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

The Thermodynamic Properties and Configuration of Trimethylhydrazine Identification and Correction for a Major Impurity[1]

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The heat capacities of trimethylhydrazine have been measured from 12 to 294°K. The triple point (201.24 ± 0.01°K.), the heat of fusion (2267 ± 1.5 cal./mole) and the heat of vaporization at 292.16°K. (7949 ± 7 cal./mole), have been measured. The vapor pressures have been measured between 257 and 287°K., and the data found to be represented by the equation $\log_{10} p = -2614.506/T - 6.873235 \log T + 28.06810$. The entropy of the ideal gas at 292.16°K. and 1 atm was found to be 79.45 ± 0.14 e.u. This value has been compared with that calculated from spectroscopic and molecular data to show that only one rotational isomer is present. The entropies of hydrazine and its mono- and dimethyl derivatives have been reviewed and shown to be consistent with barriers and isomer composition closely similar to those of the analogous hydrocarbons. A method is given for identifying and correcting for the presence of a major impurity.

Rotation about the nitrogen–nitrogen bond in trimethylhydrazine should give rise to isomerism similar to that found in hydrazine,[3a] methylhydrazine[3b,c] and the dimethylhydrazines,[4a,b] in which a skew form is favored. This paper presents the results of a calorimetric investigation of trimethylhydrazine and a comparison of the third law entropy with that from spectroscopic and molecular data, together with a discussion of the probable configuration of the molecule.

Experimental

The Trimethylhydrazine Sample.—Trimethylhydrazine was prepared by the method of Class and Aston,[5a,b] purified by distillation through a column of glass helices with approximately 100 theoretical plates, and further purified by fractional melting[6] in a glass apparatus. Unfortunately the sample still contained 2.6 mole % impurity, 2.0 mole % of which was proved to be *unsym*-dimethylhydrazine. To have effected further purification would have required a prohibitively large sample. However, since the amount and nature of the major impurity was known, this was not necessary.

TABLE I

HEAT CAPACITY OF TRIMETHYLHYDRAZINE

Mol. wt. 74.126; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
12.871	0.78	61.819	10.38	140.450	20.24
14.703	1.08	67.604	11.26	145.771	20.77
16.984	1.44	71.902	11.87	152.025	21.36
20.261	2.18	76.787	12.59	158.173	21.91
22.558	2.70	81.461	13.30	164.499	22.90 premelt
25.317	3.32	83.802	13.64		
28.431	4.05			205.378	43.34 liq.
				211.466	43.63
		91.721	14.65	217.003	43.84_5
24.257	3.11	96.865	15.26	220.797	43.93
26.013	3.50	101.818	15.87	226.183	44.05_5
28.343	4.02	106.605	16.44	232.625	44.13
31.092	4.67	111.244	16.93	239.012	44.16
36.019	5.78	116.172	17.54	248.831	44.33
39.809	6.54	121.360	18.13	257.122	44.45
43.901	7.27			263.387	44.26
49.228	8.28	111.288	16.91	269.590	44.37
53.808	9.08	117.484	17.71	275.737	44.42
58.931	9.91	123.492	18.33	281.838	44.42_5
65.235	10.92	129.312	18.99	287.890	44.44
71.889	11.86	134.960	19.66	293.881	44.45

Heat Capacity Measurements.—The heat capacities of a sample of 48.924 g. (0.66001 mole) were measured from 12 to 294°K. in calorimeter G, which was used in the work on *unsym*-dimethylhydrazine.[4b] The results are listed in Table I. Smoothed values at integral temperatures are given in Table II.

The mean deviation of the experimental points from the best curve is 1% below 20°K., 0.02% for the solid above 20°K., and less than 0.01% for the liquid.

TABLE II

HEAT CAPACITY OF TRIMETHYLHYDRAZINE AT INTEGRAL TEMPERATURES

Mol. wt. 74.126; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules.

Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	Temp., °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
13	0.80	80	13.08	195	24.225
14	0.965	85	13.80	200	24.42
15	1.125	90	14.45	201.24	24.47 cryst.
16	1.295	95	15.04		Fusion
17	1.47	100	15.65	201.24	43.12 liq.
18	1.65	105	16.235	205	43.315
19	1.85	110	16.80	210	43.56
20	2.07	115	17.39	215	43.77
21	2.305	120	17.975	220	43.93
22	2.555	125	18.54	225	44.03
23	2.80	130	19.105	230	44.10
24	3.04	135	19.67	235	44.145
25	3.265	140	20.195	240	44.18
30	4.41	145	20.695	245	44.27
35	5.56	150	21.17	250	44.345
40	6.57	155	21.63	255	44.42
45	7.48	160	22.055	260	44.40
50	8.43	165	22.45	265	44.27
55	9.28	170	22.82	270	44.375
60	10.09	175	23.155	275	44.415
65	10.89	180	23.47	280	44.425
70	11.60	185	23.75	285	44.435
75	12.325	190	24.00	290	44.44
				292.16	44.445

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Due to the presence of a large amount of impurity in the sample, premelting was observed at and above 160°K. Measurements were taken in the entire premelting region, and the heat capacity values listed in Table II between 160°K. and the melting point are based on a combination of correction and extrapolation. Values of the heat capacity of the solid near the melting point may be in error by several tenths of a per cent.

The Melting Point, the Impurity and its Effect.—Equilibrium temperatures of solid and liquid trimethylhydrazine were observed with increasing fractions of the sample melted. The data are summarized in Table III. The solid-insoluble impurity was found to be 2.6 mole %, and the calculated melting point of pure trimethylhydrazine is 201.24 ± 0.01°K.

Table III

Melting Point of Trimethylhydrazine

0°C. = 273.16°K.

Temp., °K.	1/fraction melted	Temp., °K.	1/fraction melted
193.540	8.301	199.659	1.715
197.236	4.350	200.031	1.313
197.743	3.778	200.32 (extrap.)	1
199.036	2.394	201.24 (extrap.)	0

The intuition that the major part of the impurity was *unsym*-dimethylhydrazine was quantitatively confirmed by the thermal data in the premelting region. Therefore it is possible to correct exactly for the effect of the major impurity provided there is perfect solution; this is proved below.

From the heat of fusion of *unsym*-dimethylhydrazine[4b] and that of trimethylhydrazine, the eutectic temperature of the system trimethylhydrazine–*unsym*-dimethylhydrazine is calculated to be 185.0°K., provided that Raoult's law is obeyed; the calculated eutectic composition is 0.609 mole % trimethylhydrazine and 0.391 mole % *unsym*-dimethylhydrazine; the heat of fusion of one mole of eutectic mixture is 2320 cal., assuming perfect solution.

A strong inflection was observed in the apparent heat capacity ($\Delta E/\Delta T$) curve of the sample in the vicinity of 180°K. From the calorimetric data enthalpies were calculated at the end of each energy addition. The solid upper curve of Fig. 1 shows the heat capacities derived from these enthalpies. The maximum in the heat capacities occurs at 182.2 ± 0.1°K. Using this value in conjunction with the calculated properties of the system trimethylhydrazine–*unsym*-dimethylhydrazine, it is calculated that the lowering in eutectic temperature corresponds to a third constituent present to the extent of 9.5 mole % of the eutectic or that the bulk sample contains 2.1 mole % *unsym*-dimethylhydrazine and 0.5 mole % of another impurity or impurities.

