

Summary

1. The partial vapor pressures of aqueous solutions of mono-, di- and trimethylamine have been determined over a range of concentration from approximately 0.2 to 2.5 *M*.

2. The vapor pressures and the densities of

liquid trimethylamine have been determined over a temperature range from -20 to +45°.

3. Certain free energy values and other derived quantities have been calculated from the data of the investigation.

AUSTIN, TEXAS

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[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The System Magnesium Sulfate-Urea-Water at 30°

BY COLIN W. WHITTAKER, FRANK O. LUNDSTROM AND JAMES H. SHIMP

Urea and magnesium sulfate are now common constituents of mixed fertilizers. The urea is introduced as a source of nitrogen either in the form of crystal urea or as a solution of urea in ammonia. Magnesium sulfate is an impurity in much of the crude potash imported for fertilizer use and is, therefore, often included in mixtures incidentally. The recent emphasis on the importance of the lesser elements in fertilizer practice has, however, resulted in the occasional use of magnesium intentionally as calcined kieserite or as crude potassium magnesium sulfate or in other forms. Dolomite has been found superior to calcite in some types of mixed fertilizers, and magnesium is now being introduced into mixtures quite extensively in that form. It is possible also for magnesium sulfate to be formed *in situ* by chemical reactions occurring in the mixture. It has recently been found that magnesium phosphate is formed from dolomite under certain conditions¹ and it is not unlikely that this compound would react with the calcium sulfate present in most mixed fertilizers to form magnesium sulfate and one of the calcium phosphates. In view of these considerations, a knowledge of the equilibria in the system magnesium sulfate-urea-water is an aid in understanding the chemistry of mixed fertilizers. The present paper presents data establishing the 30° isotherm in this system.

Experimental

Materials.—Urea was recrystallized from water. In order to avoid any possibility of hydrolysis the temperature of the solution was always kept below 60°. The magnesium sulfate was also recrystallized from water under such conditions that the heptahydrate was obtained. Both compounds were dried *in vacuo* over sulfuric acid, the urea

completely and the heptahydrate sufficiently to permit approximation of the amounts taken.

Methods of Analysis.—Urea was determined by the modified urease procedure recently described by Yee and Davis² except that 0.025 *N* sodium hydroxide was used to improve the accuracy of titration. Carefully calibrated burets were used. All pipets and other volumetric glassware used bore the official Bureau of Standards stamp. The urease enzyme has been reported to be sensitive to various salts and the effect of added magnesium sulfate was, therefore, determined. It was found, using about 0.15 g. of urease and digesting for twenty-five to thirty minutes, that amounts of magnesium sulfate several times greater than the urea present did not interfere. Tests of the method on the recrystallized urea described gave results ranging from 99.6 to 99.8% urea. These slightly low values are in agreement with those obtained by Yee and Davis and by Dalman,³ who used the Fox and Geldard⁴ modification of the urease procedure. Yee and Davis attribute the slightly low results to impurities in the urea rather than inaccuracy of the method, an opinion in which the writers concur.

Magnesium was weighed as magnesium hydroxyquinolate. If the solution contained urea, the aliquot was evaporated to dryness, the urea destroyed by digestion to dryness with aqua regia and the magnesium sulfate taken up with water. This preliminary destruction of urea was decided upon after experiments had shown that urea interfered slightly when determining high concentrations of magnesium sulfate. All precipitations of magnesium as the quinolate were made in the presence of ammonium acetate by adding sufficient ammonium hydroxide to give a pH of at least 9.5 to the solution containing 8-hydroxyquinoline and previously heated to 60–70°. The solution was filtered on a tared fritted glass filter (10G3), the precipitate washed with 1:40 ammonium hydroxide and dried to constant weight at 135°. The procedure was tested by analyzing a pure magnesium sulfate solution by the procedure just described and by evaporating an aliquot to dryness, adding a little sulfuric acid and heating to constant weight at 450°. Satisfactory agreement was obtained.

(2) J. Y. Yee and R. O. E. Davis, *ibid.*, **27**, 259–261 (1935).

(3) L. H. Dalman, *THIS JOURNAL*, **56**, 549–553 (1934).

(4) E. J. Fox and W. J. Geldard, *Ind. Eng. Chem.*, **15**, 743–745 (1923).

(1) W. H. MacIntire and W. M. Shaw, *Ind. Eng. Chem.*, **24**, 1401–1409 (1932).

Perhaps the best check on both analytical methods is the good agreement obtained for the solubilities of urea and of magnesium sulfate with those reported in the literature as described below.

