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

Heat Capacities and Entropies of Organic Compounds. III. Methylamine from 11.5°K. to the Boiling Point. Heat of Vaporization and Vapor Pressure. The Entropy from Molecular Data

BY J. G. ASTON, C. W. SILLER AND G. H. MESSERLY

No work has so far appeared on the entropy and free energy of simple amines. The present study of methylamine is the first of a series of investigations whose purpose is to obtain such data for the lower primary, secondary, and tertiary aliphatic amines. The results herein reported are of further interest because of the similarity of ethane and methylamine. In the case of ethane the entropy of the gas at the boiling point calculated from thermal data and the third law is 1.5 e. u. lower than that calculated from the molecular data assuming free internal rotation of the methyl groups in the gas.[1] Because the third law value is in good agreement with the value calculated from the ethane–ethylene equilibrium Kemp and Pitzer have found it necessary to discard the assumption of free rotation in the gas and to assume a potential barrier of 3150 cal. Tetramethylmethane and methyl alcohol had already shown similar discrepancies,[2,3] namely, 1.7 e. u. for methyl groups in each case. Kassel[3] pointed out that the data on the methanol equilibrium are consistent with the assumption of a potential barrier of 3000 cal. for methyl alcohol, although he hesitated to accept such a high value solely on this evidence.

In the following paragraphs it is shown that the entropy calculated for methylamine assuming free rotation differs by a like amount from that from the thermal data and the third law.

Preparation and Purification of Methylamine.—In order to eliminate di- and trimethylamine the compound was prepared by rearrangement of bromoacetamide according to the usual procedure. The hydrochloride was freed as far as possible from ammonium chloride by recrystallization from anhydrous ethyl alcohol. The amine was obtained from the hydrochloride by dropping a saturated solution onto solid potassium hydroxide and drying the resulting gas over potassium hydroxide sticks before condensing in steel cylinders. The amine was then twice distilled at 10 atm. through an efficient glass fractionating column packed with glass helices (10–15 theoretical plates).[4] A portion of the main fraction was dried by standing over metallic sodium until the characteristic blue color appeared and a middle portion distilled into the sample bulb exactly as described in the work on tetramethylmethane.[2] This sample contained 0.79 mole % of impurity as estimated from the melting point range. The sharpness of the ammonia eutectic point showed that less than 0.05 mole per cent. of the sample was other impurity than ammonia. The heat capacity measurements listed as Series I to VI, inclusive, were taken using this sample.

Because no constants have been reported on pure methylamine and further because we had overlooked an ingenious method of removing ammonia devised by François[5] we decided to further purify the material. The fraction above, as vapor, was passed over mercuric oxide as described by François, condensed over metallic potassium, and allowed to stand until it became dark blue. A middle portion of the dry amine was used for the remainder of our calorimetric measurements. It contained 0.025 mole per cent. of impurity as estimated from the melting point range and premelting heat capacities. As far as we are aware this is the first time the high efficiency of the procedure of François has been demonstrated directly.

The Heat Capacity Measurements.—The apparatus, method, temperature scale and accuracy were as already described.[2] Thermocouple S-2 was used in all measurements. As usual 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 and the density of the liquid was taken as 0.699 g./cc.[6] The results on the impure sample were corrected for the heat capacity of the 0.79 mole per cent. ammonia impurity using the data of Overstreet and Giauque[7] on the assumption of additivity.

The molal heat capacities are listed in Table I by series rather than by temperature for a reason which will be apparent later.

In the region from 95 to 175°K. the heat capacities on the solid depend upon its previous history. Series I was taken after the sample had been frozen, partially melted, and slowly cooled. The cooling to 85°K. occupied eighteen hours. Three preliminary heat capacity measurements were taken during which the sample was heated to 103°K. The sample was held at this temperature for nine hours. The sample was then cooled to 61°K., which occupied ten

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[1] Kemp and Pitzer, THIS JOURNAL, **59**, 276 (1937).

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

[3] Kassel, *J. Chem. Phys.*, **4**, 494 (1936).

[4] We wish to thank the Petroleum Laboratory for the loan of this column.

[5] François, *Compt. rend.*, **144**, 567 (1907).

[6] "International Critical Tables," McGraw-Hill Book Company, Inc., New York, Vol. 1, 1926.

[7] Overstreet and Giauque, THIS JOURNAL, **59**, 254 (1937).

