Method C.—A mixture of 0.05 mole of the quinolinol and 0.25 mole of the acid chloride was heated on an oil-bath at 150° for forty-five minutes. To the cooled product 100 cc. of water was added and the insoluble substance washed with 5% sodium carbonate solution. The product was dissolved in ether, dried over potassium carbonate and then the ether was evaporated.

The esters prepared by these methods are so indicated as A, B or C in the yield column of Table I. The products in each case are recrystallized from an organic solvent as referred to in the Appearance column of Table I.

The 4-benzyloxybenzoyl chloride and 3,4,5-tris-(benzyloxy)-benzoyl chloride were prepared according to reference 1. 3,4,5-Tri-(acetoxy)-benzoyl chloride was prepared by the method of Fischer.[21]

Catalytic Reduction of the Pyridinols, Quinolinols and their Esters.—An amount of the compound between 0.5 and 1.5 g. was dissolved in 100 cc. of ethanol or dioxane. Dioxane was used as a solvent for most of the esters. After addition of 200 mg. of Pd catalyst,[2] hydrogenation was carried out at 55° in the apparatus previously mentioned. The compounds tested and the reduction products obtained are outlined in Table III. The time required for the reductions varied from about one to three hours, most reductions requiring about two hours. The esters of the 2-benzoxypyridine type reduced in two stages as measured by the rate of hydrogen uptake. The rates of reduction are compared in Table IV. Benzyl alcohol is included as a reference standard.

2-Benzoxypyridine was reduced more slowly than the other esters. The first three molar equivalents of hydrogen were absorbed more rapidly since hydrogenolysis of the ester with subsequent reduction of the resulting aldehyde to the hydrocarbon proceeded more rapidly than reduction of the pyridinol or quinolinol rings.

Acknowledgment.—The authors wish to thank Dr. C. M. Suter and Dr. Johannes S. Buck for suggestions submitted during the course of this investigation.

Summary

1. All three monohydroxypyridines and seven monohydroxyquinolines are capable of forming aromatic esters. Esters of the 2- and 4-hydroxy bases are more readily hydrolyzed than others; the 4-esters could be prepared only under anhydrous conditions. Introduction of a methyl group in the 4-position of quinoline reduced the strength of the ester linkage in the 2-position.

2. With a palladium catalyst, 2-pyridinol was reduced to α-piperidone; 3- and 4-pyridinols did not reduce. 2-Quinolinol reduced to the 3,4-dihydro derivative, 4-quinolinol did not reduce. 3-, 5-, 6-, 7- and 8-quinolinols reduced to the corresponding 1,2,3,4-tetrahydroquinolinol. The presence of a methyl group as in 4-methyl-2-quinolinol prevented reduction.

3. The benzoyl ester of 3-pyridinol did not hydrogenate. The 3-, 5-, 6- and 7-quinolinol benzoyl esters reduced to the corresponding 1,2,3,4-tetrahydro- derivatives. The 2- and 4-pyridinol, 2- and 4-quinolinol, and 4-methyl-2-quinolinol aromatic acid esters reduced to yield the hydrocarbon of the aromatic acid with liberation of the hydroxypyridine or -quinoline which behaved according to its own nature toward further reduction. Esters of 8-quinolinol underwent reduction to the 1,2,3,4-tetrahydro derivative which rearranged to give the N-acyl derivative. This last case is similar to the rearrangement of ortho aminophenyl esters and appears to result when the grouping $R'-CO-O-\underset{|}{C}=\underset{|}{C}-NHR$ occurs in a reaction, R being H or a group which does not destroy the basic character of the nitrogen.

4. Hydrogenation of 1-isoquinolinol yielded 3,4-dihydro-1(2)-isoquinolone; 1-benzoxyisoquinoline gave toluene, the dihydroisoquinolone and a small amount of a compound which appears to be N-benzoyl-3,4-dihydro-1(2)-isoquinolone.

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[21] E. Fischer, Bergmann and Lipschitz, *Ber.*, **51**, 45 (1918).

[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 Trimethylamine. The Entropy from Spectroscopic and Molecular Data

BY JOHN G. ASTON, MALCOLM L. SAGENKAHN, GEORGE J. SZASZ, GUSTAVE W. MOESSEN AND HERBERT F. ZUHR

The Raman spectrum of trimethylamine shows a shift of 272 cm.$^{-1}$ which can be assigned to the hindered rotation of the methyl groups. Thus the determination of the entropy of trimethylamine from calorimetric data and the third law of thermodynamics is particularly desirable to compare with the entropy calculated from spectroscopic and molecular data as a verification of the assignment. Such a comparison has already been made for methylamine[1] and for dimethylamine,[2] but in those cases the comparison was used to estimate the potential barrier hindering internal rotation. The present paper records the results of calorimetric measurements on trimethylamine from 11°K. to the normal boiling point along with the other data necessary for calculating the entropy of the saturated vapor at several temperatures up to its normal boiling point. The entropy thus calculated is compared with that calculated from molecular and spectroscopic data whose assignment to the normal modes of vibration including the hindered rotation is discussed.