Preparation of Equilibrium Solutions.—The systems to be studied were prepared by mixing amounts of the three components sufficient to give convenient quantities of solution and of solid phase after establishing equilibrium conditions. The components were taken in such proportions that the composition of the resulting saturated solutions fell in the desired portion of the curve. Usually each solution was used for determining two to four points on the isotherm, additional magnesium sulfate heptahydrate or urea being added after each determination in order to adjust the composition in the desired direction. It was, of course, necessary to consider the water of crystallization when adding $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

All mixtures were stirred in glass containers in a thermostat, the temperature of which was constant to $\pm 0.01^\circ$ and was exactly 30° , as closely as it could be read on a Bureau of Standards calibrated thermometer graduated to 0.1° . The stirrers were motor driven and operated through mercury seals to keep out dust and laboratory fumes. In most cases the mixtures were stirred for three to five hours, allowed to stand overnight, stirred another two to three hours and sampled after being allowed to settle. That equilibrium was obtained is indicated by the following. Two solutions analyzed after stirring for three to five hours and standing overnight showed no significant change in composition on an additional three to five hours of stirring and again standing overnight. Some of these solutions were so viscous that settling was extremely slow. Over part of the urea branch of the curve the solid phase floated on top. Suitable precautions were taken to prevent contamination of the liquid samples with the solid phase.

Solubility of Magnesium Sulfate and of Urea

As a check on the entire procedure the solubilities of magnesium sulfate and of urea at 30° were determined. The solubility of magnesium sulfate was found to be 28.42% by weight (average of four determinations). This is higher than the value of 28.05 obtained by interpolation between the values for 29.89 and 34.72° obtained by Ting and McCabe⁶ but agrees well with the value of 28.43% (3.30 moles per 1000 g. water) given by the "International Critical Tables."⁶

The solubility of urea at 30° was found to be 57.0% (average of three determinations). The best value to take from the literature is somewhat of a problem. By plotting $\log N$ (mole fraction of urea) against $1000/T$, using what Shnidman and Sunier⁷ term their best data, the value of 57.08 was obtained. Similar plotting of the data of Dalman⁸ gave the value of 57.15%. Pinck and Kelly⁹ report a higher value of 57.63%, while graphical interpolation

(5) Hsü Huai Ting and Warren L. McCabe, *Ind. Eng. Chem.*, **26**, 1207-1208 (1934).

(6) "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, New York, 1928, p. 228.

(7) L. Shnidman and A. A. Sunier, *J. Phys. Chem.*, **36**, 1232 (1932).

(8) L. H. Dalman, *THIS JOURNAL*, **56**, 549-553 (1934).

(9) L. A. Pinck and M. Kelly, *ibid.*, **47**, 2170 (1925).

of the data of Speyers¹⁰ and of the "International Critical Tables"¹¹ yields the lower figure of 56.59%.

These results for magnesium sulfate and urea having indicated that the technique in general was satisfactory, the 30° isotherm of the system was studied. The identification of solid phases was accomplished in the usual way by analysis of the wet solid phase and the use of extrapolated tie lines.

Discussion

The results are shown in Table I and are plotted in Fig. 1. The curve shows three branches, corresponding to the stable solid phases $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$, and $\text{CO}(\text{NH}_2)_2$.

TABLE I

EQUILIBRIA IN THE SYSTEM MAGNESIUM SULFATE-UREA-WATER AT 30°

Composition of satd. soln.		Composition of wet solid		Stable solid phase
MgSO_4 Wt., %	$\text{CO}(\text{NH}_2)_2$ Wt., %	MgSO_4 Wt., %	$\text{CO}(\text{NH}_2)_2$ Wt., %	
28.42 ^a	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.16	4.13	42.33	1.41	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.00	11.15	41.28	4.56	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.17	12.23	39.19	6.20	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.08	19.42	39.23	9.74	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.44	20.52	38.50	20.00	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ + $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.20	21.18	38.20	18.52	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ + $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
28.19	22.84	36.92	23.84	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
25.96	27.36	36.19	26.82	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
25.39	29.19	34.07	27.59	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
25.16	32.57	35.57	29.53	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
23.84	36.66	36.64	30.74	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
22.71	38.54	30.23	35.10	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
21.75	43.00	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
21.64	43.40	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
21.14	46.04	31.96	38.98	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
20.82	48.88	32.03	40.35	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
20.81	49.16	30.74	41.82	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
20.79	50.35	28.97	44.38	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
21.01	53.02	24.84	56.86	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ + $\text{CO}(\text{NH}_2)_2$
20.91	53.17	16.48	64.48	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ + $\text{CO}(\text{NH}_2)_2$
21.08	53.39	12.83	69.67	$\text{CO}(\text{NH}_2)_2$
17.63	52.15	11.42	69.02	$\text{CO}(\text{NH}_2)_2$
14.18	52.93	10.07	65.33	$\text{CO}(\text{NH}_2)_2$
9.21	54.79	5.86	70.79	$\text{CO}(\text{NH}_2)_2$
4.47	55.42	2.85	71.37	$\text{CO}(\text{NH}_2)_2$
...	57.00 ^b	$\text{CO}(\text{NH}_2)_2$
Most Probable Values at Invariant Points				
28.32	20.80	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ + $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$
20.96	53.09	$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ + $\text{CO}(\text{NH}_2)_2$

