TABLE III

RATES OF ACID HYDROLYSIS, MUTAROTATION AND RACEMIZATION GIVEN IN k (SEC.$^{-1}$)

Initial compd.	(Acid)	Temp., °C.	k_1, acid hydrolysis	k_m, mutarotation	k_r, racemization
l-cis-[Co en_2Cl_2]$^{+a}$	0.012	30	2.15×10^{-4}	5.37×10^{-4}	6.13×10^{-5}
d-cis-[Co en_2F_2]$^{+b}$	.001	25	6.0×10^{-6}	8.2×10^{-6}	3×10^{-6}
	.1	25	5×10^{-5}	10.3×10^{-5}	6.5×10^{-6}
l-cis-[Cr en_2Cl_2]$^+$	.1	22	2.30×10^{-4}	2.28×10^{-4}	1.48×10^{-4}
	.1	25	3.30×10^{-4}	3.30×10^{-4}	2.0×10^{-4}

[a] Values from Mathieu.[20] [b] Values from Basolo, *et al.*[5f]

mium complexes are in part responsible for (1) the general non-labile characteristics found for cobalt and chromium complexes as compared with other first row transition metal complexes, (2) the strong similarity of cobalt and chromium complexes in ease of substitution-type reactions, and (3) the ease with which Cr(II) goes to Cr(III) in systems which can form d^2sp^3 hybrid-orbital complexes with Cr(III).

URBANA, ILLINOIS

[CONTRIBUTION NO. 62 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Pyridine: Experimental and Calculated Chemical Thermodynamic Properties between 0 and 1500°K.; a Revised Vibrational Assignment[1]

BY J. P. MCCULLOUGH, D. R. DOUSLIN, J. F. MESSERLY, I. A. HOSSENLOPP, T. C. KINCHELOE AND GUY WADDINGTON

RECEIVED APRIL 22, 1957

From studies by low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry, values were obtained for the entropy, heat capacity and heat of formation of pyridine in the ideal gaseous state. The calorimetric values of entropy and heat capacity served as guides in revising the vibrational assignments for pyridine and several deuteropyridines. The revised assignment for pyridine and molecular structure data were used in computing values of the thermodynamic functions at selected temperatures between 0 and 1500°K. Values of the heat, free energy and equilibrium constant of formation were calculated at the same selected temperatures. The experimental investigations provided the following information: values of heat capacity for the solid (13–224°K.), the liquid [$C_{\text{satd}} = 33.633 - 9.1446 \times 10^{-2}T + 3.8478 \times 10^{-4}T^2 - 3.3430 \times 10^{-7}T^3$, cal. deg.$^{-1}$ mole^{-1} (240–347°K.)], and the vapor [$C_p° = -8.262 + 10.608 \times 10^{-2}T - 5.4662 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (374–500°K.)]; the heat of fusion [1978.6 cal. mole^{-1}] at the triple point [231.49°K.]; the entropy of the liquid at 298.16°K. [42.52 cal. deg.$^{-1}$ mole^{-1}]; the vapor pressure [$\log_{10} p(\text{mm.}) = 7.04162 - 1374.103/(t + 215.014)$, (67–153°)]; the heat of vaporization [$\Delta Hv = 13077 - 10.201\ T - 4.7941 \times 10^{-3}T^2$, cal. mole^{-1} (346–388°K.)]; the second virial coefficient in the equation of state, $PV = RT\ (1 + B/V)$, [$B = -15 - 84.5 \exp(950/T)$, cc. mole^{-1} (346–500°K.)]; and the standard heat of formation of the liquid at 298.16°K. [23.89 kcal. mole^{-1}].

Thermodynamic investigations of organic nitrogen compounds were begun recently in this Laboratory as part of American Petroleum Institute Research Project 52. The objective is to provide comprehensive thermodynamic data for nitrogen compounds that are important in petroleum technology. This paper is the first of a projected series on cyclic nitrogen compounds. Results are reported for pyridine, a compound important in theoretical considerations concerning molecular structure as well as in practical considerations as an industrial chemical. Some thermodynamic data for pyridine have been reported previously,[2] but many of the basic data are not of the accuracy that can be obtained by present-day methods.

The experimental part of this investigation consisted of measurements of thermodynamic properties by the methods of low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry. Descriptions of the experiments and detailed results are given in the Experimental part of the paper. For convenience, the most important experimental results—values of the entropy, heat capacity and heat of formation for the ideal gaseous state—are collected in Table I. The entropy and heat capacity data served as guides in revising the vibrational assignment for pyridine and as checks on thermodynamic properties calculated by the methods of statistical

TABLE I

OBSERVED AND CALCULATED MOLAL THERMODYNAMIC PROPERTIES OF PYRIDINE IN THE IDEAL GASEOUS STATE

	Entropy, $S°$, cal. deg.$^{-1}$			Heat capacity, $Cp°$, cal. deg.$^{-1}$	
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
346.65	70.65	70.65	374.20	23.79	23.79
366.11	71.86	71.89	397.20	25.23	25.24
388.40	73.27	73.30	420.20	26.65	26.65
			450.20	28.43	28.40
			500.20	31.12	31.21

Heat of formation, $\Delta Hf°_{298.16}$ (obsd.) = 33.50 kcal.

---

[1] (a) 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. (b) Presented at 130th American Chemical Society Meeting, Atlantic City, N. J., September, 1956.

