only semiquantitative, because both the experimental and calculated temperature-composition points were used to draw the constant-temperature lines. The greater distance between the liquid isothermal lines shows the flatness of surface in the middle of the ternary composition diagram. The close proximity of the lines near the 2,3-dimethylbutane–chloroform and chloroform-methanol surfaces depict the steeply rising liquid surface.

NOMENCLATURE

A, B, C = Antoine constants
P_i = vapor pressure of component *i*, mm. of Hg
P_T = total pressure, mm. of Hg
T_c = calculated temperature, ° C.
T_e = experimental temperature, ° C.
x_{ic} = calculated mole fraction of component *i* in the liquid phase
x_{ic} = experimental mole fraction of component *i* in the liquid phase
y_{ic} = calculated mole fraction of component *i* in the vapor phase
y_{ie} = experimental mole fraction of component *i* in the vapor phase
α_{ij} = relative volatility of component *i* to component *j*
γ = activity coefficient
γ_{ie} = calculated activity coefficient of component *i*
γ_{ie} = experimental activity coefficient of compound *i*
λ = Wilson parameter, cal. per gram mole

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Critical Properties and Vapor Pressures of Some Organic Nitrogen and Oxygen Compounds

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EXPERIMENTAL values of *P-V-T* and other thermodynamic properties are available for only the most common substances. Usually these properties have to be estimated. One of the most frequently used tools is the Law of Corresponding States, or one of its modifications, which requires a knowledge of critical properties. Gas and liquid compressibility factors, vapor pressures, heats of vaporization, and other thermodynamic properties are given in the literature as functions of reduced temperature, reduced pressure, and usually a third parameter.

The purpose of this work was to determine the critical properties of selected organic nitrogen and oxygen compounds. Other experimental data include: vapor pressures; rectilinear diameters in the critical region for isopropylamine, *n*-heptane, and benzene; boiling points; indices of refraction; and some information on the stability of the compounds at elevated temperature and pressure. Calculated values of critical compressibility, "acentric factor," and "critical parameter" are presented to expedite the estimation of thermodynamic properties of these compounds.

PURIFICATION OF COMPOUNDS

The compounds listed in Table I were distilled by the authors. The pyrans, picolines, isopropylamine, 1,1-dimethyl hydrazine, and dimethoxymethane were treated with Drierite before distillation. In general, 80% heart cuts were taken the number of times specified in Table I in a 48- × 3/4-inch glass column packed with 1/4-inch glass helices. Reflux ratios of 60 to 80:1 were used. The boiling ranges and boiling temperatures of the final products were measured with a double-junction Chromel-Alumel thermopile capable of measuring temperature differences of the order of 0.0125° C. Attempts to purify 2-methyl pyrazine and *cis*-2,5-dimethyl piperazine

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The critical properties of some selected organic nitrogen and oxygen compounds have been measured using the method of Caillet and Colardeau. Other data obtained were vapor pressures, boiling points, and refractive indices. Compounds studied were dihydropyran, tetrahydropyran, isopropylamine, tertiary butylamine, tertiary octylamine, 2-picoline, 4-picoline, 1,1-dimethyl hydrazine, benzene, *n*-heptane, 2-methyl pyrazine, *cis*-2,5-dimethyl piperazine, dimethoxymethane, and trimethyl phosphite. Critical properties were measured for all of these compounds except tertiary octylamine, 1,1-dimethyl hydrazine, *cis*-2,5-dimethyl piperazine, and trimethyl phosphite.

in this manner resulted in discoloration of these compounds, 50% heart cuts of these latter two compounds, which were received from the supplier as 99+ mole % pure, were taken under reduced pressure (water ejector) in a packed Vigreux column.

The tertiary amines were used as received from Rohm and Haas Co., who took them from constant boiling products. The *n*-heptane used was research grade material, certified 99.9+ mole % pure, from Phillips Petroleum Co.

