plus remain reasonably constant when the concentration of the heptanes-plus fraction is decreased by a factor of approximately 2. The effect of a decrease in the heptanes-plus fraction at the concentrations studied serves mainly to extend the pressure region over which these ratios are defined. This trend could be completely reversed with a continued decrease in the heptanes-plus concentration. Decreasing the amount of the heptanes-plus fraction in this system does have a slight effect on the equilibrium ratios of the intermediate components, ethane through hexanes; the net effect is a small increase at the higher pressures.

Figure 5 shows many interesting trends regarding the equilibrium ratios of different multicomponent systems. The data of other investigators have been cross plotted to yield values at 190° F. With the exception of the C and F mixture data of Standing and Katz (18), the procedure of cross plotting on semilog paper would introduce a relatively small amount of error.

The curves as numbered in Figure 5 generally show an increase in $\frac{\partial K}{\partial p}$, and a decrease in the rate at which they approach their respective "apparent convergence pressure". With the exception of Roland's distillate system, the moles of heptanes-plus per mole of remaining components decrease as the curve numbers increase. The low molecular weight of Roland's heptanes and heavier fraction could over-ride this factor. The molecular weight of the systems shows an increase with respect to curves 1, 2, 3, and 4. The molecular weight corresponding to curve 5 is slightly less than that corresponding to curve 4. Figure 4 compares the phase behavior of the mixtures represented by curves 2, 3, and 4, in Figure 5.

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Critical Properties and Vapor Pressures of Some Ethers and Heterocyclic Compounds

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This report, a continuation of previous work (11), supplies more data on critical properties of newer organic compounds, thus permitting the law of corresponding states to be used in estimating other properties of engineering importance.

Critical properties were determined for five ethers and eight heterocyclic compounds, using the apparatus and technique of the previous work.

Correlations and equations are given for the critical temperatures and pressures of the ethers, heterocyclic compounds, and ketones.

Many organic chemicals, heretofore of only academic interest, are now being produced in tonnage quantities. Frequently engineers need to estimate certain properties of these compounds that are basic to the design of research equipment, pilot plants, and commercial installations.

The law of corresponding states, first proposed by van der Waals, has been used by many investigators for the estimation and correlation of thermodynamic data; Nelson and Obert (14) gave a brief review of various forms that are in common use. One of the more important correlations based on this law are compressibility charts, the most recent of which was prepared by Nelson and Obert (15) from 30 gases. These charts show a maximum deviation of 1.0% in the region below the critical point. In pressure ranges where P_r = 1.0 to 10.0, the maximum deviation is 2.5%, while in the high pressure ranges where P_r = 10.0 to 40.0, the maximum deviation, based on 9 gases, is about 5%.

A knowledge of critical constants permits a correction for the effect of pressure on various thermodynamic properties such as enthalpy, entropy, heat capacity, and fugacity coefficients. The concept of the law of corresponding states is now being advanced toward the calculation of transport properties such as thermal conductivity (3) and diffusion coefficients (1). Attempts are being made to generalize some physical properties on the same basis (23).

A brief review of various methods for the determination of critical properties was given by Kobe and Lynn (9), who also tabulated critical values for many compounds.

APPARATUS

The apparatus (Figure 1) differs in some respect from that described by Kobe, Crawford, and Stephenson (11). Briefly, it consists of a high pressure bomb incased in an

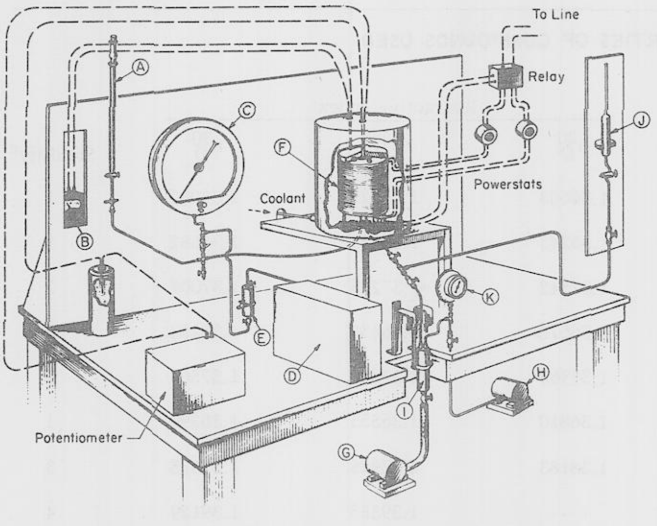

Figure 1. Apparatus for the determination of vapor pressures and critical properties

aluminum block for heating and cooling, a thermocouple for measuring temperature, a Bourdon tube for measuring pressure, a mercury reservoir for changing the free volume (available to the sample) of the bomb, and a sample buret with lines for introducing a weighed portion of a compound to the bomb. Modifications of the previous apparatus (11) are:

1. A Fenwal Thermoswitch, mounted in the heating block and set to close at 700° F., operated a relay that turned off current to the cartridge heaters in order to prevent overheating of the bomb.
2. The 9-inch gage was replaced with a 16-inch Heise Bourdon gage, having a range of 0 to 1000 pounds/square inch, in 1 pound/square inch scale divisions. It is felt that this gage, properly calibrated with the dead-weight gage tester, will give readings to 0.3 pound/square inch.
3. The mercury buret, A, was connected to the system through a graded glass-to-Kovar seal. The sample buret, J, was connected similarly but with a polyethylene section retained for flexibility.

OPERATION

Filling the mercury system, determining the bomb volume, and introducing the sample were performed essentially as before (11). However, the testing of compounds was changed as follows:

After determining a point on the vapor pressure curve, the bomb was heated at a rate which raised its temperature 10° F. in 4 minutes; then the heat input was decreased so it was just less than the heat lost, and the system was allowed to come to equilibrium. The temperature and pressure, rising more and more slowly, finally reached constant values which persisted for a minute or two, then began to fall. Maximum temperatures and pressures were recorded, although they occurred as much as three minutes apart. In the initial region, the heat input was decreased so that the rise in temperature was 3° or 4° F. in two minutes; thus data points on the pressure-temperature diagram were closer together.

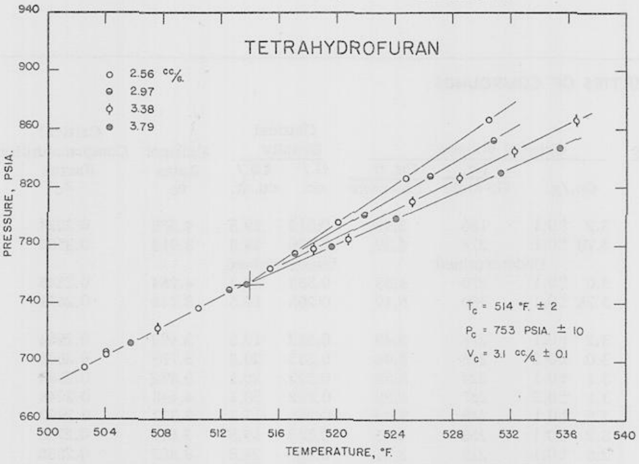

Figure 2. Critical point of tetrahydrofuran

Temperatures were corrected by a calibration curve obtained by determining the vapor pressure curve of deaereated, triple-distilled water. Pressure measurements were corrected with a dead-weight gage tester calibration; further corrections were made for hydrostatic head, vapor pressure of mercury, and change of barometric pressure. Specific volume was corrected for thermal expansion of the steel bomb and the mercury it contained.

When behavior of the sample indicated that appreciable decomposition had taken place, fresh samples were introduced and heated directly to the critical region in order to check on previous data.

Data for tetrahydrofuran (Figure 2) were plotted by the method of Ipatieff and Monroe (8).

PURIFICATION OF COMPOUNDS

Prior to purification, the compounds were treated with Drierite in order to remove any water which might be present, and those suspected of containing peroxides were treated with ferrous sulfate. The samples were distilled and 80% heart cuts were taken three times in columns