[2] (a) C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944); (b) D. P. Biddiscombe, E. A. Coulson, R. Handley and E. F. G. Herington, *J. Chem. Soc.*, 1957 (1954); (c) E. F. G. Herington and J. F. Martin, *Trans. Faraday Soc.*, **49**, 154 (1953) [and references cited there]; (d) G. S. Parks, S. S. Todd and W. A. Moore, THIS JOURNAL, **58**, 398 (1936); (e) J. N. Pearce and H. M. Bakke, *Proc. Iowa Acad. Sci.*, **38B**, 450 (1929).

mechanics. The experimental value of the heat of formation and the calculated thermodynamic properties were used in computing values of the heat, free energy and equilibrium constant of formation at selected temperatures between 0 and 1500°K. These calculations are discussed in the following section.

Calculation of Thermodynamic Properties

The Vibrational Assignment.—The vibrational spectra of pyridine and several deuteropyridines have been studied by a number of investigators.[3] Corrsin, Fax and Lord (CFL) have given detailed vibrational assignments for pyridine and pyridine-d_5.[3a] Anderson, Bak, Brodersen and Rastrup-Andersen[3b] have given assignments for 4D-pyridine, 3D-pyridine and 2D-pyridine based on the assignments of CFL. When the published vibrational assignment for pyridine was used in calculating thermodynamic properties, the results disagreed with the experimental values of $C_p°$ and $S°$ listed in Table I (the discrepancies were about 2 and 0.3%, respectively). Because the accuracy uncertainty of the observed values of $C_p°$ is 0.2%, a revision of the vibrational assignment for pyridine was required for calculating accurate thermodynamic properties. The revised assignment for pyridine and its deuterated species is given in Table II.

The vibrational assignment of CFL is based on good spectroscopic evidence. It was considered likely that the choice of only one fundamental frequency was seriously in error. To obtain agreement between calculated and observed values of both $C_p°$ and $S°$, it was apparent that a frequency near 700 cm.$^{-1}$ had to be eliminated and replaced by one near 1000 cm.$^{-1}$. Corresponding changes in the assigments for the deuteropyridines had to be made to retain consistency with the product rule for isotopic substitution.

There are only three observed frequencies near 700 cm.$^{-1}$ in the spectrum of pyridine: 675 (infrared, weak); 703 (infrared, very strong; Raman, very weak); 749 (infrared, strong; Raman, very weak) cm.$^{-1}$. These frequencies had been assigned by CFL to ν_4, ν_{11} and ν_{10b},[4] respectively. The assignment of CFL was retained for the infrared band at 675 cm.$^{-1}$, which cannot be assigned as a likely overtone or combination. The other pair of frequencies was replaced by a single fundamental frequency by interpreting the 703–749 cm.$^{-1}$ doublet as the result of Fermi resonance between an a_1 mode near 720 cm.$^{-1}$, taken to be ν_{6a}, and the overtone of ν_{16a}, 2 × 374 (a_2) = 748-(A_1). This reinterpretation necessitated revised assignments for b_2 modes ν_{10b} and ν_{11}. The frequency previously assigned to ν_{6a}, 605 cm.$^{-1}$, was reassigned to ν_{11}. The assignment of the 605 cm.$^{-1}$ frequency to a b_2 rather than an a_1 mode is consistent with the reported depolarization of the Raman line.[5] The frequency at 981 cm.$^{-1}$, previously assigned to the a_2 mode ν_{17a} in violation of the strict selection rules of C_{2v} symmetry, was chosen for the other b_2 mode. However, this frequency was assigned to ν_5 and CFL's choice for ν_5, 940 cm.$^{-1}$, was assigned instead to ν_{10b}. (The latter change was made to obtain better over-all consistency among the assignments for pyridine, benzene and their deuterated species.[3b,6]

Table II

Revised Vibrational Assignment for Pyridine and Some Deuteropyridines

Freq. No.	Species[a]	Frequency, cm.$^{-1}$ Pyridine	Pyridine-d_5	4D-Pyridine	3D-Pyridine	2D-Pyridine
1		992	962	989	980	989
2		3055[d]	2293[d]	3033	3038	3040
6a		720[b]	690[d]	720[b]	717	748
8a		1583	1530	1575	1570[c]	1576
9a	a_1	1218	887[d]	1212[d]	1195	1149
12		1030[d]	1006	1015	1033	1029
13		3055[d]	2270	2285	3053	3051
18a		1068	823	1068	1050	1059
19a		1483	1340	1476	1468	1461
20a		3035	2254	3019	3022	2258
3		1200	908	1212[d]	1217	1212
6b		653	625	635[c]	650[c]	640[c]
7b		3055[d]	2285	3069	2289	3068
8b		1571	1542	1559	1570[c]	1570
14	b_1	1377	1322	1347	1337	1357
15		1146	887[d]	1121	1108	1112
18b		1085	833	862	848	834
19b		1440	1301	1413	1416	1424
20b		3080	2293[d]	3069	3077	3075
10a		885	713	890[c]	823	814
16a	a_2	374	329	365[c]	350[c]	360[c]
17a		1030[d]	798	1015	965[d]	997
4	b_2	675	582	633[c]	632[c]	638
5		981	690[d]	968	965[d]	970
10b		940	762	834	902	901
11		605	530	597	599	600
16b		405	371	370	404	405

[a] The species designation is for C_{2v} symmetry, that of pyridine, pyridine-d_5 and 4D-pyridine. [b] Fermi resonance assumed between ν_{6a} and 2 × ν_{16a}. [c] Approximate values; see ref. 3b. [d] Frequencies assigned to more than one fundamental.

