compound $N_2O_4 \cdot 2R_2O$ can be pictured as having the structure shown in Fig. 4.

This concept is capable of explaining the relatively high melting point of the dioxane compound $N_2O_4 \cdot O(CH_2CH_2)_2O$, for the two oxygen atoms in a single dioxane molecule make possible an indefinitely extended aggregation.

If one is willing to accept the assumption that each of the nitrogen atoms in the N_2O_4 molecule is capable of accepting a pair of electrons from an ether oxygen, thus increasing the coördination number of the N-atom to four, a structure in which each oxygen atom from a given dioxane molecule is coördinated to one of the nitrogen atoms in the N_2O_4 molecule to form a bicyclic configuration (Fig. 5) may be considered.

The proof of these structures must, of course, await X-ray diffraction studies.

The results of this study are particularly interesting since they can be correlated with the recent studies of reactions of dinitrogen tetroxide with olefins in basic solvents. Since Levy, *et al.*,[4c] found that β,β'-dichlorodiethyl ether does not prevent oxidation as do other more basic ethers, the results of the present investigation that show that the dichloroether does not form an addition compound with dinitrogen tetroxide certainly lend support to the postulate that basic solvents moderate the oxidizing action of dinitrogen tetroxide through the formation of molecular addition compounds.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Heat Capacities and Entropies of Melamine and Dicyandiamide

BY C. C. STEPHENSON AND D. J. BERETS

The heat capacities of melamine and dicyandiamide have been measured from 15 to 300°K. The calculated entropies at 298.16°K. are 35.63 cal./deg./mole and 30.90 cal./deg./mole, respectively.

The recent increased importance of organic compounds containing nitrogen has made it desirable to have adequate thermal data with which to carry out thermodynamic calculations on some of these compounds. Accordingly, the heat capacities of melamine, $C_3N_6H_6$, and dicyandiamide, $C_2N_4H_4$, have been measured from 15°K. to room temperature.

Experimental

Materials.—Both compounds were prepared and purified in the Stamford Research Laboratories of the American Cyanamid Company. The melamine was recrystallized from NaOH solution and analyzed to be 100.0% pure, containing 0.002% Na and 3.7 p.p.m. Fe. The dicyandiamide was recrystallized from hot water and was analyzed spectrographically to contain no more than 0.1% impurities. Both materials were dried under high vacuum for several days, but without heating. From the anomalies in the heat capacity curves at the melting point of ice, it was calculated that the melamine contained 0.05% by weight of water and the dicyandiamide, 0.34%. The final heat capacity values have been corrected for the contribution of this amount of water.

TABLE I

HEAT CAPACITIES AT EXPERIMENTAL TEMPERATURES

Melamine		Dicyandiamide	
T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
15.62	0.63	14.40	0.54
17.04	0.77	15.59	0.64
18.43	0.94	16.89	0.75
19.87	1.17	18.33	0.92
23.03	1.65	20.18	1.16
26.15	2.16	26.61	2.14
29.31	2.72	30.33	2.84
32.76	3.35	33.72	3.46
36.42	4.01	37.31	4.11
40.25	4.71	41.22	4.83
44.44	5.46	45.40	5.58
49.09	6.30	49.81	6.35
54.14	7.17	54.82	7.16
59.44	8.04	60.11	7.97
63.64	8.69	64.26	8.60
69.29	9.58	69.19	9.22
74.88	10.36	74.18	9.86
80.46	11.11	79.26	10.41
86.00	11.81	84.43	10.94
91.61	12.52	89.67	11.47
97.40	13.22	95.03	11.98
103.45	13.94	100.62	12.50
109.65	14.68	106.42	13.00
116.09	15.43	112.52	13.54
122.48	16.18	118.67	14.06
126.63	16.64	124.83	14.57
131.75	17.23	131.29	15.10
137.20	17.83	137.74	15.60
142.92	18.50	144.18	16.15
148.89	19.19	150.62	16.69
155.15	19.97	157.12	17.25
161.73	20.77	163.74	17.80
168.48	21.55	170.81	18.39
175.45	22.40	178.13	18.99
182.78	23.25	185.53	19.57
190.24	24.17	192.97	20.19
197.81	25.06	200.49	20.78
205.46	25.98	208.12	21.37
213.15	26.88	215.43	21.99
220.55	27.76	223.12	22.57
228.30	28.68	230.86	23.19
236.09	29.63	238.72	23.81
243.90	30.56	246.37	24.38
251.74	31.47	254.17	24.99
259.16	32.39	262.12	25.64
267.04	33.50[a]	269.79	26.40[a]
275.24	34.78[a]	277.73	26.85[a]
283.58	35.32	285.97	27.50
291.73	36.30	294.63	28.14
299.95	37.31		

[a] Values are high due to melting of ice in sample.

Apparatus and Procedure.—The low temperature calorimeter has been previously described[1] and was used without modification.

A melamine sample of a little under one mole was employed. The calorimeter cooled with nitrogen refrigerant to the temperature of solid nitrogen and heat capacity measurements were made up to about 220°K. Dry Ice was then used as refrigerant for measurements to room temperature. Following this, the calorimeter was cooled with nitrogen and hydrogen refrigerant to the temperature of solid hydrogen and the interval 15 to 60°K. covered. The procedure with dicyandiamide was identical and a sample of a little over one mole was used.

