[Contribution No. 85 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines, U. S. Department of the Interior]

Pyrrolidine: Chemical Thermodynamic Properties between 0 and 1500°K.; Effect of Pseudorotation; and an Unusual Thermal Anomaly in the Liquid State[1]

By J. P. McCullough, D. R. Douslin, W. N. Hubbard, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, F. R. Frow, J. P. Dawson and Guy Waddington

Received May 8, 1959

The chemical thermodynamic properties of pyrrolidine in the ideal gaseous state (0–1500°K.) were calculated by use of calorimetric, spectroscopic and molecular structure information. In common with other saturated molecules with five-membered rings, the pyrrolidine molecule has a "pseudorotational" degree of freedom. Best agreement between calculated and observed thermodynamic properties was obtained by assuming pseudorotation to be hindered by a potential barrier of 300 cal. mole^{-1}. Experimental studies provided the following information: values of heat capacity for the solid above 13°K.; the liquid below 350°K. and the vapor between 350 and 500°K.; temperature of a first-order transition in the solid state, triple point temperature; heats of transition, fusion and vaporization; thermodynamic functions for the solid and liquid (0–360°K.); vapor pressure (43–121°); equation of state parameters; and standard heats of combustion and formation at 298.16°K. An unusual anomaly, possibly related to the effects of restricted pseudorotation and/or association, was observed in the heat capacity of liquid pyrrolidine.

A comprehensive thermodynamic investigation of pyrrolidine was made in this Laboratory as part of a continuing program of studies of organic nitrogen compounds important in petroleum technology. This paper, on a saturated five-membered-ring compound, is the second of a projected series on cyclic nitrogen compounds, the first having given results for pyridine.[2] Concurrently with the work reported here, investigations of the thermodynamic properties of pyrrolidine and extensive spectroscopic studies that proved essential to understanding some of the unusual properties of this substance were made in the laboratories of Dow Chemical Company.[3]

The experimental part of this investigation included measurements of thermodynamic properties by the methods of low temperature calorimetry, comparative ebulliometry, vapor flow calorimetry and combustion calorimetry. Descriptions of the experiments and detailed results are given in the Experimental section. From a theoretical standpoint, the most interesting results of this research stem from the effects of pseudorotation[4–6] and hydrogen bonding. The properties of pyrrolidine can be accounted for only by use of the concept of pseudorotation as originally introduced by Kilpatrick, Pitzer and Spitzer.[4] Further, pyrrolidine exhibits anomalous thermal behavior in the liquid state that may be related to the effects of hydrogen bonding and, possibly, restricted pseudorotation. These phenomena are discussed in the following sections.

Calculation of Thermodynamic Properties

The thermodynamic properties of pyrrolidine in the ideal gaseous state were computed from calorimetric, spectroscopic and molecular structure information. For convenience, the calorimetric results used in these calculations are collected in Table I.

Table 1

Observed and Calculated Molal Thermodynamic Properties of Pyrrolidine in the Ideal Gaseous State

Entropy, $S°$, cal. deg.$^{-1}$			Heat capacity, $C_p°$, cal. deg.$^{-1}$		
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
321.90	75.53	75.53	350.20	23.51	23.49
339.50	76.69	76.70	369.20	24.99	24.97
359.72	78.01	78.05	415.20	28.47	28.47
			458.25	31.53	31.57
			500.25	34.38	34.40

Heat of formation, $\Delta Hf°_{298.16}$ (obsd.) = −0.86 ± 0.22 kcal.

Vibrational Assignment.—Comprehensive spectroscopic data have been reported for pyrrolidine[7] recently. The excellent studies of Evans and Wahr[3b] were particularly useful in clearing up uncertainties in interpretation of the spectra, which are complicated by the effects of pseudorotation and of hydrogen bonding in the liquid state. The vibrational assignment used in this research is given in Table II, which also includes a tentative assignment for pyrrolidine-ND. Evans and Wahr report a vibrational assignment and discuss the spectra in detail. Except for unimportant differences in designation of normal modes of vibration, which are primarily useful only for purposes of classification in such complex molecules, the assignment of these authors differs from that of Table II in only six frequencies; they use frequencies at 560, 800, 840, 1096, 1136 and 1171 cm.$^{-1}$ instead of those in Table II at 612, 925, 980, 990, 1053 and 1239 cm.$^{-1}$. The assignment in Table II is preferred because (1) it is consistent with the assignments for cyclopentane[4,8] and thiacyclopentane,[5] also given in Table II, and (2) it is consistent with both entropy and vapor heat capacity data. The

---

[1] This investigation was performed as part of American Petroleum Institute Research Project 52 on "Nitrogen Constituents of Petroleum," which is conducted at the University of Kansas in Lawrence, Kansas, and at the Bureau of Mines Experiment Stations in Laramie, Wyoming, and Bartlesville, Oklahoma.

[2] J. P. McCullough, D. R. Douslin, J. F. Messerly, I. A. Hossenlopp, T. C. Kincheloe and G. Waddington, This Journal, **79**, 4289 (1957)

[3] (a) D. L. Hildenbrand, G. C. Sinke, R. A. McDonald, W. R. Kramer and D. R. Stull, *J. Chem. Phys.*, to be published; (b) J. C. Evans and J. C. Wahr, *ibid.*, to be published.

[4] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, This Journal, **69**, 2483 (1947).

[5] W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and G. Waddington, *ibid.*, **74**, 6052 (1952).

[6] J. P. McCullough, *J. Chem. Phys.*, **29**, 966 (1958).

[7] (a) Raman and infrared data: H. Tschamler and H. Voetter, *Monatsh. Chem.*, **83**, 302 (1952); (b) Raman data: American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, to be published; (c) infrared data: *ibid.*, Catalog of Infrared Spectral Data, to be published.

[8] F. A. Miller and R. G. Inskeep, *J. Chem. Phys.*, **18**, 1519 (1950).