TABLE I

MOLAL HEAT CAPACITY OF METHYLAMINE

Molecular weight 31.057. 0°C. = 273.16. Series I to VI 0.6398 mole, VII to XVIII 0.6752 mole

T, °K.	ΔT, °K. (approx.)	C_p
	Series I	
14.76	1.5	0.435
17.25	1.0	.681
21.19	1.1	1.194
23.05	1.4	1.417
25.01	1.9	1.685
26.75	0.7	1.845
28.70	3.4	2.145
32.47	2.5	2.706
35.48	4.0	3.147
39.83	5.0	3.828
44.62	4.8	4.561
49.05	3.9	5.199
53.72	5.2	5.757
58.55	4.4	6.305
62.84	3.8	6.873
66.93	4.2	7.276
71.11	3.9	7.696
75.64	5.0	8.125
80.39	4.5	8.604
84.70	4.1	9.009
89.12	4.3	9.383
	Series II	
85.84	5.7	9.072
91.22	5.1	9.531
96.64	5.4	10.04
101.20	3.6	15.84
105.78	5.8	10.68
111.56	5.4	10.88
117.01	5.1	11.18
122.48	4.8	11.44
	Series III	
93.89	1.3	9.690
96.25	3.4	9.943
99.55	3.3	10.17
102.70	3.1	10.37
105.58	3.0	10.55
	Series IV	
127.51	4.5	11.73
132.90	4.2	12.01
137.40	4.1	12.17
144.21	4.8	12.42
149.56	4.5	12.78
155.79	5.3	13.05
	Series V	
138.10	5.0	12.43
144.73	4.7	12.82
151.35	4.4	13.20
	Series VI	
188.35	5.6	23.85
194.27	5.4	23.78
200.90	5.2	23.86
206.64	5.1	23.92
212.47	5.0	24.07
218.72	4.7	24.16
224.28	4.6	24.08
230.84	4.5	24.15
237.09	4.3	24.22
242.61	4.9	24.38
248.63	5.0	24.39
254.73	4.6	24.38
259.28	2.7	24.33
	Series VII	
172.22	2.6	14.14
174.76	2.4	14.61
176.91	2.2	16.52
	Series VIII	
62.16	3.5	6.798
71.91	4.5	7.802
80.45	5.4	8.561
87.05	4.8	9.175
96.51	4.7	14.28
101.83	2.2	10.80
	Series XII	
90.20	5.5	9.478
95.89	2.7	10.09
99.78	4.6	10.52
104.74	4.3	10.57
111.27	5.8	10.90
116.85	5.0	11.10
	Series XIII	
12.71	2.4	0.311
15.38	2.4	.478
18.02	2.3	.733
20.39	2.6	1.041
22.69	2.0	1.325
24.85	2.0	1.595
27.13	1.6	1.900
29.77	3.1	2.291
32.77	2.4	2.718
36.16	4.1	3.267
40.63	5.1	3.938
45.67	4.9	4.717
50.66	5.2	5.361
56.28	6.0	6.010
64.50	5.5	7.101
72.81	5.5	7.857
	Series XIV	
89.77	4.4	9.384
93.05	1.8	9.708
96.53	1.7	10.02
98.66	2.2	12.39
102.60	5.7	14.04
106.69	4.6	10.62
115.81	5.1	11.05
121.86	4.7	11.39
127.37	5.8	11.69
136.43	5.3	12.17
	Series XV	
90.34	4.8	9.414
95.62	3.9	9.900
100.97	6.4	10.29
112.38	5.2	10.91

TABLE I (*Concluded*)

T, °K.	ΔT, °K. (approx.)	C_p
117.57	4.9	11.23
123.61	4.6	11.59
128.87	5.6	11.96
139.45	6.2	12.49
	Series XVI	
129.92	5.5	12.02
135.45	5.2	12.29
140.79	4.9	12.57
148.02	4.7	12.85
155.82	5.4	13.20
161.59	5.2	13.39
167.20	4.9	13.69
	Series XVII	
142.06	4.8	12.68
149.23	5.1	13.17
157.01	5.2	13.61
165.18	4.9	13.82
	Series XVIII	
186.61	3.4	23.68
191.13	3.7	23.66
195.91	4.0	23.75
201.33	4.7	23.75
206.74	4.5	23.90
213.18	5.1	23.94
219.39	4.9	23.94
227.92	4.7	24.35
233.92	5.0	24.32
239.54	4.2	24.27
245.61	5.1	24.13
252.48	5.0	24.18

hours. Two preliminary heat capacity measurements were then taken during which the sample was heated to 75°K. over a period of twelve hours. The sample was then cooled over about three hours to 10°K., and Series I started. After the measurements listed in Series I the calorimeter drifted to 97°K. over three days. It was then cooled to 82°K. and the points of Series II taken. The high point at 101.2°K. was immediately obvious from the smaller rise both in the thermocouple and the resistance thermometer, the lower temperature drifts, and the slowness with which equilibrium was attained. It was therefore decided to stop the series at 125°K. and repeat the point. The calorimeter was rapidly cooled to 93°K. and Series III started. The abnormality in the neighborhood of 101°K. was no longer present in spite of the fact that the other points checked those of the previous run fairly well. After Series III the calorimeter was heated to 124°K., having stood about twenty-four hours. The points of Series IV were then taken. The slowness of reaching equilibrium suggested that the last three points might be in error due to this cause and therefore Series V was taken. For this series the sample was frozen, partially melted and slowly cooled. The cooling to 128°K. occupied ten hours.

