Vapor Pressure Relations of 13 Nitrogen Compounds Related to Petroleum

ANN G. OSBORN and DONALD R. DOUSLIN
Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla. 74003

Compilations of vapor pressures measured by static and ebulliometric methods, covering four orders of magnitude in pressure, are given for key members of classes of pyrroles, pyridines, amines, piperidines, and pyrrolidine which were selected in a related project for a comprehensive study of their thermodynamic properties. Constants of the Antoine and Cox vapor pressure equations are provided to aid in interpolating or extrapolating the experimental results.

THERMOCHEMICAL studies of organic nitrogen compounds and hydrocarbons in or related to petroleum are in progress at the Bureau of Mines Bartlesville Petroleum Research Center. The purpose of this paper is to summarize the vapor pressure–temperature relations of 13 of the nitrogen compounds selected from the program. Previously, work on the vapor pressure relations of 36 key sulfur compounds was reported by Osborn and Douslin (*10*) from thermochemical studies conducted at the Bureau of Mines under API Research Project 48.

Vapor pressure results on pyrrolidine (*7*), pyridine (*8*), pyrrole (*14*), 2-methylpyridine (*16*), and 3-methylpyridine (*15*) have been reported; however, derived values of the constants in the correlating equations appear here recalculated in terms of the presently defined International Temperature Scale (*17*). Consequently, small differences from the constants published originally will appear.

MATERIALS

Sample materials were from research grade standard sample stocks maintained at the API Standard Sample Repository (Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.) and were prepared and purified by the Bureau of Mines Laramie Petroleum Research Center (Laramie, Wyo.) as part of API Research Project 52. Purities of the compounds (Table I) were determined from freezing temperature *vs.* fraction melted data obtained during low-temperature calorimetric measurements conducted by the Thermodynamics Group of the Bureau of Mines Bartlesville Petroleum Research Center. Additional checks on the purity of these materials were made during the ebulliometric vapor pressure measurements by simultaneous observation of the ebullition and condensation temperatures. Differences in these temperatures (column 2, Table I) confirm the calorimetric purities and indicate that the samples in the ebulliometer were represented faithfully by the purities as given. In general, the small differential temperatures indicate that the impurities had negligible effect on the measured temperatures of the boiling materials. In the pyrrolidine and 2-methylpyridine samples, which showed differential temperatures of 0.007° and 0.008°, respectively, the impurities might have contributed a small effect equal in magnitude to the precision of the thermometry itself.

EXPERIMENTAL METHODS

In the pressure range from 70 to 2026 mm. of Hg, a comparative ebulliometric method discussed by Waddington *et al.* (*18*), and more recently by Osborn and Douslin (*10*), was used on all substances. Briefly, the ebulliometric method consisted of comparing the boiling temperatures of the nitrogen compound with standard water or standard benzene under the same pressure of a helium gas blanket. Temperatures were measured with a precision of 0.001° on the International Temperature Scale [T °K. = t °C. (Int., 1948) + 273.15] (*17*), by using a 25-ohm platinum resistance thermometer that had been calibrated by the National Bureau of Standards and checked at the triple-point temperature of a certified benzoic acid cell. From the boiling temperature of the standard substance, the pres-