TABLE II

VIBRATIONAL ASSIGNMENT FOR PYRROLIDINE AND RELATED COMPOUNDS, IN $CM.^{-1}$

Description	Cyclopentane[a]	Thiacyclopentane[b]	Pyrrolidine[c]	Pyrrolidine-ND[c]
Ring def.	283	296	300	290
Ring def.	545	472	570	506
Ring def.	617	520	612	560
CH_2 rock	769	770	792	800
CH_2 rock	827	820	844	844
Ring stretch	886	882	872	860
Ring stretch	896	632	909	909
Ring stretch	949	687	925	949
Ring stretch	964	960	980	975
Ring stretch	(964)[d]	(960)	(980)	(975)
CH_2 rock	1030	1022	1025	1025
CH_2 wag	1033	1036	1053	[1053][e]
CH_2 wag	(1033)	1064	1080	1076
CH_2 twist	1104	1098	1105	1101
CH_2 twist	(1104)	1136	1205	1202
CH_2 rock	1207	1183	1220	1232
CH_2 rock	(1207)	..	..	..
CH_2 wag	1258	1196	1239	1261
CH_2 wag	(1258)	..	..	..
CH_2 twist	1283	1258	1284	1287
CH_2 twist	(1283)	..	..	..
CH_2 wag	1306	1307	1299	[1299][e]
CH_2 twist	1316	1333	1348	1346
CH_2 bend	1453(2)[f]	1442(2)	1468(2)	1468(2)
CH_2 bend	1462(3)	1466(2)	1480(2)	1480(2)
CH stretch	2900(10)	2900(8)	2900(8)	2900(8)
NH or ND stretch	..	..	3367	2495
NH or ND def.	..	..	1418	1155
NH or ND def.	..	..	990	715

[a] Fundamental frequencies from ref. 8. [b] Fundamental frequencies from ref. 5. [c] Numerical frequency values selected from data in refs. 3 and 7. [d] Frequencies in parentheses used twice. [e] Estimated to be the same as in normal pyrrolidine. [f] Number in parentheses indicates multiplicity used in thermodynamic calculations.

vapor heat capacity data, which were not available when Evans and Wahr made their assignment, provide a particularly sensitive test of the assignment of frequencies in the range of the most important differences.

The most significant change from a spectroscopic standpoint is the assignment of the out-of-plane NH deformation frequency at 990 $cm.^{-1}$ instead of 792 $cm.^{-1}$. Unfortunately, the data of Evans and Wahr[3b] for pyrrolidine-ND do not allow a positive assignment of this mode. The product rule for isotopic substitution is of little help because all vibrations of pyrrolidine are of the same species. However, if the excellent consistency of the assignments in Table II is to be retained, agreement between the calculated and observed vapor heat capacity can be obtained only if this NH deformation frequency is near 1000 $cm.^{-1}$. The observed Raman frequency at 990 $cm.^{-1}$ was so assigned. The frequency at 792 $cm.^{-1}$ was retained in the present assignment as a CH_2 rocking frequency.

Other differences in the vibrational assignments are relatively minor. The Raman line at 612 $cm.^{-1}$ was used instead of 560 $cm.^{-1}$ to give better consistency among the assignments in Table II. (The infrared absorption of the vapor from 550–582 $cm.^{-1}$ was assumed to be due to only one fundamental vibration.) The doubtful frequency at 800 $cm.^{-1}$, assigned as a fundamental by Evans and Wahr, easily can be the difference combination, $1105 - 300 = 805$ $cm.^{-1}$, if it is real. The doublet in the infrared spectrum of the vapor at 840–848 $cm.^{-1}$ was assumed to be due to only one fundamental, at 844 $cm.^{-1}$. The infrared band at 1096 was interpreted as the unresolved pair that appear at 1080 and 1105 $cm.^{-1}$ in the Raman spectrum. The frequencies at 1136 and 1171 $cm.^{-1}$ were interpreted as the combinations $300 + 844 = 1144$, and $300 + 872 = 1172$ $cm.^{-1}$.

The assignment in Table II is schematic, of course, particularly in the choice of descriptive names for the fundamental modes of vibration. However, the choice of numerical frequency values is believed to be essentially correct. Evans and Wahr report calculated and observed values of the product rule quotient for pyrrolidine and pyrrolidine-ND to be 0.380 and 0.390, respectively. The observed quotient from the assignment in Table II is 0.355. Again, the numerous fundamentals, low symmetry and diffuse spectra of pyrrolidine limit the utility of the product rule in testing the vibrational assignment.

Moments of Inertia.—Like cyclopentane, pyrrolidine is a non-planar molecule. However, because the ring is only slightly puckered and the molecular structure parameters have not been determined, the moments of inertia were computed for a planar configuration with the estimated dimensions: C–N bond distance, 1.46; C–C bond distance 1.54; C–H bond distance, 1.09; N–N bond distance, 1.02 Å.; C–N–C bond angle, 108°; C–C–C bond angle, 105° 29′; N–C–C bond angles, 111° 31′; and H–C–H bond angles, 109° 28′. For this assumed structure, the product of principal moments of inertia is 3.439×10^{-114} $g.^3$ $cm.^6$.

Pseudorotation.—If no configuration of the puckered pyrrolidine ring is favored energetically over any other, that is, if pseudorotation is "free" as in cyclopentane, only one parameter, the reduced "moment of inertia" of pseudorotation, is needed to compute the contribution of pseudorotation to the thermodynamic functions. If pseudorotation is restricted, as in thiacyclopentane,[5] a second parameter, the "barrier height," also is needed. The best agreement with the calorimetric data was obtained by assuming that pseudorotation is slightly restricted in pyrrolidine. The thermodynamic properties are insensitive to the nature of the restricting potential, so a twofold cosine-type barrier was chosen arbitrarily as the most reasonable form. The height of the barrier to pseudorotation, 300 cal. $mole^{-1}$, and the reduced moment of inertia, 8.570×10^{-40} g. $cm.^2$, were selected to give agreement between observed and calculated values of entropy and heat capacity in the vapor state.