PURITY AND PHYSICAL PROPERTIES

Information on the purities of the compounds used in this investigation may be deduced from several sources: boiling range of the final product (Table I); comparison of measured boiling points and refractive indices with literature values, where both are available; and constancy of the vapor pressure values over a wide range of specific volumes. Table II compares measured boiling points and refractive indices with literature values. Refractive indices were measured with a Bausch and Lomb Abbe-type refractometer and have a precision of ±0.00006.

Dihydropyran, Tetrahydropyran, Tertiary Butylamine ($C_4H_{11}N$), 1,1-Dimethyl Hydrazine, 2-Methyl Pyrazine, and *cis*-2,5-Dimethyl Piperazine. Literature values of boiling points and refractive indices for these compounds were taken from the Chemical Rubber Handbook (*4*) and 1,1-dimethyl hydrazine from CRC Handbook (*6*). The reliability of this information is questionable, particularly in view of the apparent uncertainty in the boiling points. None of these materials was run in the equipment over a wide enough range of specific volumes to draw any firm conclusions about sample purity.

Isopropylamine. The measured value of the boiling point appears to be in agreement with that reported by Koob *et al.* (*11*) and the measured value of n_D^{20} is in fair agreement with the same authors. No displacement of the vapor pressure curve was noted over a range of specific volumes from 2.21 to 8.80 cc. per gram.

Tertiary Octylamine ($C_8H_{19}N$). The only values of boiling point and refractive index found in the literature came from an article reporting its synthesis and giving no information about the purity of the prepared material. No information on sample purity is derivable from the vapor pressure data in the present work.

2-Picoline. There is a discrepancy between the measured n_D^{20} and that reported by both Kyte *et al.* (*13*) and Biddiscombe *et al.* (*2*). The measured boiling point agrees well with that reported by the former (128.5° C./748) and differs somewhat from the latter's (128.845° C./748). The values at 748 mm. of Hg were derived from the reported values by using $dt/dp = 0.04695$° C./mm. of Hg, as given by Biddiscombe *et al.* Although 2-picoline decomposed slightly at elevated temperatures, several fresh samples were run and the vapor pressure curve showed no apparent displacement over a range of specific volumes from 2.34 to 5.35 cc. per gram.

4-Picoline. The refractive index measured at 20° C.

Table I. Purification of Compounds

Compound	Supplier[a]	Number of Distillations	Final Product Boiling Range, ° C.
Dihydropyran, C_5H_8O	3	2	<0.0125
Tetrahydropyran, $C_5H_{10}O$	3	2	<0.0125
Isopropylamine, C_3H_9N	7	2	<0.0125
2-Picoline, C_6H_7N	6	2	0.06
4-Picoline, C_6H_7N	6	1	0.02
1,1-Dimethyl hydrazine, $C_2H_8N_2$	4	2	<0.0125
Benzene, C_6H_6	1	1	0.05
2-Methyl pyrazine, $C_5H_6N_2$	8	1	[b]
cis-2,5-Dimethyl piperazine, $C_6H_{14}N_2$	8	1	[b]
Dimethoxymethane, $C_3H_8O_2$	2	1	<0.0125
Trimethyl phosphite, $C_3H_9O_3P$	5	2	0.03

[a] Key to the suppliers index is as follows:
1. Allied Chemical and Dye Corp.
2. Celanese Corp. of America
3. E. I. du Pont de Nemours and Co.
4. Food, Machinery, and Chemical Corp.
5. Monsanto Chemical Co.
6. Reilly Tar and Chemical Corp.
7. Sharples Chemicals, Inc.
8. Wyandotte Chemicals Corp.

[b] See text under "Purification of Compounds"

