molecules, and a residual contribution, due to energetic interactions between groups:

$$\ln \gamma_i = \ln \gamma_i^{S} + \ln \gamma_i^{G} \tag{16}$$

$$\ln \gamma_i^{S} = \ln \gamma_i(\text{comb}) \qquad (\text{UNIQUAC equation}) \tag{17}$$

$$\ln \gamma_i^{G} = \sum_{k=1}^{NG} \upsilon_{ki}(\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{18}$$

Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i:

$$\ln \Gamma_k = Q_k [1 - \ln (\sum_{m=1}^{NG} \theta_m \psi_{mk}) - \sum_{m=1}^{NG} \frac{\theta_m \psi_{km}}{\sum_{j=1}^{NG} \theta_j \psi_{jm}} \tag{19}$$

$$\theta_m = \frac{Q_m X_m}{\sum_{j=1}^{NG} Q_j X_j} \tag{20}$$

$$X_j = \frac{\sum_{i=1}^{N} \upsilon_{ji} x_i}{\sum_{i=1}^{N} \sum_{m=1}^{NG} \upsilon_{mi} x_i} \tag{21}$$

$$\psi_{mk} = \exp\left[-\frac{U_{mk} - U_{kk}}{RT}\right] = \exp\left[-\frac{a_{mk}}{T}\right] \tag{22}$$

X_m is the fraction of group m in the mixture. The parameters a_{mk} and a_{km} characterize the interactions between groups m and k.

Glossary

A, B	method of correlation of ternary data (Table VI)
a_{ij}	UNIFAC group interaction parameter, K
b_{ij}	NRTL parameter, K
c_{ij}	UNIQUAC parameter, K
g_{ij}, u_{ij}	measure of the interaction energy between molecules i and j
F_1, F_2	objective functions
q_i	pure component area parameter of component i
Q_k	group-area parameter for group k
r_i	pure component volume parameter of component i
R_k	group-volume parameter of group k
R	gas-law constant
x_{ij}	molar fraction of component i in phase j
X_{ij}	weight fraction of component i in phase j
X_k	group fraction of group k
rmsd	root-mean-square deviation
z	lattice coordination number (equal to 10)

Greek Letters

α_{ij}	nonaleatory NRTL parameter
γ_i	activity coefficient of component i
Γ_k	activity coefficient of group k
$\Gamma_k^{(i)}$	activity coefficient of group k in pure component i
ϕ_i	segment fraction of component i
υ_{ki}	number of groups of type k in molecule i
ϑ_i	area fraction of component i
θ_k	area fraction of group k
τ_{ij}	NRTL of UNIQUAC parameter
ψ_{nm}	UNIFAC parameter

Registry No. PFD, 306-94-5; 1-heptene, 592-76-7; *n*-heptane, 142-82-5; *n*-hexane, 110-54-3.

Literature Cited

(1) Bernardo-Gil, G. S.; Soares, L. J. S. *J. Chem. Eng. Data* **1987**, *32*, 327.
(2) Soares, L. J. S.; Ashton, N. P.; Ellis, S. R. M. *Proceedings of ISEC'74*, *Lyon*, 1974; Vol. 2, p 1813.
(3) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(4) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(5) Fredenslund, A.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(6) Bernardo-Gil, M. G.; Soares, L. J. S. *Fluid Phase Equilib.* **1986**, *25*, 291.
(7) Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.

Received for review March 28, 1988. Accepted October 12, 1988.

Estimation Procedures for Critical Constants

G. Raam Somayajulu

Thermodynamics Research Center, Texas A&M University, College Station, Texas 77843-3111

The procedures developed by Riedel, Lydersen, and Ambrose for the calculation of critical constants of organic compounds have been reexamined, and new procedures are proposed in terms of group indices. These procedures are combined with the procedures developed by Kreglewski for the calculation of critical constants of homologous series of compounds. The treatment has also been extended to inorganic compounds.

Introduction

The knowledge of critical constants is important in the field of chemical process design in extrapolating, for example, the vapor pressures from the normal boiling point to the critical temperature (*1*). The procedures for the estimation of critical constants of organic compounds have been reviewed by several authors (*2*–*6*). Among such procedures, the procedures developed by Lydersen (*7*), Ambrose (*8*–*10*), and Kreglewski (*11*–*13*) have gained general recognition. They are noted for their simplicity and general accuracy. While the procedures developed by Lydersen and Ambrose yield satisfactory results for organic compounds of low molecular weight, the procedures developed by Kreglewski yield satisfactory results to homologous series of compounds, in general, of high molecular weight. We therefore propose to review these procedures and propose modified procedures for the calculation of critical constants. With this goal in mind we now introduce the following symbols.

