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

The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressures, Entropy and Thermodynamic Functions of Methylhydrazine[1]

BY J. G. ASTON, H. L. FINK, G. J. JANZ AND K. E. RUSSELL

The entropy of methylhydrazine vapor in the ideal gas state has been calculated from heat capacity measurements down to 14.5°K., heats of fusion, heats of vaporization and the vapor pressure. This has been compared with that calculated from the spectroscopic and molecular data on the basis of alternate assumptions concerning the ratios of the amounts of rotational isomers. The outer form apparently predominates.

Introduction

Investigations of the thermodynamic properties of the various methyl-substituted hydrazines are in progress in this Laboratory. This paper presents the experimental results on methylhydrazine, together with a discussion of the configuration of the molecule in the gaseous state based on a comparison of the calorimetric entropy with that calculated from spectroscopic and molecular data.

Experimental

The Methylhydrazine Sample.—The methylhydrazine was prepared according to the method of "Organic Syntheses."[2] Benzalazine was prepared from hydrazine, and converted to the methylhydrazine sulfate by reaction with dimethyl sulfate. The salt was decomposed with base, and the methylhydrazine distilled in an atmosphere of nitrogen. The sample was further purified by the method of fractional melting[3] in a glass apparatus. It was shown to contain 0.25 mole per cent. impurity from its melting point curve, assuming all impurity to be solid insoluble.

Apparatus.—The experimental measurements were made in an adiabatic calorimeter with a valve in the outlet line at the shield. This is described in Fig. 1 with explanatory legend. The calorimeter and valve is similar to one designed by R. B. Scott of the National Bureau of Standards,[4a] and except for the valve, to others of this Laboratory.[4b,4c] Henceforth it will be designated as calorimeter F. The valve seat is of stainless steel, and the closure disk of brass which has been tin plated. The valve is opened and closed by means of a thumb screw which gives fine control of a lever system. The valve prevents evaporation of the sample into the filling line and hence eliminates corrections to the heat capacities from this cause. It is also used to control the rate of flow of vapor during heats of vaporization. With the valve located on the shield the vaporization process does not include any effect of expansion at the valve.

An electronic circuit was designed to control accurately the temperature of the tube and two shields. When necessary this could replace manual operation.

A means of switching, in turn, the three control thermocouple voltages into a single Perkin Elmer d.c. amplifier was provided. This is made possible by the low period ($^1/_6$ sec.) of the amplifier. A motor drives two single pole triple throw switch elements. One switch element controls the input side of the amplifier (directly from the thermocouple) and the other switch element controls the output side of the Perkin Elmer d.c. amplifier (to the electronic amplifier circuit). These two switches had to be phased so that the input contact was made before the output and then the output contact broken before the input. The switches are carefully shielded to exclude stray electromotive forces. The signal received from the amplifier is stored in a condenser, for each circuit, which then controls an electronic circuit in which the output of 616 tubes is used to heat the various elements of the calorimeter assembly.

A schematic diagram showing the various connections used in the control circuit and calorimeter, etc., is given in Fig. 2. It is sometimes necessary to maintain a small temperature difference between the shields and the calorimeter. This is done by adding a small bias voltage ("balance controller") to the signal from the difference thermocouples. The control panel is arranged so that the heating current for the shields and tube is set to a higher value on switching the calorimeter heating current on. This is done by exchanging the resistance in the output circuit of the 6L6 tubes for a lower one. The time of energy input was measured on a clock driven by the output from a General Radio Company vacuum tube precision fork. The switches for the heating current and for the clock were so connected that the heating circuit and the timing circuit were switched on and off simultaneously.

The Temperature Scale.—Below 90°K. the calorimeter platinum resistance thermometer, PT. G-9, was calibrated, as previously described,[4b,4c] against the laboratory standard thermocouple S-3 which was fastened to the calorimeter. The indications of the thermocouple, S-3, were compared with temperatures from vapor pressures of hydrogen condensed in the calorimeter before the measurements were made. The change from the original calibration ($T_{S-3} - T_{obs.}$) was 0.42° at 20.3°K. A corresponding correction in microvolts was applied to the original calibration on the assumption that this was proportional to the total microvolt reading. Above 90°K. the International Temperature was used as determined by the readings of PT. G-9 at the oxygen, ice, steam and sulfur points. This scale agreed with that of the thermocouple, with its indications thus corrected, within experimental error (0.02°).

