimental Method.—Mixtures for the basic region of this system were prepared by boiling zinc sulfate solutions of various concentrations with U. S. P. zinc oxide, filtering hot to remove

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[3] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Company, New York, N. Y., 1936, pp. 65, 20.

the undissolved zinc oxide and cooling to 25°. The solid which separated out and a part of the liquid were equilibrated at 25° for about four weeks before analysis samples were removed.

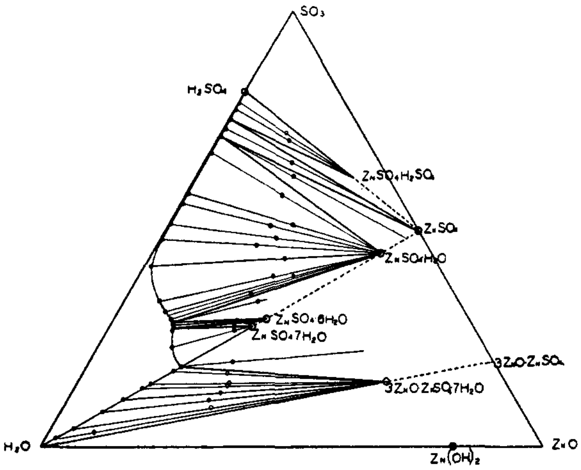

Fig. 8.—Ternary system of $ZnO-SO_3-H_2O$ at 25°.

Results.—Table II shows the data obtained for the basic range of this system and Fig. 8 is a trilinear plot of the data and that of Fig. 2 calculated to the plot for $ZnO-SO_3-H_2O$ at 25°. Tie line extrapolation on this diagram shows that from 2% sulfur trioxide to the point representing the saturated solution of zinc sulfate the solid phase is $3ZnO \cdot ZnSO_4 \cdot 7H_2O$ or $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$, the solubility of this compound being less than the experimental error of analysis over the entire range of zinc sulfate compositions at 25°.

Table II

Ternary System $ZnO-SO_3-H_2O$ at 25° Basic Range

Liquid phase, %		Wet solids, %		
ZnO	SO_3	ZnO	SO_3	
1.8	1.9	9.1	3.5	$3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$
4.4	4.4	29.4	9.1	
8.1	8.0	28.2	10.8	
10.7	10.7	29.8	12.4	
13.6	13.6	30.3	14.0	
14.5	14.5	30.3	14.6	
17.6	17.6	29.0	17.0	
18.3	18.3	(single sample)		$3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$ + $ZnSO_4 \cdot 7H_2O$

At lower zinc sulfate concentrations the solid phase is probably $Zn(OH)_2$ or ZnO. This region, however, is below 2% zinc sulfate and probably below the experimental error of zinc and sulfate analysis so that tie line extrapolation to zinc hydroxide would be meaningless.

The degree of hydration of basic zinc sulfate has been checked in the following manner. It has been found that this compound can be washed completely free of zinc sulfate solution without hydrolysis taking place if no more than fifteen minutes are required for the washing. A sample of this washed material dried at 100° loses four molecules of water (which indicates that the second formula given above is the correct one). A sample of this dried material and one still wet with the wash water were placed in a desiccator over a saturated zinc sulfate solution and allowed to equilibrate for three months. At the end of this time analysis for zinc and sulfate on the two samples showed them to be

$$3Zn(OH)_2 \cdot ZnSO_4 \cdot 4.4H_2O$$
$$3Zn(OH)_2 \cdot ZnSO_4 \cdot 3.8H_2O$$

for the samples starting with excess and deficient water, respectively.

Discussion

The data presented in Table I and shown on Fig. 5 for the solubility of zinc sulfate in pure water are in fair agreement with the work of Bury[4] and of Cohen and Hetterschij[5] between 0 and 55°. At 25° the present paper shows the solubility to be 36.8% ± 0.1 at 0.1 ± 0.1% sulfuric acid. Cohen and Hetterschij give 36.5%, Caven and Gardner[6] 36.6, Hill and Taylor[7] 36.7 and Bury 38.8. The isothermally invariant point where the hexa- and heptahydrates are in equilibrium was found to be 39° in this paper. Cohen and Hetterschij found 38.1°, the curve presented by Bury reads approximately 38°, Agde and Schimmel[8] give 39.1° and the value given in the "International Critical Tables" is 39°. Above 60° the data presented here do not agree with those found in the "Landolt-Börnstein" tables. They show an isothermal invariant point between the hexa- and monohydrates at 70° whereas Fig. 6 shows it to be 60°. Agde and Schimmel studied the region of $ZnSO_4 \cdot 7H_2O$ in sulfuric acid solutions from −10 to 30° and their data are in close agreement with those presented here except for their indication of the equilibrium between the hexa- and heptahydrates at 25.4% sulfuric acid and 18.2° which is below the quintuple point of Fig. 6. However, there is no proof given in their paper that their equilibrium is not

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[4] Bury, *J. Chem. Soc.*, Part 2V, **125**, 2538 (1924).