0021-9568/89/1734-0106$01.50/0

T_b = normal boiling temperature

T_c = critical temperature

P_c = critical pressure

V_c = critical volume

M = molar mass

MW = molecular weight or relative molecular mass

$F_t = T_b/T_c$

$G_t = T_b/(T_c - T_b)$

$G_p = (M/P_c)^{1/2}/(\text{g mol}^{-1}\ \text{bar}^{-1})^{1/2}$

$G_v = V_c/(\text{cm}^3\ \text{mol}^{-1})$

$\Delta_t(X)$ = contribution of group X to F_t or G_t

$\Delta_p(X)$ = contribution of group X to G_p

$\Delta_v(X)$ = contribution of group X to G_v

n_t = temperature index of group X = $\Delta_t(X)/\Delta_t(-CH_3)$

n_p = pressure index of group X = $\Delta_p(X)/\Delta_p(-CH_3)$

n_v = volume index of group X = $\Delta_v(X)/\Delta_v(-CH_3)$

N_t = temperature index of a molecule = $\sum n_t$

N_p = pressure index of a molecule = $\sum n_p$

N_v = volume index of a molecule = $\sum n_v$

$N_t = N_p = N_v = N$ for normal alkanes

N = number of carbon atoms in the alkane molecule

$T_\infty{}^c$ = critical temperature when N tends to infinity = 960 K

$\sum \Delta_t = b_t \sum n_t = b_t N_t$

$\sum \Delta_p = b_p \sum n_p = b_p N_p$

$\sum \Delta_v = b_v \sum n_v = b_v N_v$

N_1 = the number of $-CH_3$ groups

N_2 = the number of $>CH_2$ groups

N_3 = the number of $>CH-$ groups

N_4 = the number of $>C<$ groups

N_g = the number of gauche C–C–C–C structural features

Riedel (*14–17*) proposed eq 1, 3, 4, and 5 for the estimation of the critical properties. Equation 2 is a modification of eq 1 by Lydersen. Eq 3 was applied by Riedel to alkanes, but Ambrose extended it to various classes of organic compounds. Both Lydersen and Ambrose gave revised group constants for eq 4 and 5. Equations 1–3 for the estimation of critical temperature are fairly accurate for compounds of low molecular weight.

$$F_t = a_t + \sum \Delta_t \tag{1}$$

$$F_t = a_t + \sum \Delta_t - (\sum \Delta_t)^2 \tag{2}$$

$$G_t = \sigma_t + \sum \Delta_t \tag{3}$$

$$G_p = a_p + \sum \Delta_p \tag{4}$$

$$G_v = a_v + \sum \Delta_v \tag{5}$$

Equations 6–8 have been developed by Kreglewski for the estimation of the critical constants in homologous series of compounds.

$$\log((T_\infty{}^c - T_c)/\text{K}) = a_t - b_t N^{2/3} \tag{6}$$

$$\log(P_c/\text{bar}) = a_p - b_p N^{2/3} \tag{7}$$

$$V_c/(\text{cm}^3\ \text{mol}^{-1}) = a_v + b_v(N + N^{2/3}) \tag{8}$$

The equations developed by Kreglewski for critical temperature and critical pressure have some theoretical support. Kreglewski's equation for critical volume, however, differs significantly from the others and is not supported by experiment. The presence of $N^{2/3}$ in eq 8 lacks justification. We are, therefore, not in favor of using eq 8.

Kreglewski's equations, which are intended to apply to homologous series of compounds, employ the carbon number instead of the group contributions. In dealing with homologous series of compounds, it is advantageous to use carbon numbers instead of group contributions in the equations developed by Riedel, Lydersen, and Ambrose. In order to treat these equations on a common basis, we introduce an entity called the group index, n_i, defined as

$$n_i(X) = \Delta_i(X)/\Delta_i(-CH_3) \tag{9}$$

where i stands for t, p, or v. The molecular index N_i is obtained by the summation of the relevant group indices. If we now set $b_i = \Delta_i(-CH_3)$ and substitute $\sum \Delta_i$ by $b_i N_i$, it is possible to transform eq 1–5 into eq 10–14.

$$F_t = a_t + b_t N_t \tag{10}$$

$$F_t = a_t + b_t N_t - b_t^2 N_t^2 \tag{11}$$

$$G_t = a_t + b_t N_t \tag{12}$$

$$G_p = a_p + b_p N_p \tag{13}$$

$$G_v = a_v + b_v N_v \tag{14}$$

The molecular indices are to be calculated from the group indices listed in Table I. The group indices are obtained on the basis of the group contributions listed by both Lydersen and Ambrose in many cases. The Lydersen scheme is followed more closely in treating the unsaturated compounds. For groups such as $-C_6H_5$, $-CF_3$, etc. the indices given are built up from the indices of their consistuents listed in the same table. Such values are also listed for the convenience of the user although it increased the number of entries by 60. A few of the group indices have no experimental basis, and they are estimated on the basis of the values for similar groups and are given only to two decimal places. We shall have to revise some of these group indices when experimental values become available. It can be seen that, for normal alkanes, we have $N_t = N_p = N_v = N$ = the number of carbon atoms in the alkane molecule. We also have the advantage of using the same set of molecular indices in eq 10–12 involving the critical temperature. The constants a_i's and b_i's of eq 10–14 are recorded Table II.