The Heat Capacity Measurements.—The smoothed values of the heat capacity at integral

TABLE I

HEAT CAPACITY OF METHYLHYDRAZINE

Mol. wt. 46.074; 0 °C. = 273.16°K.; 1 cal. = 4.1833 int. joules

T, °K.	C_p	T, °K.	C_p
	Crystal	130	12.21
15	0.436	140	12.84
20	1.007	150	13.45
25	1.646	160	14.05
30	2.349	170	14.67
35	3.081	180	15.34
40	3.830	190	15.98[a]
45	4.570	200	16.60[a]
50	5.220	210	17.20[a]
55	5.835	220	17.80[a]
60	6.420	220.79	17.84[a] crystal
65	6.984		Fusion
70	7.531	220.79	31.27 liquid
75	8.085	230	31.40
80	8.570	240	31.52
85	8.996	250	31.64
90	9.389	260	31.76
95	9.760	270	31.88
100	10.13	280	32.01
110	10.83	290	32.14
120	11.52	298.16	32.25

[a] Values extrapolated.

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[1] This research was carried out on Contract N6onr-269, Task Order 3, of the Office of Naval Research.

[2] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 395.

[3] Aston and Mastrangelo, *Anal. Chem.*, **22**, 636 (1950).

[4] (a) R. B. Scott, *et al.*, to be published; see also Osborne and Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1948); (b) Aston and Szasz, THIS JOURNAL, **69**, 3108 (1947); (c) Morrison and Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