After the complete calculations were made it was evident that the points of Series V differed from the corresponding ones of Series IV by more than could possibly be attributed to lack of *thermal* equilibrium. Inasmuch as the data were not critically reviewed until all our measurements were complete, no planned investigation of this abnormality above 115°K. was made. What information we do have is a fortunate accident, but does show that a definite hysteresis exists. The heat capacities on both samples in the range 80°K. to the melting point are plotted in Fig. 1, where the points of the various series are distinguished. It is apparent that the abnormalities suffer no significant change after removal of the ammonia.

Series VI is for the liquid and needs no discussion. The points are plotted in Fig. 2 along with the rest of the heat capacity data used in calculating the entropy.

Series VII to XVII inclusive were taken upon the sample containing 0.025 mole per cent. of impurity. Series VII was obtained during the examination of the premelting range. Following this, the sample was cooled slowly over three days to 90°K., allowed to stand at this temperature for three days, cooled to 60°K. and held there for two days. Series VIII was then taken. A high point was obtained at 96.5°K. Because of trouble with the cryostat vacuum, several runs following Series VIII in which unsuccessful starts were made to reproduce the peak, have been discarded. Thus between Series VIII and Series XII, the calorimeter had been four times warmed from 60 to 90°K. over a period of four days. Series XII exhibited no abnormality. For twelve days prior to cooling to liquid hydrogen temperatures, the calorimeter was held around 90°K. The cooling from 70 to 10°K. occupied about four hours (the day before, the sample had been rapidly cooled to 60°K.). Series XIII covering the range 11 to 80°K. was then taken. The apparatus was allowed to stand at 80 − 90°K. for three days (duplicating the procedure of runs I and II), cooled slightly, and the points of Series XIV obtained. Series XIV exhibited the abnormality in the two points at 98.6 and 102.6°K. Following Series XIV the calorimeter was immediately cooled to 85°K. and the points of Series XV obtained. After Series XV a cooling was made to about 125°K. for the purpose of overlapping several points and Series XVI obtained. Series XVII was obtained after the sample had been completely melted in a heat of fusion measurement; the calorimeter was cooled only to 135°K. for this series (previously the substance was frozen and heated into the melting range). Series XVIII represents the results obtained upon the liquid with this sample.

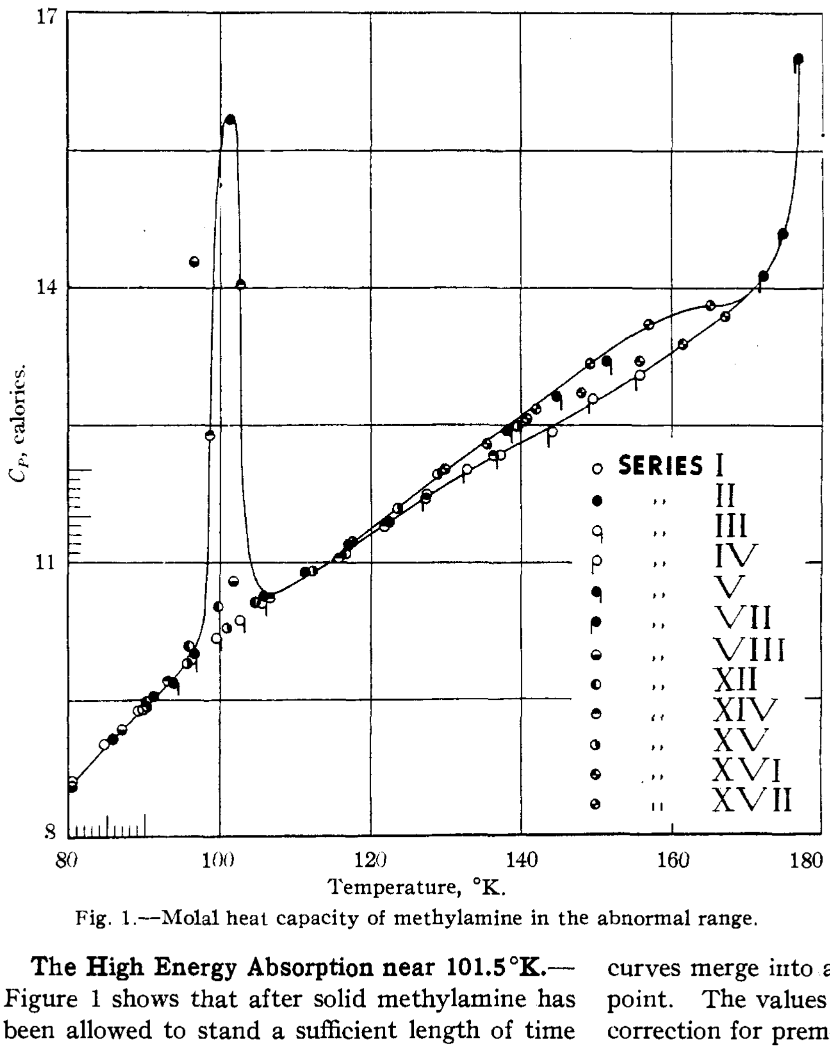

Fig. 1.—Molal heat capacity of methylamine in the abnormal range.

