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

The Thermodynamic Properties and Configuration of Unsymmetrical Dimethylhydrazine[1]

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The heat capacities of *unsym*-dimethylhydrazine have been measured from 12 to 298.16°K. The triple point (215.951 ± 0.005°K.), the heat of fusion (2407.4 ± 1.5 cal. mole^{-1}), and the heat of vaporization at 298.16°K. (8366 ± 4 cal. mole^{-1}) have been measured. The vapor pressures have been measured between 240 and 293.10°K. and the data found to be represented by the equation $\log_{10} p = 2717.132/T - 6.745741 \log T + 28.000194$. The entropy of the ideal gas at 298.16°K. and 1 atm. was found to be 72.82 ± 0.20 cal. deg.$^{-1}$ mole^{-1}. If the molecule is assumed to be entirely in the *gauche* form, this corresponds to a barrier of 3000 ± 1000 cal. mole^{-1} hindering the internal rotation of the amino group. By use of this same barrier an unlikely alternative allows 75% *trans*.

Rotation of the NH_2 group about the nitrogen-nitrogen bond in *unsym*-dimethylhydrazine would permit *trans* and *gauche* forms analogous to those possible in hydrazine.[2] This paper presents the results of a calorimetric investigation of *unsym*-dimethylhydrazine and a comparison of the third law entropy with that from spectroscopic and molecular data leading to a discussion of the probable barriers to internal rotation of the methyl and amino groups, and the configuration of the molecule.

Experimental

The *unsym*-Dimethylhydrazine Sample.—The *unsym*-dimethylhydrazine was prepared by the method of Hatt,[3] and purified by fractional distillation in a glass helix packed 40-plate column, maintained at a pressure of 680 mm. using oxygen-free nitrogen. From the change of the triple point with the fraction of sample melted (Table II), the solid-insoluble, liquid-soluble impurity was determined as 0.01 ± 0.01%. A part of this sample was used to determine the heat of combustion.[4]

The Calorimeter.—A new platinum calorimeter and assembly with platinum–rhodium filling tube, designed for adiabatic operation, was built. This will hereafter be designated calorimeter G. The assembly is similar in design to those previously reported from this Laboratory.[5a,b] Temperatures are measured with a strain-free platinum resistance thermometer Pt-G 10, which meets all requirements of the International Temperature Scale of 1948 and this scale was used above 90°K. This thermometer has been calibrated against the thermodynamic scale of the National Bureau of Standards, and by comparison with a high precision helium thermometer in this Laboratory.[6] The latter comparison was part of an investigation to provide a thermodynamic scale for this and other thermometers in the region 10–90°K. The scale below 90°K. was based on a combination of the data. This calorimeter was used in all measurements except those of the heats of vaporization which were taken in calorimeter F.[7]

Heat Capacity Measurements.—The heat capacity of the empty calorimeter in the range 12–300°K. was measured immediately previously. The heat capacities of a sample of 63.33 g. (1.0491 moles) were measured over 54 temperature intervals from 12 to 300°K. The rounded values are presented in Table I.

The mean deviation of the experimental points from the best curve is 0.02% for the crystal and 0.01% for the liquid.

TABLE I

HEAT CAPACITY OF *unsym*-DIMETHYLHYDRAZINE AT INTEGRAL TEMPERATURES

Mol. wt. 60.08, 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules

T, °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
13	0.65	145	16.255
14	.805	150	16.675
15	.95	155	17.10
16	1.105	160	17.515
17	1.28	165	17.93
18	1.46	170	18.33
19	1.64	175	18.735
20	1.82	180	19.12
21	2.00	185	19.55
22	2.18	190	19.97
23	2.36	195	20.42
24	2.535	200	20.88
25	2.72	205	21.36
30	3.74	210[a]	21.87
35	4.71	215[a]	22.36
40	5.56	215.951	22.46 cryst.
45	6.345	Fusion	
50	7.09	215.951	36.25 liq.
55	7.76	220	36.43
60	8.32	225	36.65
65	8.91	Fusion	
70	9.48	230	36.86
75	10.01	235	37.08
80	10.54	240	37.26
85	11.055	245	37.44
90	11.505	250	37.60
95	11.94	255	37.76
100	12.385	260	37.90
105	12.815	265	38.07
110	13.255	270	38.23
115	13.68	275	38.40
120	14.12	280	38.59
125	14.555	285	38.78
130	14.99	290	38.95
135	15.42	295	39.11
140	15.84	298.16	39.21

[a] From points corrected for prefusion.