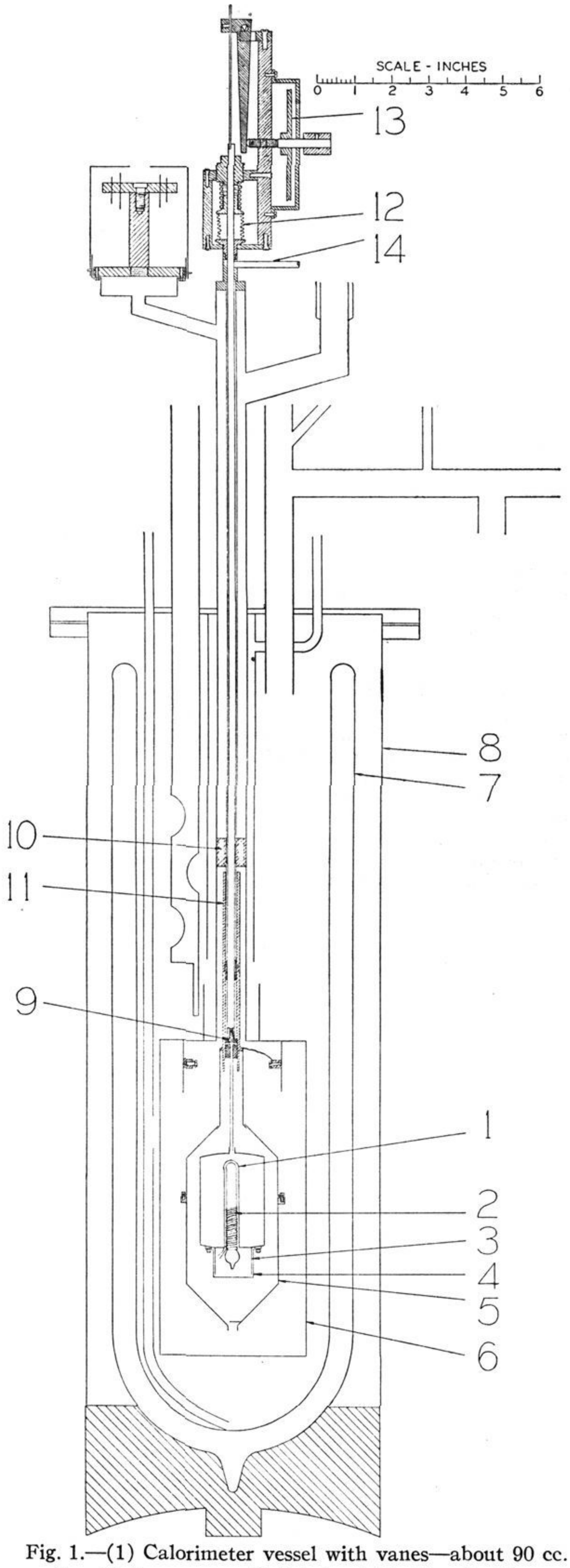

Fig. 1.—(1) Calorimeter vessel with vanes—about 90 cc. capacity, all of copper; gold plated outside, tinned with pure tin inside. (2) Thermometer well holding 25 ohm strain-free platinum resistance thermometer with the calorimeter heater of constantan wire wrapped bifilarly on the lower part. The thermometer and heater are cast in with Woods metal. (3) Collar, around which leads to heater and thermometer are wrapped so that any heat leaking along them from the heater is conducted back to the calorimeter. (4) Cap to cover collar and prevent radiation from thermometer cap and leads when at higher temperature than calorimeter. (5) Shields. (6) Vacuum tight cryostat envelope. (7) Dewar for refrigerants. (8) Dewar container. (9) Stainless steel valve seat with closure disc of tin plated brass. (10) Thermal contact of valve stem with tube leading to cryostat which serves as a thermal contact with the bath. Consists of spring-like fins of brass on stem fitting into copper bearing. (11) Tube heaters. (12) Copper bellows. (13) Valve control mechanism. (14) Filling tube for calorimeter.

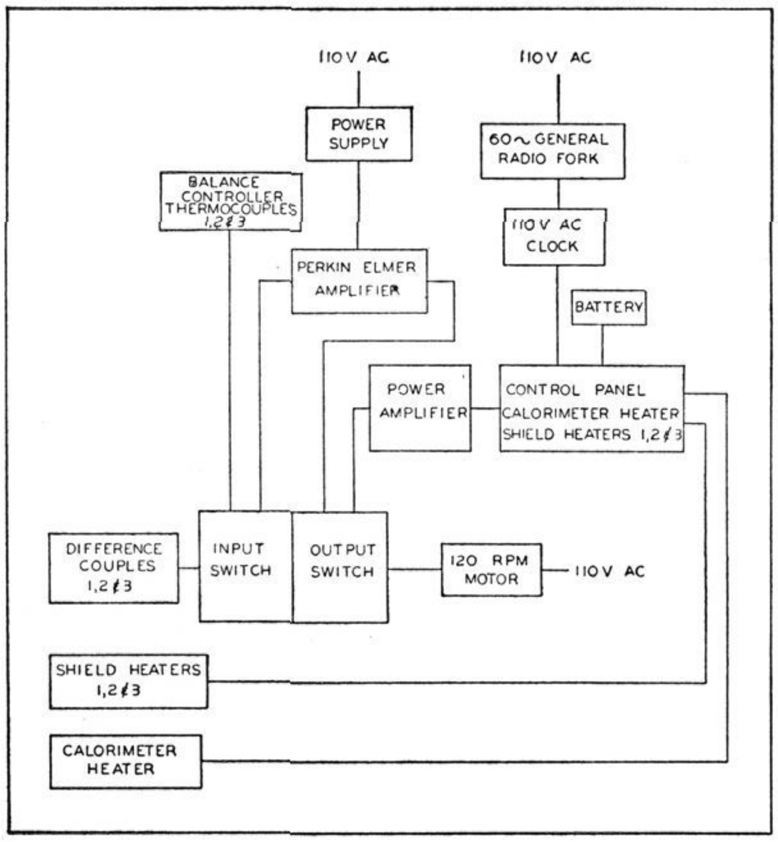

Fig. 2.—Schematic diagram of electrical connections for automatic operation of adiabatic calorimeter.

temperatures, read from the best curve through the experimental points, are listed in Table I. The precision of the results from 30 to 298°K. is 0.2%, but between 20 and 30°K. it is 0.3%, and below 20°K. the error may rise to as much as 2.5%. The uncertainty in the region 15–20°K. is due in part to the difficulty in maintaining the system adiabatic, because of the heat leak through the filling tube and valve. The heat capacity curve was extrapolated from 190°K. to the melting point (220.79°K.) because of the premelting which occurs in this region, and this may give rise to an error of 0.5% in the heat capacities at the melting point.

