

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Dimethylamine

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Comparison of the entropy of methylamine obtained from thermal data and the third law of thermodynamics with that from molecular data assuming free rotation has shown a discrepancy of 1.6 e. u. From this it may be inferred that a potential of 3000 cal. hinders the internal rotation of the methyl group.¹ Similar comparisons for tetramethylmethane^{1,2} and ethane³ yielded discrepancies which were interpreted by Kemp and Pitzer to indicate potentials of 4400 cal.⁴ and 3150 cal.,³ respectively. Similarly propane has been shown to have a potential of 3300 cal. hindering internal rotation.⁵ It would thus appear that the potential is increased slightly by additional substitution of rotating groups on the central carbon atom.

In the present paper it is shown that in dimethylamine the potential has become 3460 cal. hindering the rotation of each methyl group.

Preparation and Purification of Dimethylamine.—The dimethylamine was prepared from nitrosodimethylaniline,⁶ since by this method the product is reasonably free from other amines.

Dimethylaniline purified by fractional distillation was treated with sodium nitrite and hydrochloric acid. The *p*-nitrosodimethylaniline hydrochloride was not purified further, but was dried and then decomposed by the addition of a saturated solution of sodium hydroxide. The amine was absorbed in concentrated hydrochloric acid, and the hydrochloride, obtained by evaporation, decomposed by saturated aqueous sodium hydroxide. The amine was condensed in glass bulbs cooled in a dry ice-acetone mixture and dried with metallic potassium.

In order to remove ammonia the amine was passed over yellow mercuric oxide,⁷ and finally dried with metallic potassium.

The amine was twice distilled at 675 mm. pressure through the laboratory low temperature fractionating column⁸ and the final middle fraction used for the calorimetric measurements. It contained 0.011 mole per cent. of impurity as estimated from the melting point range and premelting heat capacities.

The Heat Capacity Measurements.—The apparatus, methods, temperature scale and accuracy were as described already.⁹ Calorimeter B (adiabatic) was used with the resistance thermometers R-200 (platinum-rhodium) and R-102 (constantan).

One calorie (15°) was taken equal to 4.1852 absolute joules and one international joule to 1.00041 absolute joules. In correcting for material vaporized into the filling line, the vapor pressure measurements described later were used. The density of the liquid was taken to be $d_4 = 0.6804 - 0.0009886t$.¹⁰ The molal heat capacities are listed in Table I and graphed in Fig. 1.

The Vapor Pressure Measurements.—The measurements were made as already described.^{1,2} In view of the high purity of the sample, except for the lowest pressures, the accuracy is determined solely by the temperature. The results for the liquid are given in Table II. Column 1 gives the absolute temperature as read by the resistance thermometer. Column 3 gives the difference between the observed pressure and that calculated from equation (1)

$$\log_{10} P_{\text{mm.}} = -2460.100/T - 8.63900 \log_{10} T + 7.60550 \times 10^{-3} T - 3.51389 \times 10^{-5} T^2 + 5.32410 \times 10^{-8} T^3 + 32.26370 \quad (1)$$

and column 4, the temperature difference corresponding to this pressure difference.

The first eleven observations were made with the calorimeter full of material. These results were used in deriving equation (1). The last two measurements were made on the material left in the calorimeter after one-half of the sample had been distilled out for the heat of vaporization measurements. These results show that the boiling point range was negligible.

The Melting Point.—The equilibrium temperature of the pure sample was observed over a period of nine hours, with several fractions of the material melted, as estimated from the heat input. The results are given in Table III. From these results and the heat of fusion, the impurity

(1) Aston, Siller and Messerly, *THIS JOURNAL*, **59**, 1743 (1937).

(2) Aston and Messerly, *ibid.*, **58**, 2354 (1936).

(3) Kemp and Pitzer, *ibid.*, **59**, 276 (1937).

(4) Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

(5) Kemp and Egan, *THIS JOURNAL*, **60**, 1521 (1938).