Preparation and Purification of Trimethylamine.—Trimethylamine was prepared by the reaction of para-

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[1] (a) Aston, Siller and Messerly, THIS JOURNAL, **59**, 1743 (1937); (b) Aston and Doty, *J. Chem. Phys.*, **8**, 743 (1940).

[2] Aston, Ridinoff and Forster, THIS JOURNAL, **61**, 1539 (1939).

formaldehyde solution with ammonium chloride[3] followed by repeated treatment with nitrous acid. The free base was distilled through the laboratory low temperature column (twelve theoretical plates) and finally dried over metallic potassium. The product was found to contain 1.38 mole per cent. impurity as determined from the equilibrium temperatures observed during melting. Further treatment with nitrous acid did not decrease the amount of impurity, a fact which may indicate oxidation by the nitrous acid.

The sample for the thermodynamic measurements was prepared from this sample by exhaustive methylation.

To a cold aqueous solution of the amine four moles of methyl iodide was added with stirring. After the addition was complete, the mixture was allowed to warm to room temperature and the quaternary iodide filtered off. Approximately two and one-half moles of wet tetramethylammonium iodide free of amine odor was obtained. The latter salt was then suspended in one liter of water and treated with a slight excess of silver oxide (prepared by adding two and one-half moles of sodium hydroxide in 30% aqueous solution to two and one-half moles of silver nitrate in 30% aqueous solution, filtering and washing the precipitated silver oxide). After permitting the silver oxide–quaternary iodide mixture to react for thirty minutes the resulting silver iodide was filtered off.

The tetramethylammonium hydroxide solution thus formed was evaporated down to one-third of its original volume. Then and only then did the distillate start to come over basic. The first portion of the distillate was neglected and the second portion was collected in a receiver containing a 100% excess of concentrated hydrochloric acid immersed in an ice-bath. The collection assembly consisted of three receivers: the first, a trap to collect the methyl alcohol and water, the second and third, the cold hydrochloric acid to collect the amine. The decomposition was continued until the evolution of gas had practically ceased.

The amine was liberated from a concentrated aqueous solution of the hydrochloride by adding a concentrated solution of sodium hydroxide, passed over solid potassium hydroxide sticks and finally collected in a liquid air trap. The new sample was once more fractionated and dried as described above. Alternate freezing by cooling to liquid air temperature with evacuation to 10^{-6} mm. and thawing removed the last traces of air before the sample was sealed into a bulb and weighed ready for introduction into the apparatus in the customary manner.[4] The sample was found to contain twenty-seven hundredths mole per cent. of impurity. Judged by the usual standards of this Laboratory the purity is not high although adequate for the purpose.

A comparison of the impurity determined from the melting point with the molecular weight as determined from density measurements shows that the impurity is probably an equimolar mixture of methyl- and dimethylamines.

The Heat Capacity Measurements.—The apparatus, method and temperature scale were as already described.[4,5] Calorimeter C with thermocouples S-7 and S-4 was used. One defined calorie was taken equal to 4.1833 international joules. The heat capacity measurements are listed in Table I and plotted in Fig. 1. The temperature rises can be estimated from the intervals between points in a given series. Series I and II (open circles on Fig. 1) were taken on a sample 0.48867 mole, series III and IV (closed circles on Fig. 1) were taken on a 0.48420-mole sample. The last four points in series III and both points in series IV were taken using the laboratory automatic timer which is similar to that described by Johnston,[6] while others were taken using a tenth second stop watch frequently calibrated against an astronomical clock which was checked against the Arlington time signals. Corrections to the heat capacities for vaporization into the filling line were made using the density determinations of Swift.[7] Table II gives the heat capacities interpolated from the data at rounded values of the absolute temperature.

TABLE I

THE MOLAL HEAT CAPACITY OF TRIMETHYLAMINE

Mol. wt. 59.112; 0.48867 mole in calorimeter for series I and II; 0.48420 mole in calorimeter for series III and IV; 0°C. = 273.16°K.