[5] Cohen and Hetterschij, *Z. physik. Chem.*, **115**, 440 (1925).

[6] Caven and Gardner, *J. Chem. Soc.*, 943 (1933).

[7] Hill and Taylor, This Journal, **60**, 1099 (1938).

[8] Agde and Schimmel, *Z. angew. Chem.*, **41**, 340 (1928)

between the hexa- and monohydrates at this point. Röntgen and Högel[9] showed that at 15° only two solid phases exist. Their solubility curve is, however, not in agreement with the data of this paper or those of Agde and Schimmel. Montemartini[10] indicates that at 12.5° three single-solid phase regions exist, hepta-, hexa- and dihydrate. We have obtained no indication in any of our work of zinc sulfate dihydrate. Joshi and Devadatta[11] obtained plots for the system $ZnSO_4-H_2SO_4-H_2O$ at 30 and 45° showing areas for the hepta-, hexa- and monohydrates at the lower temperature and for the hexa- and monohydrates only at the higher one. Their solubility curves and transition point locations, however, are not in agreement with those presented here.

Dissociation pressure measurements of zinc sulfate hydrates have been made by a dynamic method by Schumb[12] and by Bonnel and Burridge[13] who have both obtained results slightly higher than those obtained here by static methods. The data found in the "International Critical Tables" are in agreement with those shown in Fig. 6 over certain ranges but are not sufficiently consistent to allow the desired verification of the points of the ternary system.

More than twelve basic zinc sulfates have been reported in the literature but it is generally believed that the only true compounds except in extremely dilute zinc sulfate solutions are hydrates of the compound $3ZnO\cdot ZnSO_4$. Feitknecht[14] claims that the compound in equilibrium with strong zinc sulfate solutions is $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$ and if this compound be dried at 100° $3Zn(OH)_2\cdot ZnSO_4$ is obtained. This is in agreement with the observations presented here. Other authors[15,16] have claimed that basic zinc sulfate prepared in a manner similar to that employed in this study contains 6 or 8 molecules of water. We believe that our tie line extrapolation and equilibrium study definitely establish this compound to be $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$.

Summary

1. The system $ZnSO_4-H_2SO_4-H_2O$ was investigated by the usual methods over the temperature range −5 to 70° and 0 to 60% sulfuric acid.

2. A drawing of a three-dimensional model of this system and three trilinear plots showing typical isotherms are presented.

3. A projection of the model on the 0% sulfuric acid face shows the solubility curve for zinc sulfate in water and the variation of the four-phase systems (two solid phases, liquid and vapor) with temperature.

4. Isothermal invariant points in pure water were found to be: $ZnSO_4\cdot 7H_2O = ZnSO_4\cdot 6H_2O + H_2O$ at 39° and $ZnSO_4\cdot 6H_2O = ZnSO_4\cdot H_2O + 6H_2O$ at 60°. At 21° a quintuple point was found where hepta-, hexa- and monohydrate exist in contact with vapor and a solution containing 23.5% sulfuric acid and 21.5% zinc sulfate.

5. The points at 21 and 39° were substantiated by vapor pressure and decomposition pressure measurements.

6. At 25° the study was continued to 97% sulfuric acid showing the existence of anhydrous zinc sulfate and the possible existence of $ZnSO_4\cdot H_2SO_4$.

7. Some data also were obtained in the basic range of the system $ZnO-SO_3-H_2O$ at 25° which show that in equilibrium with zinc sulfate solutions the solid phase is basic zinc sulfate having the formula $3Zn(OH)_2\cdot ZnSO_4\cdot 4H_2O$.

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(9) Röntgen and Högel, *Metall u. Erz*, **25**, 295 (1928).

(10) Montemartini, *Industria Chim.*, Feb., 1929, p. 107.

(11) Joshi and Devadatta, *Proc. Ind. Chem. Soc.*, 130 (1938).

(12) Schumb, THIS JOURNAL, **45**, 342 (1923).

(13) Bonnel and Burridge, *Trans. Faraday Soc.*, **31**, 473 (1935).

(14) Feitknecht, *Helv. Chim. Acta*, **13**, 22 (1930).

(15) Fredman, *J. Applied Chem.* (*U. S. S. R.*), **8**, 227 (1935).

(16) Kraut, *Z. Anorg. Chem.*, **13**, 1 (1897).