The small volume above the methylhydrazine in the calorimeter and the low vapor pressure even at 298.16°K. (49.6 mm.) made it unnecessary to correct for the amount of material in the vapor space. However, there was some polymerization as indicated by the heat capacity of the empty calorimeter which had risen several tenths of a per cent. after the first series of measurements. A correction was applied based on the amount of sample which could be removed. The uncertainty in this correction could affect the accuracy of the results by as much as one per cent. in some regions but much less at others. The maximum effect on the entropy could not exceed 0.3 e.u.

The Melting Point and Heat of Fusion.—Equilibrium temperatures of solid and liquid methylhydrazine were observed with increasing fractions of the sample melted. From these results, the solid-insoluble impurity was found to be 0.25 mole per cent. A similar value was calculated from the premelting heat capacities showing that there was little or no solid soluble impurity in the sample. The melting point of pure methylhydrazine, obtained by correcting the melting point of the sample for the presence of 0.25 mole per cent. impurity, is 220.79°K.

The results of the heat of fusion measurements are given in Table II. The usual corrections for premelting and for heating the solid and the liquid have been applied.[4b] They were obtained during the heat capacity measurements as previously described.

TABLE II

HEAT OF FUSION OF METHYLHYDRAZINE

Mol. wt. 46.074; 0°C. = 273.16°K.; melting point = 220.79°K.; 1 cal. = 4.1833 int. joules

Temp. interval	Cor. heat input cal./mole	$C_p dT$, cal./mole	Pre-melting, cal./mole	H cal./mole
205.007–221.763	2970.8	−489.2	+ 8.2	2489.8
214.688–222.584	2701.9	−252.9	+42.2	2491.2
			Mean	2490.5 ± 3 cal./mole

The Vapor Pressures and Heats of Vaporization.—The vapor pressure of methylhydrazine at 298.16°K. is required for the calculation of the entropy of compression term to 1 atmosphere. A series of readings of vapor pressures against temperatures, taken in the usual manner,[4b] are reported in Table III. The deviations of the values in column 2 from equation 1, given at the foot of the table, are given in column 3. These are much larger than usual, possibly due to lack of equilibrium caused by adsorption on the glass capillary and walls of the manometer, possibly due to slight condensation. The vapor pressure interpolated at 298.16°K. by this equation is 49.6 mm.

TABLE III

VAPOR PRESSURE OF METHYLHYDRAZINE

g State College = 980.124 cm./sec.[2] "I.C.T.", 0°C. = 273.16°K.

T, °K.	$P_{obs.}$, mm.	$P_{calcd.} - P_{obs.}$
275.117	12.11	+0.13
284.899	22.85	+ .08
290.292	31.76	− .02
293.692	38.72	− .10
(298.16)(interpolated using eq. 1)	49.63	
298.326	50.00	+ .08

Calculated from the equation: $\log_{10}p = -7.88 \log_{10}T - 3.146/T + 31.746$ (1).

Heats of vaporization were obtained directly by introducing measured quantities of heat into the calorimeter and collecting the methylhydrazine vaporized in weighed bulbs surrounded by liquid air as described for the heat of vaporization of trimethylamine at 250°K.[5] The temperature of vaporization, as measured on a standard thermocouple attached to the calorimeter, was maintained constant by controlling the valve instead of the grooved stopcock described previously. The filling tube and valve were held at a higher temperature than the calorimeter to prevent condensation in the line, and corrections for the heat leak from this cause and from the shields were applied. The vaporizations were taken at temperatures close to 25° and the heats of vaporization at 25° were calculated using a value of the heat capacity of the vapor obtained from spectroscopic data and assumed barriers for internal rotation. The results are given in Table IV. A value calculated from equation (1) and thermodynamics is also included as a test of this equation only. Its accuracy is not to be compared with that of the measured values.

TABLE IV

MOLAL HEATS OF VAPORIZATION OF METHYLHYDRAZINE AT 298.16°K.