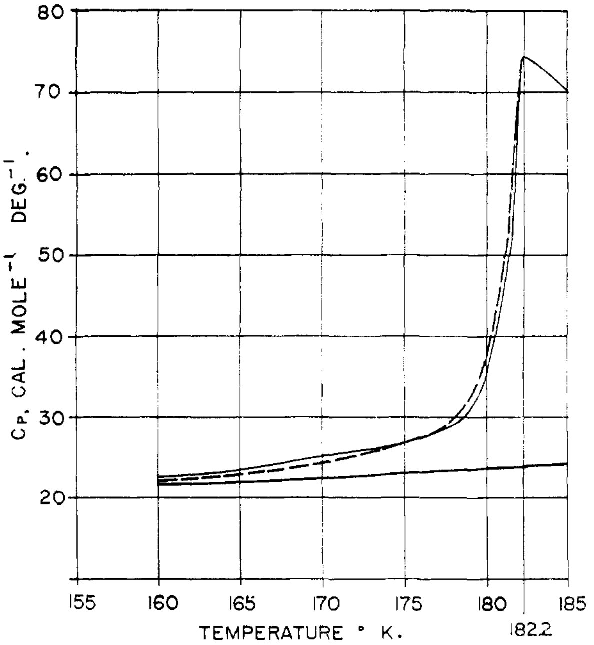

Fig. 1.

This conclusion may be checked in the following manner: In an excess of trimethylhydrazine, 0.391 mole of *unsym*-dimethylhydrazine are equivalent to one mole of eutectic mixture, and therefore the sample should contain 5.4 mole % eutectic. Now, at 182.2°K., $f = 1 = Q/(2320N)$, where f is the fraction of eutectic that has melted, N is the mole fraction of eutectic in the bulk sample, and Q is the area between the apparent heat capacity curve and the extrapolated true heat capacity curve (the lower curve of Fig. 1) of the solid up to 182.2°K. The value of Q was found to be 126 cal./mole, and hence $N = 0.054$ mole %, in agreement with the expected value.

A final argument in support of the contention that the major part of the impurity is *unsym*-dimethylhydrazine is provided by an examination of the fraction of sample melted at various temperatures up to 182.2°K. The fractions of eutectic melted may be obtained directly from the thermal data by making use of the assumed composition of the eutectic together with computed amount of other impurities to ascertain the specific heat of fusion. The results are given in the first two columns of Table IV. It is easily verified that the values of $1/f$ listed in the first column are a linear function of the temperature. The value of T_0 obtained by extrapolation to $1/f = 0$ agrees with the calculated eutectic temperature well within the limits of experimental error. Another relation between $1/f$ and T may be obtained by putting a straight line through the points ($1/f = 0$, $T = 185.0$) and ($1/f = 1$, $T = 182.2$) where f is again the fraction of eutectic that has melted. This procedure is solely based upon the hypothesis that *unsym*-dimethylhydrazine is present in the sample (which implies that $T_0 = 185.0$°K.), and is obviously independent of any assumptions regarding the quantities of *unsym*-dimethylhydrazine in the eutectic or other material in the sample. Equilibrium temperatures taken from this theoretical line are listed in the last column of Table IV. The calculated and observed temperatures must, of course, agree by hypothesis at $1/f = 1$, but the agreement at other values of $1/f$ serves to confirm the assumptions that were made.

Table IV

Fractions of Eutectic Melted

0°C. = 273.16°K.

1/fraction melted	T, °K. Obsd.	Calcd.
1.89	179.4	179.7
1.57	180.3	180.6
1.40	181.0	181.1
1.21	181.5	181.6
1.10	181.9	181.9
1	182.2	(182.2)
0	185.4 (extrap.)	185.0

The dashed curve of Fig. 1 shows the heat capacities calculated by using all the assumptions.

The values of the specific heat of *unsym*-dimethylhydrazine are so close to those of trimethylhydrazine at any temperature that no correction is necessary for the presence of 2.1 mole % of the former in the sample. Corrections of 0.5% are required in the heat of fusion and in the heat of vaporization, but since these corrections are known to about 3% of their value, their application introduces negligible uncertainty. However, the possibility remains that all results of this paper may be in error by 0.1 to 0.2% due to the presence of 0.5 mole % of the additional 0.5% impurities.

The Heat of Fusion.—Three independent determinations of the heat of fusion of trimethylhydrazine were made, and the resulting values are presented in Table V. The usual corrections[7] have been applied to the heat input.

The entropy of mixing due to impurities is calculated to be 0.26 e.u. This is automatically excluded from the entropy of fusion when the heat capacities are corrected for

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TABLE V

HEAT OF FUSION OF TRIMETHYLHYDRAZINE

Mol. wt. 74.126; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules; triple point 200.32°K.