(6) Baeyer and Caro, *Ber.*, **7**, 810 and 963 (1874).

(7) François, *Compt. rend.*, **144**, 567 (1907).

(8) To be described in a forthcoming publication.

(9) Aston and Eidinoff, *THIS JOURNAL*, **61**, 1533 (1939).

(10) Jaeger, *Z. anorg. allgem. Chem.*, **101**, 86 (1917).

TABLE I

MOLAL HEAT CAPACITY OF DIMETHYLAMINE

Molecular weight 45.085. 0°C. = 273.16°K. Sample: 0.66388 mole.

T, °K.	ΔT , °K. (approx.)	C_p	Series no.
14.32	5.0	0.696	I
18.13	2.7	1.231	I
21.01	3.0	1.769	I
23.83	2.9	2.249	I
26.72	2.9	2.692	I
29.83	3.7	3.343	I
33.50	3.8	4.004	I
37.52	4.4	4.741	I
42.02	4.5	5.597	I
46.17	3.9	6.221	I
49.72	3.3	6.749	I
53.84	4.9	7.403	I
58.83	5.2	8.093	I
64.32	5.8	8.801	I
69.80	5.2	9.522	I
74.79	4.8	10.118	I
80.07	5.8	10.688	I
85.64	5.4	11.299	I
90.00	5.2	11.766	II
90.83	5.0	11.830	I
95.09	4.9	12.296	II
99.90	4.7	12.757	II
104.50	4.5	13.185	II
108.88	4.3	13.561	II
113.10	4.1	13.918	II
118.79	5.0	14.367	II
123.70	4.8	14.754	II
128.45	4.7	15.097	II
133.04	4.5	15.443	II
137.50	4.4	15.739	II
142.35	5.3	16.075	II
146.76	5.2	16.329	III
147.64	5.1	16.425	II
151.93	5.1	16.725	III
152.90	5.0	16.794	II
156.94	4.9	17.094	III
157.81	4.8	17.124	II
161.98	4.8	17.350	III
162.56	4.7	17.377	II
166.69	4.7	17.704	III
167.20	4.6	17.643	II
171.72	4.5	18.015	II
176.11	4.3	18.457	II
180.97	Fusion		
184.82	5.4	28.996	IV
190.19	5.3	29.457	IV
195.44	5.2	29.898	IV
200.57	5.1	30.287	IV
205.60	5.0	30.650	IV
210.52	4.9	30.932	IV
215.35	4.8	31.222	IV
220.18	4.7	31.484	IV
224.83	4.6	31.648	IV
229.64	5.4	31.842	IV
234.96	5.3	31.977	IV
240.22	5.2	32.109	IV
245.70	5.1	32.202	IV

250.80	5.0	32.236	IV
255.83	5.1	32.331	IV
260.81	4.9	32.373	IV
265.83	4.8	32.469	IV
270.74	4.8	32.527	IV
275.55	4.7	32.639	IV
280.45	4.6	32.693	IV
280.04	Boiling point		

TABLE II

VAPOR PRESSURES OF LIQUID DIMETHYLAMINE

0°C. = 273.16°K. Boiling point = 280.04°K. (g for State College = 980.124 ("I. C. T.")).

T, °K.	Press. obsd., int. mm.	Press. (obsd.- calcd., 1) int. mm.	ΔT (calcd.- obsd., 1) °K.
201.387	4.86	+0.002	+0.022
213.802	14.69	- .009	- .038
222.078	28.35	- .018	- .034
232.137	58.32	- .014	- .018
242.078	110.58	+ .010	+ .008
249.630	172.13	+ .024	+ .013
256.449	249.54	+ .033	+ .013
262.977	348.06	+ .033	+ .010
270.182	491.22	+ .026	+ .006
275.934	636.50	- .008	- .001
279.960	757.37	.000	.000
After distilling off half sample			
277.680	686.45	- .37	- .012
280.018	758.62	- .53	- .017

present was found to be 0.011 mole per cent. assuming no solid solution. After correcting for this impurity, the melting point of pure dimethylamine is $180.97 \pm 0.05^\circ\text{K}$.

