

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

## Partial Vapor Pressures of Aqueous Methylamine Solutions

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### Object of the Investigation

The purpose of this investigation was the determination of the partial vapor pressures of aqueous solutions of mono-, di- and trimethylamines. This investigation was one of a series<sup>1</sup> dealing with the thermodynamic properties of these amines in relation to their use as refrigerating fluids in the absorption type of refrigerating units. The completeness of the absorption of the gaseous refrigerant by the aqueous absorber can be ascertained from the data of this investigation.

In calculating the free energy decrease attending the reaction Amine (liquid) = Amine (1 *M*), it was found that vapor pressure data for trimethylamine were lacking, except for a few scattered boiling point determinations. Accordingly, the vapor pressures and the densities of liquid trimethylamine were determined.

Incidentally, since no free energy content data for these amines are available in the literature, the data of this investigation yield information leading to a partial determination of such values. A high temperature dissociation investigation, of exploratory nature, has yielded some preliminary data for the calculation at 25° of the free energy content of these gaseous amines; the results of this investigation will be reported in a later paper.

### Previous Investigations

No data have been found for the partial vapor pressures of aqueous amine solutions.

Vapor pressure data for monomethylamine have been reported by Felsing and Thomas;<sup>1</sup> for dimethylamine, there are the data of Berthoud;<sup>2</sup> and for trimethylamine, there were found no data.

Density data for liquid trimethylamine also are very meager. Landolt-Börnstein, "Tabellen," list 0.675 g./cc. at -4°, Lange<sup>3</sup> gives 0.662 at -5°, and Elsey<sup>4</sup> gives a value of 0.702 g./cc. at -33.5°.

(1) (a) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929); (b) Felsing and Wohlford, *THIS JOURNAL*, **54**, 1442 (1932); (c) Felsing and Buckley, *J. Phys. Chem.*, **37**, 779 (1932); (d) Felsing and Jessen, *THIS JOURNAL*, **55**, 447 (1933); and (e) Felsing and Ashby, *ibid.*, **56**, 2226 (1934).

(2) Berthoud, *J. chim. phys.*, **15**, 3 (1917).

(3) Lange, "Handbook of Chemistry," Handbook Publishers, Inc., Sandusky, Ohio, 1934.

(4) Elsey, *THIS JOURNAL*, **42**, 2454 (1920).

### Methods of the Investigation

(a) The method of determining partial vapor pressures of the aqueous amine solutions was the dynamic or air-saturation method originally developed by Berkeley and Hartley.<sup>5</sup> The method embodied the modifications of Washburn and Heuse<sup>6</sup> and of Bates and Kirschman;<sup>7</sup> additional modifications were made during the investigation, but they were concerned more with minor details of size and design than with departures from the principles of the later modifications listed.

The process consisted of passing, at an optimum rate, an unmeasured volume of dry air through a series of saturators containing pure water and the solutions whose vapor pressures were to be measured. The weights of water vapor carried out by the gas from the pure water saturator,  $w_1$ , the weight of the amine absorbed by the acid absorber and the weight of the water carried out from the solutions,  $w_2$ , and the barometric pressure,  $p_B$ , were the measurements actually made.

A rocking device ensured the continual presentation of a fresh liquid film to the air passing through three sets of saturators in series. The air passed over but not through the liquids. Water vapor was removed by dehydrite-filled absorbers and the amines were absorbed by double, acid-containing absorbers. The rate of air flow varied from 1 to 5 liters per hour for periods of approximately four to five hours, depending upon the particular amine and its concentration. The whole apparatus was immersed in a thermostat maintained at 25 ± 0.05°.

The amine solutions were prepared by dissolving in cold distilled water the gaseous amines generated from c. p. Eastman hydrochlorides by concentrated potassium hydroxide solution. Standard acid and base solutions used in absorption and in titration were prepared from tested c. p. reagents and standardized against each other and against c. p. sodium carbonate. Weight burets were used throughout. The indicator was

(5) Berkeley and Hartley, *Proc. Roy. Soc.*, (London), **A177**, 156 (1906).

(6) Washburn and Heuse, *THIS JOURNAL*, **37**, 809 (1915).