Method of Calculation

We assume that the molecular indices and the critical constants will be calculated on a computer rather than on a hand calculator. The procedure followed by the author is therefore outlined below. The Fortran program written by this author requires two input files called index.inp and crit.inp. The file called index.inp contains the group numbers and the group indices for all the groups listed in Table I. The crit.dat file say

Table I. Group Indices for Calculation of Critical Constants

no.	group	n_t	n_p	n_v
1	$-CH_3$	1.000	1.000	1.000
2	$>CH_2$	1.000	1.000	1.000
3	>CH–	0.849	1.079	0.970
4	>C<	0.494	1.104	0.987
5	C–C–C–C (gauche)	–0.197	–0.133	–0.086
6	$-CH_2-$ (ring)	0.640	0.805	0.809
7	>CH– (ring)	0.640	0.805	0.809
8	>C< (ring)	0.420	0.805	0.809
9	>CH– (fused ring)	0.250	0.625	0.809
10	$=CH_2$	0.900	0.900	0.820
11	=CH–	0.800	0.800	0.780
12	=C<	0.800	0.800	0.780
13	=C=	0.400	0.600	0.400
14	trans alkene	–0.200	–0.150	0.000
15	=CH– (ring)	0.542	0.681	0.672
16	=C< (ring)	0.542	0.681	0.653
17	=C< (fused ring)	0.250	0.460	0.653
18	≡CH	1.180	0.690	0.635
19	≡C–	0.680	0.540	0.635
20	phenyl substitution[a]	–1.000	–1.000	0.000
21	isopropyl	2.849	3.079	2.970
22	isobutyl	3.849	4.079	3.970
23	*sec*-butyl	3.652	3.946	3.884
24	*tert*-butyl	3.494	4.104	3.987
25	isopentyl	4.652	4.946	4.884
26	neopentyl	4.494	5.104	4.987
27	cyclobutyl	2.560	3.220	3.236
28	cyclopentyl	3.200	4.025	4.045
29	cyclohexyl	3.840	4.830	4.854
30	phenyl	3.252	4.086	4.032
31	naphthyl	4.836	6.368	6.682
32	vinyl	1.700	1.700	1.600
33	allyl	2.600	2.600	2.560
34	–OH (water)	0.870	–0.236	0.290
35	–OH (methanol)	4.000	0.284	0.290
36	–OH (ethanol)	4.670	0.360	0.290
37	–OH (propanol)	4.080	0.280	0.290
38	–OH (butanol)	3.490	0.200	0.290
39	–OH (pentanol)	2.900	0.120	0.290
40	–OH (hexanol)	2.310	0.040	0.290
41	–OH (heptanol)	1.720	–0.040	0.290
42	–OH (octanol)	1.130	–0.120	0.290
43	–OH (phenols)	1.530	–0.100	–0.014
44	–OH and X (ortho)[b]	–0.340	–0.100	0.000
45	X and Y (ortho)[c]	–0.100	–0.100	0.000
46	X and Y (meta)[d]	0.200	0.100	0.000
47	C–C–C–OH (gauche)	–0.500	0.000	0.000
48	–O– (nonring)	0.870	0.710	0.363
49	–O– (ring)	0.800	0.710	0.363
50	>CO (nonring)	2.300	1.250	1.070
51	C–C–C=O	–0.500	0.000	0.000
52	>CO (ring)	3.300	1.540	1.100
53	–CHO	2.800	1.250	1.070
54	–C–C–CHO	–0.500	0.000	0.000
55	–CHO (aromatic)	1.250	1.100	1.070
56	–COOH	4.000	2.000	1.360
57	C–C–COOH	0.400	0.000	0.000
58	–COO– (formates)	2.100	2.080	1.433
59	–COO– (others)	2.400	2.080	1.433
60	–COO– (aromatic)	2.200	2.080	1.433
61	–CO–O–CO–	8.200	3.035	2.503
62	=O (oxides)[e]	1.000	0.660	0.290
63	$-NH_2$	1.700	0.420	0.580
64	–NH– (nonring)	1.500	0.420	0.580
65	–NH– (ring)	1.000	0.260	0.580
66	>N– (nonring)	0.600	0.800	0.580
67	$-NH_2$ (aromatic)	1.500	0.280	0.580
68	>NH (aromatic)	1.500	0.280	0.580
69	>N– (aromatic)	1.500	0.500	0.580
70	>N– (ring)	0.050	0.260	0.580
71	=N– (general)	0.542	0.355	0.580
72	N(V)	–0.400	0.040	0.580
73	–CN (normal)	3.000	1.580	1.450
74	–CN (aromatic)[f]	1.800	1.330	1.450
75	$-NO_2$	2.700	2.000	1.420
76	$-CONH_2$	4.000	1.670	1.650
77	$-ONH_2$	2.600	1.130	0.943
78	≡N	1.250	1.260	0.900
79	HN (nonbonded)[g]	2.000	–0.135	0.000
80	–SH	0.650	1.200	1.000
81	–S– (nonring)	0.760	1.200	1.000
82	–S– (ring)	0.460	1.130	0.570
83	=S	0.260	1.200	1.000
84	S(IV)	0.400	1.200	1.000
85	S(VI)	0.800	0.800	1.000
86	–F (aliphatic)	0.688	1.072	0.230
87	–Cl (aliphatic)	0.570	1.409	0.820
88	–Br (aliphatic)	0.570	2.800	1.150
89	–I (aliphatic)	0.570	4.068	1.620
90	–F (aromatic)	0.572	0.827	0.230
91	–Cl (aromatic)	0.642	1.400	0.820
92	–Br (aromatic)	0.642	2.800	1.150
93	–I (aromatic)	0.642	4.068	1.620
94	HF (nonbonded)	0.230	–0.130	0.000
95	HCl (nonbonded)	0.093	–0.040	0.000
96	HBr (nonbonded)	0.040	0.000	0.000
97	HI (nonbonded)	0.040	0.000	0.000
98	FCl (nonbonded)	0.070	0.000	0.000
99	FBr (nonbonded)	–0.030	0.000	0.000
100	FI (nonbonded)	–0.03	0.00	0.00
101	ClBr (nonbonded)	–0.030	0.000	0.000
102	ClI (nonbonded)	–0.05	0.00	0.00
103	BrI (nonbonded)	–0.05	0.00	0.00
104	FC (nonbonded)[h]	–0.230	–0.180	0.000
105	FC (nonbonded in ring and alkenes)[h]	–0.120	–0.140	–0.035
106	$-CF_3$ (normal)	3.064	4.216	1.690
107	$-CF_3$[h]	2.604	3.856	1.690
108	$>CHF_2$ (normal)	2.836	2.884	1.460
109	$>CHF_2$[h]	2.836	2.524	1.460
110	$>CH_2F$ (normal)	2.148	1.812	1.230
111	$>CF_2$ (normal)	2.376	3.144	1.460
112	$>CF_2$[h]	1.456	2.424	1.460
113	>CF– (normal)	1.688	2.072	1.230
114	>CF–[h]	0.998	1.532	1.230
115	$-CF_2-$ (ring)[h]	1.546	2.389	1.199
116	–CHF– (ring)[h]	1.328	1.467	0.969
117	>CF– (ring)[h]	–0.400	1.417	0.969
118	$=CF_2$ (normal)	2.276	3.044	1.269
119	$=CF_2$[h]	2.036	2.764	1.199
120	=CHF–[h]	1.698	1.702	1.015
121	=CF–[i]	1.138	1.522	1.015
122	$=CCl_2$[h]	1.800	3.438	2.390
123	=CHCl[h]	1.443	2.129	1.605
124	=CFCl[h]	1.988	3.101	1.800
125	=CF– (ring)[h]	1.095	1.508	0.902
126	$-CF_2Cl$ (normal)	3.086	4.553	2.280
127	$-CF_2Cl$[h]	2.626	4.193	2.280
128	$-CFCl_2$ (normal)	2.968	4.890	2.870
129	$-CFCl_2$[h]	2.508	4.530	2.870
130	$-CF_2Br$ (normal)	2.886	5.944	2.610
131	$-CF_2Br$[h]	2.426	5.584	2.610
132	–CRClBr[h]	2.378	5.921	2.610
133	$-CCl_3$ (normal)	2.710	5.227	3.460
134	$-CCl_3$[h]	2.250	4.867	3.460
135	$-CHCl_2$	2.326	3.738	2.640
136	$-CH_2Cl$	1.756	2.329	1.820
137	$-CH_2Br$	1.650	3.800	2.150
138	$-CHBr_2$	2.220	6.600	3.300
139	$-CH_2I$	1.650	5.068	2.620
140	Se(II)	0.400	2.700	1.500
141	Te(II)	0.800	3.600	1.600
142	Si(IV)	1.500	2.400	2.100
143	$-O-Si(CH_3)_2$	3.600	5.110	4.463
144	$-O-Si(C_2H_5)_2$	2.800	7.110	6.463
145	>Si< (ring)	0.800	2.400	2.100
146	C–C–Si–O	–0.900	0.000	0.000
147	Ge(IV)	2.000	3.200	2.000
148	Sn(IV)	2.000	4.500	2.400
149	Ti(IV)	1.200	1.800	2.100
150	Zr(IV)	14.000	1.800	2.200
151	Hf(IV)	20.000	3.600	2.200