The symmetry number for over-all rotation and pseudorotation is unity. (The inversion of the N–H group with respect to the ring is taken into account in the assignment of symmetry number.)

Little quantitative significance can be attached to the barrier height used in these calculations. Qualitatively, the results show that pseudorotation in pyrrolidine is either free or only slightly restricted.

The Chemical Thermodynamic Properties.—The molecular parameters discussed in foregoing paragraphs were used in computing values of the following thermodynamic functions at selected

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF PYRROLIDINE[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$C_p°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	log Kf[b]
0	0	0	0	0	0	6.66	6.66	Infinite
273.16	−60.77	11.59	3.166	72.36	17.52	−0.27	25.07	−20.06
298.16	−61.81	12.16	3.626	73.97	19.39	− .86	27.41	−20.09
300.00	−61.88	12.21	3.663	74.09	19.53	− .90	27.58	−20.09
400	−65.77	15.02	6.008	80.79	27.33	−3.02	37.41	−20.44
500	−69.46	18.20	9.100	87.66	34.39	−4.70	47.71	−20.85
600	−73.06	21.41	12.846	94.47	40.31	−5.97	58.32	−21.24
700	−76.60	24.47	17.13	101.07	45.22	−6.90	69.11	−21.58
800	−80.05	27.33	21.86	107.38	49.35	−7.56	80.01	−21.86
900	−83.42	29.98	26.98	113.40	52.85	−7.96	91.00	−22.10
1000	−86.71	32.42	32.42	119.13	55.84	−8.16	102.02	−22.30
1100	−89.91	34.67	38.14	124.58	58.40	−8.19	113.02	−22.46
1200	−93.01	36.74	44.09	129.75	60.60	−8.09	124.03	−22.59
1300	−96.03	38.65	50.24	134.68	62.50	−7.90	135.02	−22.70
1400	−98.95	40.42	56.59	139.37	64.14	−7.61	146.03	−22.80
1500	−101.80	42.05	63.08	143.85	65.56	−7.26	157.01	−22.88

[a] To retain internal consistency, some of the values in this table are given to one more decimal place than is justified by the absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant of formation by the reaction: $4C(c, \text{graphite}) + 9/2H_2(g) + 1/2N_2(g) = C_4H_9N(g)$.

temperatures between 0 and 1500°K.: $(F - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$ and $C_p°$.[9] Corrections for the effects of anharmonicity of vibrational degrees of freedom were not necessary. The results are listed in columns 2–6, Table III.

The calculated and observed values of entropy and heat capacity are compared in Table I. Agreement well within the accuracy uncertainty of the experimental data was obtained over the entire range of temperature of the experiments. It is important to note that no reasonable treatment that does not include pseudorotation allows a simultaneous fit to all of the calorimetric data.

The Heat, Free Energy and Equilibrium Constant of Formation.—The calculated values of the thermodynamic functions of pyrrolidine, the experimental value of $\Delta Hf°_{298.16}$ (Table I) and values of the thermodynamic functions of C(c, graphite),[10] $H_2(g)$[10] and $N_2(g)$[10] were used in computing values of $\Delta Hf°$, $\Delta Ff°$ and log Kf at selected temperatures between 0 and 1500°K. These results are listed in columns 7–9, Table III.

The Thermal Anomaly in Liquid Pyrrolidine

The authors are not aware of any organic substance other than pyrrolidine that exhibits such unusual thermal behavior in the liquid state as shown in Fig. 1 by the plot of heat capacity *vs.* temperature. The heat capacity curve at the melting point has *positive* slope and *negative* curvature; in the range 260–280°K., the curve shows a point of inflection. Thermal equilibration during the heat capacity measurements was abnormally slow, but replicate measurements following varying thermal pretreatment showed no effect of hysteresis. Reproducibility of results was within 0.05%. The independent study by Hildenbrand, *et al.*,[3a] who were not aware then of the work in this Laboratory, verified these findings in every detail.

A satisfactory quantitative explanation of the anomalous heat capacity results has not been found. Studies of the transport properties and the nuclear-magnetic-resonance spectrum of liquid pyrrolidine planned in other laboratories, and thermal studies of ethylenimine and piperidine planned in this Laboratory, should shed further light on the complex phenomena that must be involved. Until additional information is available, it seems best to be content with a qualitative understanding of the behavior of pyrrolidine.

On the basis of spectroscopic evidence, Evans and Wahr[3b] concluded that liquid pyrrolidine consists exclusively of hydrogen-bonded dimers at room temperature. However, pyrrolidine must be only weakly associated at the boiling point, for both the boiling point and heat of vaporization are normal for a nonassociated liquid. Further, the trends of heat of vaporization and vapor pressure with temperatures (reported in the Experimental section) do not show evidence of strong association in the liquid slightly above room temperature. Of course, the hydrogen bond energy in pyrrolidine must be very small, so the effect of association on thermal properties near room temperature also may be small.

Pronounced spectral changes occur as pyrrolidine is cooled below room temperature, and Evans and Wahr assumed that the changes cannot be due to increased molecular complexing, through hydrogen bonding, in the already associated liquid. They suggest that the spectral changes are due to the presence of puckered conformations of the molecule with different energies and spectra. Thus, Hildenbrand, *et al.*,[3a] concluded that the unusual thermal behavior was due to shifting equilibrium among conformations with different energy. However, the contribution of this "isomerism" to the heat capacity is not large enough to account for the observed anomaly.