Temp. interval, °K.	Heat input, cal./mole	$\int Cp\, dT$, cal./mole	Pre-melting, cal./mole	ΔH fusion, cal./mole
164.082–205.940	4220.0	1943.5	1.1	2277.6
162.796–203.298	4108.1	1827.9	0.0	2280.2
161.420–202.111	4088.4	1808.9	0.0	2279.5

Mean ΔH = 2279.1 ∓ 1.5

Mean ΔH, corrected for the different heat of fusion of 2.1 mole % *unsym*-dimethylhydrazine = 2267.1

premelting and all the heat due to melting assumed to be put in at the true melting point. On the other hand, if the melting phenomenon be treated in such a way that all latent heat is counted as sensible heat (*i.e.*, the measured heat capacities are used directly and the main part of fusion is treated as a heat capacity over the range 1° below the melting point), the entropy of the liquid at the melting point does include the entropy of mixing.

The entropy of the liquid at the melting point calculated by the former method is 39.06 e.u. (not corrected for the slightly different heat of fusion of *unsym*-dimethylhydrazine), and consequently the second method should result in a value of 39.32 e.u. The actual value found by the sensible heat method is 39.34 e.u. As far as the authors are aware this is the first time attention has been called to the question of entropy of mixing where there is impurity and how this is eliminated.

The Vapor Pressures.—The vapor pressure of trimethylhydrazine at 292.16°K. is required for the evaluation of the entropy of compression of the gas at that temperature. Measurements were made as for methylhydrazine.[3a] Observed values of the vapor pressure at various temperatures are listed in column 2 of Table VI. These were fitted to the equation

$$\log p = -2621.916/T - 6.920951 \log T + 28.20910 \quad (1)$$

TABLE VI

VAPOR PRESSURES OF TRIMETHYLHYDRAZINE

0°C. = 273.16°K.

T, °K.	$P_{\text{obs.}}$, mm.	$P_{\text{calcd.}} - P_{\text{obs.}}$, mm.	Cor. P, mm.
256.939	21.20	0.00	21.34
263.791	32.52	+ .01	32.73
269.058	44.41	.00	44.67
274.222	59.38	+ .02	59.72
279.568	79.19	− .01	79.59
279.576	79.25	− .03	79.63
286.986	115.44	− .01	115.98
286.995	115.51	− .02	116.05
292.16	148.05 (extrap.)		148.72

Deviations of the experimental values from this equation are tabulated in column 3. Use was made of the vapor pressure equation for *unsym*-dimethylhydrazine[4b] to correct the observed pressures for the presence of 2.1 mole % of that substance. Corrected values are listed in the last column, and are summarized by the equation

$$\log p = -2614.506/T - 6.873235 \log T + 28.06810 \quad (2)$$

The values of ΔC_p calculated from equation 1 or equation 2 agree with that estimated from the spectroscopic and molecular data for the gas along with the measured heat capacities of the liquid to about 6 cal., which is in accord with the consistency of the data. As a check on internal consistency, the value of the heat of vaporization at 292.16°K. calculated from the corrected vapor pressures as given by equation 2 is appended at the foot of Table VII for comparison with the experimental value corrected for impurity.

In spite of the thermodynamic consistency of the corrected as well as the uncorrected vapor pressures, their reliability is open to serious doubt because of the presence of 0.5 mole % of unknown impurity or impurities in the sample. The vapor pressure at 274°K. was lowered by 0.8 mm. after about one third of the sample had been distilled off, whereas the calculated drop due to enrichment of the residue in the less volatile *unsym*-dimethylhydrazine only amounts to 0.04 mm.