Table I (Continued)

no.	group	n_t	n_p	n_v	no.	group	n_t	n_p	n_v
152	V(III)	1.700	1.800	2.200	166	B(III)	1.500	2.000	1.200
153	Nb(V)	2.000	1.800	2.200	167	Al(III)	6.000	4.000	1.500
154	Ta(V)	2.000	3.500	2.400	168	Ga(III)	5.000	4.000	1.500
155	Mo(VI)	0.500	2.000	2.900	169	P(III)	1.000	1.700	1.600
156	W(VI)	0.500	3.900	2.000	170	P(V)	0.750	1.700	1.600
157	Hg(II)	0.250	3.600	0.800	171	As(III)	1.000	1.500	1.400
158	B(III)	1.500	2.000	1.200	172	Sb(III)	0.750	1.500	1.800
159	Al(III)	6.000	4.000	1.500	173	Bi(III)	0.500	1.500	1.500
160	Ga(III)	5.000	4.000	1.500	174	U(VI)	0.500	4.200	2.400
161	P(III)	1.000	1.700	1.600	175	Re(VI)	0.500	4.200	2.500
162	P(V)	0.750	1.700	1.600	176	Os(VIII)	0.500	4.200	2.500
163	As(III)	1.000	1.500	1.400	177	–D	0.100	0.050	0.000
164	W(VI)	0.500	3.900	2.000	178	Xe(IV,VI)	0.900	2.000	1.500
165	Hg(II)	0.250	3.600	0.800	179	–H (partially ionic)	3.000	0.125	0.220