To establish the magnitude of the thermal anomaly, the heat capacity of pyrrolidine was compared with that of related heterocyclic compounds, as shown in Fig. 1. In the absence of abnormal ef-

---

(9) The vibrational contributions were computed at the Bureau of Mines Computation Laboratory, Pittsburgh, Pa. The contributions of restricted pseudorotation were taken from the tables of K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

(10) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

fects, the difference in heat capacity between thiophene and thiacyclopentane would be expected to be about the same as that between pyrrole and pyrrolidine. Actually, the latter difference is much larger than the former, as Fig. 1 demonstrates. However, this comparison is complicated by the fact that the results for pyrrole also are unusual, the heat capacity curve being linear within 0.03%, probably an effect of hydrogen bonding in this substance. The plotted results for 2-methylthiophene and 1-methylpyrrole indicate that the heat capacities of corresponding nitrogen and sulfur heterocyclic compounds do not differ very much if hydrogen-bonding and pseudorotation cannot occur. Therefore, comparison of the results for pyrrolidine and thiacyclopentane leads to the conclusion that the anomalous contribution to the heat capacity of pyrrolidine is of the order of 6 cal. deg.$^{-1}$ mole^{-1} at the melting point and 2 cal. deg.$^{-1}$ mole^{-1} at room temperature.

The type of isomerism suggested by Hildenbrand, *et al.*, which is equivalent to more highly restricted pseudorotation in the liquid state than in the vapor, could not be responsible for an increase in heat capacity of more than about 2 cal. deg.$^{-1}$ mole^{-1}. It seems likely that at least part of the anomalous increase must be associated with the presence of polymeric complexes formed by hydrogen bonding. A combination of restricted pseudorotation and increased molecular association might account for the spectral changes found by Evans and Wahr.

Experimental

The reported values are based on a molecular weight of 71.120 for pyrrolidine (1951 International Atomic Weights[11]), the 1951 values of fundamental physical constants[12] and the relations: 0° = 273.16°K. and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[13] between 90 and 500°K. and the provisional scale[14] of the National Bureau of Standards between 11 and 90°K. All electrical and mass measurements were referred to standard devices calibrated at the National Bureau of Standards.

The apparatus and methods used in the continuing program of this Laboratory evolve as a result of improvements and modifications suggested by experience or required in studies of different substances. Not all of these improvements have been described in the literature, but the basic experimental techniques used for pyrrolidine are presented in published descriptions of apparatus and methods for low temperature calorimetry,[15] vapor flow calorimetry,[16] comparative ebulliometry[17] and combustion calorimetry.[18]

The Material.—The sample of pyrrolidine used for low temperature calorimetry, comparative ebulliometry and combustion calorimetry was part of the Standard Sample of Organic Nitrogen Compound, API-USBM 52-3, prepared and purified at the Laramie, Wyo., Station of the Bureau of Mines.[19] The purity, as determined by a calorimetric study of melting point as a function of fraction melted, was 99.85 mole %. For flow calorimetry, which required a larger volume of material, a sample of slightly lower purity was used.

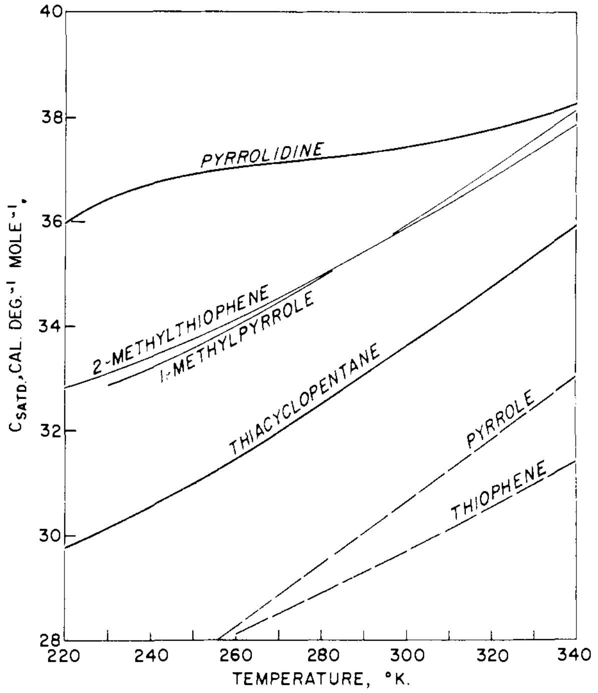

Fig. 1.—The heat capacity of liquid pyrrolidine and other heterocyclic compounds containing nitrogen and sulfur. The sources of heat capacity data are: thiophene, G. Waddington, *et al.*, THIS JOURNAL, **71**, 797 (1949); thiacyclopentane, D. W. Scott, *et al.*, *ibid.*, **74**, 6025 (1952); 2-methylthiophene, R. E. Pennington, *et al.*, *ibid.*, **78**, 2055 (1956); pyrrole and 1-methylpyrrole, unpublished results, this Laboratory.

Heat Capacity in the Solid and Liquid States.—Low temperature calorimetric measurements were made with a 46.352-g. sample sealed in a platinum calorimeter with helium (4 cm. pressure at room temperature) added to promote thermal equilibration. The observed values of heat capacity, C_{satd}, are listed in Table IV. Above 30°K. the accuracy uncertainty is estimated to be no greater than 0.2% except in the premelting region.

A small isothermal transition occurs only 8.2° below the melting point. Thermal equilibration below and above the transition was very slow, and the effect of premelting was pronounced. For these reasons, the accuracy uncertainty of the heat capacity results is larger in this region. Nevertheless, the total enthalpy change from 15–20° below the transition point to above the melting point was determined with normal precision (within ±0.1%), as shown by the results in the following section.

