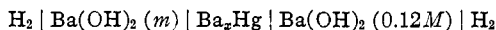


(2), and the tenth column similar values computed from the smoothed results.

The agreement of the smoothed out values with those computed by the equation is good. All three series of γ values agree well in the more concentrated solutions. In the dilute solutions, the behavior of the directly observed values in column (9) is somewhat erratic.

Summary

1. Measurements of the cells



through a concentration range from 0.002 to 0.23 M at 25° have been made.

2. The densities, d_{25} , of aqueous barium hydroxide solutions at 25° have been determined and are given to within ± 1 in the fourth decimal place by the equation

$$d_{25} = 0.9970 + 0.1878m$$

3. The activity coefficient of barium hydroxide in aqueous solution has been evaluated by employing Hückel's equation, which upon substitution of the numerical values of the constants A and B becomes

$$\log \gamma = - \frac{0.708 \sqrt{6c}}{1 + 0.696 \sqrt{6c}} + 0.0678c - \log (1 + 0.054m)$$

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS] THE HEATS OF SOLUTION OF GASEOUS METHYLAMINE

BY W. A. FELSING AND P. H. WOHLFORD

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Object of the Investigation.—In a previous paper¹ there were presented some preliminary values for the total heats of solution of gaseous monomethylamine in water at different concentrations of methylamine produced. These preliminary data were included at that time to give an idea of the order of magnitude of this heat effect and to present a more complete listing of the thermodynamic properties of methylamine with the view of using this substance as a refrigerating fluid. Since the appearance of that paper, more reliable data have been obtained; these are presented in the present paper.

Existing Data.—Besides the preliminary data of Felsing and Thomas, there are listed but few determinations or calculations of this heat effect in the literature. Bonnefoi² presents two experimental values and Moore and Winmill³ present a calculated value; the values given by Bonnefoi are 11,780 and 12,400 cal./mole of methylamine when the ratio of moles of

¹ Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

² Bonnefoi, *Ann. chim. phys.*, **23**, 362 (1905).

³ Moore and Winmill, *J. Chem. Soc.*, **101**, 1667 (1912).

water to moles of methylamine in the solutions formed are, respectively, 588.4 and 606.8.

Experimental Procedure

The total heat of solution of gaseous methylamine in water was measured by passing the dry gas into distilled water, observing the temperature rise, and determining the concentration of the methylamine solution produced.

The method used was essentially that employed by Felsing and Stiles⁴ in obtaining the heats of solution of sulfur dioxide. The exact arrangement of the apparatus is shown in the figure. The details of manipulation, in general, are identical with those of Felsing and Stiles.

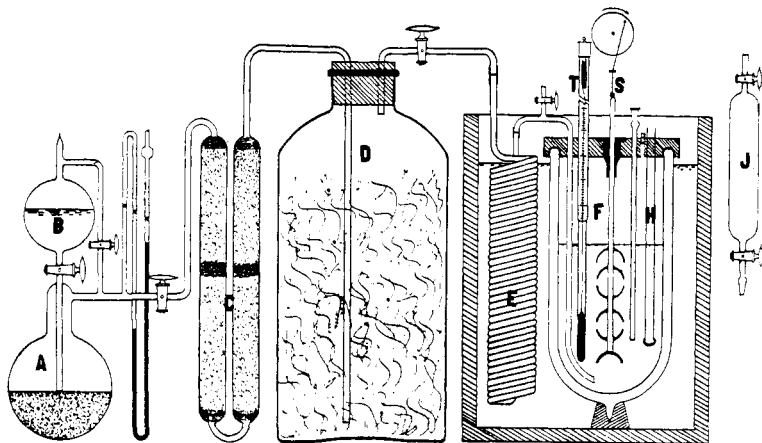


Fig. 1.

A is a generator filled with methylamine hydrochloride (free from ammonium chloride and trimethyltrimethylenetriamine); B is a reservoir of concentrated potassium hydroxide; C is a drying system containing fused barium oxide and flake sodium hydroxide; D is a large bottle filled loosely with metallic sodium ribbon; E is a coil of 6.6-mm. copper tubing about 15 meters long; and F is the calorimeter. A highly evacuated silvered Dewar flask contains a calibrated 2° Beckmann thermometer T, a motor-driven glass stirrer S, a heating element H (61 cm. of No. 24 B. and S. platinum wire, in coil form, soldered to heavy copper leads), and a weight buret sampler. The coil and the calorimeter are immersed in an accurately controlled thermostat kept at 35°.

The *water equivalent* of the calorimeter, determined in the usual manner with all precautions, was found to be 21.7 cal./deg.; the maximum deviation of six determinations was 1.1 calories.