Temp., °K.	C_p, cal./deg./mole
Series II	
11.88	0.526
13.39	0.753
16.04	1.242
18.92	1.897
21.57	2.570
25.21	3.481
29.92	4.686
33.92	5.544
38.44	6.419
42.24	7.105
47.18	7.874
52.36	8.556
57.43	9.219
62.91	9.888
Series I	
58.67	9.372
69.63	10.801
74.66	11.466
79.48	12.010
89.87	13.15
94.44	13.72
99.45	14.34
104.28	14.83
109.50	15.45
114.73	16.04
119.87	16.66
124.63	17.22
129.45	17.75
134.30	18.29
139.36	19.01
144.42	20.83
148.42	26.49
160.88	27.58
166.08	27.64
171.20	27.67
176.29	27.80
181.54	27.76
186.71	27.95
196.89	28.09
202.20	28.28
206.93	28.42
211.81	28.58
216.69	28.76
221.72	28.87
226.76	29.04
231.76	29.22
236.95	29.56
242.13	29.78
247.51	29.94
253.25	30.26
258.66	30.59
264.38	30.93
270.45	31.24
275.90	31.50
Series III	
81.55	12.24
87.75	12.94
93.14	13.55
98.34	14.24
106.99	15.15
117.63	16.40
128.78	17.66
Series IV	
240.62	29.71
245.88	29.95

The Melting Point of Trimethylamine.—The equilibrium temperature of solid and liquid trimethylamine was observed over a period of seventeen hours with various fractions of the sample melted as estimated from the heat input. From these results and the heat of fusion, the liquid-soluble solid-insoluble impurity present was found to be 0.27 mole per cent. Table III summarizes the data on the melting point which was

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(3) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 514.

(4) Aston and Messerly, THIS JOURNAL, **58**, 2351 (1936).

(5) Messerly and Aston, *ibid.*, **62**, 886 (1940).

(6) Johnston, *J. Optical Soc. Am.*, **17**, 381 (1928).

(7) Swift, THIS JOURNAL, **64**, 115 (1942).

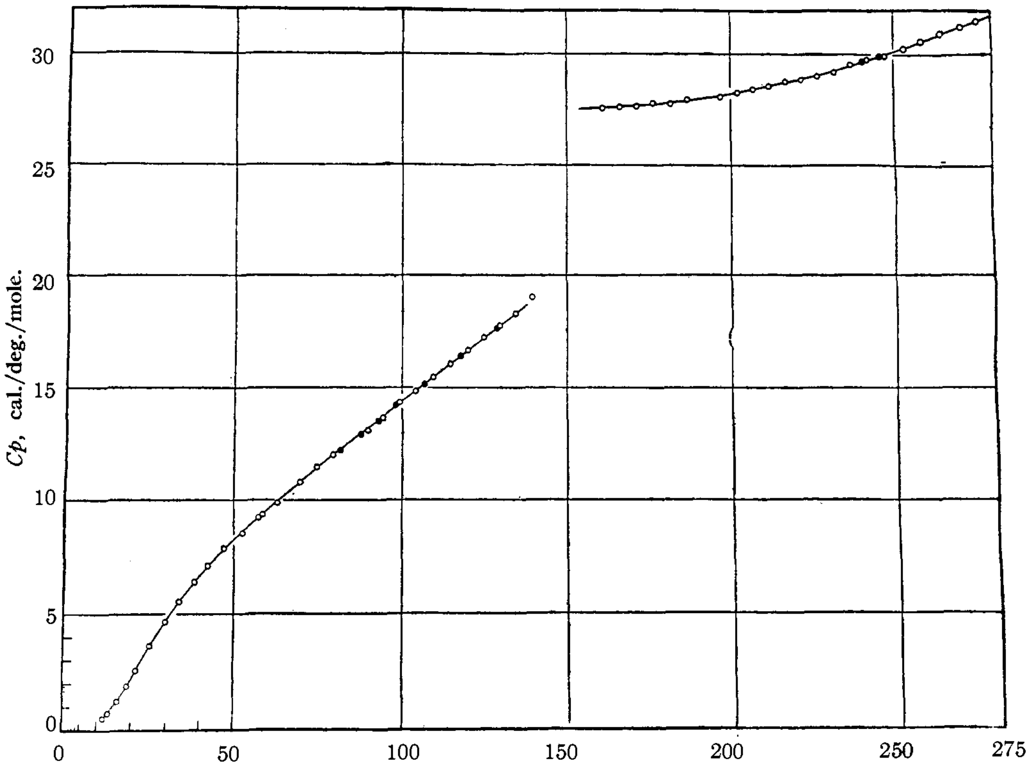

Fig. 1.—The molal heat capacity of trimethylamine: 0.48867 mole, ○; 0.48420 mole, ●

found to be 156.08 ± 0.05°K. (−117.08°C.). Other values in the literature are: Timmermans and Mattaar,[8a] −124.0°C.; Simon and Huter,[8b] −123.8°C.; Wiberg and Sütterlin,[8c] −117.3°C. With regard to the possible existence of another crystalline form, the agreement between the low values of the melting point obtained by Simon and Huter and Timmermans and Mattaar is of no real significance since the melting point of dimethylamine obtained by the latter authors differed from that found by the former by 3° whereas the values of Simon and Huter,[8b] Wiberg and Sütterlin[8c] and this Laboratory[2] were all within 1°

