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

# The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressures and Entropy of Symmetrical Dimethylhydrazine[1]

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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.

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.

**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.

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,

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[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.

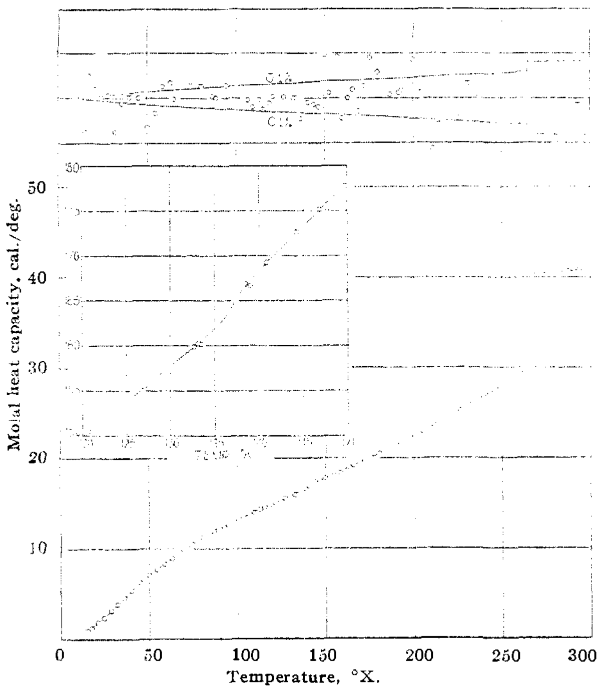

Fig. 1.—Heat capacities of dimethylhydrazine.

for which a correction was made. The heat capacity measurements could be in error by several tenths of a per cent. and the entropy by about 0.3 e.u. on this account rather than by the instrumental errors listed in Table IV.

**The Melting Point.**—Equilibrium temperatures were observed with several fractions of the sample melted. The solid insoluble impurity was calculated to be 0.4 mole per cent. and the calculated melting point of the pure material is 264.24 ± 0.04°K. The concentration of impurity was also estimated to be 0.4 mole per cent. from premelting heat capacities indicating the presence of little or no solid-soluble impurity. This included the involatile material mentioned above.

**The Heat of Fusion.**—The results of the heat of fusion measurements on *sym*-dimethylhydrazine are summarized in Table II. They were taken during the course of the heat capacity measurements and the usual corrections have been applied.[2c] One of the results was obtained in conjunction with the purity determination.

TABLE II

HEAT OF FUSION OF *sym*-DIMETHYLHYDRAZINE

Mol. wt. 60.010; 0°C. = 273.16°K.; 1 cal. = 4.1833 int. joules; melting point 264.28°K.

| Temp. interval, °K. | Heat input, cal./mole | $\int C_p dT$ cal./mole | Pre-melting, cal./mole | $\Delta H$ fusion, cal./mole |
|---|---|---|---|---|
| 245.106–266.167[a] | 4126.3 | 876.2 | 10.5 | 3260.6 |
| 242.844–266.387[b] | 4243.6 | 993.7 | 7.6 | 3257.5 |
| 243.758–266.409[b] | 4205.2 | 952.1 | 7.3 | 3260.4 |
| | | | Mean $\Delta H$ = | 3295.5 ± 5 cal./mole |

[a] Obtained in conjunction with purity determination.
Integral heat of fusion.

**Heats of Vaporization and Vapor Pressures.**—Measurements were made as for methylhydrazine.[2] As a result of five determinations listed in Table III, the heat of vaporization of *sym*-dimethylhydrazine was found to be 9,400 cal./mole at 25°. The vapor pressures below 25°, taken as described previously,[2] are given in Table IV, column 2, along with the deviations (column 3) from equation (1) given at the foot of the table. These are larger than usual, possibly due to the slow adsorption processes. To give an idea of the accuracy, the heat of vaporization calculated from equation (1) is given at the foot of Table III. The accuracy of this value, of course, does not compare with the measured one. In its calculation the vapor volumes were estimated using the modified Berthelot equation and the estimated critical constants, $T_c$ = 530°K. and $P_c$ = 90 atmospheres. Equation (1) yields a value of 70.1 mm. for the vapor pressure at 298.16°K. (Table IV). This result has been used in the calculation of the entropy correction to one atmosphere.

TABLE III

MOLAL HEATS OF VAPORIZATION OF *sym*-DIMETHYLHYDRAZINE

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

| Mole vaporized | Mean temp. of vaporization, °K. | $\Delta H$ real gas, $T$, °K. | $\Delta H$ real gas 298.16°K., cal./mole |
|---|---|---|---|
| 0.093236 | 296.46 | 9441 | 9404 |
| .093136 | 298.97 | 9388 | 9406 |
| .093329 | 298.60 | 9375 | 9385 |
| .092230 | 298.50 | 9393 | 9401 |
| .091609 | 297.81 | 9410 | 9402 |
| | | Average | 9400 ± 15 |
| Calculated from equation (1), Table IV, and estimated critical data, $T_c$ = 530°K., $P$ = 90 atm. (Berthelot correction = 21 cal.) | | | 9318 |

TABLE IV

VAPOR PRESSURES OF *sym*-DIMETHYLHYDRAZINE

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

| Temperature, °K. | Vapor pressure, mm. | $P_{\text{calcd.}}{}^{a} - P_{\text{obsd.}}$ |
|---|---|---|
| 274.531 | 17.01 | +0.33 |
| 282.892 | 29.19 | +0.23 |
| 288.970 | 42.49 | − .37 |
| 294.067 | 56.13 | − .04 |
| 297.617 | 67.99 | − .05 |
| 298.16 (extrapolated using eq. 1) | 69.9 | |

[a] Calculated using the equation: $\log_{10}p = -10.540 \log_{10}T - 3407.0/T + 39.352$ (1).