No radiation corrections were applied in the heat of solution determinations since (1) the Dewar flask was highly evacuated and silvered, (2) the stirring rate was held constant throughout, (3) the surroundings were kept at constant temperature and (4) the time of calibration (the water equivalent determinations) was made, by trial, the same in length at the time of an actual heat of solution determination. Only traces of methylamine gas escaped absorption.

⁴ Felsing and Stiles, *THIS JOURNAL*, **43**, 1543 (1926).

The dry methylamine gas was passed from the storage reservoir D into the calorimeter, where it was absorbed by a weighed quantity of distilled water. The temperature rise was noted and a 50-cc. sample of the resulting solution was removed by means of the sampling pipet J. A weighed quantity of solution was titrated against standard sulfuric acid, using methyl red as an indicator. All titrations and standardizations were made by weight; the usual precautions for highest accuracy were observed carefully and duplicate determinations were always made.

Data.—The data are listed in Table I; the order of presentation is made identical with the decreasing concentration of methylamine solution produced. It is not the order of actual determination. The functional relation which expresses the dependence of the total heat of solution upon the concentration of solution formed is given by the equation

$$-\Delta H(\text{cal./mole}) = 10,627 + 0.24193 N \quad (1)$$

where N is the ratio of the moles of water to moles of methylamine.

TABLE I
OBSERVED AND CALCULATED VALUES OF THE TOTAL HEATS OF SOLUTION OF
METHYLAMINE

No.	$\Delta t(^{\circ}\text{C.})$	CH_3NH_2 , g.	H_2O , g.	N (moles $\text{H}_2\text{O}/$ moles CH_3NH_2)	$-\Delta H(\text{calcd./mole})$	
					Observed	Calcd. by Eq. (1)
1	1.822	1.1650	197.55	292.2	10,649	10,698
2	1.588	0.8894	171.54	332.3	10,704	10,707
3	1.469	.8670	182.02	361.7	10,717	10,714
4	1.281	.7039	168.11	411.5	10,725	10,727
5	1.263	.7389	179.65	418.9	10,689	10,728
6	1.129	.6149	166.68	467.0	10,741	10,740
7	0.808	.5101	197.45	666.9	10,780	10,788
8	.728	.3948	167.12	729.3	10,810	10,803
9 ^a	.667	.3762	174.80	800.1	10,814	10,821
10	.618	.3449	170.90	853.7	10,815	10,834
11 ^a	.574	.3400	185.50	940.0	10,857	10,854
12	.518	.3190	194.07	1048.1	10,881	10,881

^a Data by W. W. Floyd.

The variation of the total heat of solution per mole with the concentration of methylamine produced, at any concentration, is given by

$$d(-\Delta H)/dN = 0.24193 \quad (2)$$

Bonnefoi, on diluting a methylamine solution containing 1 mole in 2 liters with 4 parts of water, obtained a value of 40 cal. per mole as the *heat of dilution*. The corresponding values of N are approximately 111 and 555. Integrating Equation 2 between these limits there results a value of 107.3 calories as the heat of dilution, which value is to be compared with Bonnefoi's value of 40 calories.

Summary

1. The total heat of solution of gaseous monomethylamine has been determined at 35° for various concentrations of methylamine produced.

2. The relation between $-\Delta H$ (cal./mole of methylamine) and N (moles of water/moles of methylamine) is given by the linear equation $-\Delta H = 10,627 + 0.24193 N$; the experimental values agree with the values calculated by this relation on the average to within 0.11%; the maximum deviation is 0.46%.

AUSTIN, TEXAS

NOTE

Note on the Preparation of Absolute Isopropanol

By LEWIS E. GILSON

During several years of biochemical research the writer has found many instances where isopropanol could be substituted for ethanol in laboratory work. It is cheap and there are no restrictions governing its use; nor is it likely to be an object of theft. The commercial 91% azeotropic mixture was used instead of 95% ethanol and found to be fully equal or superior to the latter as a solvent or extracting medium. Absolute isopropanol was used in place of absolute ethanol.

Absolute isopropanol is easily prepared. The 91% grade is shaken with 10% of its weight of commercial flake sodium hydroxide, separated from the aqueous layer which forms, then shaken with a little more sodium hydroxide, decanted and distilled. The product obtained mixes with eight volumes of carbon disulfide, xylene or petroleum ether without the slightest trace of turbidity.

Dilute isopropanol can be concentrated by shaking with dry sodium chloride. Water is removed as a saturated layer of brine. The upper layer contains about 87% isopropanol and 2-3% of sodium chloride. While distilling, an additional quantity of brine separates. The distillate has so nearly the composition of the 91% azeotropic mixture that it can be used as such without further treatment. Or, after shaking the dilute isopropanol with sodium chloride and separating, it can be treated directly with sodium hydroxide and the absolute grade prepared.

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