TABLE II

THE MOLAL HEAT CAPACITY OF TRIMETHYLAMINE

Temp., °K. Solid	C_p, cal./deg./mole	Temp., °K. Liquid	C_p, cal./deg./mole
12	0.54	160	27.57
15	1.03	170	27.68
20	2.17	180	27.80
25	3.47	190	27.98
30	4.71	200	28.22
35	5.75	210	28.50
40	6.70	220	28.81
50	8.24	230	29.20
60	9.53	240	29.65
70	10.85	250	30.12
80	12.06	260	30.67
90	13.21	270	31.22
100	14.38	280	31.68
110	15.51		
120	16.69		
130	17.81		
140	18.88[a]		
150	19.83[a]		

[a] Premelting range extrapolated.

TABLE III

MELTING POINT OF TRIMETHYLAMINE

0°C. = 273.16°K.

Melted, %	Total time, min.	T, °K. Res. Th.	T, °K. Thermocouple S-4	T, °K. Thermocouple S-7
11	130	155.539	155.513	155.534
26	265	155.742	155.721	155.741
41	430	155.843	155.806	155.826
57	610	155.905	155.897	155.907
74	775	155.949	155.939	155.946
91	1020	155.971	155.960	155.968
(100)				155.979
Melting point of pure trimethylamine				156.08±0.05°K. (−117.08°C.)
Mole per cent. impurity				0.27

The Vapor Pressures.—The results of the vapor pressure determinations, made as described previously,[4,5] are given in Table IV. Column 1 gives the observed pressure, column 2 the absolute temperature as read by the resistance thermometer calibrated against standard thermocouple S-7, and column 3 gives the differ-

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(8) (a) Timmermans and Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921); (b) Simon and Huter, *Z. Elektrochem.*, **41**, 28 (1935); (c) Wiberg and Sütterlin, *ibid.*, **41**, 1151 (1935).

ence between the observed pressure and that calculated from the temperature by means of equation (1). The last three measurements were made on the residue after distilling off one-third of the same sample. This residue was removed and later put back into the calorimeter for this purpose. The deviations correspond to 0.01° and indicate little effect of the impurity on the vapor pressures.

TABLE IV

THE VAPOR PRESSURE OF TRIMETHYLAMINE

0°C. = 273.16°K.; boiling point, 276.026°K.; *g* for State College = 980.124 (I.C.T.)

$P_{\text{obsd.}}$ Int. mm. Hg.	$T_{\text{obsd.}}$ °K.	$P_{\text{obsd.}} - P_{\text{calcd.}}$,[a] mm. A., S., S., M. and Z.	S. and H.[9b]	W. and S.[9c]
6.04	192.835	0.00	−0.18	+0.7
10.25	199.069	.00	− .13	+1
25.16	210.811	− .01	+ .07	+1
50.83	221.212	− .01	+ .24	0
69.79	226.308	.00	+ .32	0
94.12	231.376	+ .02	+ .32	0
132.64	237.533	+ .02	+ .56	0
192.20	244.643	.00	+ .96	−1
238.31	248.995	+ .02	+1.20	−1
288.03	252.986	+ .01	+1.37	−1
348.82	257.176	− .01	+1.51	−1
426.05	261.728	− .02	+1.65	−1
505.14	265.751	+ .03	+1.49	−1
601.61	270.037	+ .02	+0.83	0
701.27	273.930	+ .03	−0.80	+1
761.51	276.078	+ .02	−1.94	+1
After distilling off one-third of the material.				
251.23	250.083	+0.10	+1.24	−1
472.83	264.165	+0.17	+1.54	−1
777.15	276.604	+0.34	−2.42	+3

[a] $\text{Log } P_{\text{mm.}} = -(2141.7743/T) - 11.400327 \log T + 0.006349001\,T + 36.715267.$

In the range from 190°K. to the normal boiling point the vapor pressures can be fitted by equation (1)

$$\text{Log}_{10}P_{\text{mm}} = -2141.7743/T - 11.400327 \log T + 0.006349001\,T + 36.715267 \quad (1)$$

The value of the normal boiling point calculated from equation (1) is 276.03 ± 0.05°K. (2.87°C.). The values given in the literature are: Vincent and Chappuis,[9a] 9.3°C.; Hofmann,[9b] 3.3°C.; Simon and Huter,[8b] +2.9°C.; Wiberg and Sütterlin,[8c] +2.8°C.; Thompson and Linnett,[9c] 3.2°C. The third and fourth groups of investigators also report vapor pressure determinations and give their results as an equation with deviations of the experimental points. From the equations and deviation plots we have calculated what the observed pressure would be at the temperatures of our observations, allowing for the difference in ice points (270.20°K. for both European investigators and 273.16°K. in our case), by multiplying our Kelvin temperatures by 273.20/273.16. Since in neither case is any gravity correction mentioned and the results are not explicitly stated to be in international mm., we have corrected their pressures to international mm. where such a correction is significant. The deviations of their pressures from our equation are given in columns 4 and 5 of Table IV.