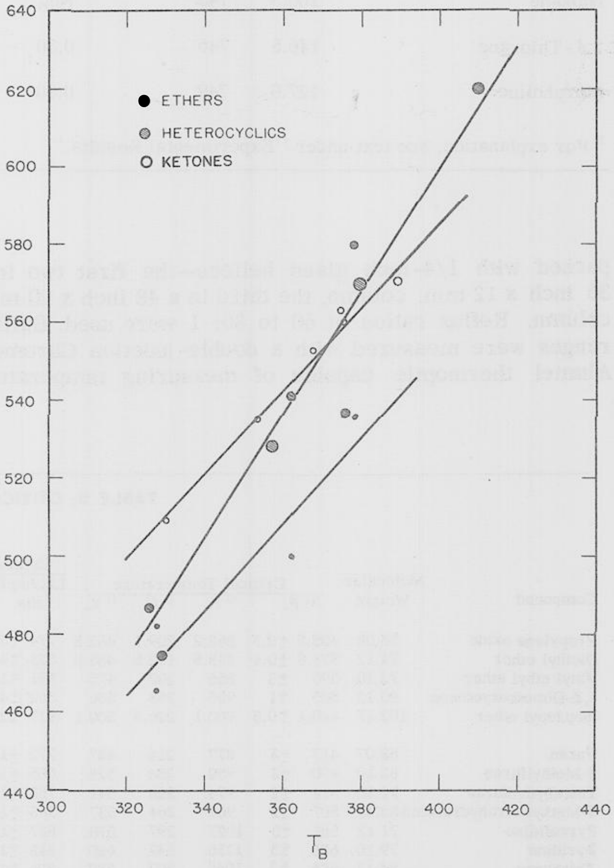

Figure 3. Correlation of critical temperature and normal boiling point

TABLE I. PHYSICAL PROPERTIES OF COMPOUNDS USED

Compound	Boiling Point ° C.	Boiling Point Mm. Hg	Boiling Range, ° C.	Refractive Index n_D^{20}	Refractive Index n_D^{25}	Refractive Index n_D^{30}	Stability[a]
Propylene oxide	33.9	754	0.05	1.36603	1.36322	1.36082	1
Diethyl ether	34.2	753	0.02	1.35243	1.34955	1.34682	1
Vinyl ethyl ether	35.4	747	0.05	1.37542	1.37288	1.37009	2
Dimethyl acetal	63.8	751	0.03	1.36678	1.36435	1.36183	3
1, 2-Dimethoxy ethane	84.6	756	Neg.	1.37963	1.37811	1.37505	2
Isopropyl ether	68.1	753	0.02	1.36810	1.36553	1.36290	1
Ethyl butyl ether	91.2	742	0.02	1.38183	1.37928	1.37685	3
Vinyl isobutyl ether	82.4	746	0.04	....	1.39385	1.39129	4
n-Butyl ether	139.7	752	0.09	1.39921	1.39683	1.39467	3
Furan	30.7	754	0.02	1.42161	1.41871	1.41562	2
2-Methylfuran	63.6	744	0.10	1.43492	1.43236	1.42889	2
Tetrahydrofuran	65.5	748	0.02	1.40716	1.40496	1.40252	1
2-Methyltetrahydrofuran	79.4	751	0.03	1.40751	1.40508	1.40270	2
Pyrrole	127.3	750	Neg.	1.50859	1.50641	1.50422	3
Pyrrolidine	85.8	748	0.12	1.44276	1.44025	1.43801	2
Pyridine	114.5	748	0.02	1.50915	1.50696	1.50460	2
Thiophene	83.2	744	0.01	1.52766	1.52038	1.52218	2
Dioxane	100.5	745	Neg.	1.42120	1.41923	1.41720	2
1,4-Thioxane	146.5	746	0.30	1.50706	....	....	4
Morpholine	127.0	749	0.30	1.45408	1.45212	1.45010	4

[a] For explanation, see text under "Experimental Results."

packed with 1/4-inch glass helices—the first two in a 36 inch x 12 mm. column, the third in a 48 inch x 20 mm. column. Reflux ratios of 60 to 80: 1 were used. Boiling ranges were measured with a double-junction Chromel-Alumel thermopile capable of measuring temperature differences of the order 1/80° C. Boiling temperatures were measured with National Bureau of Standards calibrated thermometers.

Physical properties of the compounds used are given in Table I.