The result of the foregoing changes was to eliminate from the earlier assignment a frequency near 700 cm.$^{-1}$ and leave ν_{17a} available for assignment of a frequency near 1000 cm.$^{-1}$. The a_2 mode ν_{17a} may be unobserved, for it should appear with very low intensity in the Raman spectrum and is forbidden in the infrared. Although the weak Raman line at 1043 cm.$^{-1}$ could be due to ν_{17a}, it was interpreted as the sum-combination, 374 (a_2) + 675 (b_2) = 1049 (B_1). It was assumed that ν_{17a} is obscured in the Raman spectrum by the strong line of ν_{12} at 1030 cm.$^{-1}$, and that frequency was chosen for ν_{17a}. A value of 1030 cm.$^{-1}$ for ν_{17a} results in a slightly more satisfactory product-rule ratio, r_{obsd}, for the a_2 frequencies of pyridine and pyridine-d_5.

---

(3) (a) L. Corrsin, B. S. Fax and R. C. Lord, *J. Chem. Phys.*, **21**, 1170 (1953), and earlier references cited there; (b) F. A. Anderson, B. Bak, S. Brodersen and J. Rastrup-Andersen, *ibid.*, **23**, 1047 (1955); (c) unpublished data from Chemical Research Laboratory, Teddington, Middlesex, England.

(4) The designation of normal modes of vibration is that given in ref. 3a.

(5) K. W. F. Kohlrausch, "Ramanspektren," Akademische Verlagsgesellschaft, Becker and Erler, Leipzig, 1943, p. 353.

(6) (a) C. K. Ingold and co-workers, *J. Chem. Soc.* (*London*), 222 ff. (1946); (b) R. L. Mair and D. F. Hornig, *J. Chem. Phys.*, **17**, 1236 (1949).

Two additional minor changes have been made in the assignment for pyridine. Infrared bands at 1200 and 1085 cm.$^{-1}$ were observed recently by workers at the Chemical Research Laboratory[3c] and are assigned to ν_3 and ν_{18b}. These fundamentals were previously assigned (by CFL) the same values as ν_{9a} and ν_{18a}, 1218 and 1068 cm.$^{-1}$.

The revision of CFL's vibrational assignment for pyridine made necessary corresponding changes in the previous assignments for the deuterated pyridines.[3a,3b] The revised assignments for the deuterated species, given in Table II, were made concurrently with the revision of the assignment for pyridine.

The vibrational assignments in Table II are as consistent internally as those of refs. 3a and 3b. The comparisons of observed and calculated product rule ratios, r_{obsd} and r_{calcd}, in Table III show that good agreement was retained. Also, all observed frequencies in the spectra of these compounds that were not chosen as fundamentals can be assigned readily as allowed overtones or combinations. For the most part, the intercomparison of assignments for pyridine, benzene and their deuterated species is slightly improved, although it is apparent that some of the fundamental frequencies of pyridine and benzene differ more than in the earlier assignment.[3a] Actually, spectroscopic evidence alone is not sufficient to choose between the assignment in Table II and that of CFL. The fact, discussed later, that excellent agreement between calculated and observed values of $C_p°$ and $S°$ was obtained by use of the revised assignment ensures that the set of fundamentals chosen is essentially correct. Uncertainties that may remain in the assigment of observed frequencies to particular modes of vibration can be removed only by additional spectroscopic evidence.

TABLE III

PRODUCT-RULE RATIOS FOR PYRIDINE AND PYRIDINE-d_5

Symmetry class	$r_{\text{calcd.}}$ from ref. 3a	$r_{\text{obsd.}}$ Ref. 3a	This work
a_1	5.49	5.38	5.45
b_1	5.07	4.89	4.90
a_2	1.84	1.80	1.82
b_2	2.56	2.55	2.54

TABLE IV

THE MOLAL THERMODYNAMIC PROPERTIES OF PYRIDINE[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$Cp°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10}Kf$[b]
0	0	0	0	0	0	37.52	37.52	Infinite
273.16	−55.44	10.59	2.893	66.03	16.99	33.82	44.48	−35.59
298.16	−56.40	11.19	3.336	67.59	18.67	33.50	45.47	−33.33
300	−56.47	11.24	3.372	67.71	18.80	33.48	45.54	−33.18
400	−60.07	13.97	5.588	74.04	25.42	32.38	49.74	−27.18
500	−63.49	16.85	8.425	80.34	31.11	31.52	54.18	−23.68
600	−66.81	19.62	11.772	86.43	35.72	30.88	58.77	−21.41
700	−70.03	22.20	15.54	92.23	39.44	30.41	63.47	−19.82
800	−73.15	24.55	19.64	97.70	42.49	30.07	68.21	−18.63
900	−76.17	26.69	24.02	102.86	45.04	29.86	72.99	−17.72
1000	−79.08	28.63	28.63	107.71	47.17	29.76	77.79	−17.00
1100	−81.89	30.40	33.44	112.29	48.99	29.75	82.59	−16.41
1200	−84.62	32.02	38.42	116.64	50.54	29.82	87.37	−15.91
1300	−87.23	33.49	43.54	120.72	51.88	29.92	92.18	−15.50
1400	−89.77	34.85	48.79	124.62	53.04	30.07	96.96	−15.14
1500	−92.22	36.10	54.15	128.32	54.05	30.24	101.73	−14.82

[a] To form an internally consistent set of values and to retain the higher accuracy of increments with temperature of a given property, some of the values in this table are given to one more significant figure than is justified by their absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of pyridine by the reaction: $5C(graphite) + 5/2H_2(g) + 1/2N_2(g) \rightarrow C_5H_5N(g)$.

It should be noted that the net effect of these reassignments is merely the replacement of fundamentals at 703 and 749 cm.$^{-1}$ by fundamentals at 720 and 1030 cm.$^{-1}$—that is, the change that was found necessary to obtain agreement between calculated and experimental values of both $C_p°$ and $S°$.