TABLE VII

HEATS OF VAPORIZATION OF TRIMETHYLHYDRAZINE

Mol. wt. 74.126; 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules

Mole vaporized	Mean temp. of vaporization, °K.	ΔH, real gas, T, °K.	ΔH real gas 292.16°K., cal./mole
0.047673	292.525	7984	7991
.065766	292.614	7990	7999
.030584	292.801	7978	7991
.032602	292.703	7976	7987
		Av.	7992 ∓ 7

Value cor. for presence of 2.1% *unsym*-dimethylhydrazine 7949

Calcd. from eq. 2 and estimated critical data, T_c = 500°K., P_c = 46 atm., Berthelot correction = 62 cal.) 7910

The Heat of Vaporization.—Measurements were made as for methylhydrazine[3a] except that a grooved stopcock was used instead of a valve to maintain the temperature constant. The results are presented in Table VII. Due account was taken of the temperature variation of the heat of vaporization of *unsym*-dimethylhydrazine in the correction for the presence of 2.1 mole % of that substance in the sample.

Since these determinations involved the use of stopcocks, they were made after all other measurements had been completed.

The Entropy from Calorimetric Data.—The calculation of the entropy of trimethylhydrazine from the calorimetric data is summarized in Table VIII. The correction for gas imperfection was made with the estimated critical constants given in Table VII in conjunction with the Berthelot equation.

TABLE VIII

ENTROPY OF TRIMETHYLHYDRAZINE FROM THERMAL DATA

	E.u./mole
0–15°K., Debye function, θ = 141, six degrees of freedom	0.368 ± 0.02
15–155°K.	21.311 ± .02
155–201.24°K., graphical	6.055 ± .00
Fusion, 2267.1/201.24	11.266 ± .01
201.24–292.16°K., graphical	16.445 ± .02
Entropy of liquid at 292.16°K.	55.445 ± .07
Vaporization, 7949/292.16	27.208 ± .03
Entropy real gas 292.16°K., 148.7 mm.	82.653 ± .10
Entropy ideal gas at 292.16°K., 148.7 mm.	82.689 ± .11
Compression, $R \ln 148.7/760$	− 3.241 ± .03
Entropy ideal gas at 292.16°K., 760 mm.	79.45 ± .14

While most of the work on trimethylhydrazine was in progress, this Laboratory underwent extensive structural alterations in the course of which the room temperature could not be maintained much above 20°. In order to avoid condensation of material, it was necessary to abandon the usual standard temperature of 298.16°K. in reporting results.

The Entropy from Spectroscopic and Molecular Structure Data.—The possible forms of trimethylhydrazine, in order of decreasing probability, are the *outer* form, the *inner* form, and the *trans* form, each corresponding to a sector of $2\pi/3$ for rotation about the N–N bond. Each form exhibits a pair of optical isomers. The *inner* form has the greatest clustering of methyl groups; the nomenclature is that used for methylhydrazine.[3b]

The entropy was calculated for the *outer* form, assuming all angles to be tetrahedral and using the following bond distances[8]: N–N, 1.45 Å.; C–N, 1.47 Å.; C–H, 1.09 Å.; N–H, 1.04 Å. The product of the principal moments of inertia is 6.12×10^{-114} g. cm.^{2} The reduced moments are 23.826×10^{-40} g. cm.^{2} for the methylamino group, 5.055×10^{-40} g. cm.^{2} for the methyl group of the methylamino group and the methyl group farthest removed from the methylamino group, and 5.150×10^{-40} g. cm.^{2} for the third methyl group. They were calculated by the method of Pitzer.[9a,b,c]

The frequencies used in the calculation of the vibrational entropy contribution were 307, 414, 436, 498, 712, 783, 888, 1007, 1044 (2), 1134 (2), 1168 (2), 1180, 1270, 1398 (3), 1477 (6), 2858 (4), 2970 (2), 3082, 3092 (2), 3405 cm.$^{-1}$ [10]

The entropy calculation is summarized in Table IX. The choice of barriers of 3850 ± 150 cal./mole hindering all internal rotations leads to agreement of the calculated entropy of the *outer* form with the experimental value. This is consistent with the result for the hydrocarbon analog, isopentane, which apparently exists in the C_1 form with an average barrier of about 3200 cal./mole, but with methyl barriers as high as 3620 cal./mole.[11] For completeness the data on the liquid have been extrapolated, and a calculation made based on the spectroscopic data and the derived barrier to yield the entropies of the liquid and the ideal vapor at 298.16°K. and 1 atm. The values, are, respectively, 56.34 and 80.00 e.u./mole.