The High Energy Absorption near 101.5°K.—Figure 1 shows that after solid methylamine has been allowed to stand a sufficient length of time at or below 60° a peak, discussed above, appears in the heat capacity curve with a maximum at about 101.5°K. For purposes of calculating the entropy it is simpler to ignore this peak by drawing a curve joining the "normal" heat capacity values (hereafter referred to as the "normal" curve) as has been done in Fig. 2. The additional increase in heat content corresponding to the peak is then divided by the temperature of the maximum to obtain the entropy corresponding to the "abnormal" absorption of energy. From our results it is possible to compute two values of this "abnormal" absorption of energy. The temperature interval of the result given in Table I, Series II, at 101.20°K. includes almost the entire "abnormal" energy absorption. By subtracting the energy absorption corresponding to the "normal" curve from the total energy absorption a value of 19.6 cal./mole is obtained. The total energy input of the two results of Series XIV at 98.66 and 102.60°K. treated similarly yielded a value of 26.9 cal./mole. This includes a correction of 4.8 cal./mole for the heat leak during the five hours necessary for the system to come to equilibrium after the first addition of energy. The average value taken is 23.2 cal.

The "Hysteresis" Loops above 115°K.—From Fig. 1 it is seen that in Series IV and XIV where the sample was initially cooled below 60°K. the results lie on the lowest curve. Where the sample had only been cooled to about 130°K. after freezing, the highest curve is followed as exemplified by Series V and XVII. Other series where the sample was cooled to intermediate temperatures after heating to near the melting point lie on intermediate curves (XV and XVI). It seems that all the curves merge into a single curve near the melting point. The values of Series VII after applying a correction for premelting (not applied in Table I or Fig. 1) fall on the extrapolated lower curve although the sample was previously only cooled slightly below 170°K.

It is of interest that as the methylamine was heated from low temperatures in the course of the normal heat capacity measurements, the behavior

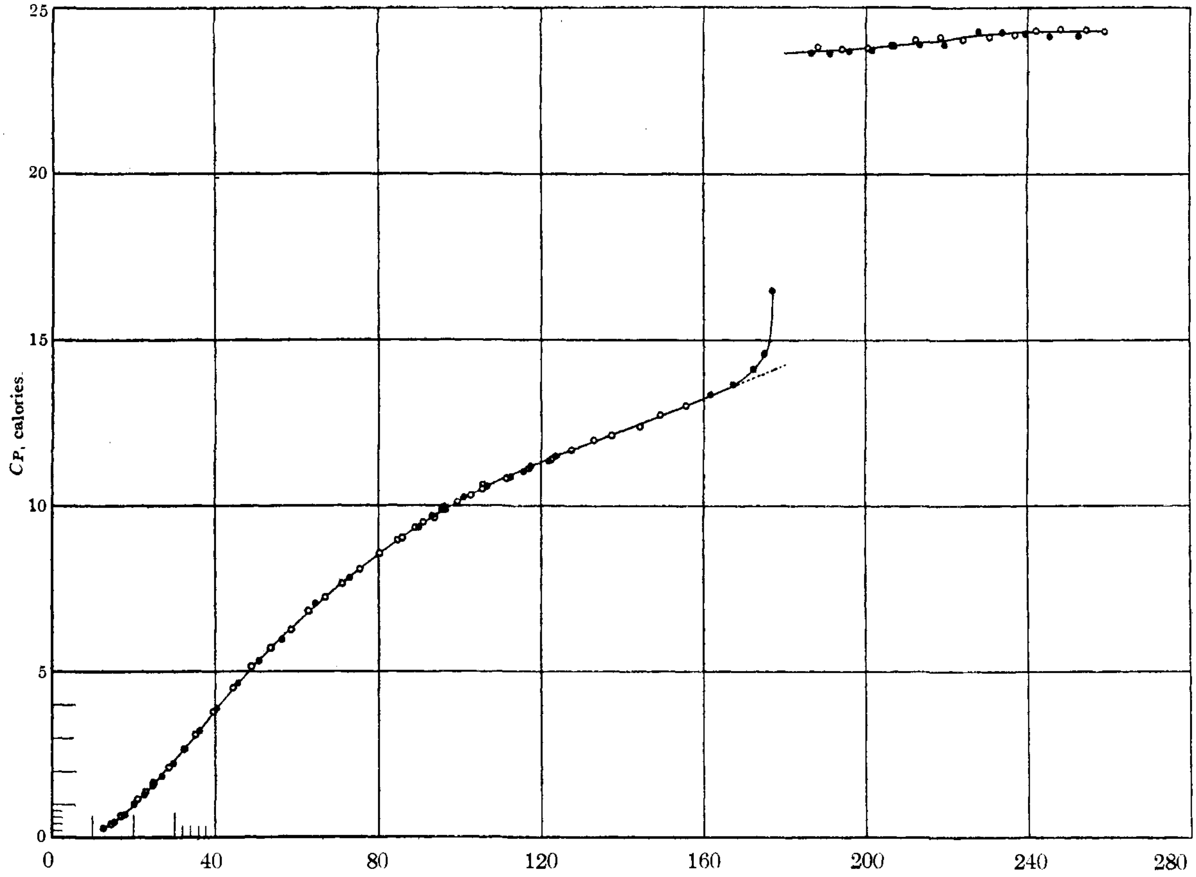

Fig. 2.—Molal heat capacity of methylamine (the lowest curve chosen in abnormal range): ○, impure sample; ●, pure sample.