The unusual shape of the heat capacity curve of liquid pyrrolidine was discussed earlier in this paper. From 260 to 360°K., the following equation represents the observed heat capacity results for the liquid with a maximum deviation of 0.03%

$$C_{\text{satd}}\ (\text{liq.}) = 13.902 + 0.24885T - 9.1996 \times 10^{-4}T^2 + 1.1733 \times 10^{-6}T^3,\ \text{cal. deg.}^{-1}\ \text{mole}^{-1} \quad (1)$$

The heat capacity data in Table IV are in excellent agreement with the slightly less precise results of Hildenbrand, *et al.*

---

[11] E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

[12] F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

[13] H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

[14] H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

[15] H. M. Huffman, *Chem. Revs.*, **40**, 1 (1947); H. M. Huffman, S. S. Todd and G. D. Oliver, THIS JOURNAL, **71**, 584 (1949); D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

[16] Guy Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947); J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and G. Waddington, *ibid.*, **76**, 4791 (1954).

[17] G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 797 (1949).

[18] W. N. Hubbard, F. R. Frow and Guy Waddington, to be published.

[19] R. V. Helm, W. J. Lanum, G. L. Cook and J. S. Ball, *J. Phys. Chem.*, **62**, 858 (1958).

TABLE IV

THE MOLAL HEAT CAPACITY OF PYRROLIDINE IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.	ΔT[c]	C_{satd}	T, °K.	C_{satd}
Crystals II[d]		100.97	5.618	13.611	Liquid	
		106.50	5.455	13.956		
13.05	0.835	112.42	6.390	14.321	218.35	35.880
13.19	0.852	118.73	6.225	14.711	220.37	35.977
14.46	1.092	124.87	6.065	15.102	222.52	36.077
14.89	1.166	131.35	6.907	15.501	222.94	36.114
15.82	1.372	138.17	6.724	15.925	226.09	36.261
16.36	1.472	144.81	6.574	16.351	227.87	36.336
17.18	1.645	151.31	6.430	16.784	228.98	36.377
17.78	1.782	157.67	6.284	17.226	232.05	36.493
18.75	2.002	159.51	2.805	17.362	236.56	36.641
19.24	2.113	161.99	6.892	17.531	241.93	36.767
20.46	2.410	164.37	6.916	17.717	247.84	36.898
20.99	2.541	168.79	6.725	18.045	252.21	36.957
22.24	2.852	171.20	6.760	18.237	262.90	37.065
23.10	3.076	175.43	6.560	18.591	274.01	37.155
24.23	3.371	175.63	6.707	18.602	285.07	37.260
25.31	3.646	177.41	6.601	18.740	286.14	37.269
26.55	3.969	182.25	6.552	19.185	294.33	37.359
27.93	4.316	183.92	6.428	19.357	305.21	37.528
29.15	4.623	188.71	6.384	19.848	316.02	37.706
32.02	5.343	189.36	4.758	19.900	326.75	37.924
35.32	6.110	190.26	6.273	20.006	338.28	38.229
39.10	6.921	194.44	5.422	20.489	350.59	38.633
43.00	7.666	195.00	6.200	20.578		
47.38	8.419	198.58	5.053	21.132		
48.51	8.605	199.77	5.265	21.293		
52.52	9.211	203.53	4.856	22.237		
53.53	9.355	204.24	3.698	22.346		
55.06	9.563					
58.95	10.070		Crystals I[d]			
59.60	10.150					
64.45	10.713	209.17	1.307	25.47		
64.67	10.759	209.64	1.235	26.78		
69.67	11.224	210.02	1.223	27.06		
69.90	11.251	210.24	1.205	27.46		
75.35	11.728	210.42	1.218	27.65		
81.04	12.226	210.82	1.138	29.65		
84.42	12.505	211.18	1.116	30.45		
86.48	12.664	211.37	1.082	31.52		
89.76	12.898	211.56	1.086	32.05		
95.27	13.257					

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase at saturation pressure. [c] ΔT is the temperature increment of each measurement. [d] Values of C_{satd} for Crystals I and II are *not* corrected for the effect of premelting.

Heats and Temperatures of Transition and Fusion.—Three determinations of the heat of transition and four determinations of the heat of fusion, ΔHm, gave the average values 129.1 ± 0.2 and 2050 ± 1 cal. mole^{-1}, with the maximum deviation from the mean taken as the uncertainty. The transition temperature, determined by observing the temperature in the two-phase region, was found to be 207.14 ± 0.1°K. The results of a study of melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, are given in Table V. Also listed in Table V are values obtained for the triple point temperature, $T_{\text{T.P.}}$, the mole fraction of impurity in the sample, N_2^*, and the cryoscopic constants,[20] $\text{A} = \Delta Hm/RT_{\text{T.P.}}^2$ and $\text{B} = 1/T_{\text{T.P.}} - \Delta Cm/2\Delta Hm$, calculated from the observed values of $T_{\text{T.P.}}$, ΔHm and ΔCm (12.31 cal. deg.$^{-1}$ mole^{-1}).

These values for heat and temperature of phase changes are in excellent agreement with those of Hildenbrand, *et al.*

TABLE V

PYRROLIDINE: MELTING POINT SUMMARY

$T_{\text{T.P.}} = 215.31 \pm 0.05$°K.; $N_2^* = \text{AF}/(T_{\text{T.P.}} - T_{\text{obsd}}) = 0.0015$; $\text{A} = 0.02225$ deg.$^{-1}$; $\text{B} = 0.00164$ deg.$^{-1}$

Melted, %	1/F	T_{obsd}, °K.	T_{graph}, °K.[b]
16.20	6.173[a]	214.8834[a]	214.8834
28.52	3.506	215.0672	215.0696
51.77	1.932	215.1788	215.1794
71.54	1.398	215.2143	215.2167
89.52	1.117[a]	215.2362[a]	215.2363
100.00	1.000		215.2445
Pure	0		215.3143

[a] A straight line through these points was extrapolated to 1/F = 0 to obtain $T_{\text{T.P.}}$. [b] Temperatures from the straight line of footnote *a*.