[a] Applies to benzene ring. [b] X stands for any group attached to an aromatic ring in the ortho position to a –OH group. [c] X and Y stand for any groups other than –OH in the ortho positions in aromatic compounds. Also, both X and Y should not be halogen atoms. [d] X and Y are any two groups in meta positions without any intervening groups in the middle. [e] Applies to oxides such as carbon dioxide, sulfur dioxide, sulfur trioxide, nitrous oxide, and dinitrogen tetraoxide. [f] These indices apply also to hydrogen cyanide, cyanogen, and trifluoroacetonitrile. See text for explanation. [g] Applies to hydrazine and its derivates. [h] Applies to perhalogenated compounds and 1-*H*-perfluoroalkanes, perhalogenated compounds, and some partially halogenated alkanes and alkenes as discussed in other footnotes. [i] Applies to perfluoroalkenes.

Table II. Values of the Constants

const	eq 10	eq 11	eq 12	eq 13	eq 14
a_i	0.567	0.567	1.242	0.339	40.00
b_i	0.020	0.020	0.138	0.226	55.00

Table III. Constants for Kreglewski's Equations[a]

homologous series	a_t	b_t	a_p	b_p
normal alkanes	6.805 31	0.209 01	4.309 98	0.272 96
1-alkenes	6.820 81	0.211 58	4.308 61	0.263 52
1-alkynes	6.746 17	0.197 50	4.588 60	0.306 21
1-alkylcyclopentanes	6.770 58	0.218 47	4.720 35	0.328 02
1-alkylcyclohexanes	6.784 67	0.224 72	4.712 20	0.326 47
1-alkylbenzenes	6.763 34	0.228 06	4.999 65	0.353 26
1-fluoroalkanes	6.680 17	0.186 36	4.257 91	0.275 10
perfluoroalkanes	6.731 31	0.149 75	3.833 99	0.277 85
1-chloroalkanes	6.540 85	0.194 61	4.339 24	0.284 01
1-bromoalkanes	6.440 39	0.192 51	4.371 40	0.286 62
1-iodoalkanes	6.333 11	0.197 75	4.370 84	0.281 28
1-alkanols	6.425 15	0.173 71	4.525 43	0.293 12
2-alkanols	6.560 48	0.194 29	4.406 09	0.267 99
1-alkanals	6.541 35	0.179 87	4.389 89	0.285 82
1-alkanoic acids	6.173 24	0.148 65	4.458 00	0.302 28
2-alkanones	6.522 27	0.178 24	4.494 83	0.303 13
normal alkyl methyl ethers	6.680 11	0.191 96	4.292 25	0.271 03
methyl alkanoates	6.517 98	0.191 96	4.292 25	0.278 53
ethyl alkanoates	6.485 12	0.174 00	4.145 86	0.250 23
normal alkyl methanoates	6.530 14	0.182 85	4.358 82	0.280 10
normal alkyl ethanoates	6.556 71	0.180 38	4.304 94	0.269 08
1-alkanamines	6.565 79	0.191 52	4.453 19	0.299 19
alkanenitriles	6.343 96	0.158 40	4.329 42	0.277 08
1-alkanethiols	6.462 43	0.194 99	4.396 12	0.292 20
2-thiaalkanes	6.546 63	0.212 68	4.337 77	0.277 04

[a] The coefficients for eq 6 are to be used with the value 960 K for the limiting critical temperature.

Table IV. Comparison of the Calculated Critical Temperatures of Normal Alkanes with Experimental Values

		T_c/K				
compound	T_b/K	obsd	eq 6	eq 10	eq 11	eq 12
methane	111.64	190.56	227.62	190.19	190.32	192.54
ethane	184.55	305.42	312.24	304.04	304.84	306.12
propane	231.05	369.85	375.62	368.50	370.63	370.57
butane	272.65	425.16	426.94	421.41	425.62	424.63
pentane	309.21	469.70	470.12	463.58	470.64	469.26
hexane	341.88	507.50	507.33	497.64	508.30	507.04
heptane	371.58	540.30	539.91	525.57	540.56	539.87
octane	398.82	568.83	568.78	548.58	568.61	568.82
nonane	423.97	594.61	594.61	567.56	593.30	594.65
decane	447.30	617.88	617.88	583.18	615.27	617.89
undecane	469.08	638.80	638.98	596.04	635.09	639.04
dodecane	489.47	658.20	658.20	606.53	653.15	658.37
tridecane	508.62		675.79	615.02	669.77	676.15
tetradecane	526.73	694.00	691.94	621.88	685.31	692.68
pentadecane	543.84		706.83	627.27	699.92	708.04
hexadecane	560.01	720.59	720.59	631.35	713.75	722.33
heptadecane	575.17		733.35	634.15	726.78	735.47
octadecane	590.22	745	745.19	636.70	740.18	748.63
nonadecane	603.68		756.22	637.47	752.16	759.91
icosane	617.15		766.50	638.21	764.75	771.36

for aniline requires the following input.