The Heat of Fusion.—The data were taken along with the heat capacities by the usual method.[4,5] The results are tabulated in Table V. Fusions 1, 2 and 3 were taken on the 0.48867 mole sample. The fourth fusion, taken on the 0.48420 mole sample, was started closer to the melting point than was the case in the first three.

TABLE V

HEAT OF FUSION OF TRIMETHYLAMINE

Mol. wt. 59.11; 0.48867 mole for first three, 0.48420 for fourth; melting point, 156.08 ± 0.05°K.

Temp. interval, °K.	Cor. heat input, cal./mole	$\int C_p\,dT$, cal./mole	ΔH fusion, cal./mole
150.137–158.172	1838.7	274.6	1564.1
150.027–158.759	1865.9	301.5	1564.4
149.989–158.071	1839.7	275.3	1564.4
151.835–160.370	1871.8	308.7	1563.1
		Average	1564.0 ± 1.0

Heats of Vaporization at the Normal Boiling Point.—These heats of vaporization were measured using an apparatus for collecting the vapor similar to that described by Giauque and Johnston,[10,11] in conjunction with calorimeter C. The pressure in this method is maintained constant by controlling automatically the pressure behind the mercury in a three-liter collecting vessel with a solenoid valve actuated by contact in a manometer. Thus, as the pressure behind it decreases, the mercury is allowed to fall, increasing the volume of the collected vapor and thus reducing its pressure. This action takes place quite rapidly and in such a way as to keep the pressure constant to within a few millimeters. The vapor thus collected was condensed in a bulb and weighed.

TABLE VI

MOLAL HEAT OF VAPORIZATION OF TRIMETHYLAMINE AT THE NORMAL BOILING POINT

Mol. wt. = 59.11; boiling point = 276.03 ± 0.05°K.

Moles vaporized	Mean temp. of vapor, °K.	Total cor. heat input, cal./mole	$\int C_p\,dT$, cal./mole	ΔH at N.B.P. to real gas state cal./mole
0.13237	276.081	5469.8	10.4	5480.8
0.12621	275.942	5525.6	41.7	5483.9
			Mean	5482.4 ± 7
Calculated from equation (1) and critical data of Vincent and Chappuis[9a] (T_c = 433.7°K., P_c = 41 atm. Berthelot correction = 205 cal.).				5523

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(9) (a) Vincent and Chappuis, *Compt. rend.*, **103**, 380 (1886). (b) Hofmann, *Ber.*, **22**, 703 (1889), gives the value 3.2 to 3.8° C. at 764.6 mm. The average had been corrected to 1 atm. using our pressure coefficient. (c) Thompson and Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

(10) Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

(11) Kennedy, Sagenkahn and Aston, *ibid.*, **63**, 2267 (1941).

Table VI summarizes the data on the heat of vaporization. This table also compares the measured heat of vaporization with that calculated from equation (1) and thermodynamics using the modified Berthelot equation of state with the critical constants determined by Vincent and Chappuis.[9a] Needless to say, the measured heat of vaporization is the more accurate.

Heats of Vaporization at 250°K.—These vaporizations were taken in calorimeter C using a different method to collect the vapor.[12] The pressure was held constant by maintaining a pressure drop through a grooved stopcock which could be very finely adjusted. The pressure on one side of this stopcock was that of the vaporization while on the other side it corresponded to the condensing pressure of the trimethylamine in liquid air, *i. e.*, effectively zero pressure. The material was condensed into a duplicate bulb while the stopcock was being set; when the pressure, as read on a Société Génévoise cathetometer, remained constant, condensation into the main sample bulb was started by turning a three-way stopcock from the duplicate to the main sample bulb. After a measured time had elapsed, the three-way stopcock was turned again to the duplicate bulb whose contents was returned to the calorimeter after the measurements were complete. By frequently adjusting the grooved stopcock during vaporization it was found possible to control the pressure to better than 0.5 mm.; without this adjustment the pressure varied as much as 15 mm. The average pressure during vaporizations was obtained by plotting the pressure against the time, integrating and dividing by the total time. The value thus obtained corresponded to a temperature never more than 0.2° different from the temperature of S-4 (soldered to the calorimeter top). The difference of 0.2° corresponds to but 3 cal./mole difference in the heat of vaporization. If the 0.2° indicates superheating of the vapor, the error produced on the heat of vaporization will be 3 cal./mole in the opposite direction. Thus it is immaterial which temperature is chosen as representing that of the vaporization. The temperature corresponding to that of the vapor pressure was finally chosen.

