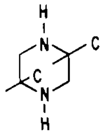
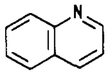
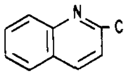
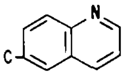
Table II. Properties of Organic Nitrogen Compounds (*Continued*)

Compound		Freezing Point, °C.	Purity, Mole %	Boiling Point, °C., 760 Mm.	Density G./Ml., d_4^{20}	Refractive Index n_D^{20}	Refractive Index n_g^{20}	Derived Functions: Refractivity intercept $n_D^{20} - d_4^{20}/2$	Derived Functions: Specific dispersion, $(n_g^{20} - n_D^{20})10^4/d_4^{20}$	Derived Functions: Molecular refraction, $M(n^2-1)/d(n^2+2)$	Spectra Catalog Serial Numers: UV	Spectra Catalog Serial Numers: IR 2–15µ	Spectra Catalog Serial Numers: IR 14–25µ	Spectra Catalog Serial Numers: Mass	Spectra Catalog Serial Numers: Raman
cis-2,5-Dimethylpiperazine[j]		18.9	[b]	101.1[d]	0.9218	1.4731	1.4853	1.0122	132.35	34.76	772	2031	2032	1559	
Quinoline[e]		−14.9	[b]	161.9[d]	1.0941							2598	2599		
2-Methylquinoline[l]			[b]	171.5[d]	1.0636										
6-Methylquinoline[l]		−26.0	[b]	181.4[d]	1.0664	1.6165	1.6577	1.0833	386.35	46.95	773	2033	2034	1560	

[a] Original sample donated by University of Kansas, Lawrence, Kan. [b] Purity estimated 99.0 mole % or better (*8*). [c] Insufficient sample for this measurement. [d] Boiling point at 100 mm. [e] Original sample donated by Mellon Institute of Research, Pittsburgh, Pa. [f] 14—40µ. [g] Original sample donated by Bureau of Mines, Laramie, Wyo. [h] Original sample purchased from Aldrich Chemical Co., Milwaukee, Wis. [i] Original sample purchased from Du Pont Organic Chemicals, Wilmington, Del. [j] Original sample purchased from Wyandotte Chemical Corp., Wyandotte, Mich. [k] Original sample purchased from Union Carbide Corp., New York, N. Y. [l] Original sample purchased from Matheson Co., Inc., East Rutherford, N. Y.

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RECEIVED for review June 20, 1968. Accepted October 16, 1968. Work done under a cooperative agreement between the Bureau of Mines, U.S. Department of Interior, and the University of Wyoming, an adjunct of American Petroleum Institute Research Projects 48 and 52, sponsored cooperatively by the Bureau of Mines and the American Petroleum Institute. Reference to specific brand names or models of equipment is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

Vapor Pressure of Primary *n*-Alkyl Chlorides and Alcohols

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The vapor pressures of 1-alkyl chlorides and of 1-*n*-alkanols were determined by differential thermal analysis between 5 and 760 Torr. The experimental data were correlated by the Antoine vapor pressure equation, and the Antoine constants for the compounds are presented.

DIFFERENTIAL thermal analysis provides a relatively new technique for determining the vapor pressure of compounds over a wide range of temperature and pressure (*8*). The dynamic nature of the technique avoids problems of decomposition and decontamination of the compounds under test and the method can provide data of excellent accuracy.

Experimental determinations of vapor pressure of the primary alcohols and the corresponding alkyl chlorides have been reported in many places, but the data available are neither complete nor entirely reliable. For example, Winslow (*14*) shows that fair amounts of data are available for the first eight members of the series, especially for the even numbered homologs, but above this point the data are sparse and of unknown reliability. Li and Rossini (*10*) have shown that most of the reliable data for the alkyl chlorides apply to the first four homologs, but even within these data there are many discrepancies. For instance,

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[1] Present address: American Cyanamid Co., Bound Brook, N. J.

Dreisbach and Martin (*5*) report the boiling point of 1-chlorobutane at 760 Torr as 78.44° C., while Lenth (*9*) measures 77.5° C. This discrepancy is equivalent to a variation in vapor pressure of about 25 Torr.

