[CONTRIBUTION NO. 138 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF TEXAS]

The Heats of Solution of Gaseous Di- and Trimethylamines

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Object of the Investigation.—In a previous paper[1] there were reported calorimetrically determined values for the heats of solution of gaseous monomethylamine in water at different concentrations of methylamine produced. Since the di- and trimethylamines have been investigated[2] partially in this Laboratory with the view of determining their value in refrigerating systems of the absorption type and since it would be desirable to complete the heats of solution for this series of amines, this investigation was undertaken.

Existing Data.—Very few data on the heat of solution of these amines are recorded in chemical literature.

Bichowsky and Rossini[3] estimated the heat of solution of dimethylamine gas to be 12,700 cal. Other values, estimated in various ways, are due to Bonnefoi[4] (14,635 cal.), to Moore and Winmill[5] (12,290 cal.), and the "International Critical Tables"[6] (14,581 cal.), based upon data by Bonnefoi.[7] In no instance was there specified the concentration of the dimethylamine solution produced.

The values for the heats of solution for gaseous trimethylamine are also discordant. Berthelot[8] gives the value of 12,900 cal. when one mole of the amine is dissolved in 270 moles of water (*i. e.*, at $N = 270$). Other values are those of Moore and Winmill[5] (12,820 cal.), of the "International Critical Tables"[6] (12,908), and of Colson,[9] who gave a value of 8750 cal. for the heat of solution of *liquid* trimethylamine. This value may be combined with the molal heat of vaporization of 5540 cal./mole at 30°, based upon the data of Felsing and Phillips,[2] yielding a value of 14,290 cal./mole for the heat of solution.

Berthelot[8] cites some values for the heats of dilution of a saturated trimethylamine solution (410 g./1000 g. of water at 19°) and of some solutions ranging in concentration from near saturation to about one-half molar, the solutions in each case being diluted to approximately one-fourth molar.

Experimental Procedure.—The total heat of solution of these gaseous amines was determined by passing the dry gas into distilled water, observing the temperature effect, and determining the concentration of the amine solution produced. The method of procedure is that of Felsing and Wohlford;[1] only minor modifications were introduced.

The energy equivalent of the calorimeter system was determined by the usual electrical energy input method. Approximately 200 g. of distilled water measured to 0.001 g. was used for each of the seven determinations. The maximum deviation (a single determination) from the *mean* was 0.32 cal. (0.14%), whereas the average deviation was only 0.147 cal. (0.067%). The international calorie was used, 1 calorie being 4.1833 international joules.

No radiation corrections were applied to the heat of solution determinations since: (1) the time of a calibration run (the energy equivalent determinations) was made, by actual trial, the same as the time of a heat of solution determination; (2) the temperature rise of the calibration runs was made the same as the *average* rise of a heat of solution determination; (3) the stirring rate was held constant throughout; (4) the calorimeter vessel (a special Dewar flask) was highly evacuated and silvered; and (5) the surroundings were kept constant at 30 ± 0.05°. The initial temperature of each run was exactly 30°.

The gaseous amines were generated from the Eastman c. p. hydrochlorides by treatment with 50% potassium hydroxide in the apparatus of Felsing and Wohlford. The gases were dried by passing through tubes filled with pellet potassium hydroxide and were completely dried by storage over sodium wire. These dried gases (mixed with a very small amount of hydrogen resulting from the sodium wire drying process) were allowed to pass into the water of the calorimeter, the temperature rise was noted on a calibrated 2° Beckmann thermometer, and two samples (approx. 50 cc.) of the resulting solution were removed by

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(1) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932).

(2) Felsing and Phillips, *ibid.*, **58**, 1973 (1936).

(3) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 50.

(4) Bonnefoi, *Ann. chim. phys.*, [7] **23**, 367 (1901).

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

(6) "I. C. T.," Vol. V, p. 182.

(7) Bonnefoi, *Compt. rend.*, **127**, 576 (1898).

(8) Berthelot, *Ann. chim. phys.*, [5] **23**, 247 (1881).

(9) Colson, *ibid.*, [6] **19**, 407 (1890).