NOTE ADDED IN PROOF. J. K. Wilmshurst and H. J. Bernstein of the Canadian National Research Council have recently made new spectroscopic studies of pyridine and some deuteropyridines. Dr. Bernstein courteously provided us with a copy of his manuscript, which is soon to be published. The data of Wilmshurst and Bernstein require further revision of the vibrational assignment for pyridine. In their forthcoming paper, Wilmshurst and Bernstein will present a new vibrational assignment that is consistent with the available spectroscopic and calorimetric data. Use of their assignment in calculating thermodynamic properties results in no significant changes in the calculated values listed in Tables I and III of this paper.

The Moments of Inertia and Anharmonicity Contributions.—The moments of inertia of the pyridine molecule have been determined in several recent microwave studies.[7-9] The difference between values of the product of principal moments of inertia calculated from the results of these studies is not significant, but the value actually used in calculation of thermodynamic properties, 5.691×10^{-113} g.^{3} cm.^{6}, was computed from the data of ref. 9. The symmetry number of over-all rotation is 2.

The contributions of anharmonicity to the thermodynamic functions were treated by the empirical

---

(7) K. E. McCulloh and G. F. Pollnow, *J. Chem. Phys.*, **22**, 681 (1954).

(8) B. B. DeMore, W. S. Wilcox and J. H. Goldstein, *ibid.*, **22**, 876 (1954).

(9) B. Bak, L. Hansen and J. Rastrup-Andersen, *ibid.*, **22**, 2013 (1954).

method described in an earlier paper from this Laboratory.[10] The parameters $Z = 0.340$ cal. deg.$^{-1}$ mole^{-1} and $\nu = 750$ cm.$^{-1}$ were selected to give agreement with the calorimetric values of $C_p°$. The contributions of anharmonicity to the thermodynamic properties are small at 400°K., 0.03 and 0.11 cal. deg.$^{-1}$ mole^{-1} in $S°$ and $C_p°$, but increase to 0.62 and 0.92 cal. deg.$^{-1}$ mole^{-1} in $S°$ and $C_p°$ at 1500°K.

The Chemical Thermodynamic Properties.—The vibrational assignment, product of principal moments of inertia and anharmonicity parameters given in preceding paragraphs were used in computing values of the following thermodynamic functions at selected temperatures between 0 and 1500°K.: $(F° - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$ and $C_p°$. The results are listed in columns 2–6 of Table IV.[11]

The calculated and observed values of $C_p°$ and $S°$ are compared in Table I. Agreement within 0.1% was obtained over the entire range of temperature of the experimental data. Because the observed values of $S°$ and $C_p°$ are entirely independent, the excellent agreement obtained for $S°$ is another confirmation of the third law of thermodynamics.

The Heat, Free Energy and Equilibrium Constant of Formation.—The calculated values of the thermodynamic functions of pyridine, the experimental value of $\Delta Hf°_{298.16}$ (Table I) and values of the thermodynamic functions of C(graphite),[12] H_2(g)[12] and N_2(g)[12] were used in computing values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10}Kf$ at selected temperatures between 0 and 1500°K. These results are listed in columns 7–9 of Table IV.

Experimental

Physical Constants.—The 1951 International Atomic Weights[13] and the 1951 values of fundamental physical constants[14] were used. The results are based on a molecular weight of 79.098 for pyridine and the following 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[15] between 90 and 500°K. and the provisional scale[16] of the National Bureau of Standards between 11 and 90°K. Measurements of mass, energy and resistance were made in terms of standard devices calibrated at the National Bureau of Standards.

The Material.—The sample of pyridine used in the low temperature thermal studies, vapor pressure measurements and heat of combustion experiments was part of the Standard Sample of Nitrogen Compound, API-USBM-52-1, prepared and purified by American Petroleum Institute Research Project 52b at the Laramie, Wyoming, Station of the Bureau of Mines. In a calorimetric study of the melting point to be discussed subsequently, the purity of this sample was found to be 99.92 mole %. A second sample of 99.8 mole % purity was used in studies of the heat of vaporization and vapor heat capacity.

The samples of pyridine were received in sealed ampoules and were dried in the liquid phase with CaH_2. Transfers of sample were made by distillation under vacuum.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal studies were made in an adiabatic calorimeter system similar to that described in previous publications.[17] The sample, 0.66591 mole, was sealed in a platinum calorimeter. About 27 mm. helium pressure, at room temperature, was left in the calorimeter to promote thermal equilibration at low temperatures.

The observed values of heat capacity at saturation pressure, C_{satd}, are recorded in Table V. No adjustment for the effect of premelting has been applied to these data. The temperature increments used in the measurements were small enough that corrections for non-linear variation of C_{satd} with temperature were unnecessary. Generally, the precision of the results is within ±0.1%; and it is estimated that above 30°K., the accuracy uncertainty is not greater than 0.2%.

The heat capacity curve, C_{satd} *vs.* T, for solid pyridine is smooth and regular from 13 to 200°K. A very small "bump" was observed in the curve between 200 and 215°K. (about 20° below the melting point). When the sample was cooled rapidly from a point above 215°K., the "bump" was not detected. It is believed that this anomaly was due to melting of the eutectic between pyridine and an impurity, and that rapid cooling caused the eutectic mixture to supercool. The excess energy associated with the "bump" was only 1.3 cal. mole^{-1}. This amount of energy corresponds to about 0.06 mole % impurity if the heat of fusion of the eutectic mixture is assumed to be about 2000 cal. mole^{-1}. In Table V, the values indicated by asterisks define the anomalous "bump." These points were disregarded in drawing the smoothed heat-capacity curve of pyridine.