Table II. Physical Properties—Comparison with Literature Values

Compound	Boiling Point, ° C./Mm. Hg.		Refractive Indices				Stability^a
	This work	Literature (Ref.)	This work			Literature (Ref.)	
			n_D^{20}	n_D^{25}	n_D^{30}		
Dihydropyran	85.0/745	86–87/760 (*4*)	1.44231	1.44003	1.43779	n_D^{19} = 1.4402 (*4*)	2
Tetrahydropyran	87.6/747	88/760 (*4*)	1.42084	1.41862	1.41630	n_D^{18} = 1.4195 (*4*)	1
Isopropylamine	31.5/753	31.7/760 (*11*)	1.37363	1.37058	1.36759	n_D^{20} = 1.3742 (*11*)	1
Tertiary butylamine	43.6/760^b	45.2/760 (*4*)	1.37764	1.37462	1.37188	n_D^{20} = 1.3786 (*4*)	1
Tertiary octylamine	140.6/771^b	138/760 (*17*)	1.42372	1.42153	1.41938	n_D^{27} = 1.4222 (*17*)	3
2-Picoline	128.5/748	129.5/770 (*13*) 129.408/760 (*2*)	1.49913	1.49686		n_D^{20} = 1.50102 (*13*) n_D^{20} = 1.50101 (*2*)	2
4-Picoline	143.7/751.5^c	145.356/760 (*2*) 145.0/765 (*13*)	1.50566	1.50322	1.50063	n_D^{20} = 1.50584 (*2*) n_D^{20} = 1.50584 (*13*)	1
1,1-Dimethyl hydrazine	60.8/750	63/760 (*6*)	1.40765	1.40504	1.39961	n_D^{22} = 1.4075 (*6*)	3
Benzene	79.7/750	79.673/750 (*1*)	1.50015	1.49715	1.49415	n_D^{20} = 1.50112 (*1*) n_D^{25} = 1.49792 (*1*)	1
n-Heptane		98.427/760 (*1*)	1.38764	1.38508	1.38287	n_D^{20} = 1.38764 (*1*) n_D^{25} = 1.38511 (*1*)	1
2-Methyl pyrazine	133.5/747.2^c	135/760 (*4*)	1.50504	1.50265	1.50049	n_D^{19} = 1.5067 (*4*)	2
cis-2,5-Dimethyl piperazine	164.5/746^b	162/760 (*4*)	1.47289		1.46843		3
Dimethoxymethane	41.8/755	41.5/754 (*18*) 41.6/760 (*7*) 41.9/755 (*14*)	1.35373	1.35132	1.34852	n_D^{20} = 1.35298 (*18*) n_D^{25} = 1.3515 (*7*)	2
Trimethyl phosphite	111.2/755.7	111/760 (*5*)	14.0836	1.40611	1.40385	n_D^{20} = 1.40843 (*5*)	3

[a] 1. Compounds which were stable and needed no allowance for decomposition.
2. Compounds which decomposed slightly, but were stable enough to allow determination of the critical properties.
3. Compounds unstable to the extent that only vapor pressure data below the critical region were obtained.

[b] Reported by supplier.

[c] Measured in a Cottrell boiling point apparatus.

agrees well with the value reported by both sets of researchers mentioned in the discussion of 2-picoline. Again the measured boiling point agrees better with Kyte *et al.* (144.3° C./751.5) than with Biddiscombe *et al.* (144.940° C./751.5), but in neither case is the agreement good. The reported values were corrected to 751.5 mm. of Hg using $dt/dp = 0.04887°$ C./mm. of Hg from Biddiscombe *et al.* 4-Picoline was not run in the equipment over a wide enough range of specific volumes to draw any firm conclusions about sample purity.

Benzene. The boiling point obtained for benzene agrees with that published in API Project **44** (*1*) within the precision of the former. No displacement of the vapor pressure curve was noted over a range of specific volumes from 1.96 to 7.59 cc. per gram. On the other hand, measured refractive indices do not agree with the values reported in API Project **44** within the precision of the former. The authors have no explanation for this inconsistency.

***n*-Heptane (C_7H_{16}).** The refractive indices measured here agree very well with the values reported in API Project **44**. No displacement of the vapor pressure curve was noted over a range of specific volumes from 2.48 to 7.28 cc. per gram.

Dimethoxymethane. A critical cross check of the available literature data shown in Table II shows that the values of boiling point and refractive indices reported in this work lie in the range of values reported by other researchers.

No information on purity is available from vapor pressure data.

Trimethyl Phosphite. Values of boiling point and n_D^{20} measured in this work agree well with the values reported by Foxton *et al.* (*5*). No information on purity is available from vapor pressure data.