**Entropy from the Thermal Data.**—The entropy calculation is summarized in Table V. A correction for gas imperfection has been made using the Berthelot equation and assumed critical constants of $T_c$ = 530°K., $P_c$ = 90 atmospheres. As with methylhydrazine, the uncertainty is less than 0.005 e.u.

## Discussion

**The Entropy from Spectroscopic and Molecular Structure Data.**—The most probable forms of symmetrical dimethylhydrazine are the three skew forms,[2a] with the outer–outer, the inner–outer, and the inner–inner placement of methyl

TABLE V

ENTROPY OF *sym*-DIMETHYLHYDRAZINE FROM THERMAL DATA

| | B.u./mole |
|---|---|
| 0–15°K. Debye function ($\theta$ = 118, 3° of freedom) | 0.306 ± 0.02 |
| 15°K.–264.28°K. graphical | 30.055 ± 0.07 |
| Fusion (3259.5/264.28) | 12.334 ± 0.02 |
| 264.28–298.16°K. graphical | 4.903 ± 0.01 |
| Entropy of liquid at 298.16°K. | 47.598 ± 0.12 |
| Vaporization (9400/298.16) | 31.527 ± 0.05 |
| Entropy real gas at 298.16°K. and 69.8 mm. | 79.125 ± 0.17 |
| Entropy ideal gas at 298.16°K. and 69.8 mm. | 79.135 ± 0.18 |
| Compression *R* ln (69.9/760) | −4.740 ± 0.01 |
| Entropy ideal gas at 760 mm. and 298.16° K. | 74.39 ± 0.2 |

groups. From stereo-chemical reasoning it is likely that the amount of the inner–inner form in the vapor at room temperature is very small, so that the two low energy forms are the outer–outer and the inner–outer.

The moments of inertia were calculated using the following bond distances, N–N, 1.45 Å.; C–N, 1.47 Å.; C–H, 1.09 Å.; N–H, 1.04 Å., and assuming all angles to be tetrahedral. The product of the principal moments of the outer–outer form is $1.309 \times 10^{-114}$ (g. cm.$^2$).[3] The reduced moment of the methyl group is $4.524 \times 10^{-40}$ g. cm.$^2$ for the outer–outer form, and the reduced moment of the methylamino group is $1.636 \times 10^{-39}$ g. cm.$^2$. For the inner–outer form, the product of the principal moments is $1.573 \times 10^{-114}$ (g. cm.$^2$)[3] and the reduced moments of the methyl and methylamino groups are $4.986 \times 10^{-40}$ g. cm.$^2$ and $1.897 \times 10^{-39}$ g. cm.$^2$, respectively. The moments of the methylamino group were calculated by the method of Pitzer.[4] The symmetry number for the external rotation is unity for the inner–outer form and two for the outer–outer form.

The frequencies used in the calculation of the vibrational entropy contribution were 422, 483, 720, 801, 865, 1019, 1045 (2), 1099, 1114 (2), 1132, 1197, 1405 (2), 1456 (2), 1476 (2), 2824, 2845, 2916 (2), 2946 (2), 3223, 3294 cm.$^{-1}$.[5]

Approximate barriers of 3000 cal./mole have been assigned to the hindered rotation of both the methyl and methylamino groups. The calculations are summarized in Table VI.

TABLE VI

ENTROPY OF *sym*-DIMETHYLHYDRAZINE FROM MOLECULAR DATA

| | Outer–outer form | Inner–outer form |
|---|---|---|
| *S* translation | 38.186 | 38.186 |
| *S* vibration | 2.850 | 2.850 |
| *S* ext. rotation | 22.692 | 24.253 |
| *S* methyl internal rotation | 4.194 | 4.370 |
| *S* methylamino internal rotation | 3.294 | 3.436 |
| *S* mixing optical isomers | 1.377 | 1.377 |
| *S* total, e.u. | 72.59 | 74.47 |
| *S* observed, e.u. | 74.39 | 74.39 |

Two alternatives are allowed by the entropy study. The entropy calculated for the inner–outer form is equal to the observed entropy within the limits of experimental error. One possibility is therefore that *sym*-dimethylhydrazine vapor at 25° consists almost entirely of the inner–outer form. Supporting evidence comes from dipole moment data.[1] West and Killingsworth[1] conclude that *sym*-dimethylhydrazine is predominantly in the inner–outer form.

The entropy study allows a second alternative. A mixture of about 70 mole per cent. outer–outer form with 30 mole per cent. inner–outer form gives an entropy equal to the observed value. This corresponds to an energy difference of about 1000 cal. between the two forms. If such a high proportion of a second form were also present in liquid *sym*-dimethylhydrazine at room temperature, it would be expected that the Raman spectrum would contain lines due to both forms. Spectra taken at two different temperatures might show variations in relative intensities of some lines, giving evidence for this second alternative.

The above discussion assumes that *sym*-dimethylhydrazine does not possess a zero-point entropy. The barriers to internal rotation are not known exactly, although the values chosen are probably not in serious error.

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[4] Pitzer, *J. Chem. Phys.*, **14**, 239 (1946).

[5] Axford, Janz and Russell, to be published.