Previous data on the boiling point and melting point of dimethylamine are listed in Table IV.

TABLE III

MELTING POINT OF DIMETHYLAMINE

0°C. = 273.16°K.

% melted	T, °K. R-200	T, °K. Thermocouple S-9
3	180.885	180.890
6	180.908	180.912
12	180.922	180.929
23	180.934	180.936
46	180.936	180.943
70	180.938	180.953
70 ^a	180.936	180.953
93	180.941	180.960
100	180.941	180.960

^a This observation was taken one hour after the previous one.

Heat of Fusion and Vaporization.—The method has been described before.^{2,9} The results are summarized in Tables V and VI.

During the first four vaporizations listed in the table, the pressure was held constant by having the condensation bulb immersed in a cryostat

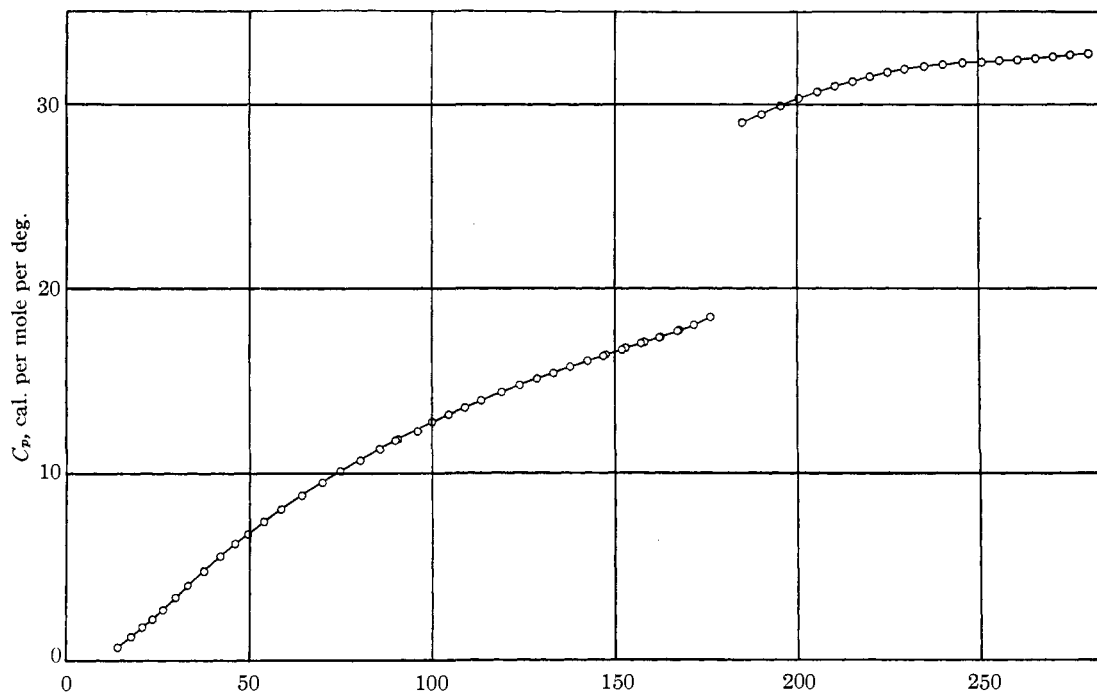


Fig. 1.—Molal heat capacity of dimethylamine.

TABLE IV

MELTING AND BOILING POINT TEMPERATURES OF DIMETHYLAMINE

M. p., °C.	B. p., °C.	Observer
	7.2	Berthoud ¹¹ (1917)
	7.1-7.2	Hofmann ¹² (1889)
-93.0	7.0	Simon and Huter ¹³ (1935)
-96.0		Timmermans and Mataar ¹⁴ (1921)
-92.9	7.0	Wiberg and Sutterlin ¹⁵ (1935)
-92.19 (180.97°K.)	6.88 (280.04°K.)	This research

consisting of a well stirred benzene-benzene ice mixture with excess water. The benzene (Eastman thiophene-free) was purified by several crystallizations. In this way a bath was obtained whose temperature was constant and reproducible

TABLE V

HEAT OF FUSION OF DIMETHYLAMINE

Mol. wt., 45.085; 0.66388 mole; melting point, 180.97°K.