An empirical equation that represents the observed heat capacity data for liquid pyridine between 240 and 347°K. with an average deviation of 0.01% is

$$C_{satd}(\text{liq.}) = 33.633 - 9.1446 \times 10^{-2}T + 3.8478 \times 10^{-4}T^2 - 3.3430 \times 10^{-7}T^3, \text{ cal. deg.}^{-1}\text{ mole}^{-1} \quad (1)$$

The Heat of Fusion.—Two determinations were made of the heat of fusion. Measurements were made of the enthalpy change over a finite temperature interval that included the melting point. Subtraction of the energy absorbed non-isothermally by the crystals and liquid gave the latent heat of fusion, 1978.6 ± 0.6 cal. mole^{-1}; the indicated uncertainty is the deviation of the two results from the mean. Corrections for premelting were applied in calculating the heat of fusion. The energy associated with the anomaly at about 210°K. is included in the value given.

The Triple Point Temperature, Cryoscopic Constants and Purity of Sample.—For determination of the triple point temperature and purity of sample, a study of the melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, was made by the procedure outlined in an earlier publication.[18] The results are summarized in Table VI. Values of T_{obsd} were plotted as a function of $1/F$. The triple point temperature, $T_{T.P.} = 231.49 \pm 0.05$°K., was obtained by linear extrapolation to zero value of $1/F$. If the impurities present form ideal solutions in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N^*_2, and melting point depression, $\Delta T = T_{T.P.} - T_{obsd}$, is[19]

$$-\ln(1 - N_2) = A\Delta T(1 + B\Delta T + \ldots..) \quad (2)$$

where $N_2 = N^*_2/F$. The cryoscopic constants, $A = \Delta H_{fusion}/RT^2_{T.P.} = 0.01358$ deg.$^{-1}$ and $B = 1/T_{T.P.} -$

---

[10] J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, THIS JOURNAL, **76**, 2661 (1954).

[11] The harmonic oscillator contributions to the thermodynamic functions were taken from H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," NAVEXOS P-646, Office of Naval Research, Department of the Navy, Washington, D. C., July, 1949. Anharmonicity contributions were computed from the tables of R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

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

[13] Edward Wichers, THIS JOURNAL, **74**, 2447 (1952).

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

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

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

[17] R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943); H. M. Huffman, S. S. Todd and G. D. Oliver, *ibid.*, **71**, 584 (1949); D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver, and H. M. Huffman, *ibid.*, **74**, 883 (1952); H. M. Huffman, *Chem. Revs.*, **40**, 1 (1947).

[18] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

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

$\Delta C_{\text{fusion}}/2\Delta H_{\text{fusion}} = 0.00255$ deg.$^{-1}$ were evaluated from the values for $T_{\text{T.P.}}$ and ΔH_{fusion} and from $\Delta C_{\text{fusion}} = 6.99$ cal. deg.$^{-1}$ mole^{-1} (Table VII). Application of eq. 2 in its simplified form (for $N^*_2 << 1$), $N^*_2 = AF\Delta T$, yielded a value of 0.08 mole % for the indicated concentration of impurity in the Standard Sample of pyridine.

TABLE V

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

T, °K.[a]	ΔT[b]	C_{satd}[c]	T, °K.[a]	ΔT[b]	C_{satd}[c]
	Crystals		169.31	6.005	16.396
13.08	1.311	1.063	172.38	7.155	16.606
13.61	1.270	1.204	172.49	6.402	16.624
14.37	1.283	1.359	173.90	5.889	16.728
14.97	1.381	1.454	174.19	5.895	16.752
15.84	1.675	1.646	178.13	11.633	17.049
16.25	1.193	1.722	179.26	7.146	17.107
17.46	1.586	1.999	179.44	6.969	17.150
17.67	1.662	2.041	179.72	5.767	17.154
19.23	1.948	2.406	180.58	6.905	17.250
19.43	1.901	2.448	186.32	6.792	17.707
21.26	2.126	2.888	187.39	6.728	17.807
21.42	2.089	2.930	189.24	6.714	17.945
23.42	2.211	3.410	193.02	6.622	18.276
23.55	2.183	3.446	193.43	6.630	18.327
25.78	2.508	3.975	193.48	6.527	18.310
25.88	2.489	3.998	194.02	6.561	18.369
28.53	2.820	4.610	195.86	6.536	18.558
28.61	3.166	4.625	198.37	3.269	18.756
31.74	3.595	5.306	199.54	6.452	18.881
35.36	3.663	6.049	199.97	6.456	18.958
39.20	4.025	6.738	200.49	6.388	19.006
43.54	4.652	7.429	200.75	3.276	18.995
48.14	4.549	8.060	201.61	3.223	19.081
53.18	5.545	8.669	204.00	3.234	19.294
54.23	3.647	8.784	204.80	3.183	19.368
58.52	5.128	9.228	205.88	6.256	19.636*
58.63	5.148	9.243	206.33	6.286	19.597
64.01	5.607	9.739	206.84	4.180	19.549
70.06	6.509	10.203	207.20	3.194	19.609
76.40	6.173	10.646	207.28	7.210	19.821*
82.91	6.857	11.093	207.93	3.118	19.883*
85.74	4.830	11.279	210.75	3.938	19.938
89.62	6.568	11.515	211.98	6.121	20.151
90.50	4.681	11.568	212.16	5.388	20.183
95.57	5.465	11.839	212.53	6.117	20.299*
101.39	6.192	12.156	212.55	7.108	20.311*
107.41	5.853	12.499	213.43	6.099	20.389*
111.70	4.261	12.735	215.70	6.014	20.605
113.19	5.701	12.823	217.99	5.939	20.943
117.78	7.905	13.086	218.70	4.954	21.076
119.37	6.600	13.175	219.42	5.885	21.320
125.29	7.112	13.527	223.53	4.747	22.278
125.93	6.476	13.560	223.74	5.613	22.545[d]
132.30	6.910	13.954			
132.32	6.314	13.940		Liquid	
138.56	6.160	14.329			
138.91	6.319	14.346	239.70	4.616	29.213
144.89	6.516	14.727	245.82	7.638	29.431
145.61	7.076	14.769	254.41	9.564	29.765
151.57	6.844	15.161	263.90	9.445	30.159
152.58	6.888	15.227	273.75	10.256	30.575
158.32	6.672	15.613	283.92	10.116	31.040
159.38	6.716	15.693	293.96	9.974	31.521
161.87	6.152	15.861	303.85	9.841	31.997
163.24	6.142	15.957	307.16	8.668	32.159
165.75	6.112	16.106	316.61	10.254	32.641
166.02	6.555	16.158	326.79	10.102	33.177
167.60	7.294	16.265	336.81	9.954	33.712
167.95	6.018	16.292	346.69	9.809	34.246