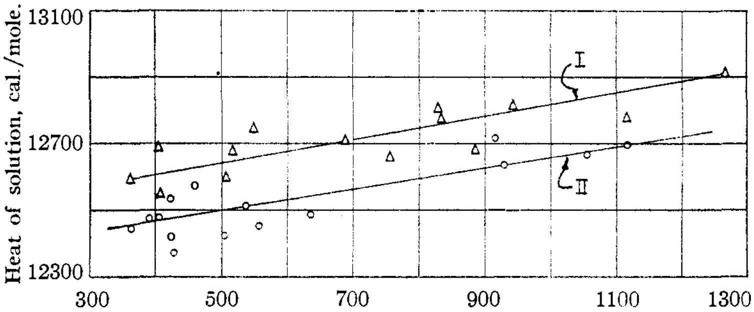

Fig. 1.—N, Moles water/moles amine; I, Dimethylamine; II, Trimethylamine.

means of a sampling pipet. From this pipet the sample was added to a weighed quantity of standard sulfuric acid, containing one drop of methyl red indicator, until faint alkalinity was indicated. To this essentially neutral solution was added the standard sulfuric acid to produce a slightly acid solution. This excess was then titrated with standard sodium hydroxide, the whole procedure being that of Moore and Winmill.[5] The use of methyl red as indicator has been recommended by Treadwell and Hall[10] and by Thompson.[11] All titrations and standardizations were made by weight; duplicate determinations always were made and the usual precautions for highest accuracy were observed.

A. DIMETHYLAMINE

Δt, °C.	$(CH_3)_2NH$, g.	H_2O, g.	N (moles H_2O/moles amine)	Heat of solution (cal./mole) Obsd.	Calcd. by Eq. (1)
0.514	0.4008	203.069	1267	12,912	12,915
.580	.4609	204.774	1111	12,765	12,860
.686	.5348	201.401	941	12,815	12,800
.703	.5363	197.407	920	12,863	12,793
.725	.5883	207.655	882	12,660	12,780
.776	.5872	208.649	832	12,779	12,763
.777	.6266	194.723	829	12,824	12,761
.853	.7064	212.061	750	12,646	12,733
.934	.7506	206.393	687	12,713	12,711
1.025	.8565	211.229	505	12,588	12,647
1.171	.9199	202.112	549	12,761	12,662
1.232	.9401	194.537	517	12,690	12,651
1.564	1.2659	205.094	405	12,543	12,612
1.592	1.3145	212.232	403	12,693	12,612
1.747	1.4066	204.550	363	12,586	12,597

Maximum deviation, 0.93%; average deviation, 0.43%.

B. TRIMETHYLAMINE

Δt, °C.	$(CH_3)_3N$, g.	H_2O, g.	N (moles H_2O/moles amine)	Heat of solution (cal./mole) Obsd.	Calcd. by Eq. (2)
0.574	0.6067	207.225	1123	12,700	12,697
.607	.6471	207.928	1053	12,653	12,697
.687	.7117	201.516	928	12,653	12,637
.833	.8763	207.921	913	12,724	12,632
.994	1.0572	204.613	634	12,498	12,544
1.128	1.2285	208.853	557	12,435	12,520
1.186	1.2617	205.783	538	12,510	12,514
1.225	1.3554	208.138	583	12,402	12,503
1.357	1.3898	197.689	466	12,579	12,491
1.455	1.6003	209.814	430	12,363	12,480
1.466	1.6238	212.323	428	12,412	12,479
1.506	1.6222	208.259	421	12,540	12,477
1.550	1.6187	200.385	406	12,489	12,472
1.620	1.7343	206.106	390	12,499	12,467
1.745	1.8104	199.712	361	12,533	12,458

Maximum deviation, 0.93%; average deviation, 0.43%.

The Data.—The data are listed in the table, in the order of increasing amine concentration; this is not necessarily the order of determination. A plot of the heat of solution against N (the ratio of moles of H_2O to moles of amine) was made for each amine. A straight line represents best the variation of the total heat of solution with change in the concentration of the solution produced for each of the amines. These functional relations are given by

$$\text{Dimethylamine:}\quad -\Delta H_1\ (\text{cal./mole}) = 12{,}470 + 0.35149N \quad (1)$$

$$\text{Trimethylamine:}\quad -\Delta H_2\ (\text{cal./mole}) = 12{,}344 + 0.31645N \quad (2)$$

These relations apply only to the range of concentrations investigated.