TABLE IX

ENTROPY OF TRIMETHYLHYDRAZINE FROM MOLECULAR DATA AT 292.16°K.

	Outer form, e.u.
S, translation	38.723
S, vibration	4.897
S, external rotation	25.555
S, mixing optical isomers ($R \ln 2$)	1.377
	70.552
S, int. rot. Me ($V = 3850$)	1.877
S, int. rot. Me	1.862
S, int. rot. Me	1.862
S, int. rot. $NHCH_3$ ($V = 3850$)	3.292
Sum	79.44
Obsd.	79.45 ± 0.14

Discussion

The potential barrier hindering rotation about the nitrogen–nitrogen bond in hydrazine[12] has the same magnitude as the methyl barrier in ethane.

For methylhydrazine, several choices for the barrier hindering internal rotation of the methyl group were considered[3a]: A barrier of 2800 cal./mole if the molecule be entirely in the *outer* form; 3200 cal./mole for a mixture of 96 mole % *outer* form and 4 mole % *inner* form; 3500 cal./mole for a mixture of 92 mole % *outer* form and 8 mole % *inner* form. This latter corresponds to an energy difference of 1450 cal./mole. An assignment of 3500 cal./mole agrees within limits of experimental error with the methyl barrier of the hydrocarbon analog, propane (3400 cal./mole).

The case of *sym*-dimethylhydrazine will be considered later in some detail. Regardless of the interpretation of experimental results, the choice of methyl barriers in *sym*-dimethylhydrazine of 3000 cal./mole is compatible with the value for its hydrocarbon analog, butane (3300 cal./mole).[13]

Only one assignment is possible for the methyl barriers of *unsym*-dimethylhydrazine in order to obtain agreement between the calculated and the observed entropy, namely, 3700 cal./mole,[4b] which corresponds to the existence of the molecule in the *skew* "gauche" form and agrees within limits of experimental error with the value of the methyl barriers in the hydrocarbon analog, isobutane (3620 cal./mole).[13]

The results for trimethylhydrazine show so much similarity to those for isopentane as to suggest a revision of the conclusions that were drawn from an entropy study of *sym*-dimethylhydrazine.[4a] There will be three forms, *outer–outer, inner–outer* and *inner–inner*, both of the latter corresponding to the gauche configuration of butane. Denoting an *inner* interaction energy by the letter i, and a gauche interaction energy by the letter g, the three forms (oo, io and ii) of *sym*-dimethylhydrazine have the interaction energies

$$oo = 0, io = i + g, ii = 2i + g$$

Adopting Pitzer's value[14] of 800 cal./mole for the energy difference between potential minima (gauche interaction energy), the *inner* interaction energy required to obtain agreement with the observed entropy is 400 cal./mole, and *sym*-dimethylhydrazine exists as a mixture of approximately 75 mole % *outer–outer* form, 20 mole % *inner–outer* form and 5 mole % *inner–inner* form. It has not been possible to relate any of the lines in the spectrum to these forms.[15] Strong hydrogen bonding in the liquid would make a study of the temperature dependence difficult. A determination of the gaseous heat capacities of all the methyl-substituted hydrazines is obviously the best way to verify the conclusions.

It should be noted that the *inner* interaction energy for *sym*-dimethylhydrazine is due to the effect of the interaction of one hydrogen atom with the inner methyl group, the other part of the interaction being absorbed in the 800 cal./mole gauche interaction. Therefore, twice the value of 400 cal./mole or 800 cal./mole is to be compared with the value of 1450 cal./mole found for the energy difference between the two forms of methylhydrazine. If the value of 800 cal./mole be adopted for this *inner* interaction, and using a methyl barrier of 3500 cal./mole, the value obtained for the entropy of methylhydrazine is 67.06 e.u., compared with the experimental value of 66.61 ± 0.2 e.u. at 298.16°K. This corresponds to 21 mole per cent. of the *inner* form and to a dipole moment of 1.76 D. The measured value is 1.68 ± 0.14 D.[16]

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