[a] T is the mean temperature of each heat capacity measurement. [b] ΔT is the temperature increment used in each heat capacity measurement. [c] C_{satd} is the heat capacity of the condensed phase under its own vapor pressure. [d] The data below the melting point have *not* been corrected for the effect of premelting caused by impurities.

TABLE VI

PYRIDINE: MELTING POINT SUMMARY

Melted, %	$1/F$	T, °K. Obsd.	Graph.[b]
11.56	8.648	231.1659	231.13
25.66	3.897	231.3397	231.330
49.99	2.000	231.4076	231.4086
70.08[a]	1.427[a]	231.4310[a]	231.4310
90.18[a]	1.109[a]	231.4440[a]	231.4440
100.00	1.000		231.4485
Pure	0.0		231.489[c]

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple-point temperature, $T_{\text{T.P.}}$ [b] Temperatures read from the straight line of footnote *a;* deviations from T_{obsd} indicate slight departure from assumed conditions. [c] Triple-point temperature.

Biddescombe, Coulson, Handley and Herington[2c] report a value for $t_f°$, the freezing point in air at 1 atm., that is 0.12° higher than the triple-point temperature found in this investigation. However, recent unpublished studies by these authors[20] on a purer sample of pyridine gave a value of $t_f°$ that is 0.10° lower than their reported value, in better consistency with the results of this work.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the free energy function, heat content function, heat content, entropy and heat capacity at selected temperatures between 10 and 350°K. were computed from the low-temperature calorimetric data for pyridine. The values at 10°K. were calculated from a Debye function for 4 degrees of freedom with $\theta = 107.40°$; these parameters were evaluated from the heat capacity data between 13 and 22°K. The thermodynamic properties above 10°K. were computed from the values of the heat of fusion and triple-point temperature, and from increments computed by numerical integration of values of C_{satd} read from a large scale plot of the data in Table V. The results are given in Table VII. Corrections for the effect of premelting have been applied to the "smoothed" data recorded in Table VII.

The results in Table VII agree with those of Parks, Todd and Moore[2d] within the 1% accuracy uncertainty of the earlier data. The results of Pearce and Bakke[2e] seem to be in error.

The Vapor Pressure.—The vapor pressure of pyridine at temperatures between 67 and 153° was measured with an improved version of the twin ebulliometer system described in an earlier publication.[21] Observations were made of the boiling and condensation temperatures of pyridine and water as the two compounds boiled simultaneously at a common pressure. The pressures corresponding to the observed boiling points of the water were obtained from the data of Osborne, Stimson and Ginnings.[22] The results are presented in Table VIII. The difference between the boiling and condensation temperatures of the sample was observed to be 0.004° or less; this observation indicates that the material was essentially free of impurities of different volatility. The constants in an Antoine equation

$$\log_{10} p \text{ (mm.)} = 7.04162 - 1374.103/(t + 215.014) \quad (3a)$$

were obtained from the data in Table VIII by a least squares treatment.[23] Also, to provide a more accurate means of

---

(20) Communicated by Dr. J. D. Cox, Chemical Research Laboratory, Teddington, Middlesex, England (1955–1956).

(21) Guy Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 797 (1949).

(22) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

(23) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

TABLE VII

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

T, °K.	$-(F_{\text{satd}} - H°_0)/T$, cal. deg.$^{-1}$	$(H_{\text{satd}} - H°_0)/T$, cal. deg.$^{-1}$	$H_{\text{satd}} - H°_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
			Crystals		
10	0.042	0.124	1.243	0.166	0.491
15	.137	.393	5.895	.530	1.439
20	.303	.798	15.961	1.101	2.588
25	.531	1.276	31.89	1.807	3.789
30	.809	1.792	53.75	2.601	4.937
35	1.125	2.316	81.07	3.441	5.977
40	1.468	2.831	113.24	4.299	6.874
45	1.830	3.324	149.58	5.154	7.638
50	2.205	3.789	189.45	5.994	8.294
60	2.972	4.634	278.01	7.606	9.377
70	3.743	5.373	376.1	9.116	10.199
80	4.504	6.020	481.5	10.524	10.895
90	5.247	6.598	593.8	11.845	11.538
100	5.970	7.119	711.9	13.089	12.080
110	6.670	7.596	835.5	14.266	12.640
120	7.350	8.040	964.7	15.390	13.212
130	8.011	8.460	1099.8	16.471	13.802
140	8.652	8.864	1240.9	17.516	14.420
150	9.278	9.255	1388.2	18.533	15.059
160	9.887	9.639	1542.1	19.526	15.728
170	10.483	10.018	1703.0	20.501	16.440
180	11.066	10.395	1871.1	21.461	17.193
190	11.639	10.774	2047.1	22.413	18.022
200	12.201	11.158	2231.5	23.359	18.876
210	12.754	11.547	2424.7	24.301	19.773
220	13.300	11.943	2627.3	25.243	20.755
230	13.841	12.348	2840.1	26.189	21.797
231.49	13.920	12.410	2872.7	26.330	21.958
			Liquid		
231.49	13.920	20.957	4851	34.87	28.950
240	14.68	21.245	5098	35.92	29.228
250	15.55	21.571	5392	37.12	29.588
260	16.40	21.887	5690	38.29	29.995
270	17.24	22.195	5992	39.43	30.41
273.16	17.49	22.291	6089	39.79	30.54
280	18.05	22.497	6299	40.55	30.85
290	18.84	22.793	6610	41.64	31.33
298.16	19.48	23.032	6867	42.52	31.72
300	19.62	23.086	6925	42.71	31.81
310	20.38	23.375	7246	43.76	32.30
320	21.13	23.662	7571	44.79	32.81
330	21.86	23.948	7902	45.81	33.34
340	22.58	24.232	8238	46.81	33.88
350	23.29	24.516	8580	47.80	34.43