TABLE II. CRITICAL PROPERTIES OF COMPOUNDS

Compound	Molecular Weight	Critical Temperature				Critical Pressure		Critical Volume			Critical Density		Critical Ratio	Critical Compressibility Factor
		° F.	° R.	° C.	° K.	Lb./sq.in. abs.	Atm.	Cc./g.	Cc. / G.-mole	Cu. ft. / Lb.-mole	G./ cc.	Lb./ cu. ft.	r_c	z_c
Propylene oxide	58.08	408.5 ±0.7	868.2	209.1	482.3	714 ±5	48.6	3.2 ±0.1	186	2.98	0.312	19.5	4.378	0.2284
Diethyl ether	74.12	378.8 ±0.4	838.5	192.6	465.8	523 ±4	35.6	3.70 ±0.1	274	4.39	0.270	16.8	3.918	0.2552
Vinyl ethyl ether	72.10	396 ±3	856	202	475	591 ±10	40.2	Undetermined			Undetermined		..	..
1,2-Dimethoxyethane	90.12	505 ±1	965	263	536	562 ±4	38.2	3.0 ±0.1	270	4.33	0.333	20.8	4.264	0.2345
Isopropyl ether	102.17	440.4 ±0.3	900.1	226.9	500.1	417 ±2	28.4	3.78 ±0.1	386	6.19	0.265	16.5	3.744	0.2671
Furan	68.07	417 ±3	877	214	487	772 ±15	52.5	3.2 ±0.1	218	3.49	0.312	19.5	3.492	0.2864
2-Methylfuran	82.10	490 ±3	950	254	528	685 ±15	46.6	3.0 ±0.2	246	3.94	0.333	20.8	3.779	0.2646
Tetrahydrofuran	72.10	514 ±2	974	268	541	753 ±10	51.2	3.1 ±0.1	224	3.58	0.322	20.1	3.872	0.2583
2-Methyltetrahydrofuran	86.13	507 ±2	967	264	537	545 ±10	37.1	3.1 ±0.2	267	4.28	0.322	20.1	4.448	0.2248
Pyrrolidine	71.12	567 ±3	1027	297	570	827 ±15	56.3	3.5 ±0.1	249	3.99	0.286	17.8	3.337	0.2997
Pyridine	79.10	656 ±3	1116	347	620	818 ±15	55.6	3.2 ±0.1	253	4.05	0.312	19.5	3.617	0.2765
Thiophene	84.13	585 ±2	1045	307	580	826 ±10	56.2	2.6 ±0.1	219	3.51	0.385	24.0	3.867	0.2586
Dioxane	88.10	598 ±2	1058	315	588	755 ±10	51.4	2.7 ±0.1	238	3.81	0.370	23.1	3.943	0.2536

TABLE III. VAPOR PRESSURES OF SOME ETHERS AND HETEROCYCLIC COMPOUNDS

ETHERS

Temp., °F.	Vapor pressure, lb./sq. inch abs.							
	Propylene oxide	Diethyl	Vinyl ethyl	Dimethyl acetal	1, 2-Dimethoxyethane	Isopropyl	Ethyl butyl	n-Butyl
160		47						
170		54						
180		62						
190	77	72						
200	87	82	78					
210	98	94	90					
220	112	106	102					
230	126	120	115	58				
240	142	134	129	64				
250	160	151	145	73				
260	178	168	163	82	48		44	
270	200	187	182	93	56		50	
280	223	207	201	105	64		56	
290	247	230	223	118	73		63	
300	273	253	246	132	82	116	71	
310	301	280	271	146	92	129	79	
320	330	308	300	163	103	143	89	
330	364	332	329	181	115	158	98	
340	401	369	361	199	128	174	108	
350	438	406	395	219	143	193	120	
360	479	444	433	242	158	212	132	
370	521	485	471	265	175	232	146	
380	567		513	290	193	253	160	
390	617		562	318	212	275	176	
400	668			347	233	298	193	
410					254	326	211	
420					278	356	231	
430					305	386	252	
440					333		275	
450					362		299	
460					394		324	117
470					429			130
480					462			142
490					506			154
500					548			166
510								181
520								197
530								214
540								232
550								251
560								272

HETEROCYCLIC COMPOUNDS

Temp., °F.	Vapor pressure, lb./sq. inch abs.								
	Furan	2-Methylfuran	Tetrahydrofuran	2-Methyltetrahydrofuran	Pyrrole	Pyrrolidine	Pyridine	Thiophene	Dioxane
200	91								
210	103								
220	117								
230	132	52							
240	148	60							
250	167	68	63						
260	188	78	74						
270	209	88	84						
280	233	100	96						
290	257	113	108						
300	284	129	121			77		70	
310	313	142	132	92		88		85	59
320	344	158	146	103		99		90	67
330	377	175	162	116		112		106	76
340	412	193	179	129		124		118	85
350	451	213	198	143	52	138	67	130	95

TABLE III. VAPOR PRESSURES OF SOME ETHERS AND HETEROCYCLIC COMPOUNDS (Contd.)
HETEROCYCLIC COMPOUNDS (Contd.)