Thermodynamic Properties in the Solid and Liquid States.—Values of the thermodynamic properties of the condensed phases were computed from the calorimetric data for selected temperatures between 10 and 360°K. The results are given in Table VI. The values at 10°K. were computed from a Debye function for 4.5 degrees of freedom with $\theta = 121.8°$; these parameters were evaluated from the heat capacity data between 13 and 21°K. Corrections for the effects of premelting were applied in calculating the "smoothed" data recorded in Table VI.

The value of the entropy of liquid pyrrolidine at 298.16°K. in Table VI, 48.76 cal. deg.$^{-1}$ mole^{-1}, is in excellent agreement with that reported by Hildenbrand, *et al.*, 48.78 cal. deg.$^{-1}$ mole^{-1}.

Vapor Pressure.—Observed values of vapor pressure, determined by comparative ebulliometry with water as the reference substance, are listed in Table VII. At one atm. pressure, the ebullition temperature was 0.009° higher than the condensation temperature. The Antoine and Cox equations selected to represent the results are

$$\log p\,(\text{mm.}) = 6.92534 - 1180.451/(t + 205.304) \qquad (2)$$

$$\log P\,(\text{atm.}) = A(1 - 359.718/T) \qquad (3)$$

where

$$\log A = 0.919436 - 9.48362 \times 10^{-4}T + 9.22187 \times 10^{-7}T^2$$

In these equations, *t* is in °C. and *T* is in °K. Comparisons of the observed and calculated vapor pressure for both equations are given in Table VII. The normal boiling point, calculated from either equation, is 86.56° (359.72°K.).

The vapor pressure data reported by Hildenbrand, *et al.*,[3] are in poor agreement with those in Table VII near the normal boiling point.

Heat of Vaporization, Vapor Heat Capacity and Effects of Gas Imperfection.—In the course of the flow-calorimetric experiments, which normally extend over a period of several weeks, the observed values of heat of vaporization were found to increase slightly with time. Pyrrolidine is known to be sensitive to oxygen in concentration of a few parts per million. Therefore, it was assumed that the change in heat of vaporization was caused by slight contamination owing to reaction with oxygen, which could not be entirely eliminated from the system. Twice during the experiments the sample was removed from the system, dried with CaH_2 and distilled under vacuum conditions. Results obtained after this treatment agreed with those obtained at the beginning with the original material. Nine to 16 determinations were made at each of the three temperatures of the experiments. Because the maximum change noted was less than 0.4% and because the change at each temperature was a linear function of time (measured as hours of operation *after* placing the original or repurified sample in the calorimeter), the heat of vaporization of the pure material could be estimated without significant loss of accuracy. Replicate measurements of vapor heat capacity showed that this property was not affected by the slight contamination that occurred.

The experimental values of heat of vaporization and vapor heat capacity are given in Tables VIII and IX. The estimated accuracy uncertainty of the values of ΔHv and $Cp°$

---

[20] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

TABLE VI

THE MOLAL THERMODYNAMIC PROPERTIES OF PYRROLIDINE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{satd} - H°_0)/T$, cal. deg.$^{-1}$	$(H_{satd} - H°_0)/T$, cal. deg.$^{-1}$	$H_{satd} - H°_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
			Crystals II		
10	0.032	0.097	0.966	0.129	0.383
15	.108	.314	4.710	.422	1.194
20	.244	.667	13.341	.911	2.292
25	.439	1.118	27.950	1.557	3.563
30	.688	1.632	48.96	2.320	4.842
35	.980	2.178	76.21	3.158	6.035
40	1.307	2.728	109.10	4.035	7.100
45	1.659	3.264	146.86	4.923	8.020
50	2.030	3.781	189.03	5.811	8.836
60	2.806	4.741	284.47	7.547	10.198
70	3.603	5.601	392.0	9.204	11.256
80	4.401	6.363	509.0	10.764	12.136
90	5.191	7.049	634.4	12.240	12.914
100	5.966	7.668	766.8	13.634	13.552
110	6.724	8.231	905.4	14.955	14.174
120	7.464	8.752	1050.2	16.216	14.800
130	8.183	9.241	1201.3	17.424	15.416
140	8.885	9.704	1358.6	18.589	16.038
150	9.570	10.148	1522.2	19.718	16.694
160	10.239	10.578	1692.4	20.817	17.364
170	10.892	10.998	1869.6	21.890	18.074
180	11.532	11.413	2054.2	22.945	18.868
190	12.161	11.828	2247.3	23.989	19.760
200	12.778	12.249	2449.7	25.027	20.760
207.14	13.213	12.556	2600.8	25.769	21.56
			Crystals I		
207.14	13.213	13.179	2729.9	26.392	21.29
210	13.394	13.295	2791	26.689	22.04
215.31	13.730	13.527	2912	27.257	23.42
			Liquid		
215.31	13.730	23.048	4962	36.778	35.73
220	14.229	23.321	5130	37.55	35.96
230	15.278	23.881	5492	39.15	36.42
240	16.305	24.411	5858	40.71	36.73
250	17.312	24.908	6226	42.22	36.92
260	18.298	25.372	6596	43.67	37.04
270	19.264	25.806	6967	45.07	37.12
273.16	19.565	25.937	7084	45.50	37.15
280	20.209	26.212	7339	46.42	37.21
290	21.136	26.593	7711	47.72	37.31
298.16	21.878	26.887	8016	48.76	37.42
300	22.044	26.952	8085	48.99	37.44
310	22.933	27.293	8460	50.22	37.60
320	23.805	27.618	8837	51.42	37.78
330	24.660	27.929	9216	52.58	38.00
340	25.498	28.229	9597	53.72	38.28
350	26.320	28.521	9982	54.84	38.61
359.72	27.105	28.798	10359	55.90	38.96

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

is 0.2%. Empirical equations selected to represent the results are

$$\Delta Hv = 13{,}660 - 14.609T - 0.3980 \times 10^{-2}T^2 \quad \text{cal. mole}^{-1}\ (321\text{-}360°\text{K.}) \qquad (4)$$

$$Cp° = -9.653 + 0.11028T - 4.452 \times 10^{-5}T^2 \quad \text{cal. deg.}^{-1}\ \text{mole}^{-1}\ (350\text{-}500°\text{K.}) \qquad (5)$$

Equation 5 represents the experimental values of $Cp°$ within 0.03%.