(7) Bates and Kirschman, *ibid.*, **42**, 1992 (1919).

methyl red, as recommended by Treadwell and Hall<sup>8</sup> and by Thompson.<sup>9</sup>

(b) The vapor pressures and the densities of pure liquid trimethylamine were determined by the method of Felsing and Thomas.<sup>1</sup>

### The Results Attained

(a) The partial pressures of the amines were determined at four concentrations; four to six acceptable determinations were made at each concentration, the mean of which is reported in the table. The partial pressures were calculated by the relation

$$P \text{ (amine from solution)} = \frac{p_w \frac{N_2}{N_1} \left[ 1 - \frac{(1-F)p_w}{p_B - p_w} \right]}{1 + p_w \frac{N_2}{N_1} \left[ \frac{1}{p_B - p_w} \right]}$$

in which  $F$  is the ratio  $p_s/p_w$ , where  $p_w$  is the vapor pressure of pure water at 25° and  $p_s$  the partial water vapor pressure of the amine solution and  $N_2/N_1$  is the ratio of the number of moles of amine to water. It was assumed that the vapors of the amines consisted of simple, non-associated molecules and that they obeyed the ideal gas law.

The following table presents the partial vapor pressures of the amines from their solution as calculated by means of the relation above.

Concn. (molar)	$p$ , mm.	$p/c$ , obsd.	"Best" $K$
Monomethylamine			
0.250	1.88	7.52	
.525	4.01	7.64	
1.030	8.03	7.79	
2.205	17.08	7.75	7.75
Dimethylamine			
0.261	2.81	10.76	
.500	5.59	11.18	
.952	10.62	11.15	
2.379	25.58	10.75	11.15
Trimethylamine			
0.248	16.93	68.26	
.538	38.30	71.18	
1.071	72.67	67.85	
1.961	133.10	67.86	67.87

The value of "best"  $K$  was obtained by plotting the data and determining the equation for the "best" straight line that could be drawn through the data; a straight line represents best the data over the range investigated.

(b) The vapor pressures of liquid trimethylamine were measured over a temperature range

(8) Treadwell and Hall, "Analytical Chemistry," Vol. II, 7th Ed., 1928, p. 470.

(9) R. T. Thompson, *Analyst*, **53**, 315 (1928).

of -20 to +45°. The following equation represents the data obtained, approaching equilibrium at each temperature from above and below:  $\log_{10} p(\text{mm.}) = -1410.5/T + 8.57435 - 0.0021158T$ . The over-all accuracy of these data is believed to be better than 1 part in 2500. The normal boiling point calculated by this relation is 2.90°.

The densities of liquid trimethylamine were determined over the same temperature range as were the vapor pressures. The relation which reproduced the observed data is density (g./cc.) =  $0.87406 - 4.433 \times 10^{-4} T - 1.29236 \times 10^{-6} T^2$ . This relation presents true values of the density, it is believed, to within 1 part in 5000.

### Derived Quantities

(a) The Free Energy of Solution.—The partial vapor pressures of the amine solutions at exactly 1 molar were determined, by interpolation, to be 7.60 mm. for the mono-, 11.64 mm. for the di- and 67.64 mm. for the trimethylamine. With the aid of these data, the following free energy values were calculated for the reaction: Amine (760 mm.) = Amine (1  $M$ ) + ( $-\Delta F$ ). The values of  $-\Delta F$  were found to be 2727 cal./mole for the mono-, 2502 cal./mole for the di-, and 1434 cal./mole for the trimethylamine.

From the sources cited and from the data of this investigation, the vapor pressures of the three liquid amines at 25° were found to be 2681 mm. for the mono-, 1763 mm. for the di- and 2299 mm. for the trimethylamine. From these values, the free energy decrease attending the change Amine ( $p$ , mm.) = Amine (760 mm.) was calculated and then combined with the preceding free energy value to yield the free energy decrease attending the change: Amine (liquid) = Amine (1  $M$ ) + ( $-\Delta F$ ). The results attained for  $-\Delta F$  were 3474 cal./mole for the mono-, 2991 cal./mole for the di-, and 2090 cal./mole for the trimethylamine.

(b) Heat of Vaporization of Trimethylamine.—

$$\Delta H_v = T(v_2 - v_1) dp/dT$$

The exact Clapeyron equation was applied at the normal boiling point, 2.90°. The molal volume of the vapor,  $v_2$ , was calculated by means of the ideal gas law, since data for another equation of state were lacking, and the molal volume of the liquid,  $v_1$ , was calculated from the experimental density relation. The heat of vaporization was thus found to be 95.6 cal./g. or 5706 cal./mole.

### 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.

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## The System Magnesium Sulfate-Urea-Water at 30°

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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 conditions<sup>1</sup> 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 Davis<sup>2</sup> 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,<sup>3</sup> who used the Fox and Geldard<sup>4</sup> 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).