

TABLE III  
ENTROPIES OF THE LIQUID METHYLNONANES PER MOLE  
Molecular weight: 142.276

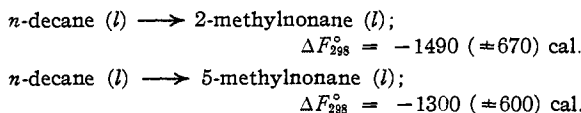
Substance	Crystals		Fusion	Liquid	$S_{298}^{\circ}$	$\Delta S$ isomerization
	0-80°K.	Above 80°K.				
2-Methylnonane	19.46	31.86	21.04	28.07	100.4	-2.3
<i>d-l</i> ,3-Methylnonane	18.57	28.72	23.72	31.05	102.1	
3-Methylnonane, pure <i>d</i> or <i>l</i>					100.7	-2.0
<i>d-l</i> ,4-Methylnonane	18.88	25.95	20.79	36.06	101.7	
4-Methylnonane, pure <i>d</i> or <i>l</i>					100.3	-2.4
5-Methylnonane	19.38	28.96	21.30	31.67	101.3	-1.4

TABLE IV  
THERMAL DATA AT 298.16°K. FOR THREE DECANES  
In calories per mole. Molecular wt. 142.276

Substance	$\Delta H_{298}^{\circ}$ , cal.	$\Delta S_{298}^{\circ}$ , e. u.	$\Delta F_{298}^{\circ}$ , cal.
<i>n</i> -Decane ( <i>l</i> )	-72,370	-254.4	3480
2-Methylnonane ( <i>l</i> )	-74,550	-256.7	1990
5-Methylnonane ( <i>l</i> )	-74,090	-255.8	2180

of the table. In view of the accuracy of the contributing data, the uncertainty in these values is probably within 600 calories.

Similar data for *n*-decane, taken from a previous study by Parks,<sup>13</sup> also have been included in Table IV for the purpose of comparison. Thus we find for the two isomerizations



(13) Parks, *Chem. Rev.*, **27**, 75 (1940).

This slightly greater stability, at room temperature, of the branched isomers as compared with the normal hydrocarbon is in general accord with the free energy data published recently by Rossini and Prosen<sup>14</sup> for the isomeric hexanes.

### Summary

1. The specific heats of the four methylnonanes have been measured between 80 and 298°K. The corresponding heats of fusion also have been determined.

2. The entropies of these hydrocarbons in the liquid state at 298.16°K. have been calculated from the foregoing heat capacity data.

3. The corresponding free energies of the 2-methyl- and 5-methylnonane also have been calculated. These are lower than the free energy of *n*-decane by 1490 and 1300 cal., respectively.

(14) Rossini and Prosen, *This Journal*, **62**, 2250 (1940).

STANFORD UNIV., CALIF. RECEIVED JANUARY 28, 1941

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 811]

## The Vapor Density of Hydrazine

BY PAUL A. GIGUÈRE<sup>1</sup> AND ROBERT E. RUNDLE

In connection with their measurements of the heat capacity of gases by the hot wire method Eucken and Krome<sup>1a</sup> reported recently that hydrazine vapor is largely associated according to the equation  $2N_2H_4 \rightleftharpoons N_4H_8$ . They stated that a vapor density determination by the Dumas method indicated complete association at 105.8° and 340 mm. They also measured the dissociation constant, which they give as  $\log K_p = 8.68 - 3060/T$  (pressure in mm.). From this the heat of dimerization was estimated to be 14.0 kcal./mole. These results seemed to us surprising as

(1) Research Fellow of the Provincial Government of Quebec, Canada.

(1a) A. Eucken and H. Krome, *Z. physik. Chem.*, **B45**, 175 (1940).

they are not to be expected from the structure of hydrazine or from analogy with closely related compounds. Furthermore, in the course of molecular structure investigations carried out some time ago in these Laboratories a number of electron-diffraction photographs of hydrazine vapor were obtained, of which none revealed the presence of double molecules. Since no other reference to this matter could be found in the literature, we decided to redetermine vapor density at various temperatures and pressures. The results reported here show that gaseous hydrazine is not associated to any appreciable extent.

The hydrazine used was prepared by repeatedly

refluxing and distilling the hydrate over barium oxide in an all-glass apparatus filled with hydrogen. After two fractional crystallizations the final product analyzed 99.4% by the iodate method of Rimini.<sup>2</sup> A first determination was made by the Dumas method at atmospheric pressure and 131°. Special care was taken to exclude moisture while transferring the liquid to the bulb. This determination gave a molecular weight of 31.8. The experimental conditions are recorded in Table I.