Only the heat capacities 6° below the melting point were affected by prefusion. These have been corrected for the effect of 0.01 mole per cent. impurity. Correspondingly the heats of fusion presented in Table III have been corrected for the small amount melted in the prefusion. The correction for vaporization into the filling line was only 0.1% at the highest temperature and therefore neglected. The heat capacity of the calorimeter, at various temperatures, was redetermined after the sample had been removed. It was within 0.1% of the original value. The weight of the

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[1] This research was carried out on Contract N6-onr-269, Task Order III of the O.N.R.

[2] W. G. Penney and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **30**, 902 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

[3] H. H. Hatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 211.

[4] J. G. Aston, E. J. Rock and S. Isserow, THIS JOURNAL, **74**, 2484 (1952).

[5] (a) J. G. Aston and G. J. Szasz, *ibid.*, **69**, 3108 (1947); (b) J. A. Morrison and G. J. Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

[6] J. G. Aston and G. W. Moessen, *et al.* to be published. All the data had not been computed at the time this paper was written.

[7] J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, THIS JOURNAL, **73**, 1939 (1951).

sample was determined after removal and indicated no loss of sample which had been confined and transferred without stopcocks (seals breakable magnetically were used).

The Melting Point.—Equilibrium temperatures of solid and liquid *unsym*-dimethylhydrazine were observed with increasing fractions of the sample melted. These data are presented in Table II along with the reciprocal of the fraction melted.

TABLE II

TRIPLE POINT TEMPERATURES OF *unsym*-DIMETHYLHYDRAZINE

0°C. = 273.16°K., solid insoluble, liquid soluble impurity: 0.01 mole per cent., calculated triple point for zero impurity: 215.951°K.

Temp., °K.	$\frac{1}{\text{Fraction melted}}$
215.863	23.14
215.934	3.86
215.940	2.11
215.945	1.45
215.947	1.04

The Heat of Fusion.—Three independent determinations of the heat of fusion of *unsym*-dimethylhydrazine were made, and the resulting values are presented in Table III. The usual corrections for premelting, and for the heating of the solid and of the liquid have been applied.[5a] For comparison, the value obtained by summing the heat input in determining the triple point, is appended. This value is not used in the evaluation of the mean heat of fusion to be used in the entropy calculation.

The Vapor Pressures.—The vapor pressure of *unsym*-dimethylhydrazine at 298.16°K. is required for the evaluation of the entropy of the ideal gas at this temperature. A series of measurements of the vapor pressure at various temperatures were made between the melting point and 298.16°K. A stirred low temperature cryostat of the type described by Scott and Brickwedde[8a,b] was used. Temperatures, which could be held constant to 0.01°, were measured by a strain-free platinum resistance thermometer filling the requirements of the International Temperature Scale. Its oxygen, ice, steam and sulfur points had been determined in this Laboratory in the conventional manner. A 10-cc. vapor pressure bulb was used along with a 13-mm. bore, copper cased manometer. The latter was read with a Société Genevoise cathetometer with two telescopes with a precision of better than 0.01 mm. The results were fitted to the equation

$$\log p = -2717.132/T - 6.745741 \log T + 28.000194 \quad (1)$$

TABLE IV

VAPOR PRESSURES OF *unsym*-DIMETHYLHYDRAZINE

g for State College = 980.124 cm./sec^2., 0°C. = 273.16°K.

T, °K.	$P_{\text{obsd.}}$, mm.	$P_{\text{calcd.}}$, mm.	$T_{\text{obsd.}} - T_{\text{calcd.}}$
237.75	3.51	3.49	−0.04
249.83	8.92	8.92	.00
255.79	13.62	13.64	+ .02
260.03	18.20	18.19	− .006
269.04	32.29	32.35	+ .03
271.09	36.65	36.65	.00
278.22	55.62	55.57	− .01
282.92	72.07	72.11	+ .01
288.37	96.39	96.30	− .02
293.095	122.40	122.44	+ .006
298.16	Extrap.	156.75	

TABLE V

HEATS OF VAPORIZATION OF *unsym*-DIMETHYLHYDRAZINE

Mol. wt. 60.08, 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules

Vaporized, mole	Mean temp. of evapn., °K.	ΔH, T, °K.	ΔH real gas 298.16°K., cal./mole
0.05246	297.76	8376	8376
.05226	296.50	8412	8373
.07465	297.66	8385	8373
.07674	300.63	8292	8350
		Average	8366 ± 16
From equation 1 and thermodynamics (Berthelot (modified) correction of 84 cal. based on T_c = 522°K. and P_c = 60 atm.)			8353

TABLE III

HEAT OF FUSION OF *unsym*-DIMETHYLHYDRAZINE

Mol. wt. 60.08, 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules, m.p. 215.951°K.