Mol. wt. 46.074, 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules

Mole vaporized	Mean temp. of vaporization, °K.	ΔH at T °K. cal./mole	ΔH at 298.16°K. cal./mole
0.12022	296.69	9684	9660
.11959	297.15	9672	9655
.092195	299.39	9618	9638
.12279	302.27	9602	9669
.12440	297.96	9623	9620
		Av.	9648
Calculated from eq. (1) (Table III) and estimated critical data, T_c = 530°K.; P_c = 75 atm. (Berthelot correction 19 cal.)			9701

The Entropy from Calorimetric Data.—The calculation of the entropy of methylhydrazine from calorimetric data is summarized in Table V.

TABLE V

ENTROPY OF METHYLHYDRAZINE FROM THERMAL DATA

	E.u./mole
0–15°K. Debye function θ = 193, six degrees of freedom	0.073
15–220.79°K. graphical	18.780
Fusion 2490.5/220.79	11.279
220.79–298.16°K. graphical	9.530
Entropy of liquid at 298.16°K.	39.66 ± 0.07
Vaporization 9648/298.16	32.36 ± 0.11
Entropy real gas at 298.16°K.	72.02 ± 0.18
Entropy ideal gas at 298.16°K.	72.03 ± 0.18
Compression R ln 49.6/760	−5.42 ± 0.02
Entropy ideal gas 760 mm., 298.16°K.	66.61 ± 0.20

The small correction for gas imperfection was made using the Berthelot equation

$$PV = RT\left[1 + \frac{9PT_c}{128P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right] \quad (2)$$

with assumed critical constants of T_c = 530°K. and P_c = 75 atm. Although the critical constants and the Berthelot correction itself are only estimates, the uncertainty is probably less than 0.005 e.u.

Discussion

Thermodynamic Functions from Spectroscopic and Molecular Data.—Rotational isomerism in methylhydrazine can give rise to a *trans* form and

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(5) Aston, Sagenkahn, Szasz, Moessen and Zuhr, THIS JOURNAL, 66, 1171 (1944).

two skew forms. It has been shown in the case of hydrazine that the *trans* form is excluded[6] and it is probable that the same result applies to methylhydrazine.[7] The skew form of methylhydrazine with the methyl group farthest from the hydrogens of the amino group is termed the "outer" form, and the other is known as the "inner" form. It is considered that the outer skew form is more stable than the inner since the interactions between the hydrogens of the methyl group and the rest of the molecule are less for this form. This is assumed as the main form.

Moments of inertia of this form have been calculated using the following data: N–N, 1.45 Å.; N–C, 1.47 Å.; N–H, 1.04 Å.; C–H, 1.09 Å.,[8] and assuming all angles to be tetrahedral. The product of the principal moments of inertia is 1.803×10^{-115} g. cm.^{2}, and the reduced moments of the methyl and amino groups are 4.32×10^{-40} g. cm.^{2} and 2.85×10^{-40} g. cm.^{2}. The reduced moments were calculated by the method of Pitzer and Gwinn.[9]

The vibrational assignment has been discussed elsewhere.[7] The frequencies used in the thermodynamic calculations were 443, 770, 816, 886, 969, 1103, 1122, 1137, 1197, 1412, 1441, 1474, 1587, 2865, 2933, 2965, 3177, 3245, 3317 cm.$^{-1}$. The frequencies corresponding to torsional oscillations were not observed directly.

In the calculation of entropy decreases due to restricted internal rotation, a three-fold cosine-type barrier was taken for the methyl hindered rotation. The shape of the barrier restricting rotation of the amino group is not known, but a barrier of the type suggested for hydrazine has been assumed with each form occupying one-third of a revolution.[10,7] A series of possible values for the potential barriers has been chosen and in each case the calculated entropy has been brought into accord with the observed by means of the entropy of mixing of inner and outer forms. The contributions due to hindered internal rotation were calculated using the difference tables of Pitzer and Gwinn. The calculations are summarized in Table VI.

Table VI

Entropy of Methylhydrazine

$T = 298.16$°K.: $P = 1$ atm.