PURIFICATION OF MATERIALS

The 11 primary alkyl chlorides studied ranged from 1-chloropropane to 1-chlorohexadecane. They were purified by preparative gas chromatography, using the Wilkens Model 700A preparative chromatograph. Sample purities are shown in Table I. The 11 normal primary alcohols studied ranged between 1-propanol and 1-hexadecanol. The C_6, C_8, C_{10}, and C_{12} isomers were each better than 99 mole % pure as received. The C_3 to C_5 isomers were carefully fractionated through a helix-packed Todd distillation column, and cuts were obtained which were better than 99 mole % pure, as shown by chromatographic analysis and by boiling range. The C_9, C_{14}, and C_{16} isomers could not be adequately purified or analyzed by gas chromatography; the compounds apparently decomposed on the columns used. Purification was achieved by careful vacuum fractionation at 50 to 1 reflux ratio through a Nester-Faust annular spinning band fractionating column. The arbitrary cuts taken were analyzed by determining their boiling range over a wide pressure spread and choosing those fractions which showed a minimum boiling range. Only the C_{14} and C_{16} homologs showed boiling ranges greater than 0.1° C. in the best cuts.

Boiling Point Range. Variation in sample purity is a major cause of difference in vapor pressures reported in the literature. The static methods which require the establishment of vapor-liquid equilibrium over a substantial period of time do not readily demonstrate the presence of trace impurities nor the generation of impurities in unstable samples refluxing at high temperatures. Independent tests of purity are often employed such as gas chromatography (*1*), determination of the freezing point (*1, 6*), or measurements of refractive index (*11*). In the present instance, gas chromatography of some of the higher alcohols and chlorides led to decomposition, which vitiated the utility of this method. Refractive index is useful only if the correct value for an authentically pure sample is known. Contiguous fractions of the alcohols and chlorides, of different purity levels, still demonstrated refractive indices identical within the limits of experimental error. Freezing points of the higher alcohols were difficult to test because of their tendency to supercool.

Table I. Purification of Raw Materials

Carbon Number	Purification Method	Estimate of Purity, Mole %
	n-ALKYL CHLORIDES	
3	Gas chromatography	99+
4	Gas chromatography	99+
6	Gas chromatography	99+
7	Gas chromatography	99+
8	Gas chromatography	99+
9	Gas chromatography	99+
10	Gas chromatography	99+
11	Gas chromatography	99+
12	Gas chromatography	99+
14	Gas chromatography	99
16	Gas chromatography	99
	1-*n*-ALKANOLS	
3	Todd column	99+
4	Todd column	99+
5	Todd column	99+
6	None	99
7	Gas chromatography	99+
8	None	99+
9	Spinning band	99+
10	None	99+
12	None	99+
14	Spinning band	99+
16	Spinning band	99+

If the material is sufficiently pure, its boiling point at any set pressure should not vary by more than the sensitivity of the temperature-measuring device employed in the vapor pressure determination. Indeed, a most common purity test is the boiling point range of the fractionated sample used (*2-4, 7, 13*). The DTA technique described below invariably produced vertical exotherm traces as the sample boiled off only if the boiling point was constant within 0.1° C. from initial boiling point to the dry point. A nonvertical exotherm indicated the presence of impurities during the actual determination, and this constituted a very sensitive check on the purity and stability of each sample at the moment of use. The limit of 0.1° C. represents the maximum sensitivity of the X-Y plotter used to demonstrate the exotherm trace. Only tetradecanol and hexadecanol produced endotherms which were not vertical within the width of the recorder line.

VAPOR PRESSURE DETERMINATION

The basic DTA instrument used was the Du Pont 900 differential thermal analyzer. Modifications made in this instrument are to be published elsewhere (*8*). The vacuum system varied by no more than 0.1 Torr in 90 minutes, while a set of three replications at a single pressure setting required no more than 30 to 40 minutes. Vacuum measurements were made with a precision Zimmerli gage from 5 to 100 Torr and with a Wallace & Tiernan mercurial barometer in the 100- to 760-Torr range.