TABLE VII

THE VAPOR PRESSURE OF PYRROLIDINE

Boiling point, °C. Water	Boiling point, °C. Pyrrolidine	p(obsd.),[a] mm.	p(obsd.) − p(calcd.), mm. Antoine, eq. 2	p(obsd.) − p(calcd.), mm. Cox, eq. 3
60.000	43.158	149.41	+0.03	+0.01
65	48.439	187.57	− .01	.00
70	53.760	233.72	− .02	− .01
75	59.122	289.13	− .03	− .01
80	64.523	355.22	+ .01	+ .02
85	69.969	433.56	.01	.00
90	75.456	525.86	.01	− .01
95	80.987	633.99	− .01	− .05
100	86.558	760.00	+ .05	+ .01
105	92.173	906.06	.06	.03
110	97.833	1074.6	.00	.0
115	103.537	1268.0	− .1	.0
120	109.280	1489.1	.0	.1
125	115.072	1740.8	.0	.0
130	120.905	2026.0	.0	.0

[a] From the vapor pressure data for water given by N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

TABLE VIII

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF PYRROLIDINE

T, °K.	P, atm.	ΔHv, cal.	B, cc. Obsd.	B, cc. Calcd.[a]
321.90	0.2500	8545	−1399	−1382
339.50	0.5000	8242	−1180	−1183
359.72	1.0000	7890	−1001	−1015

[a] Calculated from eq. 6.

TABLE IX

THE MOLAL VAPOR HEAT CAPACITY OF PYRROLIDINE IN CAL. DEG.$^{-1}$

T, °K.	350.20	369.20	415.20	458.25	500.25
Cp (1.000 atm.)		25.826	28.869	31.782	34.540
Cp (0.500 atm.)	24.080	25.385			
Cp (0.250 atm.)	23.789	25.192	28.566	31.589	34.415
$Cp°$ (obsd.)	23.510	24.989	28.470	31.526	34.375
$-TB''$ (obsd.)[a]	1.096	0.777	0.381	0.247	0.161
$-TB''$ (calcd.)[b]	1.078	.786	.404	.239	.153

[a] $-TB'' = -T(\mathrm{d}^2B/\mathrm{d}T^2)$; units are cal. deg.$^{-1}$ atm.$^{-1}$ mole^{-1}. [b] Calculated with eq. 6.

TABLE X

THE MOLAL ENTROPY OF PYRROLIDINE IN THE IDEAL GASEOUS STATE IN CAL. DEG.$^{-1}$

T, °K.	298.16	321.90	339.50	359.72
S_{satd}(liq.)	48.76	51.65	53.67	55.90
$\Delta Hv/T$	30.07	26.55	24.28	21.93
$S^* - S$[a]	0.04	0.08	0.12	0.18
$R \ln P$[b]	−4.94	−2.75	−1.38	0.00
$S°$(obsd.) ± 0.15[c]	73.93	75.53	76.69	78.01

[a] The entropy in the ideal gas state less that in the real gas state. [b] Entropy of compression, calculated from eq. 3. [c] Estimated accuracy uncertainty.

The effects of gas imperfection were correlated by the procedure described in an earlier publication.[21] The empirical equation for B, the second virial coefficient in the equation of state, $PV = RT(1 + B/V)$, is

$$B = -249 - 27.24 \exp(1200/T), \text{ cc. mole}^{-1} \qquad (6)$$

Comparisons of "observed" values of B and $-T(\mathrm{d}^2B/\mathrm{d}T^2) = \lim_{P\to 0} (\partial C_p/\partial P)_T$ with those calculated from eq. 6 are given in Tables VIII and IX.

---

[21] J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and G. Waddington, THIS JOURNAL, **77**, 6119 (1955).

TABLE XI[a,b]

PYRROLIDINE: ENERGY OF THE IDEALIZED COMBUSTION REACTION

m' (pyrrolidine)	0.84171	0.81791	0.72529	0.78609	0.78709	0.78382
$\Delta t_c = t_f - t_i - \Delta t_{cor.}$, deg.	2.10741	2.07168	2.00238	1.98199	2.00311	2.00112
$\mathcal{E}$(calor.)($-\Delta t_c$), cal.	−8203.37	−8064.28	−7794.52	−7715.15	−7797.37	−7789.62
$\mathcal{E}$(cont.)($-\Delta t_c$), cal.[c]	−10.48	−10.28	−9.96	−9.79	−9.89	−9.89
ΔE_{ign}, cal.	2.70	1.35	2.70	1.35	1.35	1.35
$\Delta E_{dec.}$ ($HNO_3 + HNO_2$), cal	17.84	18.05	16.29	17.03	17.08	18.20
ΔE, cor. to st. states,[d] cal.	2.16	2.12	2.07	2.04	2.02	2.05
$-n''\Delta Ec°$(auxiliary oil), cal.	214.00	299.78	906.04	256.89	324.30	345.53
$-n'''\Delta Ec°$(fuse), cal.	15.50	15.69	16.56	15.54	15.50	15.69
$n'\Delta Ec°$(pyrrolidine), cal.	−7961.65	−7737.57	−6860.82	−7432.09	−7447.01	−7416.69
$\Delta Ec°/M$(pyrrolidine), cal. g.$^{-1}$	−9458.90	−9460.17	−9459.41	−9454.50	−9461.45	−9462.23

Av. value and standard dev. of the mean: -9458.44 ± 1.11 cal. g.$^{-1}$

[a] The symbols and abbreviations in this table are those used in ref. 24, except as noted. The values of $\Delta Ec°/M$ for the auxiliary oil and fuse are −10,983.7 and −3923 cal. g.$^{-1}$, respectively. [b] Auxiliary data: $\mathcal{E}$(calor.) = 3892.63 cal. deg.$^{-1}$; V(Bomb) = 0.344 l.; physical properties of pyrrolidine at 25°, ρ = 0.74045 g. ml.$^{-1}$, $(\partial E/\partial P)_T = -0.013$ cal. g.$^{-1}$ atm.$^{-1}$, Cp = 0.526 cal. deg.$^{-1}$ g.$^{-1}$. [c] $\mathcal{E}^i$(cont.)(t_i − 25°) + $\mathcal{E}^f$(cont.)(25° − t_f + Δtcor). [d] Items 81–85 incl., 87–90 incl., 93 and 94 of the computation form of ref. 24.