Temp. interval, °K.	Corr. heat input, cal./mole	$\int C_p dT$, cal./mole	Pre-melting, cal./mole	ΔH , cal./mole
174.871-185.932	1751.9	332.8	0.6	1419.7
174.774-184.736	1711.9	292.2	.5	1420.2
172.079-185.489	1806.6	386.5	.3	1420.4
				Mean 1420.1 \pm 0.5

(11) Berthoud, *J. chim. phys.*, **15**, 3 (1917).(12) Hofmann, *Ber.*, **22**, 702 (1889).(13) Simon and Huter, *Z. Elektrochem.*, **41**, 28 (1935).(14) Timmermans and Mataar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).(15) Wiberg and Sutterlin, *Z. Elektrochem.*, **41**, 15 (1935).

TABLE VI

HEAT OF VAPORIZATION OF DIMETHYLAMINE

Mol. wt., 45.085; boiling point, 280.04°K.

Moles vaporized	Mean temp. of vapn., °K.	Total input cal./mole	$\int C_p dT$, cal./mole	ΔH ideal at 280.04 cal./mole	ΔH real at 280.04 cal./mole
0.04270 ^a	278.71	7176	849	6352	6302 ^a
.11919	279.17	6821	473	6381	6331
.12539	278.95	6682	328	6383	6333
.11252	278.72	6812	460	6377	6327
				Average of last three	6330 \pm 3
0.10845	273.46	6757	313	6369	6319 \pm 6

^a Due to the small sample a large error can arise from the uncertainty in the correction for the vapor in the lines. This result was therefore excluded from the average.

Calculated at one atmosphere from equation (1) and thermodynamics; Berthelot correction = 190 cal. 6408 cal.

to within 0.03°. As a check on the accuracy of the vaporization method, a well stirred water-ice cryostat was used in the fifth vaporization.

In order to compare the heats of vaporization at the freezing point of benzene with that near the ice point, all were calculated for the ideal gas at the boiling point. In this calculation the difference in heat content between the real and ideal gas was calculated using the modified Berthelot equation of state. The heat capacity of the ideal gas was obtained by correcting the gaseous heat capacity data of Felsing and Jesson¹⁶ to the ideal gas state using the modified Berthelot equation of

(16) Felsing and Jesson, *THIS JOURNAL*, **55**, 4418 (1933).

state. Column 5 of Table VI gives these ideal heats of vaporization. Column 6 gives the heats of vaporization of the real gas at the boiling point.

The heat of vaporization also has been calculated from equation (1) and thermodynamics using the modified Berthelot equation with $T_c = 437.8^\circ\text{K}$. and $P_c = 52.39$.¹¹

Considering the accuracy of the measured heats of vaporization, the comparison indicates that the modified Berthelot equation gives volumes that are too large by almost 35% of the reduction from the perfect gas law. A similar result has been noted also for methylamine.¹ This would make one doubtful of the correction for the pressure effect in calculating the heat of vaporization at the boiling point from that at 0° . For this reason the error at the boiling point is estimated = 6 instead of = 3 for this determination; it is thus consistent with the rest.

The Entropy from the Thermal Data.—The calculation is summarized in Table VII. The correction for gas imperfection is based on the modified Berthelot equation of state and is probably in error accordingly.