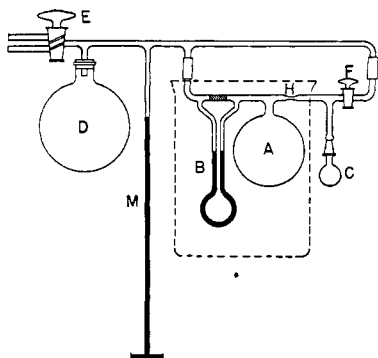


Fig. 1.—Vapor density apparatus.

A number of determinations were also made at reduced pressures by means of the apparatus shown in Fig. 1. The required amount of hydrazine was carefully weighed in the ampoule C fitted with a ground glass joint and closed with a glass stopper. This ampoule was then quickly connected to the system previously filled with dry air and the liquid was frozen in a dry-ice-acetone bath. After the apparatus had been thoroughly evacuated the stopcock F was closed, and the hydrazine was allowed to warm up and to distill into the bulb A, now cooled in dry-ice. When all of the sample had distilled over the constriction at H was sealed and the bulb with the small mercury manometer B was immersed in a beaker of clear oil. The temperature of this oil-bath was kept constant to  $\pm 0.2^\circ$  for five minutes before the corresponding pressure was read on the manometer M. The mercury in the two arms of the manometer B was kept leveled by admitting air or by evacuating through the stopcock E. Any abrupt changes of pressure were prevented by the large volume of the flask D attached to the system. Two sets of measurements made with this system over a two-day interval gave the same results within the limits of experimental error, showing that no appreciable decomposition of the hydrazine in contact with the mercury occurred at the temperatures of the experiment. The volume of the system was then determined by sealing off the small manometer B and weighing the bulb full of water. This water was analyzed for hydrazine as a further check on the weight of the sample used. Because of the presence of a small amount of water in the hydrazine the amount of hydrazine found by analysis was about 0.5% less than the original weight.

(2) W. C. Bray and E. J. Cuy, *THIS JOURNAL*, **46**, 858 (1924).

The results of the vapor density measurements presented in Table I show conclusively that hydrazine, like ammonia, water, and hydrogen peroxide, is not associated in the vapor state. For

TABLE I  
THE VAPOR DENSITY OF HYDRAZINE

Temp., °C.	Pressure, mm.	Vol. of system, cc.	Sample, g.	Mol. wt.
90	265	213	0.0778	31.2
95	273	213	.0778	30.6
100	277	213	.0778	30.6
110	287	213	.0778	30.3
120	294	213	.0778	30.4
131 <sup>a</sup>	747	220	.2090	31.8

<sup>a</sup> By the Dumas method.

conditions such as those under which our experiments were carried out, the equilibrium constant reported by Eucken and Krome leads to much larger values of the effective molecular weight, ranging from 61.5 to 62.6. Although hydrazine shows no association in the vapor phase, the liquid is evidently associated to an appreciable extent, as indicated by its high boiling point, 114°, its entropy of vaporization, 25.8 cal./mole deg.,<sup>3</sup> which is larger than the Trouton constant 21 for normal liquids, its great viscosity, etc. This association of the liquid can be explained by the formation of hydrogen bonds.<sup>4</sup> In this connection it may be of interest to evaluate the average energy of the hydrogen bonds in hydrazine. The heat of sublimation, 11.0 kcal./mole,<sup>5</sup> after subtraction of an estimated 4.0 kcal./mole for the van der Waals energy, leads to the value 3.5 kcal./mole for each of the two N—H—N bonds per molecule. This value is somewhat smaller than that for water and hydrogen peroxide, 4.5, as would be expected from the smaller ionic character of the N—H bond than of the O—H bond.<sup>6</sup>

Since we have shown that hydrazine vapor is not associated, the fact that the heat capacity determined experimentally<sup>1a</sup> agrees exactly with that calculated for single molecules from the infrared spectrum<sup>3</sup> is no longer surprising. Consequently the assumptions made by Eucken and Krome to explain this coincidence are unnecessary.

### Summary

The vapor density of 99.4% pure hydrazine,

(3) W. Fresenius and J. Karwei, *Z. Physik. Chem.*, **B44**, 1 (1939).

(4) J. Goubeau, *ibid.*, **B45**, 237 (1940).

(5) W. Wieber and A. Woener, *Z. Elektrochem.*, **40**, 252 (1934).

(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1940.

$N_2H_4$ , has been measured both at atmospheric and at lower pressures. In contradiction to the claim made by Eucken and Krome,<sup>1a</sup> the results obtained show that hydrazine is not associated in

the vapor phase. This conclusion is also confirmed by electron diffraction and spectroscopic investigations.