RESULTS AND DISCUSSION

The apparatus and experimental procedure used in this work have been discussed in previous papers (*8*, *10*). Briefly, the method consisted of determining the vapor pressure curve of the compound and taking the critical temperature as the highest point of deviation from the curve when either of the one-phase regions was entered.

The precision of temperature measurement is 0.05° F. However, since the one-phase curve rapidly approaches the vapor pressure curve as the critical volume is approached, the limiting factor in measuring the critical temperature is the closeness with which the break at the phase boundary can be determined. Because of the uncertainty involved here, no critical temperature was determined closer than ±0.5° F. In addition, when the compound is partially unstable, further uncertainty develops in the critical region; this is reflected in the assessment of accuracy in Table III.

The critical pressure is the pressure measured at the critical temperature, and the critical density is determined by interpolation between isometrics obtained on both sides of the critical density. In the case of isopropylamine, *n*-heptane, and benzene, sufficient data were taken to determine the rectilinear diameters, and the critical densities in these cases were determined by extrapolation to the critical temperature.

A summary of the experimentally determined critical properties appears in Table III. Tertiary octylamine, 1,1-dimethyl hydrazine, *cis*-2,5-dimethyl piperazine, and trimethyl phosphite proved to be too unstable at elevated pressures and temperatures to allow determination of the critical properties.

As regards the stability of the compounds at elevated

Table III. Critical Properties

Compound	Critical Temperature				Critical Pressure		Critical Density	
	° F.	° R.	° C.	° K.	P.s.i.a.	Atm.	G./cc.	Lb./ft.^{3}
Dihydropyran	551.0 ± 1.5	1011.0	288.5	561.7	662 ± 7	45.0	0.314 ± 0.02	19.6
Tetrahydropyran	570.0 ± 0.5	1030.0	299.0	572.2	692 ± 2	47.1	0.328 ± 0.01	20.5
Isopropylamine	389.5 ± 0.5	849.5	198.7	471.9	660 ± 2	44.8	0.268 ± 0.002	16.73
Tertiary butylamine	411.0 ± 0.5	871.0	210.7	483.9	558 ± 2	37.9	0.250 ± 0.01	15.6
2-Picoline	658.0 ± 1.0	1118.0	347.9	621.1	667 ± 4	45.4	0.278 ± 0.02	17.4
4-Picoline	703.3 ± 0.5	1163.3	373.1	646.3	677 ± 2	46.0	0.286 ± 0.01	17.8
2-Methyl pyrazine	681.7 ± 1.0	1141.7	361.1	634.3	726 ± 4	49.4	0.333 ± 0.01	20.8
Dimethoxymethane	405.5 ± 1.5	865.0	207.4	480.6	574 ± 6	39.0	0.357 ± 0.02	22.3
n-Heptane	513.5 ± 0.5	973.5	267.6	540.8	400 ± 2	27.2	0.234 ± 0.002	14.61
Benzene	552.0 ± 0.5	1012.0	289.0	562.2	712 ± 2	48.4	0.316 ± 0.002	19.72

Third Parameters

Compound	Acentric Factor $\omega = (-\log P_R - 1.00)T_R =_{0.7}$	Critical Parameter $\alpha_c = (d \log P/d \log T)_T = _{T_c}$	Critical Compressibility $Z_c = P_cV_c/RT_c$
Dihydropyran	0.245	6.71	0.262
Tetrahydropyran	0.214	6.84	0.263
Isopropylamine	0.261	7.23	0.255
Tertiary butylamine	0.308	7.13	0.274
2-Picoline	0.292	7.27	0.297
4-Picoline	0.282	7.20	0.283
2-Methyl pyrazine	0.318	7.34	0.268
Dimethoxymethane	0.273	7.17	0.211

Table IV. Vapor Pressures

(Pressure in p.s.i.a. Temperature in ° R.)