TABLE VII
THE ENTROPY OF DIMETHYLAMINE
Mol. wt., 45.085

	E. u./mole
0–14.79°K. Debye function $h\nu_m/k = 124$ (three degrees of freedom)	0.264
14.79–180.97°K. graphical	19.777
Fusion 1420.1/180.97	7.847
180.97–280.04°K. graphical	13.662
Vaporization 6330/280.04	22.604
Entropy of actual gas at boiling point	64.154
Correction for gas imperfection	0.122
Entropy of ideal gas at boiling point	64.28 = 0.05
Entropy of ideal gas at 298.16°K.	65.24 = .05
Entropy of liquid at 298.16°K.	43.58 = .05

For completeness the entropy of the superheated liquid has been estimated at 298.16°K. by a linear extrapolation of our heat capacity curve. The entropy of the ideal gas has been calculated at 298.16°K. from the heat capacity data of Felsing and Jesson.¹⁵

The Entropy from Molecular Data.—The CN distance was taken to be 1.46Å,¹⁷ the C–N–C and H–N–C angles as $108^\circ 06'$, the N–H distance as 1.016 Å,¹⁷ and the C–H distance as 1.11 Å. As usual the tetrahedral angle was assumed for the carbon bonds.

(17) Bauer, *THIS JOURNAL*, **60**, 524 (1938).

By trial it was found that three potential barriers of 3460 calories hindering the rotation of each methyl group give an entropy in agreement with the calorimetric data. Using the method of Pitzer⁴ the rotational and translational entropy is given by equation 2.

$$S_{T+R} = 22.8750 \log_{10} T - 4.5750 \log_{10} P_{\text{atm.}} + 10.1907 - 2(S_f - S)_{3460 \text{ cal.}} \quad (2)$$

A symmetry number of three was used for each methyl group. For evaluating $(S_f - S)$ the reduced moment of the methyl group was found to be 5.0×10^{-40} .

The following frequency assignment was made on the basis of the Raman data and discussion of Edsall¹⁸

$$\begin{aligned} &^2\nu(\pi)_{\text{CH}_3}, 2906; \quad ^4\nu(\sigma)_{\text{CH}_3} 2803; \quad ^2\delta(\pi)_{\text{CH}_3} 1450 \\ &^4\delta(\sigma)_{\text{CH}_3}, 1479; \quad \nu_{\text{RNH}}, 3339; \quad \delta_{1\text{RNH}}, 1137; \quad \delta_{2\text{RNH}}, 1189 \\ &\delta_{1\text{HCN}} \sim \delta_{2\text{HCN}} \sim \delta_{3\text{HCN}} \sim \delta_{4\text{HCN}} \sim 1080; \quad \nu(\pi)_{\text{RNR}}, 930 \\ &\quad \quad \quad \nu(\sigma)_{\text{RNR}}, 1082; \quad \delta_{\text{RNR}}, 415 \end{aligned}$$

The subscripts refer to the following assumed vibrating systems: CH₃, methyl group internally; RNH, hydrogen on nitrogen; HCN, variation of angle of CH bonds relative to CN bond; RNR, "three atom system" composed of two methyl groups and one NH group. Except for this, the nomenclature is that used in the previous paper.¹

The four HCN frequencies due to the angular oscillation of the hydrogen atoms of each methyl group, as a whole were taken as 1080 by consideration of the heat capacity results of Felsing and Jesson on the gas.¹⁶ To the heat capacity contributions of all the rest of the vibrations was added 3*R* cal. for the rotation and translation of the rigid molecule. The contribution of the two rotating methyl groups was then added. Anticipating, the latter was obtained directly from Pitzer's tables⁴ on the basis of three potential barriers of 3460 cal. hindering the rotation of each methyl group. The value thus obtained was increased by *R* plus a correction to the real gas state calculated assuming the modified Berthelot equation of state. The difference between this and the C_p 's of the gas is due to the four HCN frequencies. About 1080 cm.⁻¹ gave the best fit with the experimental data as can be seen from Table VIII which compares the experimental values (col. 2) with those calculated using these frequencies (col. 3).