Table I. Constants of the Antoine and Cox Vapor Pressure Equations

Compound	Δt,[a] °C.	Purity, Mole %	Constants of Antoine Equation			Standard Deviation, Mm. Hg	Constants of Cox Equation				Standard Deviation, Mm. Hg
			A	B	C		a	$b \times 10^{-4}$	$c \times 10^{-7}$	Φ	
Piperidine	0.003	99.94	6.85699	1239.577	205.528	0.07	0.900350	−8.84317	8.32088	379.369	0.02
2-Methylpiperidine	0.004	99.87	6.81646	1273.280	205.242	0.09	0.895997	−8.82746	8.29686	391.436	0.11
Pyrrolidine	0.007	99.85	6.92527	1180.409	205.299	0.04	0.916424	−9.31541	−8.98787	359.708	0.04
Pyridine	0.004	99.92	7.04144	1373.990	215.001	0.05	0.856586	−6.60597	5.93625	388.384	0.03
2-Methylpyridine	0.008	99.90	7.03192	1415.424	211.589	0.10	0.866637	−6.80114	6.00534	402.536	0.06
3-Methylpyridine	0.001	99.88	7.05389	1484.307	211.544	0.10	0.854256	−6.02835	5.00169	417.287	0.01
4-Methylpyridine	0.002	99.97	7.04490	1482.840	210.743	0.09	0.857781	−6.17282	5.14739	418.504	0.06
Pyrrole	0.002	99.994	7.30275	1506.877	210.995	0.26	0.872196	−5.54923	4.30369	402.915	0.06
1-Methylpyrrole	0.001	99.998	7.08790	1370.499	213.009	0.08	0.872518	−6.92885	6.20419	385.893	0.05
2,5-Dimethylpyrrole	0.003	99.90	7.21263	1516.019	182.470	0.27	0.964614	−7.64658	5.61755	440.639	0.04
1-Propylamine	0.001	99.97	6.92646	1044.028	210.833	0.03	0.922208	−10.51259	11.25530	320.379	0.03
2-Propylamine	0.001	99.993	6.89017	985.650	214.071[b]	0.06	0.921664	−11.29607	12.83991	304.916	0.03
2-Methyl-2-propylamine	0.001	99.993	6.78204	992.719	210.423	0.16	0.932434	−12.07020	13.63914	317.190	0.07

[a] Ebullition minus condensation temperature. [b] Antoine equation fitted to the ebulliometric results only.

sure in the ebulliometers and the manifold connecting the ebulliometers was determined by reference to the International Steam Tables (*9, 11*) for the vapor pressure of water and to the API Research Project 44 Tables (*13*) for the vapor pressure of benzene. A note concerning the congruity of the two reference scales is given (*10*). Some of the nitrogen compounds react readily with oxygen or carbon dioxide, and in order not to introduce an impurity from this source, the helium was passed over activated charcoal at liquid nitrogen temperature before entering the ebulliometers.

For the low-pressure, static measurements below room temperature, an inclined-piston apparatus was used; it has been described previously by Douslin and McCullough (*3*) and Douslin and Osborn (*4*). Briefly, the method consists of balancing the known weight, W, of a free piston declined from the horizontal by a measured angle, θ, against the pressure exerted by the vapor of the sample that was kept in a thermostated bath. From the measured area and weight of the piston, the angle of declination, and the acceleration of gravity, the vapor pressure was calculated directly as a primary quantity

$$p = (g/g_{\mathrm{std}})\ (W \sin \theta)/A$$

Corrections were applied, when significant, for the vapor head between piston face and the surface of the liquid.

RESULTS

Observed values of the vapor pressure are given in Table II. Table I gives derived values of the constants A, B, and C for the Antoine (*1*) equation

$$\log p = A - B/(t + C) \qquad (1)$$

constants Φ, a, b, and c for the Cox (*2*) equation,

$$\log (p/760) = A(1 - \Phi/T)$$

where

$$\log A = a + bT + cT^2$$

and the standard deviations were based on unit weight for each point. Constants in the Antoine equation were obtained by a least-mean-square method described by Willingham *et al.* (*19*). This method minimizes the sum of the square deviations of the function $t \log p - (AC - B) - At + C \log p$ and has the effect of introducing an additional variable weighting factor beyond the assigned

Table II. Experimental Vapor Pressure Results at the Indicated Temperatures (° C.)

Pressure, Mm. of Hg	Piperidine	2-Methyl-piperidine	Pyrrolidine
71.87	42.361	51.480	...
81.64	45.141	54.374	...
92.52	47.924	57.280	...
104.63	50.725	60.197	...
118.06	53.529	63.132	...
132.95	56.355	66.078	...
149.41	59.198	69.048	43.158
187.57	64.904	75.011	48.439
233.72	70.655	81.035	53.760
289.13	76.459	87.103	59.122
355.22	82.311	93.229	64.523
433.56	88.209	99.412	69.969
525.86	94.164	105.650	75.456
633.99	100.167	111.941	80.987
760.00	106.219	118.286	86.558
906.06	112.324	124.689	92.173
1074.6	118.481	131.146	97.833
1268.0	124.687	137.655	103.537
1489.1	130.946	144.222	109.280
1740.8	137.254	150.843	115.072
2026.0	143.613	157.529	120.905