of the gold resistance thermometer indicated an abnormal expansion of the material. Deviations as high as 0.2° from the usual calibration curves were observed in a direction which indicated stretching of the thermometer (fortunately within the elastic limit). Upon cooling the methylamine to an intermediate temperature the abnormal deviation of the previous run was not present but an abnormal deviation would develop again on further heating. This behavior was more or less reproducible. Fortunately the calibration curves during any run were regular so that, as it was our invariable practice to calibrate the resistance thermometer against the standard thermocouple in each run, no error in the heat capacities could arise from this cause. To remove any possible doubt a new comparison of the thermocouple (S-2) was made (Nov. 12, 1936) against the vapor pressures of oxygen, from 65 to 90°K. The results were in excellent agreement with those of March 28, 1935.[8]

The Vapor Pressure Measurements.—The measurements were made as already described.[2] The manometer, whose temperature was kept uniform to within 0.2° by its brass case, was read by a Société Génévoise cathetometer with two telescopes accurate to 0.01 mm. Thus, 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 thermocouple S-2. Column 3 gives the difference between the observed pressure and that calculated from equation (1a)

$$\log_{10} P_{\text{mm.}} = -(2089.100/T) - 6.059200 \log_{10} T + 2.61668 \times 10^{-4}\, T - 5.47880 \times 10^{-7}\, T^2 + 25.44187 \quad \text{(1a)}$$

and column 4 the temperature difference corresponding to this pressure difference. Column 5 gives the temperature difference corresponding to pressure differences calculated from the simpler equation (1b)

$$\log_{10} P_{\text{mm.}} = -(2089.100/T) - 6.059200 \log_{10} T + 25.41093 \quad \text{(1b)}$$

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[8] Aston, Willihnganz and Messerly, THIS JOURNAL, **57**, 1642 (1935).

TABLE II

VAPOR PRESSURES OF LIQUID METHYLAMINE

0°C. = 273.16°K. Boiling point = 266.84°K. (*g* for State College = 980.124 ("I. C. T.")).

T, °K.	Pressure obsd., int. mm.	Pressure (obsd. − calcd., 1a)	ΔT, (calcd. 1a − obsd.)	ΔT, (calcd. 1b − obsd.)
190.008	4.06	−0.009	−0.021	−0.002
198.904	9.59	− .009	− .010	− .001
206.932	19.19	− .027	− .017	− .010
214.265	34.75	+ .034	+ .013	+ .014
221.976	60.67	+ .004	+ .001	+ .004
228.484	94.29	− .041	− .007	− .016
236.460	155.86	+ .028	+ .003	− .008
244.402	247.20	+ .100	+ .007	− .004
249.535	326.65	+ .100	+ .006	− .004
255.598	446.09	− .111	− .005	− .011
260.602	569.33	− .314	− .012	− .014
264.791	693.03	+ .318	+ .010	+ .014
266.874	761.55	+ .314	+ .009	+ .015
After distilling off half sample				
236.049	151.85	−0.055	−0.006	−0.017
239.759	189.68	+ .093	+ .008	− .003
243.524	235.42	+ .175	+ .013	+ .002
255.928	453.40	+ .206	− .009	− .015
262.465	621.74	+ .214	− .007	− .007
267.212	773.25	+ .285	+ .008	+ .015

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

The Melting Point.—The equilibrium temperature of the pure sample was observed over twenty 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 present was found to be 0.025 mole per cent., assuming no solid solution. The melting point of pure methylamine calculated on this basis is 179.70 ± 0.05°K. (The freezing point of our sample was 179.69°K.) Preliminary measurements on the less pure sample showed 0.79 mole per cent. impurity and a freezing point of 179.37°K. From these earlier results the melting point calculated for pure methylamine is 179.72 ± 0.05°K.

TABLE III

MELTING POINT OF METHYLAMINE

0°C. = 273.16°K.

Observation	% melted	T, °K. Resistance thermometer	T, °K. Thermocouple S-2
3	4	179.500	179.505
4	17	179.643	179.628
5	30	179.667	179.659
7	41	179.675	179.678
8[a]	41	179.674	179.671
9	50	179.672	179.667
11	94	179.689	179.690
(Extrapolated)	100	179.691	

[a] Observation 8 taken one-half hour after observation 7.