	(1) $V_{CH_3} =$ 2800 $V_{NH_2} =$ 2650	(2) $V_{CH_3} =$ 3200 $V_{NH_2} =$ 3000	(3) $V_{CH_3} =$ 3500 $V_{NH_2} =$ 3400
S transitional	37.393	37.393	37.393
S vibrational	1.767	1.767	1.767
S ext. rot.	22.094	22.094	22.094
S int. rot. (CH_3 and NH_2)	3.985	3.679	3.421
S mixing (optical isomers)	1.377	1.377	1.377
S total (outer form)	66.61	66.31	66.05
S mixing (with inner form)	0.00	0.30	0.56
S total (mixture)	66.61	66.61	66.61
S observed	66.61	66.61	66.61

If a value of 2800 cal./mole is assigned to the barrier hindering the methyl rotation and 2650 cal./mole to that hindering the amino rotation, the calculated entropy agrees with the observed value, if the system exists entirely in the outer skew form. For barriers of 3200 and 3000 cal./mole for the methyl and amino hindered rotations, respectively, the system is shown to exist as an equilibrium mixture of 96 mole per cent. outer form and 4 mole per cent. inner form (with an energy difference of 1880 cal. between the two forms). If barriers as high as 3500 and 3400 cal./mole are assigned to the methyl and amino rotations, the calculated entropy for a mixture of 92 mole per cent. outer form and 8 mole per cent. inner form agrees with the observed entropy. This corresponds to an energy difference of 1445 cal. between the two forms. If a comparison may be made with barriers reported for hydrazine, the simple aliphatic amines and hydrocarbons, it is probable that values of 3200 and 3000 cal./mole are the most reasonable. Over the whole range of barriers discussed, however, it is shown that one form predominates, leading to the conclusion that methylhydrazine exists primarily in the skew outer form.

In the foregoing discussion it has been assumed that methylhydrazine does not possess residual entropy at the absolute zero. It has been suggested that hydrazine may possess a small zero point entropy,[10] and it is possible that compounds such as methylamine and dimethylamine, which have been used as comparison substances for barrier estimates, also possess a definite entropy at the absolute zero. If a zero point entropy occurs evenly through the amines and the hydrazines, however, it will change the values given for the potential barriers, but will not materially affect the above discussion concerning rotational isomers. Some additional evidence in favor of the predominance of the skew outer form for methylhydrazine may be obtained from dipole moment data. The moments for the skew forms can be calculated by vector addition of group moments. Using the values given by West and Killingsworth[11] for the N–H, N–C and H–N–CH_3 group moments and a value of 1.48 *D* for the H–N–H moment, the resultant moments of these forms were found to be

Inner form	Outer form	Observed[12]
1.13 *D*	1.92 *D*	1.68 ± 0.14 *D*

The moments were calculated assuming a 90° rotation from the *cis*-configuration, and if, as is possible, this angle is greater than 90°, the calculated dipole moment for the outer form approaches the observed value still more closely. The dipole moment was observed for a dilute solution of methylhydrazine in benzene, and it might be expected that there would be a little difference between the configuration of methylhydrazine in such a system and in the gaseous state.

Values of the free energy function, heat content function, entropy and heat capacity of methylhydrazine were calculated using the spectroscopic and molecular data already mentioned. These are listed in Table VII. In the calculation the barriers,

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(6) Penney and Sutherland, *Trans. Faraday Soc.*, **30**, 902 (1934); *J. Chem. Phys.*, **2**, 492 (1934).

(7) Janz and Russell, *ibid.*, **17**, 1352 (1949), have given preliminary results of the investigation.

(8) W. H. Beamer, This Journal, **70**, 2979 (1948).

(9) Pitzer and Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(10) Scott, Oliver, Gross, Hubbard and Huffman, This Journal, **71**, 2293 (1949).

(11) West and Killingsworth, *J. Chem. Phys.*, **6**, 1 (1938).

(12) Ulich, Peisker and Audrieth, *Ber.*, **B68**, 1677 (1935).