1. Compound id.: aniline
2. Molecular weight: 93.128
3. Normal boiling point: 457.6
4. Group number of the phenyl group: 30
5. Number of phenyl groups: 1
6. Group number of the -CN group: 67
7. Number of -CN groups: 1
8. End

After the program encounters the End, it calculates the molecular indices of the compound and uses them in the required formulas to calculate the critical constants. The program then proceeds to the next compound in the crit.inp file. In the above example aniline is treated as consisting of one phenyl group and one amino group. Alternatively, one has to treat it as consisting of five =CH— groups, one =C< group, and one —NH_2 group. If we had to build the group index of a macro group such as -C_6H_5 each time from its constituent group indices, the procedure would become extremely cumbersome. This is particularly true in the case of halogenated compounds. For this reason, we have listed the increments for several large groups and increased the entries by 60.

In case the user wishes to submit the formula and not the molecular weight, then the input requires an additional file called mass.inp listing various elements and their atomic weights.

We have recorded in Table III the constants of the Kreglewski equations for critical temperature and critical pressure for a number of homologous series. The coefficients for eq 6 are to be used with the value 960 K for the limiting critical temperature. In order to apply Kreglewski's equations, one requires data from the fourth member of a homologous series to the tenth member. Such data are often unavailable. Use is, therefore, made of the above procedures, namely, eq 10–14, for estimating such data. Using such estimated data for the lower members of a homologous series, one can es-