TABLE IV

MELTING AND BOILING POINT TEMPERATURES OF METHYLAMINE

M. p., °C.	B. p., °C.	Observer
	−8	D'Andreeff[9] (1859)
	−6	Hofmann[10] (1889)
	−6.6	Gibbs[11] (1905)
	−6.3	Berthoud[12] (1917)
−92.5		Timmermans and Mattaar[13] (1921)
	−6.79	Felsing and Thomas[14] (1929)
	−6.54 (266.56°K.)	Plank and Vahl[15] (1931)
−93.46 (179.70°K.)	−6.32 (266.84°K.)	This research

Previous data on the boiling point and melting point of methylamine are listed in Table IV. In view of the higher value for the melting point determined by Timmermans it is significant that an indirect comparison of our temperature scale with the sublimation point of carbon dioxide showed agreement within the accuracy claimed (0.05°).

Heats of Fusion and Vaporization.—The methods already described[2] were used. The results are summarized in Tables V and VI.

The pressure during the heat of vaporization measurements was held constant by having the condensation bulb immersed in a constant temperature bath consisting of a well stirred sodium thiosulfate–ice eutectic mixture contained in a one-liter Dewar. Finely shaved ice and finely powdered sodium thiosulfate ("Baker's Technical" without further purification) were added alternately in small quantities to a Dewar flask with vigorous stirring until a sufficient quantity of mixture had been prepared. Most of the saturated solution was poured off before use. In this way a bath was obtained whose temperature was constant and reproducible to ±0.05°. The

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(9) D'Andreeff, *Ann. chim. phys.*, [3] **56**, 332 (1859).

(10) Hofmann, *Ber.*, **22**, 699 (1889).

(11) Gibbs, THIS JOURNAL, **27**, 851 (1905).

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

(13) Timmermans and Mattaar, *Bull. soc. chim. belg.*, **30**, 213 (1921).

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

(15) Plank and Vahl, *Forsch. Gebiete Ingenieurw. A.*, **2**, 11 (1931).

TABLE V

HEAT OF FUSION OF METHYLAMINE

Mol. wt., 31.057; 0.67521 mole

Temp interval, °K.	Corrected heat input, cal./mole	$\int C_p dT$ cal./mole	Pre-melting, cal./mole	ΔH, cal./mole
174.159–182.449	1643.8	179.8	2.4	1466.4
172.411–184.407	1731.8	267.0	1.0	1465.8
170.681–184.193	1757.1	292.4	0.4	1465.1
				Mean 1465.8 ± 2.0

TABLE VI

HEAT OF VAPORIZATION OF METHYLAMINE

Mol. wt., 31.057. Boiling point, 266.84°K.

Moles vaporized	Mean temp. of vaporization, °K.	Total input, cal./mole	$\int C_p dT$ cal./mole	ΔH at[a] 266.84°K. cal./mole
0.07168	263.92	7819	1648	6133
.07380	263.58	6711	480	6189
.10408	263.78	6594	371	6184
				Mean 6169 ± 30
Calculated at one atmosphere from equation (1) and thermodynamics; Berthelot correction = 143 cal.				6195

[a] ΔC_p (gas-liquid) = 13.0 cal./mole used to calculate results at 1 atmosphere from those at $Pe = 1/t \int_0^t P\,dt$.

temperature of this eutectic was −10.11 ± 0.05°C. ("I. C. T." value −11°C.).

The heat of vaporization has also been calculated from equation (1) and thermodynamics using the modified Berthelot equation with $T_C = 156.9°$, $P_C = 73.6$ atm.[12] The agreement of this value with that obtained calorimetrically is a justification for the later use of the modified Berthelot equation, with these constants, to calculate the correction necessary to convert the calorimetric entropy of the real gas to that of the ideal gas.

The Entropy.—For the calculation of the calorimetric entropy we have used only the data of Series I, II, IV, VII, XIII, XIV, and the last two points of XVI on the solid, and VI and XVIII on the liquid. Thus except in the premelting range only points where the solid had previously been cooled below 90°K. were used. This choice is arbitrary and corresponds to choosing the lower envelope of the curves in the region of "hysteresis." A choice of the upper envelope would yield a value 0.35 e. u. higher. The treatment of the high energy absorption already has been discussed.

Table VII summarizes the calculation of the entropy of the gas at the boiling point from the calorimetric data plotted in Fig. 2. The entropy of the ideal gas also has been calculated at 298.16°K. and 1 atmosphere from the gaseous heat capacity data of Felsing and Jesson.[16] For completeness the entropy of the superheated liquid has also been estimated at 298.16°K. from a linear extrapolation of our liquid heat capacities.