Temp. interval, °K.		Heat input, cal./mole	$\int C_p dT$, cal./mole	Heat of fusion, cal./mole	Pre-melting, cal./mole	ΔH fusion, cal./mole
206.808	219.193	2891.50	482.97	2408.53	+0.02	2408.5
207.950	219.141	2847.20	440.77	2406.43	+ .10	2406.5
212.142	217.231	2668.25	262.32	2404.93	+1.17	2407.1
					Mean ΔH =	2407.4 ± 1.50
213.490[a]	221.182	2772.67		2411.14	3.45	2414.59

[a] From melting point determination.

The observed vapor pressures are tabulated in Table IV along with those calculated from equation 1. In the last column are tabulated the temperature differences $T_{\text{obsd}} - T_{\text{calcd}}$ by which the observed temperature exceeds that calculated from equation 1 at the observed pressure. Measurements were also made after distilling off half the material without significant change.

The heats of vaporization computed from equation 1 agree satisfactorily with the measured values as can be seen from Table V.

The values of ΔC_p calculated from equation 1 agree with those estimated from the spectroscopic and molecular data for the gas along with those measured on the liquid to about

TABLE VI

ENTROPY OF *unsym*-DIMETHYLHYDRAZINE

Mol. wt. 60.08, 0°C. = 273.16°K., 1 cal. = 4.1833 int. joules

	Cal. deg.$^{-1}$ mole^{-1}
0–15°K. Debye function	0.24 ± 0.01
15 = six degrees of freedom 215.951°K.	24.28 ± .05
Fusion 2407.4/215.951	11.15 ± .01
215.951–298.16	12.19 ± .05
Entropy of liquid at 298.16°K.	47.86 ± .12
Vaporization 8366/298.16°K.	28.06 ± .05
Entropy real gas at 298.16°K., 156.75 mm.	75.92 ± .17
Entropy ideal gas 298.16°K., 156.75 mm.[a]	75.95 ± .20
Compression R ln 156.75/760	−3.13 ± .002
Entropy ideal gas at 298.16°K. and 760 mm.	72.82 ± 0.20 e.u.

[a] $S_{\text{ideal}} - S_{\text{real}} = 27\,RT_c^3P/32T^3P_c$ with T_c = 522°K. (estimated), P_c = 60 atm. (estimated).

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(8) (a) R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **6**, 401 (1931); (b) W. H. Keesom and B. G. Dammers, *Physica*, **2**, 1080 (1935); Comm. Phys. Lab. Univ. Leiden, No. 239[a] (1935).

7.0 cal. which is in accord with the consistency of the data. The vapor pressure extrapolated to 298.16°K. on the basis of these data is 156.75 ± 0.20 mm.

The Heat of Vaporization.—Four independent values of the heat of vaporization were obtained directly by vaporizing small fractions of the sample from the calorimeter into weighed bulbs cooled with liquid nitrogen. The method used, and the corrections applied, are as described for methylhydrazine.[7] The results are presented in Table V. The values at 298.16°K. were obtained from those at the experimental temperatures using values of ΔC_p obtained from the heat capacity of the gas, calculated from the spectroscopic data and barriers discussed later, along with the observed liquid heat capacities.

The value at 298.16°K. calculated from thermodynamics using the modified Berthelot equation with T_c estimated as 522°K. and P_c as 60 atm. is also recorded in Table V.

The Entropy from Calorimetric Data.—The entropy of *unsym*-dimethylhydrazine calculated from the above calorimetric data is summarized in Table VI. The correction for the vapor imperfection at 298.16°K. was estimated to be 0.03 cal. deg.$^{-1}$ mole^{-1} using the modified Berthelot equation with the critical constants mentioned above.