Values of the heat of vaporization at 298.16°K., $\Delta Hv_{298.16}$, were calculated by extrapolation with eq. 4 (8953 cal. mole^{-1}), by the Clapeyron equation with eq. 3 and 6 (8958 cal. mole^{-1}), and by a thermodynamic network involving primarily the observed value of S_{satd} and the calculated value of $S°$ (8978 cal. mole^{-1}): the value selected is $\Delta Hv_{298.16}$ = 8965 ± 15 cal. mole^{-1}. From this value and eq. 6, the standard heat of vaporization was calculated, $\Delta Hv°_{298.16}$ = 8980 ± 15 cal. mole^{-1}.

These results for heat of vaporization, heat capacity and second virial coefficient are those to be expected for a normal unassociated substance of the molecular weight of pyrrolidine. Therefore, neither the liquid nor the vapor is associated to an unusual degree at the temperatures of this investigation.

Hildenbrand, *et al.*, reported a measured value of $\Delta Hv_{298.16}$ of 8990 cal. mole^{-1}, in fair agreement with the result given here. Their calculated value of ΔHv at the normal boiling point is in poor agreement with the observed value in Table VIII.

Entropy in the Ideal Gaseous State.—The entropy in the ideal gaseous state at 1 atm. pressure was calculated as shown in Table X.

Heat of Combustion.—The heat of combustion was determined by bomb calorimetry. The bomb, Ta-1,[22] and calorimeter system, BMR-1,[23] have been described. Rotation of the bomb is not required in the combustion calorimetry of nitrogen compounds such as pyrrolidine. The samples were contained in Pyrex ampoules. One gram of water was added to the bomb. The bomb was purged with oxygen to remove air originally present and charged to 30 atmospheres with pure oxygen. Each combustion experiment was initiated at 23°, and the quantities of pyrrolidine and auxiliary oil (Sample USBM-P3a) were chosen to produce a temperature increment of 2°. The mass of sample was used as a measure of the amount of reaction occurring in the bomb. The amount of reaction was checked by determining the amount of carbon dioxide in the combustion products, which was $100.02_5 \pm 0.02_5$% of that predicted from the sample mass. Corrections to standard states[24] were applied to the results of all experiments. The energy equivalent of the calorimetric system, $\mathcal{E}$ (Calor.), was determined by combustion of benzoic acid (National Bureau of Standards Sample 39g). The calorimetric results are summarized in Table XI. The experimental values of $\Delta Ec°/M$ apply to the following idealized combustion reaction at 298.16°K.

$$C_4H_9N(liq) + 6.25\ O_2(g) = 4CO_2(g) + 4.5\ H_2O(liq) + 0.5\ N_2(g)$$

For this reaction, the standard change in internal energy, $\Delta Ec°_{298.16}$, is −672.76 ± 0.18[25] kcal. mole^{-1} and the standard heat of combustion, $\Delta Hc°_{298.16}$, is −673.80 ± 0.18 kcal. mole^{-1}. This value of $\Delta Hc°_{298.16}$ is in excellent agreement with that reported by Hildenbrand, *et al.*,[3] −673.83 ± 0.20 kcal. mole^{-1}.

The Heat of Formation and Related Properties.—The value of $\Delta Hc°_{298.16}$ of pyrrolidine and values of heat of formation of carbon dioxide[26] and water[10] were used to compute the heat of formation in the liquid state for the reaction

$$4C(c, graphite) + 9/2\ H_2(g) + 1/2\ N_2(g) = C_4H_9N(liq.)$$

$$\Delta Hf°_{298.16}(liq.) = -9.84 \pm 0.20 \text{ kcal. mole}^{-1}$$

This value of $\Delta Hf°_{298.16}$, the value of S_{satd} (298.16) in Table VI, and values of entropy of the elements[10] were used to compute the entropy, free energy and common logarithm of the equilibrium constant of formation

$$\Delta Sf°_{298.16}(liq.) = -120.02 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta Ff°_{298.16}(liq.) = 25.95 \text{ kcal. mole}^{-1}$$

$$\text{Log } Kf_{298.16}(liq.) = -19.02$$

Addition of $\Delta Hv°_{298.16}$, $8.98_0 \pm 0.01_5$ kcal. mole^{-1}, to $\Delta Hf°_{298.16}$(liq.) yields the heat of formation in the ideal gaseous state, given in Table I.

BARTLESVILLE, OKLA.

---

(22) W. N. Hubbard, J. W. Knowlton and H. M. Huffman, *J. Phys. Chem.*, **58**, 396 (1954).

(23) G. Waddington, S. Sunner and W. N. Hubbard, "Experimental Thermochemistry," F. D. Rossini, Editor, Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 7, pp. 149–179.

(24) W. N. Hubbard, D. W. Scott and G. Waddington, ref. 23, Chapter 5, pp. 75–128.

(25) "Uncertainty interval" equal to twice the final "over-all" standard deviation. See F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(26) E. J. Prosen, R. S. Jessup and F. D. Rossini, *J. Research Natl. Bur. Standards*, **33**, 447 (1944).