	Pyridine	2-Methyl-pyridine	3-Methyl-pyridine	4-Methyl-pyridine
71.87	...	...	74.036	75.052
81.64	...	...	77.115	78.135
92.52	...	...	80.202	81.229
104.63	...	...	83.303	84.333
118.06	...	...	86.403	87.448
132.95	...	...	89.524	90.576
149.41	67.299	79.794	92.658	93.719
187.57	73.154	85.853	98.946	100.022
233.72	79.045	91.942	105.270	106.371
289.13	84.974	98.074	111.640	112.754
355.22	90.946	104.252	118.052	119.184
433.56	96.958	110.472	124.508	125.659
525.86	103.008	116.736	131.008	132.178
633.99	109.101	123.038	137.551	138.747
760.00	115.234	129.386	144.137	145.354
906.06	121.408	135.773	150.767	152.007
1074.6	127.622	142.207	157.441	158.701
1268.0	133.878	148.683	164.156	165.445
1489.1	140.174	155.201	170.918	172.223
1740.8	146.509	161.761	177.721	179.060
2026.0	152.886	168.356	184.568	185.925

Pressure, Mm. of Hg	Pyrrole	1-Methyl-pyrrole	2,5-Dimethyl pyrrole
71.87	65.671	48.962	100.560
81.64	68.522	51.766	103.523
92.52	71.374	54.577	106.491
104.63	74.233	57.400	109.464
118.06	77.098	60.228	112.450
132.95	79.970	63.067	115.443
149.41	82.847	65.926	118.448
187.57	88.622	71.649	124.468
233.72	94.422	77.400	130.516
289.13	100.244	83.202	136.598
355.22	106.096	89.033	142.707
433.56	111.972	94.908	148.853
525.86	117.875	100.815	155.030
633.99	123.806	106.761	161.241
760.00	129.765	112.743	167.489
906.06	135.753	118.767	173.768
1074.6	141.768	124.827	180.084
1268.0	147.812	130.925	186.435
1489.1	153.884	137.060	192.820
1740.8	159.984	143.230	199.239
2026.0	166.109	149.440	...

	1-Propyl-amine	2-Propyl-amine	2-Methyl-2-propylamine
3.304[a]	...	−60.069	...
5.000[a]	...	−55.442	...
7.509[a]	...	−50.627	...
11.499[a]	...	−45.301	...
16.636[a]	...	−40.429	...
23.871[a]	...	−35.417	...
33.323[a]	...	−30.542	...
233.72	...	+3.922	...
289.13	22.973	8.471	19.325
355.22	27.750	13.055	24.177
433.56	32.564	17.677	29.075
525.86	37.414	22.336	34.016
633.99	42.304	27.032	39.006
760.00	47.229	31.766	44.040
906.06	52.193	36.539	49.120
1074.6	57.195	41.349	54.246
1268.0	62.235	46.199	59.417
1489.1	67.314	51.087	64.642
1740.8	72.430	56.014	69.908
2026.0	77.587	60.978	75.212

[a] Inclined-piston data.

weight of unity for each experimental point. This procedure did not necessarily give a set of constants which minimized the standard deviation of pressures calculated with unit weighting factors; however, the difference is a relatively minor one. Constants in the Cox equation were obtained by a least-mean-square criterion involving the use of orthogonal polynomials. The Cox equation (*2*) in the form

$$\log \frac{\log P}{(1 - \Phi/T)} = \sum_{i=0}^{m} a_i T^i \ (m = 2, \text{usually})$$

was fitted to the experimental points with assigned weight factors $[(P_i \ln P_i)/(\sigma_P)_i]^2$, where $(\sigma_P)_i$ is the estimated uncertainty in P_i. For the present series of measurements, the estimated uncertainty in any point i was made proportional to pressure according to the relation $(\sigma_P)_i = s + tP_i$, in which s and t are constants with assigned values of 5×10^{-6} and 2×10^{-5}, respectively.

Piperidine and 2-Methylpiperidine. No other vapor pressure values, of comparable accuracy to the present work, exist in the published literature upon which a comparison is justified in terms of a general correlation. Data in the present experimental range, extending from 72 to 2026 mm. of Hg, have been represented adequately for piperidine and 2-methylpiperidine by both Antoine and Cox equations. For piperidine, deviations from the Cox equation at upper pressures and temperatures are significantly smaller than from the Antoine equation. But 2-methylpiperidine is the only compound reported for which the standard deviation from the Cox equation exceeds that from the Antoine equation.