TABLE VII

THE ENTROPY OF METHYLAMINE

Mol. wt., 31.057

	E. u./mole
0–12.59°K. Debye function $h\nu_m/k = 149.0$ (three degrees of freedom)	0.093
12.59–101.47°K. graphical	8.283
"Peak" 23.3/101.5	0.230
101.47–179.70°K. graphical	6.938
Fusion 1465.8/179.70	8.157
179.70–266.84°K. graphical	9.505
Vaporization 6169/266.84	23.119
Entropy of actual gas at boiling point	56.325
Correction for gas imperfection	0.095
Entropy of ideal gas at boiling point	56.42 ± 0.3
Entropy of ideal gas at 298.16°K. and one atm.	57.73
Entropy of liquid at 298.16°K.	35.90

The Entropy from Molecular Data.—The C–N distance in methylamine can be estimated to be 1.47 Å. from the electron diffraction data[17] on the C–N linkage and its independence of substituted groups. From the fact that electron diffraction data show a bond angle for the nitrogen pyramid in trimethylamine of 108 ± 4° which is within experimental error the same as that for ammonia (108°06′) it may be assumed that the ammonia pyramid suffers little distortion in methylamine. We therefore take for both the angles H–N–H and C–N–H the angle H–N–H in ammonia; namely, 108°06′[18] and for the NH distance the value 1.016 Å. found for ammonia.[18] For C–H we have as usual taken 1.11 Å.

If zero potential is associated with the internal rotation of the methyl group we find by conventional methods[19] the value

$$S_{T+R} = 20.5876 \log_{10} T - 4.5750 \log_{10} P + 7.3333 \quad (2)$$

for the classical rotational and translational entropy. The symmetry number has been taken as 3 and the nuclear spin entropy neglected.

The vibrational entropy has been calculated on the basis of the following frequency assign-

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

(17) Brockway and Jenkins, *Rev. Modern Phys.*, **8**, 261 (1936); Brockway, THIS JOURNAL, **58**, 2036 (1936).

(18) Migeotte and Barker, *Phys. Rev.*, **50**, 418 (1936).

(19) Eidinoff and Aston, *J. Chem. Phys.*, **3**, 379 (1935); Kassel, *ibid.*, **4**, 276 (1936). Using Kassel's notation the terms of the matrix of moment of inertia are $(xy) = -1.76 \times 10^{-40}$, $(yz) = (zx) = 0$ $(xx) = 3.53 \times 10^{-40}$, $(yy) = 33.0 \times 10^{-40}$, $(zz) = 4.98 \times 10^{-40}$, $(\lambda\lambda) = (\nu\nu) = (\lambda\mu) = (\mu\nu) = (\nu\lambda) = 0$, $(\mu\mu) = K = 5.47 \times 10^{-40}$.

ment: $\nu(\pi)_{CH}$, 2945; ${}^2\nu(\sigma_{CH})$, 2879; $\delta(\pi)_{CH}$, (1360); ${}^2\delta(\sigma)_{CH}$, 1466; $\nu(\pi)_{NH}$, 3312; $\nu(\sigma)_{NH}$, 3372; $\delta(\pi)_{NH}$, 1109; $\nu_{CH_3NH_2}$, 1039; $\delta_{1\,RR'} \sim \delta_{2\,RR'} \sim \delta_{3\,RR'} \sim \delta_{4\,RR'} \sim$ (768). The nomenclature is similar to that used by Bartholomé and Sachsse[20] for methyl alcohol and is based on association of all except the last five frequencies with the internal vibrations of the methyl and amino groups. These last two frequencies are due, respectively, to the stretching of the C–N bond and the bending involving the amino and methyl groups as a whole. The frequencies, with the exception of those in brackets, are from the Raman spectrum as reported by Kohlrausch.[21] The frequency $\delta(\pi)_{CH}$ is missing from the Raman spectrum and the corresponding value for methyl alcohol has been used. The four frequencies $\delta_{RR'}$ have been obtained from the specific heat data of Felsing and Jesson[16] on the gas. To the rotational and translational specific heat was added that due to the other eight frequencies in addition to a Berthelot correction to the real gas state. The value at 25° was subtracted from the experimental value. The difference was taken to be due to four equal frequencies. The heat capacities calculated using these frequencies agree fairly well with the observed values at 0° (calcd. 12.2, obsd. 11.7) and 50° (calcd. 13.6, obsd. 13.8). The calculations at the boiling point are summarized and compared with the experimental values in Table VIII.

TABLE VIII

COMPARISON OF CALORIMETRIC AND "SPECTROSCOPIC" ENTROPIES OF METHYLAMINE AT ONE ATMOSPHERE AND 266.84°K.

		E. u./mole
I	Translational and rotational	57.28
II	Vibrational (${}^4\delta_{RR'} = 768$)	0.67
III	Vibrational (other modes)	.11
IV	Total (less nuclear spin)	58.06
V	Calorimetric corrected to ideal gas state	56.42
VI	Discrepancy	1.64

To illustrate the effect of the uncertainty of choosing the four $\delta_{iRR'}$ frequencies on the entropy, a similar calculation has been made in which two of them were arbitrarily chosen as $\delta_1 = \delta_2 = 1100$. This yields $\delta_3 = \delta_4 = 548$ and a calculated entropy at the boiling point only 0.27 e. u. higher.

The discrepancy of 1.64 e. u. is considerably outside the experimental error or that of estimating the vibrational entropy. It may be due to lack of equilibrium in the solid or to neglect of the potential associated with the rotation of the methyl group. The general similarity of methylamine to ethane shows that a calculation similar to the above only assuming a potential barrier of 3000 cal. would bring the calculated value into fair agreement with the theoretical value. A detailed calculation would supply no further information in view of the latitude allowed in the choice of the four $\delta_{iRR'}$ frequencies.