Table V. Comparison of Predicted Critical Constants with the Experimental Values

							T_c/K		P_c/bar		G_v	
formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	obsd	calcd	obsd	calcd	obsd	calcd
CH_4	methane	1.000	1.000	1.000	16.043	111.64	190.56	192.54	46.04	50.26	98.9	95.0
CD_4	deuteriomethane	1.400	1.200	1.000	20.040	111.68	189.20	189.49	46.60	53.82	98.0	95.0
C_2H_6	ethane	2.000	2.000	2.000	30.070	184.55	305.42	306.12	48.80	48.06	147.0	150.0
C_3H_8	propane	3.000	3.000	3.000	44.097	231.05	369.82	370.57	42.47	42.64	200.0	205.0
C_4H_{10}	butane	4.000	4.000	4.000	58.123	272.65	425.18	424.63	37.97	37.62	255.0	260.0
C_4H_{10}	2-methylpropane	3.849	4.079	3.970	58.123	261.42	408.15	408.85	36.48	36.56	263.0	258.3
C_5H_{12}	pentane	5.000	5.000	5.000	72.150	309.21	469.70	469.26	33.69	33.43	304.0	315.0
C_5H_{12}	2-methylbutane	4.652	4.946	4.884	72.150	301.03	460.43	460.81	33.81	34.00	306.0	308.6
C_5H_{12}	2,2-dimethylpropane	4.494	5.104	4.987	72.150	282.63	433.78	434.40	31.99	32.39	303.0	314.3
C_6H_{14}	hexane	6.000	6.000	6.000	86.177	341.88	507.50	507.04	30.12	30.00	370.0	370.0
C_6H_{14}	2-methylpentane	5.652	5.946	5.884	86.177	333.41	497.50	498.30	30.10	30.43	367.0	363.6
C_6H_{14}	3-methylpentane	5.455	5.813	5.798	86.177	336.42	504.50	505.07	31.24	31.55	367.0	358.9
C_6H_{14}	2,2-dimethylbutane	5.100	5.838	5.815	86.177	322.88	488.78	488.82	30.80	31.33	359.0	359.8
C_6H_{14}	2,3-dimethylbutane	5.304	5.892	5.768	86.177	331.13	499.98	498.88	31.27	30.88	358.0	357.2
C_7H_{16}	heptane	7.000	7.000	7.000	100.204	371.58	540.30	539.87	27.36	27.15	432.0	425.0
C_7H_{16}	2-methylhexane	6.652	6.946	6.884	100.204	363.19	530.37	531.34	27.34	27.50	421.0	418.6
C_7H_{16}	3-methylhexane	6.455	6.813	6.798	100.204	364.99	535.26	536.12	28.14	28.39	404.0	413.9
C_7H_{16}	3-ethylpentane	6.258	6.680	6.712	100.204	366.64	540.64	540.77	28.91	29.32	416.0	409.1
C_7H_{18}	2,2-dimethylpentane	6.100	6.838	6.815	100.204	352.35	520.50	521.44	27.73	28.22	416.0	414.8
C_7H_{16}	2,3-dimethylpentane	6.107	6.759	6.682	100.204	362.93	537.35	537.02	29.08	28.76	393.0	407.5
C_7H_{16}	2,4-dimethylpentane	6.304	6.892	6.768	100.204	353.64	519.79	521.09	27.37	27.86	393.0	412.2
C_7H_{16}	3,3-dimethylpentane	5.706	6.572	6.643	100.204	359.21	536.40	536.21	29.46	30.11	414.0	405.4
C_7H_{18}	2,2,3-trimethylbutane	5.555	6.651	6.613	100.204	354.01	531.17	530.26	29.54	29.53	398.0	403.7
C_8H_{18}	octane	8.000	8.000	8.000	114.231	398.82	568.83	568.82	24.87	24.78	492.0	480.0
C_8H_{18}	2-methylheptane	7.652	7.946	7.884	114.231	390.81	559.64	560.88	24.84	25.07	488.0	473.6
C_8H_{18}	3-methylheptane	7.455	7.813	7.798	114.231	392.09	563.67	564.76	25.46	25.79	464.0	468.9
C_8H_{18}	4-methylheptane	7.455	7.813	7.798	114.231	390.87	561.74	563.00	25.42	25.79	476.0	468.9
C_8H_{18}	3-ethylhexane	7.258	7.680	7.712	114.231	391.70	565.49	566.29	26.08	26.54	455.0	464.1
C_8H_{18}	2,2-dimethylhexane	7.100	7.838	7.815	114.231	380.01	549.87	551.05	25.29	25.65	478.0	469.8
C_8H_{18}	2,3-dimethylhexane	7.107	7.759	7.682	114.231	388.77	563.49	563.67	26.28	26.09	468.0	462.5
C_8H_{18}	2,4-dimethylhexane	7.107	7.759	7.682	114.231	382.59	553.52	554.71	25.56	26.09	472.0	462.5
C_8H_{18}	2,5-dimethylhexane	7.304	7.892	7.768	114.231	382.27	550.06	552.17	24.87	25.35	482.0	467.2
C_8H_{18}	3,3-dimethylhexane	6.706	7.572	7.643	114.231	385.81	562.02	562.81	26.54	27.17	443.0	460.3
C_8H_{18}	3,4-dimethylhexane	6.910	7.626	7.596	114.231	390.88	568.85	568.91	26.92	26.85	466.0	457.8
C_8H_{18}	2-methyl-3-ethylpentane	6.910	7.626	7.596	114.231	388.81	567.09	565.90	27.00	26.85	443.0	457.8
C_8H_{18}	3-methyl-3-ethylpentane	6.312	7.306	7.471	114.231	391.42	576.58	576.66	28.08	28.84	455.0	450.9
C_8H_{18}	2,2,3-trimethylpentane	6.358	7.518	7.527	114.231	383.00	563.50	563.71	27.30	27.50	436.0	454.0
C_8H_{18}	2,2,4-trimethylpentane	6.752	7.784	7.699	114.231	372.37	543.96	543.67	25.68	25.95	468.0	463.4
C_8H_{18}	2,3,3-trimethylpentane	6.161	7.385	7.441	114.231	387.90	573.56	573.30	28.20	28.33	455.0	449.2
C_8H_{18}	2,3,4-trimethylpentane	6.759	7.705	7.566	114.231	386.62	566.41	564.40	27.30	26.39	461.0	456.1
C_8H_{18}	2,2,3,3-tetramethylbutane*	5.806	7.410	7.455	114.231	379.60	567.80	565.38	28.70	28.17	461.0	450.0
C_9H_{20}	nonane	9.000	9.000	9.000	128.258	423.97	594.60	594.65	22.88	22.78		535.0
C_9H_{20}	2-methyloctane*	8.455	8.813	8.798	128.258	416.43	582.90	589.31	23.10	23.61		523.9
C_9H_{20}	2,2-dimethylheptane	8.100	8.838	8.815	128.258	405.85	576.80	577.83	23.50	23.50		524.8
C_9H_{20}	2,2,5-trimethylhexane*	7.752	8.784	8.699	128.258	397.24	570.00	569.07		23.74		518.4
C_9H_{20}	2,2,3,3-tetramethylpentane	6.412	8.144	8.286	128.258	413.44	607.70	607.83	27.41	27.00		495.7
C_9H_{20}	2,2,3,4-tetramethylpentane	7.010	8.464	8.411	128.258	406.18	592.70	590.02	26.02	25.29		502.6
C_9H_{20}	2,2,4,4-tetramethylpentane	7.200	8.676	8.630	128.258	395.44	574.70	572.32	24.85	24.25		514.6
C_9H_{20}	2,3,3,4-tetramethylpentane	6.616	8.198	8.239	128.258	414.72	607.70	607.16	27.16	26.70		493.1
$C_{10}H_{22}$	decane	10.000	10.000	10.000	142.285	447.30	617.70	617.89	21.04	21.06		590.0
$C_{10}H_{22}$	3,3,5-trimethylheptane	8.161	9.385	9.441	142.285	428.85	609.70	609.94	23.17	23.51		559.2
$C_{10}H_{22}$	2,2,3,3-tetramethylhexane	7.412	9.144	9.286	142.285	433.48	623.20	624.87	25.10	24.59		550.7
$C_{10}H_{22}$	2,2,5,5-tetramethylhexane	8.200	9.676	9.630	142.285	410.63	581.60	583.63	21.86	22.30		569.6
$C_{11}H_{24}$	undecane	11.000	11.000	11.000	156.312	469.08	638.80	639.04	19.66	19.59		645.0
$C_{12}H_{26}$	dodecane	12.000	12.000	12.000	170.338	489.47	658.20	658.37	18.24	18.30		700.0
$C_{13}H_{28}$	tridecane	13.000	13.000	13.000	184.365	508.62	676.00	676.15	17.20	17.17		755.0
$C_{14}H_{30}$	tetradecane	14.000	14.000	14.000	198.392	526.73	694.00	692.68	14.40	16.17		810.0
$C_{16}H_{34}$	hexadecane*	16.000	16.000	16.000	226.446	560.01	722.00	722.33		14.48		920.0
$C_{18}H_{38}$	octadecane*	18.000	18.000	18.000	254.500	590.22	745.00	748.63		13.10		1030.0
$C_{20}H_{42}$	icosane*	20.000	20.000	20.000	282.553	617.15	768.00	771.36		11.97		1140.0
C_3H_6	cyclopropane	1.920	2.415	2.427	42.081	240.34	398.30	399.83	55.79	53.75	163.0	173.5
C_4H_8	cyclobutane*	2.560	3.220	3.236	56.108	285.70	460.00	464.79	49.90	49.31	210.0	218.0
C_5H_{10}	cyclopentane	3.200	4.025	4.045	70.134	322.40	511.70	513.89	45.08	44.98	260.0	262.5
C_6H_{12}	cyclohexane	3.840	4.830	4.854	84.161	353.88	553.50	553.60	40.70	41.12	308.0	307.0
C_7H_{14}	cycloheptane	4.480	5.635	5.663	98.188	391.63	604.20	602.16	38.10	37.76	353.0	351.5
C_8H_{16}	cyclooctane	5.120	6.440	6.472	112.215	422.00	647.20	638.57	35.60	34.85	410.0	395.9
C_6H_{12}	methylcyclopentane	4.200	5.025	5.045	84.161	344.95	532.73	534.32	37.84	38.70	319.0	317.5
C_7H_{14}	ethylcyclopentane	5.200	6.025	6.045	98.188	376.62	569.50	568.81	33.97	33.95	375.0	372.5
C_7H_{14}	1,1-dimethylcyclopentane*	5.000	6.025	6.045	98.188	361.00	547.00	547.85	33.00	33.95	360.0	372.5
C_7H_{14}	methylcyclohexane	4.840	5.830	5.854	98.188	374.08	572.20	569.94	34.71	35.78	368.0	362.0
C_8H_{16}	*trans*-1,4-dimethylcyclohexane	5.840	6.830	6.854	112.215	392.50	587.70	584.16		31.66		417.0
C_9H_{18}	1-*trans*-3,5-trimethylcyclohexane	6.840	7.830	7.854	126.242	413.70	602.20	602.96		28.39		472.0
$C_{10}H_{18}$	*cis*-decalin	5.620	7.690	8.090	138.253	468.96	702.30	701.40	32.00	32.05		484.9
$C_{10}H_{18}$	*trans*-decalin	5.620	7.690	8.090	138.253	460.46	687.10	688.69		32.05		484.9
C_2H_4	ethylene	1.800	1.800	1.640	28.054	169.38	282.34	283.03	50.39	50.44	130.0	130.2