Instead of weighing the vaporization samples, they were evaporated into the large collecting bulb described above whose volume was known to ±0.05 cc.; the bulb is located in a thermostat whose temperature was maintained to ±0.005°C. as read on an accurately calibrated Beckmann thermometer. The pressure of this material was then read on the Société Génévoise cathetometer. It was then possible to calculate the amount of sample without weighing it by using the above data together with the density data presented in the next section. The advantage of this procedure lies in the fact that each vaporization can be started with a full calorimeter without having to wait for the weighing and reintroduction of the sample, which is a rather lengthy procedure at best.

Table VII summarizes the data on the low pressure heats of vaporization. This table also compares the measured heat of vaporization with that calculated from equation (1) and thermodynamics using the modified Berthelot equation of state with the critical constants of Vincent and Chappuis.

TABLE VII

MOLAL HEAT OF VAPORIZATION OF TRIMETHYLAMINE AT 250.00°K AND 250.01 MM. PRESSURE

Moles vaporized	Mean temp. of vaporization, °K.	Total cor. heat input, cal./mole	$\int C_p\, dT$, cal./mole	ΔH at 250.00°K. and 250.01 mm. to real gas state cal./mole
0.11000	252.345	6102.2	275.7	5826.5
0.11898	250.049	5777.8	41.0	5818.8
			Average	5822.6 ± 7
Calculated from equation (1) and same critical data as given in Table VI (Berthelot correction 98 cal.)				5844

The Vapor Densities.—The temperatures, pressures and volumes of the density samples were measured as described for the low pressure vaporization samples. Measurement was made in the range 0.8 to 0.95 atmosphere. At the completion of the above measurements, the samples were condensed into weighed sample bulbs.

The densities were fitted by the equation

$$d/P = 0.000079051P + 0.00241364 \qquad (2)$$

where d is the g. per cc. and p in atmospheres.

Extrapolation of equation (2) to zero pressure gives a molecular weight of 59.052 compared to a molecular weight for the pure material of 59.112. Assuming that the discrepancy is due to an equimolar mixture of methyl and dimethylamines, the impurity is calculated to be 0.28 mole per cent., which is in excellent agreement with the melting point determination value of 0.27 mole per cent.

Essentially the same limiting density is obtained using an equation of the form

$$\frac{P}{d} = \left(\frac{P}{d}\right)_0 + \left(\frac{RT}{\text{mol. wt.}^2}\right)Bd \qquad (3a)$$

in which the average molecular weight of the impure material must be used. The equation thus obtained from the data by the method of least squares is

$$P/d = -5331.75d + 414.358 \qquad (3b)$$

Table VIII summarizes the density data. The first column gives the pressure, the second gives the density, the third gives d/P, the fourth gives the values of d/P calculated from equation (2), and the last column gives the values of the second virial coefficient calculated therefrom using the molecular weight calculated from the limiting density. For completeness, below the table is given the second virial coefficient calculated from the modified Berthelot equation at this tempera-

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[12] Aston, Fink and Schuman, THIS JOURNAL, 65, 341 (1943).

ture. The accuracy of this value is not to be compared with that determined by experiment. The only other determinations of the vapor density have been made by Muller.[13]

Table VIII

The Vapor Densities of Trimethylamine at 298.16°K.

Pressure in atm.	Density, g./cc.	d/P (obs.)	d/P calcd.[a]	B,[c] 1./mole
0.94670	0.00235584	0.00248848	0.00248848	−0.758
.88324	.00219402	.00248400	.00238346	− .767
.87801	.00218014	.00248305	.00248305	− .761
.79968	.00198018	.00247622	.00247685	− .758
0[b]	....	....	.00241364	...

[a] $d/P = 0.000079051\ P + 0.00241364$. [b] Extrapolated. [c] $B = -0.723$ calculated from the Berthelot equation, $B = (9\ PVT_c/128\ P_cT)(1 - 6T_c^2/T^2)$.

The Entropy from the Calorimetric Data.—The calculation for the liquid at the melting point and at the normal boiling point is summarized in Table IXa, while the calculations at 200, 250 and 176.03°K. for the liquid, saturated vapor and ideal gas are given in Table IXb.

Table IXa

The Molal Entropy of Trimethylamine at 156.08, 276.03 and 298.16°K.

Mol. wt. 59.11, 0°C. = 273.16°K.