The rate of change of the total heats of solution per mole with change in concentration of amine solution produced, for any concentration over the limited range investigated, is given by

$$d(-\Delta H_1)/dN = 0.35149, \text{ for dimethylamine}$$
$$d(-\Delta H_2)/dN = 0.31645, \text{ for trimethylamine}$$

The data of Berthelot[8] on trimethylamine apply only to the dilution of concentrated solutions up to a concentration which is even greater than the most concentrated of this investigation. Hence his data cannot be compared with the results of the heat of dilution relations of this investigation.

Summary

1. The total heats of solution for gaseous di- and trimethylamines have been determined at 30° for various concentrations of amine solution produced.

2. The relation between $-\Delta H$ (heat of solution in cal./mole of amine) and N (moles water/mole amine) is given by two linear equations:

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

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

$-\Delta H_1$ (dimethylamine) $= 12{,}470 + 0.35149N$ and $-\Delta H_2$ (trimethylamine) $= 12{,}344 + 0.31645N$. The experimental values agree with the values calculated by these relations on the average to 0.43%; the maximum deviation is 0.93%.

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The Densities of Fine Powders. II

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In a recent study of the apparent densities of fine powders made in this Laboratory[1] the differences in values obtained when different liquids were used as the buoying fluids were noted and conclusions were reached which were somewhat at variance, in their detail, from those reached by previous investigators. In a second study[2] there was evident a rough correlation between apparent density values and the heats of wetting of the powders when wetted by the same liquids. Further studies seemed desirable in order to test the conclusions reached in that work, and it was proposed that these should be developed along two lines, namely, (a) density determinations should be made of the fine powders used in the previous work (silica gel and active, practically ash-free, charcoal) using a number of liquids not yet investigated and (b) a study should be made of apparent densities of a non-porous powder in liquids of different types.

In the previous work[1] the conclusion was reached that variations in the apparent density of a porous powder might be due either to differences in the degree of penetration of the porous solid by the liquids or to differences in the degree of compression of the liquids at the solid–liquid interface. In either case the density differences noted must have been due primarily to the differences in surface energy decrease on wetting the solid, though in the second case differences in the compressibilities of the liquids would have been a conditioning factor. The measurements on a non-porous powder were proposed with the hope that by such means the first of these possible explanations might be confirmed or disproved.

Experimental.—In the previous work[1] a modification of the method of Harkins and Ewing[3] was used. Since this method requires considerable time, the method used by Tschapek[4] was investigated. This in brief consists of weighing a sample of the solid into a suitable specific gravity bottle and adding to the sample liquid sufficient to submerge it. The bottle is then placed in a vessel provided with suitable means of air-tight closure and a connection to a vacuum pump. This vessel is then evacuated to a pressure slightly below the vapor pressure of the liquid used on the sample. With such a pressure the adsorbed air is removed rapidly from the surface of the solid particles and after a sufficient time period (determined by increasing to time intervals yielding constant value determinations) the vacuum is broken, the specific gravity bottle filled, brought to the standard temperature and weighed. After making the necessary buoyancy corrections, the density is calculated directly. Tests of this method in comparison with that used in the previous work[1] demonstrated a satisfactory agreement, and, since it is considerably faster than the one formerly used, it was adopted for the present investigations.

Results and Discussion.—In the first study, samples of the same solid materials as were used previously[1] were employed. These were powdered silica gel and active ash-free charcoal. The methods for their preparation have been described.[1] Water, benzene, nitrobenzene, carbon disulfide, acetone, ethyl alcohol, and *n*-butyl alcohol were purified carefully by standard methods and used in the density determinations. The density values for each of the solids in each liquid are given in Table I(a). It is of interest also to add to these values those of Table I(b) taken from the previous work.

TABLE I(a)

Liquid used	Density values, g./cc. at 25°	
	SiO_2	C
Acetone	2.310	2.047
Ethyl alcohol	2.248	2.012
Water	2.247	1.861
Nitrobenzene	2.239	2.011
n-Butyl alcohol	2.236	1.976
Carbon disulfide	2.216	2.029
Benzene	2.183	2.005

TABLE I(b)

Carbon tetrachloride	2.13	1.86
Petroleum ether	2.12	2.08

Harkins and Ewing found charcoal density to be a function of the compressibility of the liquid

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[1] Culbertson and Dunbar, THIS JOURNAL, **59**, 306 (1937).

[2] Culbertson and Winter, *ibid.*, **59**, 308 (1937).

[3] Harkins and Ewing, *ibid.*, **43**, 1787 (1921).

[4] M. W. Tschapek, *Kolloid-Z.*, **63**, 343 (1933).