If the free rotation of methyl groups is assumed, the four frequencies to fit the heat capacity data best are somewhat lower than 720

(18) Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

TABLE VIII
HEAT CAPACITIES OF DIMETHYLAMINE (Perfect Gas)

Temp., °K.	C_p Obsd. ¹⁸ cal./deg./mole	C_p calcd. ($V = 3460$) cal./deg./mole	C_p calcd. ($V = 0$) cal./deg./mole
283.2	15.80	16.30	16.03
285.2	15.97	16.40	16.14
298.2	16.62	16.89	16.62
313.2	18.03	17.47	17.20
323.2	18.66	17.85	17.59

cm.⁻¹ as can be seen from Table VIII, col. 4, which is calculated on the basis of this frequency and zero potential hindering the rotation of the methyl groups.

In the case of methylamine¹ the four similar frequencies, due to the angular oscillation of the methyl and amino groups, were calculated in a similar manner, assuming free rotation, to be 768 cm.⁻¹.

The discrepancy between the experimental entropy and that calculated from the molecular data, assuming free rotation, was then 1.64 e. u. This indicated about 3000 cal. for the potential of the three barriers hindering rotation. If the four frequencies from the heat capacities are now calculated, assuming such barriers with a reduced moment of 2.0×10^{-40} for the rotation, the frequency is found to be 915 cm.⁻¹. Using this to calculate the entropy from molecular data on the basis of 3000 cal. barriers gives a value in agreement with experiment.

The figures 915 and 1080 cm.⁻¹, respectively, for these angular oscillations of the groups of hydrogen atoms in methylamine and dimethylamine seem to accord better with theoretical estimates for them than those calculated on the basis of free rotation.

Table IX summarizes the calculation of the entropy data assuming three 3460 cal. potential barriers hindering the rotation of each methyl

TABLE IX
COMPARISON OF CALORIMETRIC AND SPECTROSCOPIC ENTROPIES OF DIMETHYLAMINE AT ONE ATMOSPHERE AND 280.04°K.

	E. u./mole
I Translational and rotational, ($V = 3460$)	63.00
II Vibrational ($\delta_{\text{HCN}} = 1080$)	0.20
III Vibrational (other modes)	1.10
IV Total (less nuclear spin)	64.30
V Experimental	64.28

For 3460 cal. potentials $2(S - S) = 3.17$

group and the above frequency assignment. The agreement between the calculated and observed is a result of the empirical calculation of the potential.

The translational and rotational entropy assuming free rotation is given by equation 3

$$S_{T+R} = 22.8750 \log_{10} T - 4.5750 \log_{10} P + 9.9977 \quad (3)$$

This together with a vibrational entropy calculated using the above frequencies gives a result 3.03 e. u. higher than the calorimetric entropy at the boiling point. If, for consistency, 720 cm.⁻¹ be used for the four frequencies δ_{HCN} this discrepancy is increased further by about 0.7 e. u.

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Summary

1. The heat capacity of dimethylamine has been determined from 11.8°K. to the boiling point.

2. The melting point of dimethylamine is 180.97°K. (−92.19°) and the boiling point is 280.04°K. (6.88°).

3. The heats of fusion and vaporization of dimethylamine are, respectively, 1420.1 ± 0.5 and 6330 ± 3 cal./mole.

4. The vapor pressure of liquid dimethylamine over the range 201°K. to the boiling point is given by the equation: $\log_{10} P_{\text{mm.}} = -2460.100/T - 8.63900 \log_{10} T + 7.60550 \times 10^{-3} T - 3.51389 \times 10^{-5} T^2 + 5.32410 \times 10^{-8} T^3 + 32.26370$.

5. The molal entropy of the ideal gas calculated from the experimental data at the boiling point is 64.28 ± 0.05 e. u.

6. To bring the value calculated from molecular data into agreement with the experimental value requires a potential of 3460 cal. hindering the internal rotation of each methyl group.

7. The molal entropies of the superheated liquid at 298.16°K. and ideal gas at 298.16°K. and one atmosphere are, respectively, 43.58 ± 0.05 and 65.24 ± 0.05 e. u.

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