	E.u.
0-11.89°K. Debye extrapolation (Θ = 143°K., 6 degrees of freedom)	0.178
11.89-156.08°K., graphical $\int C_p\ d \ln T$	20.658
156.08°K., (1564.1/156.08) fusion	10.021
Entropy of liquid at the melting point	30.857 ± 0.09
156.08-276.03°K., graphical $\int C_p\ d \ln T$	16.423
Entropy of liquid at the normal boiling point	47.28 ± 0.14
276.03-298.16°K., graphical $\int C_p\ d \ln T$	2.54
Entropy of superheated liquid at 298.16°K.	49.82

Table IXb

The Molal Entropy of Gaseous Trimethylamine at Certain Temperatures

Mol. wt. 59.11, 0°C. = 273.16°K.

	E. u. 200.00°K.	250.00°K.	276.03°K.
Liquid at melting point	30.857	30.857	30.857
156.08 − T, °K. graphical	6.893	13.368	16.423
Vaporization at T, °K.	32.192[b]	23.305[d]	19.868[c]
Gas imperfection cor.[a]	0.060	0.070	0.159
Correction to 1 atm.	−8.402	−2.209	0
Entropy ideal gas at T, °K., 1 atm.	61.60 ± 0.14	65.39 ± 0.16	67.31 ± 0.19

[a] $S_{\text{ideal}} - S_{\text{real}} = 27RT_c^3P/32T^3P_c$; P_c = 41.0 atm.; T_c = 433.7°K. [b] This value was calculated from the vapor pressure equation. [c] The value at 276.03°K. is the measured value. [d] The value at 250.00°K. is the measured value.

The Spectroscopic Assignment.—The frequencies were taken from the work of Kohlrausch and Wagner[14a] and Kohlrausch.[14b] The frequency assignment was made by standard methods of group theory, a few missing frequencies being assigned by consideration of analogous molecules. Table X, using the nomenclature of Kohlrausch,[14b] shows the group theory table on which the assignment was based. The frequencies chosen in cm.$^{-1}$ were as follows

Skeleton $\omega_1 = 368\ (0)$, $\omega_2 = 827\ (0.26)$, $\omega_{3,4} = 424\ (\text{d}p)$, $\omega_{5,6} = 1050\ (0.82)$.

Hydrogen stretching $\nu_1 = 2766\ (p)$, $\nu_2 = 2943\ (p)$, $\nu_3 = [3000]$, $\nu_{4,5} = 2970\ (\text{d}p)$, $\nu_{6,7} = 2970\ (\text{d}p)$, $\omega_{8,9} = 2970\ (\text{d}p)$

Hydrogen bending $\delta_1 = 1441\ (0.79)$, $\delta_2 = 1466\ (0.79)$, $\delta_3 = [1400]$, $\delta_{4,5} = 1466\ (0.79)$, $\delta_{6,7} = 1441\ (0.79)$, $\delta_{8,9} = 1441\ (0.79)$.

Rocking $\gamma_1 = 1179\ (0.24)$, $\gamma_2 = [1040]$, $\gamma_{3,4} = 1276\ (\text{d}p)$, $\gamma_{5,6} = 1040\ (0.82)$.

Internal rotation $\Gamma_1 = [272]$, $\Gamma_{2,3} = 272\ (0.88)$.

The polarization as given by Kohlrausch and Wagner is enclosed in brackets after each frequency.

Table X

The Frequency Assignment of Trimethylamine, Point Group C_{3v}

Type	C_{3z}	σx	Raman	Infrared	Frequencies
A_1	s	s	p	M_z	Skeleton; ω_1, ω_2 Hydrogen (internal); δ_1, δ_2, ν_1, ν_2 Hydrogen (rocking); γ_1 Hydrogen (internal); δ_3, ν_3
A_2	s	as	v	ia	Hydrogen (rocking); γ_2 Internal rotation; Γ_1
E	e	e	dp	$M_\perp$	Skeleton; $\omega_{3,4}$, $\omega_{5,6}$ Hydrogen (internal); $\delta_{4,5}$, $\delta_{6,7}$, $\delta_{8,9}$ $\nu_{4,5}$, $\nu_{6,7}$, $\nu_{8,9}$ Hydrogen (rocking); $\gamma_{3,4}$, $\gamma_{5,6}$ Internal rotation; $\Gamma_{2,3}$

Estimated frequencies are enclosed in square brackets. The frequency, γ_2, at 1040 cm.$^{-1}$ was estimated in a way discussed in the next sections. The frequency at 272 cm.$^{-1}$ can hardly be other than that due to the doubly degenerate mode corresponding to the internal rotation of two methyl groups in one sense and the third in the opposite sense. To calculate the potential barrier hindering the internal rotation of the methyl groups it is probably permissible to use the equation[15]

$$V = 8\pi^2 I_{\text{red.}}(C\bar{\nu})^2/n^2 \qquad (3)$$

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(13) Muller, *Bull. soc. chim. Belg.*, **20**, 116 (1910).