Samples of 4 to 12 μl. of compound were mixed with approximately 40 mg. of 100-micron glass beads. An equal mass of beads was used as the inert reference material. Samples to be run below ambient temperature were first placed, together with the thermocouples and the heater cartridge, in the aluminum furnace block. The assembled unit was chilled in powdered dry ice in a closed container to well below the desired starting temperature. The block was then inserted into the DTA chamber which was evacuated by a roughing pump to within several Torr of the desired pressure. The sample chamber was then connected through a manifold to the previously adjusted vacuum system.

The temperature of the furnace was then raised at the desired heating rate, generally about 10° C. per minute, while the DTA trace is recorded. At the first indication of an endothermic departure from the recorder base line, a K-3 potentiometer was switched into the circuit to read the sample thermocouple e.m.f. First balanced roughly, then exactly balanced during the boiling period indicated by the vertical endotherm, the K-3 potentiometer was used to measure sample temperature precisely.

Accuracy and Precision of the Method. The Chromel-Alumel thermocouples supplied by the manufacturer were calibrated by measuring the e.m.f. produced at the boiling points of a number of pure reference materials. By varying the pressure, calibration was carried out at 10° to 20° C. intervals from −40° to 305° C. with six compounds. These materials were chosen so that their known vapor pressure ranges overlapped, to ensure that the calibration be independent of the reference materials. From −40° to 90° C., the calibration points were estimated to be accurate to within ±0.1° C., while from 110° to 305° C., the calibration was accurate to ±0.01° C.

The boiling point of a single sample of doubly distilled water was determined at 233.9 Torr over a period of 15 months. At this pressure, pure water boils at 70.0° C. During this period, a single calibrated thermocouple was in constant

Table II. Vapor Pressure Measurements

Mm. Hg	°C.	Mm. Hg	°C.	Mm. Hg	°C.	Mm. Hg	°C.
1-CHLOROPROPANE		1-CHLOROBUTANE		1-CHLOROHEXANE		1-CHLOROHEPTANE	
28.8	−25.1	10.1	−16.7	5.0	15.0	5.1	34.4
39.9	−19.6	15.2	−10.5	10.4	26.7	10.5	46.6
55.4	−13.7	19.8	−6.2	15.0	33.1	15.2	53.5
79.5	−6.9	29.6	0.8	20.1	38.6	20.1	59.1
120.5	1.2	40.2	6.2	30.1	46.7	30.1	67.5
200.2	12.1	54.8	12.0	39.9	52.6	39.8	73.6
303.9	21.8	79.8	19.7	55.0	59.7	55.0	81.1
504.0	34.9	121.6	28.8	79.8	68.4	81.9	90.9
776.0	47.1	203.1	41.1	125.6	79.5	121.6	101.1
		302.0	51.3	203.2	92.6	203.0	115.6
		499.1	65.5	305.7	104.6	302.6	127.9
		758.8	78.5	500.9	120.3	502.5	145.1
				774.0	135.6	753.4	160.1
1-CHLOROOCTANE		1-CHLORONONANE		1-CHLORODECANE		1-CHLOROUNDECANE	
5.6	54.1	5.1	69.1	5.5	86.2	5.5	101.4
9.8	63.9	5.5	70.8	10.5	98.9	10.4	114.3
15.3	72.4	9.6	80.6	15.0	106.2	15.1	122.3
20.3	78.2	15.1	89.9	20.2	112.8	19.8	128.4
30.3	87.1	19.6	95.4	30.8	122.7	30.1	138.5
40.1	93.4	29.5	104.6	40.1	129.2	39.8	145.6
55.2	101.1	39.6	111.5	54.7	137.1	55.6	154.5
80.5	110.7	55.0	119.8	80.0	147.7	81.0	165.1
121.2	121.8	79.7	129.5	120.5	159.3	120.5	176.8
201.0	136.7	121.2	141.3	201.6	175.7	203.0	193.7
301.6	149.8	200.5	156.7	301.4	189.5	308.0	208.7
501.0	167.4	301.6	170.3	501.5	208.6	499.1	227.6
773.2	184.1	501.8	188.6	754.7	225.6	499.8	227.6
		752.8	204.8			763.0	245.4
1-CHLORODODECANE		1-CHLOROTETRADECANE				1-CHLOROHEXADECANE	
5.5	116.0	5.2	141.7			5.1	165.6
5.6	116.1	9.9	155.1			10.0	180.2
10.0	128.1	14.9	164.6			15.2	190.3
15.1	137.1	20.4	172.2			20.0	197.2
20.1	143.9	29.5	181.8			30.2	208.3
29.9	153.7	41.0	190.7			39.8	216.1
40.0	161.3	55.2	199.1			54.8	225.6
55.3	170.1	80.0	210.5			79.9	237.5
80.3	180.9	122.4	223.8			122.2	251.3
120.6	193.0	203.8	242.6			204.6	270.2
204.2	210.5	311.2	258.2			295.5	285.1
300.5	224.9	498.4	277.7			501.5	306.9
504.9	245.5	764.2	297.0			766.6	326.8