Temp., °F	Furan	2-Methylfuran	Tetrahydrofuran	2-Methyltetrahydrofuran	Pyrrole	Pyrrolidine	Pyridine	Thiophene	Dioxane
	Vapor pressure, lb./sq. inch abs.								
360	492	234	218	158	58	153	73	144	106
370	535	257	240	176	66	170	82	158	117
380	580	282	258	195	74	187	92	174	131
390	628	308	288	213	83	206	102	191	144
400	678	337	313	233	94	227	113	209	159
410	727	366	341	255	106	248	126	230	175
420		399	370	277	117	272	138	250	192
430		434	402	301	130	296	152	272	209
440		469	436	326	144	323	168	296	229
450		507	472	353	157	352	184	321	250
460		547	509	372	172	382	200	348	272
470		590	549	413	190	413	217	376	296
480		636	592	444	209	442	237	406	321
490		685	637	469	227	483	256	437	348
500			683	516	249	520	277	470	377
510			733		271	559	300	504	406
520					295	601	324	541	443
530						646	348	580	473
540						693	376	617	509
550						742	405	659	545
560						792	435	702	586
570							462	747	629
580							499	793	667
590							533		716
600							572		
610							612		
620							650		
630							693		
640							738		
650							788		

EXPERIMENTAL RESULTS

Although pressure existing in the bomb may be determined within 0.3 pound/square inch, some points on vapor pressure curves deviate by as much as 2 or 3 pounds/square inch. These deviations are probably caused by a nonuniform approach to equilibrium plus instability and impurity of the sample. Because the isometric curves, when plotted as in Figure 2, break away from the vapor pressure curve in the critical region at very small angles, a small error in an important point may be magnified many times in the values of critical properties. Therefore, conservative estimates of accuracy have been made.

For the compounds used in this investigation, no attempt was made to determine either the extent of decomposition or the identity of products resulting therefrom. However, with respect to stability, the compounds may be classified into four groups (Table I):

1. Those which were stable and needed no allowance for decomposition.
2. Those whose decomposition, though appreciable, did not prevent determination of the critical point.
3. Those unstable at higher temperatures, so that only vapor pressure data well below the critical region were obtained.
4. Those so unstable that no reliable pressure volume-temperature data were obtained.

Critical properties are given in Table II. Vapor pressures (Table III) are generally accurate to ±2 pounds/square inch; for vinyl ethyl ether and the heterocyclics at higher temperatures, however, the accuracy is probably ± 4 pounds/square inch. Table IV compares results of this work with those of other investigators.

CORRELATIONS OF CRITICAL PROPERTIES

Because many compounds decompose at temperatures and pressures below the critical point, it is important that methods of estimating the critical properties be available. A resume of various correlations has been given by Kobe and Lynn (10).

A popular correlation of critical temperature is that of Meissner and Redding (13)

$$T_c = 1.027\ T_b + 159 \qquad (1)$$

where, in degrees Kelvin, T_c is critical temperature and T_b is normal boiling point.

Riedel (18, 19) in 1949 proposed a method of obtaining the critical constants by adding the contributions assigned to different atoms and groups. Lydersen (7, 12) extended this procedure and proposed

$$\frac{T_b}{T_c} = 0.567 + \Sigma\Delta_T - \left(\Sigma\Delta_T\right)^2 \qquad (2)$$

where $\Sigma\Delta_T$ is a summation of group contributions.

The form

$$\frac{T_b}{T_c} = a + bT_b \qquad (3)$$

TABLE IV. COMPARISON OF EXPERIMENTAL WITH PUBLISHED VALUES

Compound	T_c, °C.	P_c, atm.	D_c, G./cc.	Reference
Diethyl ether	193.4	34.98	0.265	(22)
	194.6	35.6	0.265	(21)
	192.3	. .	. .	(2)
	192.7	35.6	0.270	This work
Pyridine	344.2	. .	. .	(17)
	. .	60.0	. .	(5)
	347	55.6	0.312	This work
Thiophene	302.7	55.0	. .	(20)
	317.3	47.7	. .	(16)
	307	56.2	0.385	This work
Dioxane	312	50.7	0.36	(6)
	314	51.4	0.37	This work