The above assignment of frequency for methylamine brings out the not unexpected fact that the frequencies $\delta_{iRR'} \sim 768$ involving the methyl group as a whole do not differ greatly from the corresponding ones in methyl alcohol (about 700) and in ethane (about 800). In our previous calculation on tetramethylmethane[2] the $\delta_{iRR'}$ frequencies due to this bending were missing and no specific heat data were available on the gas for their estimation. The calculation took into account the nine frequencies due to the carbon skeleton and the twelve due to the distortion of the methyl group which together with the external and internal rotations and the three degrees of freedom of translation totalled thirty-one. Twelve of the remaining twenty frequencies are due to CH stretching and would be so high as to contribute nothing to the entropy. The other eight degrees of freedom are those due to an angular oscillation of the methyl group as a whole ($\delta_{iRR'}$). If these frequencies are of the same order of magnitude as in methylamine they would make a total contribution of about 1.4 e. u. to the entropy. The discrepancy in the case of tetramethylmethane would thus become 8.6 e. u. or 2.15 e. u. per methyl group.

The larger discrepancy per methyl in the case of tetramethylmethane than for methyl alcohol, ethane or methylamine suggests hindered rotation, as here one would expect a greater hindrance to rotation.

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(21) Kohlrausch, *Monatsh.*, **68**, 349 (1936).

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Summary

1. The heat capacity of methylamine has been determined from 11.5°K. to the boiling point. In the range 95 to 175°K. the heat capacity of solid methylamine exhibits hysteresis effects.

2. The melting point of methylamine is 179.70° (−93.46°C.) and the boiling point is 266.84°K. (−6.32°C.).

3. The heats of fusion and vaporization of methylamine are 1465.8 and 6169 cal./mole, respectively.

4. The vapor pressure of liquid methylamine has been determined over the range 190°K. to the boiling point and is represented by the equation:

$$\log_{10} P_{\text{mm.}} = -(2089.100/T) - 6.05920 \log_{10} T + 2.61668 \times 10^{-4}\, T - 5.47880 \times 10^{-7}\, T^2 + 25.44187$$

5. The "spectroscopic" entropy of methylamine calculated from the Raman spectrum and moments of inertia, is 58.06 e. u. per mole at one atmosphere and 266.84°K.

6. The molal entropy of the ideal gas at the boiling point, calculated from the experimental data, is 56.42 ± 0.3 E. u. This value is 1.6 E. u. less than the corresponding "spectroscopic" value.

7. The molal entropies of the superheated liquid and ideal gas at 298.16°K. and one atmosphere are 35.90 and 57.73 E. u. respectively.

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Multilayers of Sterols and the Adsorption of Digitonin by Deposited Monolayers

BY IRVING LANGMUIR, V. J. SCHAEFER AND HARRY SOBOTKA

In a recent note[1] it was shown that digitonin is adsorbed as a visible film on a properly oriented monolayer of cholesterol deposited upon a substrate of barium stearate multilayers of critical thickness. To test the specificity of this reaction we have studied the adsorption of digitonin on some other sterols. We have also built up multilayers of these sterols to determine the thickness of each monolayer and other properties.

Multilayers of Sterols.—The technique for making built-up films was similar to that which has been developed by Dr. Blodgett for barium stearate films.[2,3]

The plates upon which the films were deposited were rectangular pieces of polished chromium-plated brass 1″ × 3″ (2.5 × 7.6 cm.) The surface of the metal was covered with a thin layer of molten ferric stearate which was rubbed vigorously with a clean cloth while cooling. This gives a very uniform monolayer which we shall call the initial layer.

We now select two areas on the plate, which we designate as *blocks*, to be used for two separate purposes. One of these, the *sample block*, is to contain one or more monolayers of the sterol as a "sample" for investigation. The monolayers are deposited upon a *base* consisting of a barium–copper stearate multilayer. The other block, which we shall call the *reference block*, is a barium–copper stearate multilayer to be used as a standard (24.2 Å. per layer) for measuring the thickness of the sample layers. Each block is built up until its thickness lies within a *critical range* giving a minimum in the intensity of reflected polarized light from a sodium vapor lamp at some angle of incidence *i*, lying between 67–83°, at which angles the intensity of the reflected light is a very sensitive indicator of the thickness of the film.

The *critical thickness* corresponding to the minimum at an observed angle of incidence can be determined, with a sensitivity of about 1.5 Å., by making the film in steps (of about 2 monolayers) and finding the angle *i* at which adjacent steps match in intensity. The thickness which corresponds to the minimum is the average of the thicknesses of the two steps.

The stearate multilayers which we use for both the reference block and the base layers of the

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(2) K. B. Blodgett, *ibid.*, **57**, 1007 (1935).

(3) K. B. Blodgett and I. Langmuir, *Phys. Rev.*, **51**, 964 (1937).