use with a wide variety of samples, subject to repeated thermal cycling. The pressure system was reset each time to the desired 233.9 Torr and, based on eight replications, the accuracy of the method is indicated by the following statistics:

Boiling point range (including 70.0° C.)	0.13° C.
Standard deviation	±0.005°
95% confidence interval	±0.1°

These results illustrate the stability and reliability of the method and indicate as well an accuracy within 0.1° C., the present limit of instrumental discrimination of a constant boiling point

EXPERIMENTAL RESULTS

About 13 vapor pressure–temperature data pairs were determined for each compound. The points were spaced approximately 15° C. apart so that each point should carry equal weight in subsequent regression analysis. The experimental data are given in Table II. The temperature values are averages of several replications at the stated pressures; at most they varied by ±0.1° C. between replications.

Decomposition of Samples. Because some of the organic materials studied were exposed to relatively high temperatures, it was necessary to consider the problem of molecular degradation. The higher alcohols could be expected to dehydrate to either olefins or ethers at 350° to 450° C., but boiling points constant to ±0.1° shown by the samples indicate no significant decomposition occurred. The decomposition of the higher alkyl chlorides was shown by the formation of a white vapor cloud in the vacuum chamber at temperatures above 240° C. Indicator paper in the chamber showed these vapors to contain hydrogen chloride.

Chlorides heavier than chlorodecane were subject to sufficiently high temperatures to bring about decomposition. However, only chlorotetradecane and chlorohexadecane showed boiling ranges detectably greater than 0.1° C. The products of decomposition appear to form in the vapor phase and they have no perceptible effect on the boiling points of the liquids.

Data Correlation. The experimental data obtained for each compound were fitted to the Antoine vapor pressure equation. The equation

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

where P is the vapor pressure in torr and t is the corresponding boiling point in °C., was linearized in the form

$$\log P = A + (A \times C - B)/t - C\,(\log P/t) \qquad (2)$$

If one sets $y = \log P$, $x_1 = 1/t$, and $x_2 = (\log P)/t$, a for 1-Chloroalkanes and 1-Alkanols