Pyrrolidine. Present measurements, extending from 150 to 2026 mm. of Hg, overlap the reported results of Hildenbrand *et al.* (*6*). In the overlap range, measured boiling temperatures of pyrrolidine are from 0.01° to 0.08° higher than those given by Hildenbrand *et al.* Because the sample purities are comparable (99.91 mole % Hildenbrand *et al.* *vs.* 99.85 mole % present), the small differences in boiling temperatures might be traced to peculiarities of the methods or apparatus. The ebulliometric methods appear to be equivalent; actually, they are different in one critical respect of boiler design that could account for the lower boiling temperatures reported by Hildenbrand *et al.* When the percolation tube is completely immersed within the boiling substance and the boiler also is enclosed in a Dewar vessel, as in the ebulliometers used by Hildenbrand *et al.*, substances that are prone to superheat will give apparent boiling temperatures and calculated pressures that are in error on the high side. Therefore, if the standard substance, water, superheats more than the compound being studied, boiling temperatures will be measured for the compound that are too low for its apparent calculated pressures. In the present measurement, superheat effects were eliminated by providing an unlagged section of the percolation tube outside of the boiler (*10*) where partial condensation of vapor and reduction of superheat took place. To promote necessary slight cooling of the unlagged percolation tube, surrounding air temperatures were always kept at least 10° or 20° below boiler temperature.

Pyridine. Present measurements, 150 to 2026 mm. of Hg, overlap several sets of values reported in the literature in the range 150 to 765 mm. of Hg. A good summary of previously published results was provided by Herington and Martin (*5*) in terms of a deviation plot showing temperature differences from their derived Antoine equation. Because no later results have appeared, a comparison of the present vapor pressure values with only those of Herington and Martin should furnish a satisfactory comparison with previous significant results from the literature. This comparison shows that the Cox equation that was derived to represent present results gives calculated pressures that are higher than those of Herington and Martin by less than 0.1% over most of the temperature range. The agreement with the results of Herington and Martin is relatively good in comparison with the results from other sources, and the differences observed might be attributed entirely to small differences in sample purity provided the impurities in both samples are mostly higher boiling substances.

2-, 3-, and 4-Methylpyridine. Present measurements on 2-methylpyridine extend from 150 to 2026 mm. of Hg and thus overlap much of the pressure range investigated by Herington and Martin (*5*) from 79 to 773 mm. of Hg and by Riley and Bailey (*12*) from 6 to 760 mm. of Hg. Comparison of the pressures calculated with the Cox equation derived from the authors' data shows that the Herington and Martin values are in good agreement, being lower by less than 0.1% over much of the range, but the values given by Riley and Bailey show rather large, positive and negative deviations. As with pyridine, the difference between the values of Herington and Martin and present values can be attributed entirely to small differences in sample purity, provided the impurities in both samples are mostly higher boiling substances.

Present measurements on 3- and 4-methylpyridine extend from 71 to 2026 mm. of Hg and overlap the measurements of Herington and Martin (*5*) which extend from 96 to 779 mm. of Hg and from 78 to 762 mm. of Hg, respectively. Agreement is very close between the measurements of Herington and Martin and the present Cox equations for 3- and 4-methylpyridine. The differences are both positive and negative and generally less than 0.05%.

Pyrrole, 1-Methylpyrrole, and 2,5-Dimethylpyrrole. Present measurements extend from 72 to 2026 mm. of Hg. No significant vapor pressure measurements have been published previously. The data have been represented by Antoine and Cox equations and the standard deviations are shown to be much smaller for the Cox equation in the case of pyrrole and 2,5-dimethylpyrrole. Furthermore, for these two substances, the Antoine equation given does not represent the data within experimental accuracy and is recommended only when its relatively simpler form justifies its use.

1-Propylamine, 2-Propylamine, and 2-Methyl-2-propylamine. Measurements on 1-propylamine and 2-methyl-2-propylamine were made with the ebulliometric method. No other significant vapor pressure measurements are available for comparison with the present results.