[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.

extrapolation to temperatures beyond the range of the experiments, the following Cox equation[24] was derived

$$\log_{10}P\ (\text{atm.}) = A(1 - 388.394/T) \qquad (3b)$$

$$\log_{10}A = 0.858631 - 6.7114 \times 10^{-4}T + 6.0722 \times 10^{-7}T^2$$

In these equations, t is in °C. and T is in °K. Comparisons of the observed and calculated vapor pressures for both the Antoine and Cox equations are given in Table VIII. The normal boiling point of pyridine, calculated from either equation, is 115.23° (388.39°K.).

TABLE VIII

THE VAPOR PRESSURE OF PYRIDINE

Boiling point, °C. Water	Boiling point, °C. Pyridine	p(obsd.),[a] mm.	p(obsd.) − p(calcd.) Eq. 3a	p(obsd.) − p(calcd.) Eq. 3b
60.000	67.299	149.41	+0.02	+0.02
65	73.154	187.57	− .02	− .01
70	79.045	233.72	− .02	− .01
75	84.974	289.13	.00	+ .01
80	90.946	355.22	.00	.00
85	96.958	433.56	.00	− .01
90	103.008	525.86	+ .03	+ .01
95	109.101	633.99	+ .02	− .01
100	115.234	760.00	+ .02	.00
105	121.408	906.06	+ .01	.00
110	127.622	1074.6	.00	+ .1
115	133.878	1268.0	− .1	.00
120	140.174	1489.1	− .1	.00
125	146.509	1740.8	.0	.00
130	152.886	2026.0	.0	− .1

[a] From vapor pressure data for water given in ref. 22.

The results in Table VIII are in good agreement with those of Herington and Martin.[20] In the range of temperature of the experimental data, values of the boiling point differ by 0.02° or less.

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of pyridine were measured in the flow calorimeter system described in previous publications.[25] The modified apparatus and procedure of ref. 25b were used. The results of measurements of the heat of vaporization at boiling points corresponding to 1/4, 1/2 and 1 atm. pressure are summarized in Table IX. The estimated accuracy uncertainty of the values of the heat of vaporization reported in Table IX is ±0.1%. The following empirical equation was derived for interpolation in the temperature range of the measurements (346 to 388°K.)

$$\Delta Hv = 13077 - 10.201T - 4.7941 \times 10^{-3}T^2,\ \text{cal. mole}^{-1} \qquad (4)$$

The standard heat of vaporization at 298.16°K. was calculated by three methods: (1) from eq. 3b, 4 and 6 (given in the following section) and the relationship, $\Delta Hv° = \Delta Hv - BRT/V + (\mathrm{d}B/\mathrm{d}T)RT^2/V$; (2) from the Clapeyron equation with the aid of eq. 3b and 6; and (3) from a thermodynamic network that used the experimental value of S_{satd} (Table VII), the calculated value of $S°$ (Table IV) and eq. 3b. The results are 9612, 9599 and 9606 cal. mole^{-1}, respectively, and the average value, 9606 ± 7 cal. mole^{-1}, was selected as $\Delta Hv°_{298.16}$.

TABLE IX

THE MOLAL HEAT OF VAPORIZATION AND SECOND VIRIAL COEFFICIENT OF PYRIDINE

T, °K.	P, atm.	ΔHv(obsd.), cal.	B, cc. Obsd.	B, cc. Calcd.[a]
346.65	0.250	8965 ± 1[b]	−1292	−1326
366.11	0.500	8700 ± 2	−1157	−1147
388.40	1.000	8392 ± 4	− 990	− 990

[a] Calculated by use of eq. 6. [b] Maximum deviation from the mean of 3 to 5 determinations.

The Vapor Heat Capacity and the Effect of Gas Imperfection.—The vapor heat capacity of pyridine was measured at two or more pressures at each of five temperatures between 374 and 500°K. The results are summarized in Table X.

To correlate the thermal data, an equation of state for pyridine was obtained from data for the vapor pressure, heat of vaporization and vapor heat capacity. "Observed" values of the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$, were computed by use of the exact Clapeyron equation. Values of $\mathrm{d}^2B/\mathrm{d}T^2$ were determined from the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -(1/T)(\partial C_p/\partial P)_T$, in terms of which the variation

---

[24] E. R. Cox, *Ind. Eng. Chem.*, **28**, 613 (1936).