TABLE VII

THERMODYNAMIC FUNCTIONS FOR METHYLHYDRAZINE

Temp., °K.	$H - E_0$ cal./mole	$-(F - E)_0/T$ cal./deg./mole	S, cal./deg./mole	C_p, cal./deg./mole
298.16	3,438	55.08	66.61	17.0
300	3,469	55.16	66.72	17.11
400	5,382	58.74	72.20	21.0
500	7,658	61.97	77.29	24.3
600	10,230	64.88	81.93	27.1
700	13,040	67.67	86.30	29.3
800	16,080	70.23	90.33	31.3
900	19,290	72.58	94.02	33.1
1000	22,630	74.99	97.63	34.6
1200	29,830	79.32	104.18	37.1
1500	41,420	85.28	112.90	39.8

listed under (2) in Table VI were used with an energy difference of 1880 cal. mole^{-1} between the isomers. In some cases the values are given to more significant figures than is justified by their absolute accuracy in order to retain internal consistency among the different functions.

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BY J. G. ASTON, G. J. JANZ AND K. E. RUSSELL

The entropy of *sym*-dimethylhydrazine vapor in the ideal gas state has been calculated from heat capacity measurements down to 14.5°K., heats of fusion, heats of vaporization and the vapor pressure. This has been compared with that calculated from the spectroscopic and molecular data for both the inner–outer and the outer–outer forms.

Introduction

Symmetrical dimethylhydrazine may exhibit rotational isomerism to give a number of forms analogous to the "inner" and "outer" skew forms of methylhydrazine.[2a,b,c] This paper presents the results of a calorimetric investigation of *sym*-dimethylhydrazine, with a discussion of the relative amounts of the rotational isomers occurring in the vapor at room temperature.

Experimental

The *sym*-Dimethylhydrazine Sample.—Symmetrical dimethylhydrazine was prepared according to the method of "Organic Syntheses,"[3] liberated by the addition of base, and purified by distillation in an atmosphere of nitrogen through a column of glass helices with approximately 100 theoretical plates.

Heat Capacity Measurements.—The measurements were taken in calorimeter F which was used for the work on methylhydrazine.[2] Smoothed values of the heat capacity at integral temperatures are given in Table I, extrapolated values being used from 230°K. to the melting point because of premelting. The heat capacity data are plotted against temperature in Fig. 1. There is a sharp rise of about 0.1 cal./mole in the heat capacity in the region of 138°K. (see insert at the left of Fig. 1). The effect constitutes 3% of the total heat capacity, compared with a precision of about 0.2% at these temperatures as indicated by the deviation plot in the upper part of Fig. 1. It can be seen from Fig. 1 that the discontinuity does not affect the smoothness of the values in Table I below 130°K. or above 150°K. but that the first differences in this region are not in keeping with the rest in the table. If the phenomenon involves a transition, then the heat of transition must be close to zero. Heat capacities taken in the region of 138°K. show an abnormal afterdrift of the order of 0.001° per minute for a period of about 2 hours.

TABLE I

HEAT CAPACITY OF *sym*-DIMETHYLHYDRAZINE AT INTEGRAL TEMPERATURES

Mol. wt. 60.010; 0 °C. = 273.16 °K.; 1 cal. = 4.1833 int. joules.

Temp., °K.	C_p, cal./deg./mole	Temp., °K.	C_p, cal./deg./mole
15	0.936	100	13.14
16	1.054	110	14.06
17	1.180	120	14.95
18	1.318	130	15.77
19	1.455	140	16.83
20	1.602	150	17.79
21	1.760	160	18.66
22	1.922	170	19.56
23	2.088	180	20.50
24	2.258	190	21.49
25	2.435	200	22.50
30	3.430	210	23.53
35	4.430	220	24.59
40	5.330	230	25.70[a]
45	6.192	240	26.83[a]
50	6.990	250	28.01[a]
55	7.750	260	29.23[a]
60	8.465	264.28	29.74[a] Crystal
65	9.172		Fusion
70	9.854	264.28	40.31 Liquid
75	10.49	270	40.40
80	11.09	280	40.56
85	11.65	290	40.72
90	12.15	298.16	40.88
95	12.66		

[a] Extrapolated.

A small amount of involatile material remained in the calorimeter from the methylhydrazine measurements, which increased the heat capacity of the calorimeter by about 1% at the higher temperature,

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

[2] (a) West and Killingsworth, *J. Chem. Phys.*, **6**, 1 (1938); (b) Janz and Russell, *J. Chem. Phys.*, **17**, 1352 (1949); (c) Aston, Fink, Janz and Russell, THIS JOURNAL, **73**, 1939 (1951).

[3] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 208.