Mm. Hg	°C.	Mm. Hg	°C.	Mm. Hg	°C.	Mm. Hg	°C.
1-PROPANOL		1-BUTANOL		1-PENTANOL		1-HEXANOL	
14.7	19.3	5.5	22.6	4.3	33.9	5.7	52.2
14.9	19.8	10.3	30.9	9.5	45.6	9.7	60.4
20.4	24.5	14.8	36.2	15.2	52.5	15.3	67.4
29.4	30.3	19.6	40.7	19.8	56.7	20.5	72.6
29.5	30.3	31.0	48.2	29.4	63.6	29.8	79.2
39.7	35.2	39.6	52.4	40.7	69.3	40.7	85.0
56.4	41.3	55.3	58.3	54.8	74.9	55.3	91.1
81.3	48.1	81.4	65.8	82.7	83.1	80.0	98.7
120.4	55.4	121.4	73.5	119.1	90.7	120.8	107.6
199.4	65.7	208.0	85.1	200.0	102.4	201.0	119.7
300.0	74.6	303.5	93.8	302.0	112.3	301.8	130.1
499.5	86.6	507.0	106.5	502.1	125.8	500.0	144.5
758.5	97.3	766.0	117.8	765.4	138.0	757.3	157.3
1-HEPTANOL		1-OCTANOL		1-NONANOL		1-DECANOL	
4.7	63.6	5.3	78.9	5.6	91.7	5.6	105.0
10.9	76.1	10.2	88.8	10.5	102.1	10.2	114.5
15.0	81.5	15.0	95.4	15.3	108.9	15.0	121.7
21.1	87.6	21.0	101.5	20.3	114.4	20.1	127.3
30.2	94.3	30.0	108.4	30.2	122.4	29.9	135.6
40.2	99.9	39.5	114.0	40.6	128.8	40.1	142.2
55.5	106.4	54.4	120.9	55.5	135.8	56.0	149.9
80.5	114.5	85.4	131.2	80.4	144.7	81.1	159.2
122.4	124.1	123.8	140.3	120.7	155.0	121.3	169.9
201.0	136.5	315.5	166.1	201.4	169.0	198.0	183.9
303.5	147.8	507.6	181.2	302.4	181.0	303.0	197.4
501.0	162.8	760.0	195.3	502.5	198.0	504.8	215.3
760.8	176.4			763.9	213.6	757.6	231.0
1-DODECANOL		1-TETRADECANOL		1-HEXADECANOL			
5.3	126.5	5.2	151.6	5.9	172.1		
9.8	138.3	10.5	163.0	10.3	185.3		
14.6	146.0	15.3	171.0	15.1	193.4		
30.1	162.5	19.9	177.0	19.8	201.0		
40.9	169.5	32.1	188.4	30.1	211.0		
55.6	177.1	48.4	199.1	40.4	218.6		
81.2	187.1	80.1	213.3	55.3	227.3		
122.3	198.7	120.0	225.7	80.3	238.7		
201.3	214.5	202.8	243.1	120.3	251.6		
300.2	228.4	302.6	257.8	200.5	269.3		
499.0	247.7	501.2	277.9	302.1	285.0		
503.7	247.8	755.2	295.9	502.4	305.9		
766.0	265.4			759.2	325.1		

Table III. Antoine Constants for the 1-Alkanols and 1-Alkyl Chlorides, 5 to 760 Torr

Carbon Number	Antoine Constants			Correlation Coefficient	Variance of Estimate × 10^4	% Error of Estimate	
	A	B	C			Av.	Max.
1-ALKANOLS							
3	8.18894	1690.864	221.346	0.99944	4.227	0.397	0.880
4	7.42117	1351.555	179.810	0.99960	4.233	0.667	1.525
5	7.55787	1492.549	181.529	0.99974	2.908	0.447	2.243
6	7.28781	1422.031	165.444	0.99991	0.970	0.540	1.307
7	6.85450	1256.783	139.663	0.99990	0.995	0.619	1.565
8	6.62354	1196.639	124.107	0.99993	0.831	0.714	1.334
9	6.83667	1373.417	133.968	0.99999	0.129	0.338	0.674
10	6.39379	1180.306	104.321	0.99989	1.132	1.004	2.189
12	6.68662	1454.635	117.235	0.99997	0.363	0.535	1.973
14	6.48407	1412.907	95.368	0.99996	0.472	0.793	1.665
16	7.04183	1880.126	127.123	0.99984	0.166	1.180	3.569
1-ALKYL CHLORIDES							
3	6.96655	1126.383	229.370	0.99729	17.955	0.418	1.251
4	6.87098	1182.903	218.265	0.99321	61.825	0.677	1.230
6	6.76886	1304.968	200.058	0.99966	3.716	0.738	1.646
7	6.83820	1410.064	195.639	0.99992	0.901	0.402	0.983
8	6.84310	1469.829	187.157	0.99991	0.923	0.548	1.161
9	6.94063	1586.937	185.505	0.99995	0.536	0.361	1.194
10	6.99172	1676.793	182.017	0.99999	0.136	0.212	0.820
11	6.97249	1713.225	173.366	0.99999	0.095	0.270	0.544
12	6.96976	1754.079	165.632	0.99998	0.256	0.431	0.889
14	6.88717	1776.491	146.180	0.99995	0.549	0.659	2.050
16	7.00109	1924.969	140.341	0.99997	0.331	0.638	1.466

linear equation is obtained of the form

$$y = a + bx_1 + cx_2 \qquad (3)$$

where $a = A$, $c = -C$, and $b = (A \times C - B)$.