Discussion

The Entropy from Spectroscopic and Molecular Structure Data.—By considering rotation about the nitrogen–nitrogen bond, the possible forms of *unsym*-dimethylhydrazine are the *trans* form, corresponding to a sector of $2\pi/3$ and two *gauche* forms, each corresponding to a sector of $2\pi/3$. The entropy is calculated for both forms, assuming all angles tetrahedral, and the following bond distances and angles[9]: N–N, 1.45 Å.; C–N, 1.47 Å.; C–H, 1.09 Å.; N–H, 1.04 Å.; $\angle$C–N–C = $\angle$C–N–N = 110°. The product of the principal moments of inertia, ABC, for the *trans* form is 1.519×10^{-114} g. cm.^{2} and for the *gauche* forms 1.495×10^{-114} g. cm.^{2}. The reduced moments of the methyl and amino groups were calculated by the method of Pitzer.[10]

For the *trans* form, the reduced moment of each of the methyl groups is 5.03×10^{-40} g. cm.^{2}, and that of the amino group is 3.04×10^{-40} g. cm.^{2} while for the *gauche* forms that of the methyl groups is 5.02×10^{-40} g. cm.^{2} and that of the amino group 3.03×10^{-40} g. cm.^{2}. The symmetry number for external rotation is 1 in both cases, three for the methyl group internal rotation and one for that of the amino group, but R ln 3 must be subtracted from the free rotational entropy to limit the amino group to a sector of $2\pi/3$.

The frequencies used in the calculation of the vibration entropy contribution were: *Skeleton*, 418, 445 (2), 803, 904, 961; *Rocking*, 961, 1139, 1046 (2), 1090 (2); Hydrogen Bend, 1301 (4), 1405, 1457, 1593; Hydrogen Stretch, 2950 (3), 2988, 3141 (2), 3330 (2) cm.$^{-1}$.[11]

The contributions to the entropy are presented in Table VII. Comparison with related compounds leads to the choice of a barrier of approximately 3,700 cal. mole^{-1} hindering the rotation of the methyl groups.[12] For the internal rotation of the amino group a barrier of 3000 cal. mole^{-1} was assumed.

If the potential functions be of cosine form for the methyl and amino groups these barriers give libration frequencies of 255 and 295 cm.$^{-1}$, respectively. Examination of the Raman spectrum of the liquid shows a marked broad band around 285 cm.$^{-1}$, with a spread of approximately 30 wave numbers in keeping with these assumptions. As has been pointed out by Penney and Sutherland[2] and confirmed by comparison of third law entropies with those calculated from molecular data for hydrazine,[13] methylhydrazine[7] and *sym*-dimethylhydrazine[14] the *trans* form has a higher energy than the *gauche* forms and exists in negligible quantities at room temperatures. Such would also be expected for unsymmetrical dimethylhydrazine.

TABLE VII

ENTROPY OF *unsym*-DIMETHYLHYDRAZINE FROM MOLECULAR DATA AT 298.16°K.

	trans form, cal. deg.$^{-1}$ mole^{-1}	*gauche* form, cal. deg.$^{-1}$ mole^{-1}
S translation	38.19	38.19
S vibration	3.57	3.57
S external rotation	23.96	24.18
S mixing optical isomers (R ln 2)	0	1.38
S int. rot. Me (V = 3700)	3.89	3.89
S int. rot. NH_2 (V = 3000)	1.76	1.78
Sum	71.37	72.99
S int. rot. (V = 3700)	1.54	1.54
Sum	71.15	72.77
Observed	72.83 ± 0.20	72.83 ± 0.20

Comparison of the experimental value with the entropy calculated for an equimolar mixture of *d*- and *l*-*gauche* forms with none of the *trans* form shows satisfactory agreement for the barrier of 3000 cal. mole^{-1}. However, agreement with the experimental value can be obtained assuming a mixture of 75% of *trans* and 25% of an equimolar mixture of the *d*- and *l*-*gauche* forms.

If a barrier of 3700 cal. mole^{-1} be chosen the entropy is decreased from 0.16 above to 0.06 cal. deg.$^{-1}$ mole^{-1} below the experimental value. This is within the experimental error in either case. The barrier found in hydrazine is 2800 cal. mole^{-1}.[13] If the effect of substitution of methyl groups were as in trimethylamine the barrier for the amino group could be increased to as high as 3700 cal. mole^{-1}, a value not excluded by our data. It is of interest that the value of the amino group in methylhydrazine[14] could possibly be as high as 3400 cal. mole^{-1} which is the value to be expected by analogy with dimethylamine.

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