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[CONTRIBUTION FROM THE METALLURGICAL FUNDAMENTALS SECTION, METALLURGICAL DIVISION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

## The Specific Heats at Low Temperatures of Crystalline Boric Oxide, Boron Carbide and Silicon Carbide<sup>1</sup>

By K. K. KELLEY<sup>2</sup>

In continuation of a program of study of the thermodynamic properties of metallurgically important substances by the Metallurgical Division of the Bureau of Mines, the specific heats of crystalline  $B_2O_3$ ,  $B_4C$ , and  $SiC$  have been determined in the temperature range  $51^\circ$  to  $298^\circ K$ . Crystalline boric oxide has been known for only a relatively short time, having been reported first by McCulloch<sup>3</sup> in 1937 and by Kracek, Morey and Merwin<sup>4</sup> in 1938.<sup>5</sup> Crystalline  $B_4C$  in relatively pure form also is a substance of recent origin. The methods of manufacture and some of its physical properties were described by Ridgway<sup>6</sup> in 1934. These three substances are similar in that they have relatively low average atomic heats below room temperature and hence, it will be seen, are particularly satisfactory for study with the equipment of this Laboratory, which now enables us to reach a temperature of about  $51^\circ K$ .

**Materials.**—Crystalline boric oxide was prepared from boric acid by one of the methods of Kracek, Morey and Merwin.<sup>4</sup> A weighed quantity of boric acid was heated for one week at  $120^\circ$ , after which the temperature was raised  $10^\circ$  daily until the material was at  $200^\circ$  for one day. At this point about 40% additional boric acid (based upon the original weight) was added with stirring. The resulting mixture crystallized completely over a period of two days with the evolution of steam. The temperature was raised to  $400^\circ$  and maintained there for two days to complete the removal of water. The product obtained, a stony material, was crushed, screened, and reheated at  $400^\circ$ . Analysis showed 99.7% boric oxide. Of the re-

maining 0.3%, 0.1% appeared to be water, and 0.1% was accounted for by the impurities in the original boric acid. This preparation and analysis were made by Dr. G. W. Marks of this Laboratory, to whom the author expresses his appreciation. A sample of 161.5 g. was employed in the measurements, and correction was made for 0.1% water.

The  $B_4C$  was furnished by the Norton Company through the courtesy of Dr. R. R. Ridgway. This material was in granular, crystalline form and was reported to be 96%  $B_4C$  and 4% free and included graphite. The sample used for specific heat measurements contained 144.3 g. Correction for the graphite content was made in the results.

The silicon carbide ( $SiC$ ) also was furnished by Dr. R. R. Ridgway of the Norton Company. This material, light green and semitransparent, was reported to be 99% silicon carbide, the principal impurity being 0.6% silicon dioxide for which correction was made in the specific heat results. A 220.4-g. sample was studied.

**Apparatus.**—The  $B_4C$  and silicon carbide were studied in the apparatus previously described.<sup>7</sup> Before the crystalline boric oxide measurements several alterations were made that should be recorded. (1) A new calorimeter of the same design and dimensions as that used previously was constructed. (2) A new heavy surrounding shield or "block" was made for us by Mr. G. F. Nelson, Head Mechanic, Department of Chemistry, University of California. This "block" is identical in design with those used in the laboratory of Prof. W. F. Giaque of the University of California. (3) The temperature scale now employed is that of the National Bureau of Standards. Through the kind cooperation of Dr. F. G. Brickwedde, copper-constantan thermocouples were calibrated for us between liquid hydrogen and room temperatures. These couples are employed in conjunction with a gold heater-resistance thermometer in exactly the manner described by Giaque and Wiebe.<sup>8</sup> (4) In addition, a Kinney vacuum pump of 15 cu. ft. per min. displacement has replaced the rather cumbersome combination of pumps used heretofore for evacuating the liquid and solid nitrogen. With the new pumping facilities a temperature of  $51.1^\circ K$ . is reached readily.

**Specific Heats.**—The results, expressed in defined calories (1 calorie = 4.1833 int. joules), are

(7) Millar, *THIS JOURNAL*, **50**, 1875 (1928); Anderson, *ibid.*, **52**, 2296 (1930).

(8) Giaque and Wiebe, *ibid.*, **50**, 101 (1928).

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(2) Chemist, Metallurgical Division, Bureau of Mines.

(3) McCulloch, *THIS JOURNAL*, **59**, 2650 (1937).

(4) Kracek, Morey and Merwin, *Am. J. Sci.*, **35A**, 143 (1938).

(5) The earlier report of "crystalline  $B_2O_3$ " of Taylor and Cole, *THIS JOURNAL*, **56**, 1648 (1934), and *J. Am. Ceram. Soc.*, **18**, 55 (1935), is considered to be erroneous. The material they prepared melted at  $294^\circ$  whereas McCulloch obtained  $460^\circ$  and Kracek, Morey and Merwin  $450^\circ$  for their preparations.

(6) Ridgway, *Trans. Amer. Electrochem. Soc.*, **66**, preprint 25, 293 (1934).