has been suggested by Varshni (24); it is equivalent in form to that of Meissner and Redding,

$$\frac{1}{T_c} = (a)\left(\frac{1}{T_b}\right) + b \qquad (4)$$

which uses reciprocals and gave slightly better results than that of Varshni. The method of least squares applied to the experimental data produced for the two groups of compounds (Figure 3), the equations

$$\text{Ethers} \qquad T_c = 1.111\ T_b + 130.9 \qquad (5)$$

$$\text{Heterocyclics} \qquad T_c = 1.570\ T_b + 2.8 \qquad (6)$$

The equation previously determined (11) for ketones (Figure 3) is

$$T_c = 1.0788\ T_b + 155.3 \qquad (7)$$

and the probable error assigned to its experimental value is indicated by the relative size of the datum point. Table V compares experimental values with results obtained from the correlations of Meissner and Redding and of Lydersen.

Correlations of critical pressure appear to be mainly of two types: those containing other critical properties as parameters, and group contribution methods. Meissner and Redding's equation is

$$P_c = 20.8\ T_c / (V_c - 8) \qquad (8)$$

where P_c is critical pressure in atmospheres and V_c is critical volume in cubic centimeters per gram mole.

Lydersen's correlation is

$$\sqrt{M/P_c} = 0.34 + \Sigma\Delta p \qquad (9)$$

where M is molecular weight and $\Sigma\Delta p$ is a summation of group contributions.

A simple equation was desired which would not contain V_c; it is the critical constant least accurately measured and also has not been correlated accurately. The form

$$\frac{T_c}{MP_c} = C \qquad (10)$$

where C is a constant was suggested by Grunberg (4). The best results were obtained by adding another constant, and equations for three groups of compounds using the method of least squares (Figure 4) were determined:

$$\text{Ethers} \qquad P_c = 5.732\ \frac{T_c}{M} + 1.492 \qquad (11)$$

$$\text{Heterocyclics} \qquad P_c = 7.459\ \frac{T_c}{M} - 2.044 \qquad (12)$$

$$\text{Ketones} \qquad P_c = 4.538\ \frac{T_c}{M} + 7.666 \qquad (13)$$

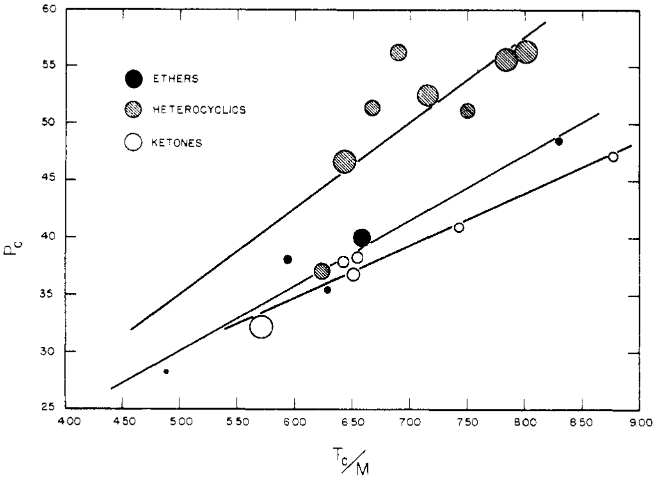

Figure 4. Correlation for critical pressure

TABLE V. CORRELATIONS OF CRITICAL TEMPERATURE

Compound	Experimental, T_c, °K.	Authors' Correlation T_c, °K.	Authors' Correlation Dev., %	Meissner and Redding T_c, °K.	Meissner and Redding Dev., %	Lydersen T_c, °K.	Lydersen Dev., %
Propylene oxide	482.3	472.3	-2.07	474.8	-1.55	494.7	2.67
Diethyl ether	465.8	472.7	1.48	474.9	1.95	467.8	0.43
Vinyl ethyl ether	475	474.3	-0.15	476.4	0.29	471.2	-0.80
1,2-Dimethoxyethane	536	528.7	-1.36	526.7	-1.73	530.7	-0.99
Isopropyl ether	500.1	510.6	2.10	510.0	1.98	505.9	1.16
	Av. Deviation		1.43%		1.50%		1.21%
Furan	487	482.3	-0.96	472.7	-2.94	490.7	0.76
2-Methylfuran	528	531.9	0.74	505.2	-4.14	527.2	-0.15
Tetrahydrofuran	541	539.0	-0.36	507.1	-6.26	539.3	-0.32
2-Methyltetrahydrofuran	537	560.8	4.43	519.1	-3.33	539.2	0.41
Pyrrolidine	570	567.2	-0.49	528.3	-7.32	559.4	-1.86
Pyridine	620	614.6	-0.87	559.3	-9.89	621.9	0.31
Thiophene	580	564.5	-2.67	526.6	-9.20	579.9	-0.02
Dioxane	588	590.3	0.39	543.4	-7.58	584.4	-0.61
	Av. Deviation		1.36%		6.33%		0.56%