Measurements on 2-propylamine were made from 3 to 33 mm. of Hg with the inclined-piston method and from 234 to 2026 mm. of Hg by the ebulliometric method.

Boiling Point Tables. Tables of boiling temperatures at even pressures based on the Cox equations of Table I are available to interested persons. Requests should be addressed to the Thermodynamics Group, Bureau of Mines, Bartlesville Petroleum Research Center, Bartlesville, Okla. 74003.

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Heats of Solution of Five Substituted Pyridines in 2*N* Hydrochloric Acid

J. W. WILSON and I. J. WORRALL
Department of Chemistry, The University of Lancaster, Lancaster, England

The heats of solution of five substituted pyridines have been determined in 2*N* HCl: 4-ethylpyridine, 2-picoline, 3-picoline, 4-picoline, and 2,6-lutidine. The values are discussed and compared with pK$_a$ values.

WE HAVE RECENTLY investigated the thermochemistry of some Group 3 halide pyridine and substituted pyridine complexes (*6*). The methods used involved the determination of the heats of hydrolysis of the complexes, together with the heats of solution of the pure ligands in 2*N* HCl.

Since previous work (*5*) has involved determination of the heats of solution of the ligands at very low acid concentration, we feel it desirable to report the present results, since these are useful in determination of the heats of formation for the type of complexes described above.

EXPERIMENTAL

The substituted pyridines were dried by refluxing over potassium hydroxide, fractionally distilled, and transferred to a vacuum line. They boiled at: 2-picoline 129.2° (760 mm.), 3-picoline 144.1° (760 mm.), 4-picoline 145.3° (760 mm.), 2,6-lutidine 143.4° (749 mm.), 4-ethylpyridine 167.8° (762 mm.). The pyridines were transferred to fragile glass bulbs, which were evacuated and sealed under vacuum. The calorimeter (*2*) was checked by measuring the heat of reaction of 0.1*N* hydrochloric acid with tri(hydroxymethyl)aminomethane: $-\Delta H$ = 7.06, 7.12, 7.16 (av. 7.11 ± 0.05) kcal. per mole at 25.0° C. (literature value 7.104) (*3*).

RESULTS AND DISCUSSION

The results are presented in Table I.

ΔH_s is the heat of solution and is given by

$$B_{(\text{liquid})} + \text{excess } 2N\ \text{HCl} \xrightarrow{\Delta H_s} BH^+ (\text{in } 2N\ \text{HCl}) + Cl^- (\text{in } 2N\ \text{HCl})$$

The weights (in grams) of the base are shown; the temperature rise, ΔT, is expressed in microvolts and the electrical calibration, C, is in terms of the thermochemical calorie (4.1840 joules) per microvolt.

Table II compares heats of solution ($-\Delta H_s$), heats of ionization ($-\Delta H_i$), and pK$_a$ values.

There is an over-all increase in $-\Delta H_s$ as the base strength, pK$_a$, increases. However, this comparison is misleading, since pK$_a$ concerns the ionization equilibria:

$$B_{(aq)} + H_3O^+ = BH^+_{(aq)} + H_2O \qquad (1)$$

Table I. Heats of Solution of Bases in Excess 2*N* HCl

Base	Wt. of Base in 100 Ml. 2*N* HCl, G.	ΔT, μv.	C, Cal./μv.	$-\Delta H_s$, Kcal./Mole
2-Picoline	0.2978	187.0	0.1735	
	0.3919	246.0	0.1737	10.17 ± 0.04
	0.2726	172.0	0.1739	
3-Picoline	0.3407	195.0	0.1737	
	0.2502	142.0	0.1744	9.27 ± 0.05
	0.1968	113.0	0.1743	
4-Picoline	0.2821	167.0	0.1738	
	0.2358	141.0	0.1738	9.64 ± 0.06
	0.1796	107.0	0.1745	
4-Ethylpyridine	0.4116	213.0	0.1718	
	0.3116	162.5	0.1717	9.57 ± 0.04
	0.2614	136.0	0.1720	
	0.3793	197.0	0.1716	
2,6-Lutidine	0.3049	196.0	0.1741	
	0.3904	251.0	0.1740	11.99 ± 0.02
	0.2173	139.0	0.1746	