(14) (a) Kohlrausch and Wagner, *Z. physik. Chem.*, **52**, 185 (1942); (b) Kohlrausch, "Der Smekal-Raman Effekt," Julius Springer, Berlin, 1938, p. 144.

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

where $\bar{\nu}$ is the wave number of the vibration, $I_{\text{red.}}$ is the reduced moment of the methyl group (see below) and n is the number of identical potential maxima hindering the internal rotation (in this case three). This amounts to the assumption that the third internal rotational frequency Γ_1 has also the value 272 cm.$^{-1}$. The value thus obtained is 4270 cal./mole and this is used later to compute the effect of the hindered rotation on the internal entropy.

The Entropy from Spectroscopic and Molecular Data.—The atomic distances used[16] were C–N, 1.47Å., C–H, 1.09Å.; C–N–C angle 108°; H–C–H angle 109°28′. The value obtained for the product of the principal reduced external moments of inertia was: ABC = 1.151×10^{-114} (g. cm.^{2}).[3] The reduced moment of the methyl group is 5.07×10^{-40} g. cm.^{2}. The symmetry number for the rigid molecule is 3 (class C_{3v}). Using the method of Kassel,[17] the entropy due to translation, external and free internal rotation of the three methyl groups is given by

$$S_{\text{t + r + int. rot.}} = 25.163 \log_{10} T - 4.575 \log_{10} P + 8.413 \cdots \quad (4)$$

The value of ABC given above is that of the determinant in equation 11 of Kassel's paper.

Equation (4) must be reduced by three times the difference between the free and restricted rotational entropy of a methyl group, of reduced moment 5.07×10^{-40} g. cm.^{2} and with three equal barriers of 4270 cal./mole. This quantity, $(S_f - S)$ was obtained from Pitzer's tables.[15]

The frequency γ_2 was guessed as 1000 cm.$^{-1}$ by analogy. However, at 200°K. it contributes only 0.01 e. u. to the entropy; so that the conclusions based on the comparison at 200° K. are independent of this frequency. It will be noted that $\gamma_{5,6}$ has been taken as accidentally degenerate with $\omega_{5,6}$ since there is no other line on the Raman spectrum corresponding to this depolarized frequency. If this assignment is in error it could affect the comparison at 200°K. by 0.06 e. u. so that the agreement at higher temperatures between the spectroscopic and calorimetric entropies confirms the vibrational assignment.

Table XI gives a summary of the calculation of the entropy from molecular and spectroscopic data at 200.00, 250.00 and 276.03°K.

TABLE XI

THE ENTROPY OF TRIMETHYLAMINE IN THE IDEAL GAS STATE FROM MOLECULAR AND SPECTROSCOPIC DATA AT CERTAIN TEMPERATURES

	200°K.	250°K.	276.03°K:
Translation, external and internal rotation	66.31	68.75	69.83
Vibrational	1.45	2.46	3.08
$-(S_F - S) \times 3$ $V = 4270$ $I_{\text{red.}} = 5.07 \times 10^{-40}$	−6.27	−5.79	−5.50
Total	61.49	65.42	67.41
Calorimetric	61.60	65.39	67.31

The excellent agreement between the spectroscopic and calorimetric entropy at 200°K. is an indication that the frequency of 272 cm.$^{-1}$ has been correctly assigned to the hindered internal rotation. It is perhaps the best example of the spectroscopic manifestation of such internal modes in that the frequency in question has the correct polarization and yields barriers in agreement with experiment. The barrier of 4270 cal./mole for trimethylamine is to be compared with values of 3000 cal./mole for methylamine[1a] and 3460 for dimethylamine.[2] It should be noted that the value of 3000 cal./mole for methylamine was calculated roughly to fit the calorimetric data and a more precise calculation has confirmed this value. A value of 1540 cal./mole has been calculated from a doubtful line at 270 cm.$^{-1}$ in the Raman spectrum[1b] but we attach little significance to it in view of the fact that the line may be due to another cause.

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Summary

1. The heat capacities of solid and liquid trimethylamine have been measured from 11.40 to 278.13°K.

2. The equilibrium temperature and heat of fusion have been determined.

3. The heats of vaporization at 276.03° and 250.00°K. have been determined calorimetrically. The vapor pressures have been measured in the range 200 to 278°K. and used to calculate values of the heat of vaporization at 200.00, 250.00 and 276.03°K.

4. An assignment of the Raman spectrum has been made. Entropies calculated from the molecular and spectroscopic data, using the Raman shift of 272 cm.$^{-1}$ for the torsional frequency, agree with the calorimetric values. This frequency corresponds to a barrier of 4270 cal./mole.

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(16) Brockway and Jenkins, THIS JOURNAL, **58**, 2036 (1936).

(17) Kassel, *J. Chem. Phys.* **4**, 27 (1936).