The temperature and energy inputs were measured by means of a platinum–rhodium thermometer-heater having the laboratory designation R222. The resistance of this thermometer agreed with its original calibration[1] at the triple point of hydrogen and the freezing point of water. The calorie was taken to be 4.1833 international joules. The absolute temperature of the ice point was taken as 273.16°K.

Data and Discussion

Heat Capacity.—The experimental results for melamine and dicyandiamide are presented in Table I.

The accuracy of these results is estimated to be 0 2% above 35°K., 1% at 20°K., and 5% at 15°K.

Except for the values near 0°, all the results are corrected for the presence of water in the sample, as mentioned in a previous paragraph.

Entropy.—The contribution to the entropy of the heat capacity in the region 15 to 298.16°K. has been computed from the area under a large scale graphical plot of C_p/T *vs.* T. Around 15°, the heat capacity values of both compounds merge smoothly with the values of a Debye function of characteristic temperature $\theta = 175°$ and six degrees of freedom. The 0–15°K. contribution to the entropy is thus 0.20 e.u.

The entropy at 298.16°K. is for melamine 35.63 ± 0.03 e.u., and for dicyandiamide 30.90 ± 0.03 e.u.

Other Thermal Data.—The entropies of formation of melamine and dicyandiamide are calculated to be −199.39 and −125.78 e.u., respectively, employing entropy data for C, N_2 and H_2 from the tables of the National Bureau of Standards.[2] The heats of formation of melamine and dicyandiamide have been given by Salley and Gray[3] as −17.13 and 5.96 kcal./mole. Hence the free energies of formation of melamine and dicyandiamide are calculated to be 42.33 and 43.50 kcal./mole, respectively.

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(1) R. W. Blue and J. F. G. Hicks, THIS JOURNAL, **59**, 1962 (1937).

(2) Selected Values of Properties of Hydrocarbons, National Bureau of Standards, Circular C461 (1947).

(3) D. J. Salley and J. B. Gray, THIS JOURNAL, **70**, 2650 (1948).

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2,2,3,3-Tetramethylbutane: Heat Capacity, Heats of Transition, Fusion and Sublimation, Vapor Pressure, Entropy and Thermodynamic Functions

BY D. W. SCOTT, D. R. DOUSLIN, M. E. GROSS, G. D. OLIVER AND H. M. HUFFMAN[1]

The heat capacity of solid 2,2,3,3-tetramethylbutane was studied between 12°K. and the melting point, 373.97 ± 0.05°K. The transition temperature (152.5 ± 0.2°K.), heat of transition (478 cal. mole^{-1}), and heat of fusion (1802 cal. mole^{-1}) were determined. The entropy of the solid at 298.16°K. was found to be 65.43 ± 0.15 cal. deg.$^{-1}$ mole^{-1}. The vapor pressure was measured from 0 to 65° and the following equation was selected to represent the data: $\log_{10} p = 7.92864 - 1709.428/(t + 233.634)$. The heat of sublimation calculated from the vapor pressure data is 10,365 ± 50 cal. mole^{-1}. The standard entropy of the vapor at 298.16°K. was found to be 93.05 ± 0.30 cal. deg.$^{-1}$ mole^{-1}. By utilizing the results of relatively detailed normal coördinate calculations as a guide in interpreting the spectra, a vibrational assignment adequate for purposes of thermodynamic computations was obtained. The average height of the potential barriers hindering internal rotation that is required to give agreement with the observed value of the entropy is 4700 cal. mole^{-1}. Using this value of the average barrier height, the vibrational assignment, and other pertinent molecular-structure data, the thermodynamic functions $-(F^0 - H_0^0)/T$, $H^0 - H_0^0$, S^0, and C_p^0 for 2,2,3,3-tetramethylbutane were computed for selected temperatures up to 1500°K.

Because of the interest of the petroleum industry in highly branched paraffin hydrocarbons, a study of certain thermodynamic properties of 2,2,3,3-tetramethylbutane (hexamethylethane) was undertaken by the Thermodynamics Laboratory of the Petroleum and Natural Gas Branch of the Bureau of Mines.

The molecule of 2,2,3,3-tetramethylbutane is the most compact and most highly symmetrical of the isomeric octane molecules and is the only one of these that does not have rotational isomers. By virtue of this high molecular symmetry and lack of rotational isomers, the detailed methods of statistical mechanics could be used in a particularly straightforward manner to calculate the thermodynamic functions of 2,2,3,3-tetramethylbutane. Of the molecular-structure parameters required for such calculations, the moments of inertia and vibrational frequencies could be obtained from available electron-diffraction and spectroscopic data, respectively. However, information about the potential barriers hindering internal rotation required an experimental value of some thermodynamic property such as a value of the entropy of the ideal gas obtained from third-law studies.

This paper presents (a) the results of calorimetric and vapor-pressure measurements by which the necessary entropy value was obtained and (b) the calculated thermodynamic functions made possible by these experimental results.

Relative to most hydrocarbons of about the same molecular weight, 2,2,3,3-tetramethylbutane has a high melting point (100.81°) and an unusually

(1) Deceased.