TABLE VI. CORRELATIONS OF CRITICAL PRESSURE

Compound	Experimental, P_c, atm.	Authors' Correlation P_c, atm.	Authors' Correlation Dev., %	Lydersen P_c, atm.	Lydersen Dev., %
Propylene oxide	48.6	49.10	1.03	51.40	5.76
Diethyl ether	35.6	37.52	5.39	37.39	5.03
Vinyl ethyl ether	40.2	39.26	-2.34	39.56	-1.59
1,2-Dimethoxyethane	38.2	35.59	-6.83	36.66	-4.03
Isopropyl ether	28.4	29.54	4.01	30.58	7.68
		Av. Deviation	3.92%		4.82%
Furan	52.5	51.32	-2.25	58.79	11.98
2-Methylfuran	46.6	45.93	-1.44	48.35	3.76
Tetrahydrofuran	51.2	53.92	5.31	50.41	-1.54
2-Methyltetrahydrofuran	37.1	44.46	19.84	42.06	13.37
Pyrrolidine	56.3	57.74	2.56	48.48	-13.89
Pyridine	55.6	56.42	1.47	51.43	-7.50
Thiophene	56.2	49.38	-12.14	58.83	4.68
Dioxane	51.4	47.74	-7.12	50.87	-1.03
		Av. Deviation	6.52%		7.22%

Equation 13 gives average and maximum deviations only slightly greater than those given by the equation

$$P_c = a/M + b \qquad (14)$$

used by Kobe and coworkers (11) for ketones. Equation 14 gave poor correlations for the critical pressures of ethers and heterocyclics.

Table VI compares experimental values, correlations by equations 10 and 11, and Lydersen's correlation.

The correlations developed here are of the form usually applied to homologous series. The ethers and heterocyclics tested cannot be regarded as members of such series; therefore, these correlations are less accurate than those which might be developed if critical properties of several members of an homologous series were known. Group contribution methods seen most promising. Lyderson states that many of his group contributions are based on insufficient data for accuracy. More experimental data, as given here, should improve this method.

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Benedict Equation of State

Methane–n-Pentane System

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Equations of state find industrial application in predicting the thermodynamic properties of fluids.

Coefficients for the Benedict equation of state were determined by least squares methods from experimental data for mixtures of the methane-n-pentane system. Values were obtained for the interaction constants for groupings of the Benedict coefficients corresponding to the second and third virial coefficients.

In the liquid and gas phases at pressures up to 5000 pounds per square inch between 100° and 460° F. the accuracy of description of the volumetric behavior was improved severalfold by use of interaction constants evaluated by least squares methods over constants calculated by the method suggested by Benedict. Such methods may prove useful in evaluating interaction constants for mixtures as a function of the characteristics of the system involved.

Benedict, Webb, and Rubin (3-7) developed an empirical equation of state which describes the volumetric behavior of gaseous hydrocarbons with satisfactory accuracy at pressures up to 4000 pounds per square inch and gives a good prediction of the phase behavior of many hydrocarbon mixtures. Brough, Schlinger, and Sage (8) proposed an analytical method based on least squares techniques for evaluating the coefficients, which extended earlier proposals of Benedict (2). Selleck, Opfell, and Sage (15) extended the application of this equation for propane to pressures up to 10,000 pounds per square inch in the temperature interval between 40° and 460° F. and included a description of the behavior of the liquid phase. Similarly Opfell (12, 13) evaluated coefficients of the Benedict equation for nine of the lighter hydrocarbons from methane through n-decane for describing the volumetric behavior in both the liquid and gas phases for the range of pressures and temperatures covered by Selleck (15). The coefficients suggested by

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