Riedel's Equation

Compound	A	$-B$	$-C$	$D \times 10^{18}$	Temp. Range, ° R.
Dihydropyran	35.4674	5665.23	9.0945	0.2539	645–1011
Tetrahydropyran	26.9574	4925.81	6.4807	0.1592	650–1027.9
Isopropylamine	30.9525	4600.58	7.8192	0.4964	549–849.5
Tertiary butylamine	35.2702	5039.60	9.1725	0.5279	570–871
2-Picoline	21.6280	5012.44	4.7389	0.0640	724–1118
4-Picoline	35.2567	6664.74	8.7808	0.0898	754.6–1163.3
2-Methyl pyrazine	5.3795	3428.77	0.16176	0.0046	731–1141.7
cis-2,5-Dimethyl piperazine	16.9728	21032.0	49.029	0.6291	787–1096
Dimethoxymethane	26.0226	4283.54	6.2882	0.3740	567–865
Tertiary octylamine	16.9612	19671.7	49.508	0.9622	745–981

Clausius-Clapeyron Equation

	E	$-F$	Temp. Range, ° R.
1,1-Dimethyl hydrazine	6.04255	2923.06	660–760
Benzene	5.65750	2784.05	940–1010
n-Heptane	5.75280	3067.74	920–980
Trimethyl phosphite	5.68240	3085.66	760–890

Table V. Comparison of Experimental Critical Properties with Published Values

Compound	T_c, ° C.	P_c, Atm.	d_c, G./Cm.^{3}	Source
n-Heptane	267.0	27.0	0.235	Kobe and Lynn (*9*)
	267.0	27.0	0.232	Kudchadker *et al.* (*12*)
	267.6	27.2	0.234	This work
Benzene	289	48.6	0.300	Kobe and Lynn (*9*)
	288.94	48.34	0.302	Kudchadker *et al.* (*12*)
	289.0	48.4	0.316	This work
Dimethoxymethane	224			Kudchadker *et al.* (*12*)
	215.2			Bourgom (*3*)
	207.4			This work
2-Picoline	348			Kudchadker *et al.* (*12*)
	347.9			This work
4-Picoline	373			Kudchadker *et al.* (*12*)
	373.1			This work

temperatures and pressures, no attempt was made to determine either the extent of decomposition or the identity of the products of decomposition. All of the unstable compounds appeared to crack to lower-boiling products except trimethyl phosphite, which appeared to form higher-boiling products.

Values of the most commonly used third parameters, critical compressibility (Z_c), acentric factor (ω), and critical parameter (α_c) (*16*), are also given in Table III.

The rectilinear diameters for isopropylamine, *n*-heptane, and benzene are:

Isopropylamine

$$\frac{d_L + d_G}{2} = 0.487 - 2.576 \times 10^{-4}T \text{ (815 to 849.5° R.)}$$

***n*-Heptane**

$$\frac{d_L + d_G}{2} = 1.099 - 8.889 \times 10^{-4}T \text{ (955 to 973.5° R.)}$$

Benzene

$$\frac{d_L + d_G}{2} = 0.684 - 3.363 \times 10^{-4}T \text{ (980 to 1012° R.)}$$

where d_L and d_G are liquid and vapor density, respectively, in grams per cubic centimeter and T is in °R.

The vapor pressures of the compounds were correlated with Plank and Riedel's (*15*) vapor pressure equation

$$\log_{10}P = A + B/T + C \log_{10}T + DT^6$$

when data were obtained over a wide enough range for the constants to be properly determined. In the case of the compounds with narrow ranges of data, the vapor pressures were fitted to the Clausius-Clapeyron vapor pressure equation

$$\log_{10}P = E + \frac{F}{T}$$

over the range for which the data were consistent. In both cases, the method of least squares was used as the criterion of fit. Table IV presents the equation constants and the temperature range for which the equations are valid. With very few excepted points, these equations fitted the experimental vapor pressures within 1 p.s.i. The accuracy of the vapor pressure data is ±2 p.s.i.

COMPARISON WITH LITERATURE

Other published values of critical properties are available for some of the compounds studied in this work. These were summarized by Kobe and Lynn (*9*) and/or Kudchadker *et al.* (*12*). Table V shows a comparison of the present authors' values with the "selected values" of the two reviewers. One value for dimethoxymethane which was overlooked in the summaries was a critical temperature determination by Bourgom (*3*) of 215.2° C.

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