The constants of linear Equation 3 were evaluated by multilinear least squares regression. This method of linearization was used because it permits explicit solution of Equation 2 for either log P or t. The Antoine constants are listed in Table III together with several statistical parameters showing the goodness of fit of the equations to the experimental data. The maximum error of 3.6% was obtained for hexadecanol, one of the two alcohols which appeared to contain detectable trace impurities. However, this maximum error is well within the expected maximum error for the Antoine equation which is reported to be about 5% (*12*).

ACKNOWLEDGMENT

H. R. Kemme was recipient of an NDEA Fellowship. Part of this work was supported by a grant from the Foundation for Advancement of Graduate Study at the Newark College of Engineering. The authors are especially grateful to Margaret A. Nichols for assistance with programming and computations.

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RECEIVED for review August 21, 1967. Accepted August 28, 1968.

Enthalpies of Combustion of Toluene, Benzene, Cyclohexane, Cyclohexene, Methylcyclopentane, 1-Methylcyclopentene, and *n*-Hexane

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The enthalpies of combustion of toluene, benzene, cyclohexane, cyclohexene, methylcyclopentane, 1-methylcyclopentene, and *n*-hexane were measured in a bomb calorimeter. Values, in kilocalories per mole based on the mass of sample, for the enthalpies of combustion, $\Delta Hc^{\circ}_{298.15}$, of the liquid hydrocarbons in gaseous oxygen to form gaseous carbon dioxide and liquid water are toluene, −934.49 ± 0.12; benzene, −780.95 ± 0.10; cyclohexane, −936.87 ± 0.13; cyclohexene, −896.75 ± 0.12; methylcyclopentane, −941.28 ± 0.14; 1-methylcyclopentene, −897.17 ± 0.13; and *n*-hexane, −995.03 ± 0.13. Values of the enthalpy of formation of the liquids were derived. They were compared to existing hydrocarbon data and can be used to check the internal consistency of the existing selections of data for the several families of hydrocarbons. The best means of measuring the amount of reaction in combustion calorimetry were reconsidered. Both sample mass and carbon dioxide recovery were used as measures of the amount of reaction. A new carbon dioxide absorbent was used and was superior to older absorbents.

THE BUREAU OF MINES is conducting thermodynamic studies at the Bartlesville Petroleum Research Center on selected hydrocarbons under American Petroleum Institute Research Project 62, "Thermodynamics of Hydrocarbons from Petroleum." In this project, research in combustion calorimetry is being done to extend and improve the existing thermochemical data for the hydrocarbons (*1*) largely produced by Johnson, Prosen, Rossini, and coworkers of the National Bureau of Standards.

The work on hydrocarbons by the National Bureau of Standards was planned carefully. Series of measurements on isomeric families of compounds gave highly accurate values of the heats of isomerization. Other studies gave precise values of the —CH_2— increment to the enthalpy of formation, and values for larger families of compounds were made internally consistent by studying single isomers from each of several smaller families in one carefully planned series of experiments. For example, all the alkanes were interrelated by studying the *n*-alkanes. The internal consistency of the enthalpies of formation of the alkanes probably would not be improved now by repeated studies.

The method of calibration differed from that used by Johnson, Prosen, Rossini, and collaborators. Earlier calibration was done with electrical energy, but later benzoic acid combustion was the means of calibration. For many good reasons (*4*), today most precision combustion calorimetry uses benzoic acid calibration. It is possible, however, that changes over the years have introduced lack of agreement between families of compounds. The principal reason for the research reported here was to check the consistency of the values for the alkanes, benzenes, cyclohexanes, cyclohexenes, and cyclopentenes.