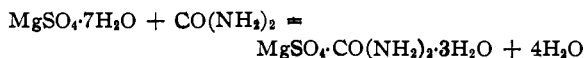
^a Average of four determinations. ^b Average of three determinations.

(10) C. L. Speyers, *Am. J. Sci.*, IV, **14**, 263-302 (1902).

(11) "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, New York, 1928, p. 251.

The tie lines do not all pass exactly through the points corresponding to the composition of the three solid phases mentioned, but it must be considered that the analytical errors become greatly magnified as the tie lines are extended. No evidence of the existence of solid phases other than the three mentioned was obtained. So far as the writers are aware, the compound $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ has not been reported previously.

A curious feature of this isotherm is the practically unchanged solubility of magnesium sulfate over a wide range of urea concentration (0-21%). Mixtures of solid urea and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, of such composition that the resulting equilibrium solution falls in the range represented by the middle branch of the isotherm, at first go completely or almost completely into solution, but on continued stirring the reaction



takes place quite rapidly and is probably complete in an hour or so after it starts. The crystals of the complex so obtained are very small. Attempts to prepare large crystals for detailed examination have, so far, been unsuccessful.

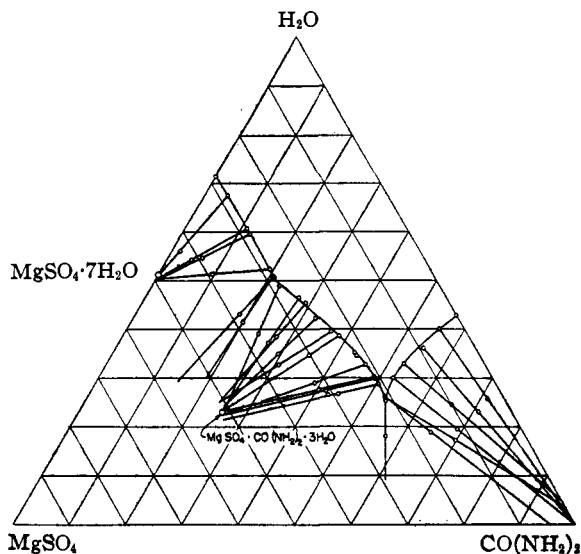


Fig. 1.—The system magnesium sulfate-urea- H_2O at 30° .

Summary

Data were obtained establishing the 30° isotherm of the system magnesium sulfate-urea-water. It was found to consist of three branches corresponding to the solid phases $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$.

WASHINGTON, D. C.

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Optical Crystallographic Data for Some Salts of the Cinchona Alkaloids

BY MARY LOUISE SHANER AND M. L. WILLARD

Introduction

Very few data on the optical properties of the salts of quinine, quinidine, cinchonidine and cinchonine can be found in the literature. Groth,¹ Poe and Swisher,² Wright,³ and Wherry and Yanovsky⁴ have listed some optical properties of these four alkaloids. However, the information is very scant.

Many salts of quinine were available, while just a few of quinidine, cinchonidine and cinchonine could be obtained. All salts were of commercial origin.

Optical Crystallographic Data

The optical properties, given in the table, were

- (1) Groth, "Chemische Kristallographie," 1908-1919.
- (2) Poe and Swisher, *THIS JOURNAL*, **57**, 748 (1935).
- (3) Wright, *ibid.*, **38**, 1647 (1916).
- (4) Wherry and Yanovsky, *ibid.*, **40**, 1063 (1918).

determined by methods given by Chamot and Mason.⁵ Refractive indices were determined by the Becke line method. In several cases it was impossible to determine the indices because the crystals dissolved in the immersion oils. The quartz wedge and selenite plate were used in various determinations.

The fluorescence of the salt and its aqueous solution were determined by means of an ultraviolet lamp.

All crystals were found to be biaxial and to give parallel extinction, except in the case of quinine bihydrochloride carbamate and quinine tetrasulfate where oblique extinction was obtained. The sign of elongation was positive in all cases except quinine nitrate and picrate.

- (5) Chamot and Mason, "Handbook of Chemical Microscopy." Vol. I, John Wiley and Sons, Inc., New York, New York, 1930.