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

TABLE X

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

T, °K.	374.20	397.20	420.20	450.20	500.20
C_p(1.00 atm.)		25.877	27.110	28.753	31.336
C_p(0.50 atm.)	24.199	25.540			
C_p(0.25 atm.)	23.991	25.390	26.761	28.512	31.170
$C_p°$(obsd.)	23.79	25.23	26.65	28.43	31.12
$-T(d^2B/dT^2)$,[a] obsd.	0.79	0.60	0.44	0.30	0.21
$-T(d^2B/dT^2)$,[a] calcd.[b]	.80	.59	.45	.33	.20

[a] $-T(d^2B/dT^2) = \lim_{p\to 0}(\partial C_p/\partial P)_T$; units are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$. [b] Calculated by use of eqs. 5 and 6.

of vapor heat capacity with the pressure is represented, with slight approximations,[25b] by

$$C_p = C_p° - T\left(\frac{d^2B}{dT^2}\right)P + 2\left(\frac{B}{R}\right)\left(\frac{d^2B}{dT^2}\right)\left(1 - \frac{3BP}{RT}\right)P^2 \quad (5)$$

The value of the last term in eq. 5 (0.04 cal. deg.$^{-1}$ mole^{-1} or less) was estimated for each experimental point and subtracted from C_p(obsd.). The adjusted values of C_p at each temperature were plotted against P. The intercept and slope of the resulting straight lines were taken as $C_p°$(obsd.) and $\lim_{p\to 0}(\partial C_p/\partial P)_T = -T(d^2B/dT^2)$(obsd.), respectively. Constants in the following empirical equation for B were evaluated from the values of B(obsd.) and (d^2B/dT^2)(obsd.).

$$B = -15 - 84.5 \exp(950/T), \text{ cc. mole}^{-1} \text{ (346–500°K.)} \quad (6)$$

Iteration using eq. 6 with eq. 5 and the experimental data produced no change in the correlation. The values of $C_p°$(obsd.) so determined are given in Table X. Observed values of B and $T(d^2B/dT^2)$ are compared in Tables IX and X with values calculated by using eq. 6.

The accuracy uncertainty of the values of $C_p°$(obsd.) listed in Table X should not exceed 0.2%. The following empirical equation represents these data within ±0.07% from 374 to 500°K.

$$C_p° = -8.262 + 10.608 \times 10^{-2}T - 5.4662 \times 10^{-5}T^2, \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (7)$$

Gas density measurements on pyridine were recently made at the Chemical Research Laboratories, Teddington, England.[20] Values of B calculated from an equation representing these data are −1258, −1126 and −993 cc. mole^{-1} at 346.65, 366.11 and 388.40°K. (the temperatures at which data were obtained in this Laboratory). These values of B are in excellent agreement with those listed in Table IX.

The Entropy in the Ideal Gaseous State.—The experimental and derived data given in the foregoing sections were used in computing "observed" values of the entropy in the ideal gaseous state at one atmosphere pressure. These calculations are summarized in Table XI.

TABLE XI

THE MOLAL ENTROPY OF PYRIDINE IN CAL. DEG.$^{-1}$

0–10°K.	Debye extrapolation	0.166
10–231.49°	Crystals, $\int C_{satd}\, d \ln T$	26.164
231.49°	Fusion, 1978.6/231.49	8.547
231.49–298.16°	Liquid, $\int C_{satd}\, d \ln T$	7.639
S_{satd}(liq.), 298.16°K. [±0.09][a]		42.52

T, °K.	346.65	366.11	388.40
S_{satd}(liq.)	47.48[b]	49.38[c]	51.50[c]
$\Delta Hv/T$[d]	25.86	23.76	21.61
S(ideal) − S(real)[e]	0.06	0.10	0.16
$R \ln P$[f]	−2.75	−1.38	0.00
$S°$(obsd).[±0.15][a]	70.65	71.86	73.27

[a] Estimated accuracy uncertainty. [b] Interpolated in Table VII. [c] Extrapolation by use of eq. 1. [d] Entropy of vaporization; from data in Table IX. [e] Entropy of gas imperfection; calculated by use of eq. 6. [f] Entropy of compression; calculated with the aid of eq. 3b.

The Heat of Formation and Related Properties.—The heat of combustion of pyridine was determined by precise combustion calorimetric experiments, details of which will appear as part of another publication.[26] From this study, the heat of formation of liquid pyridine, $\Delta Hf°_{298.16}$ (liq.), was found to be 23.89 kcal. mole^{-1}. Addition of the standard heat of vaporization, 9.606 kcal. mole^{-1}, given in a preceding section, yields the heat of formation of pyridine in the ideal gaseous state, 33.50 kcal. mole^{-1}, as presented in Table I.

The value of S_{satd} (liq.) from Table VII and values of the entropy of C(graphite),[12] H_2(g)[12] and N_2(g)[12] were used in computing values of the entropy, free energy and logarithm of the equilibrium constant of formation of liquid pyridine according to the reaction

$$5C(\text{graphite}) + 5/2H_2(g) + 1/2N_2(g) \longrightarrow C_5H_5N(l)$$

$\Delta Hf°_{298.16}$ = 23.89 kcal. mole^{-1}; $\Delta Sf°_{298.16}$ = −65.20 cal. deg.$^{-1}$ mole^{-*}; $\Delta Ff°_{298.16}$ = 43.33 kcal. mole^{-1}; $\log_{10}Kf$ = −31.76

NOTE ADDED IN PROOF.—Dr. Kun Li of Jones and Laughlin Steel Corporation, Pittsburgh, Pa., recently has published a paper [*J. Phys. Chem.*, 61, 782 (1957)] in which the earlier thermodynamic data for pyridine are correlated and extended. With the exception of the heat of formation and vapor pressure data (refs. 2b and 2c of this paper), the accuracy of the experimental data used by Li is significantly lower than that of the data given in this paper. Those thermodynamic properties derived from the less accurate experimental data are also subject to greater uncertainty than the corresponding values listed in this paper.

BARTLESVILLE, OKLAHOMA

---

(26) W. N. Hubbard, F. R. Frow and Guy Waddington, to be published.