Table V (Continued)

formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	T_c/K		P_c/bar		G_v	
							obsd	calcd	obsd	calcd	obsd	calcd
C_3H_6	propene	2.700	2.700	2.600	42.081	225.46	364.85	365.10	46.01	46.71	181.0	183.0
C_4H_8	1-butene	3.700	3.700	3.600	56.107	266.89	419.57	419.17	40.23	40.63	240.0	238.0
C_4H_8	*cis*-2-butene	3.600	3.600	3.560	56.107	276.86	435.58	436.08	42.45	42.23	234.0	235.8
C_4H_8	*trans*-2-butene	3.800	3.750	3.560	56.107	274.03	428.63	429.16	39.85	39.85	238.0	235.8
C_4H_8	2-methylpropene	3.700	3.700	3.600	56.107	266.20	417.90	418.09	40.00	40.63	239.0	238.0
C_5H_{10}	1-pentene	4.700	4.700	4.600	70.134	303.11	464.78	463.43	35.27	35.72		293.0
C_5H_{10}	*cis*-2-pentene	4.600	4.600	4.560	70.134	310.08	475.00	475.30	36.90	36.90		290.8
C_5H_{10}	*trans*-2-pentene	4.800	4.750	4.560	70.134	309.49	471.00	472.00	35.20	35.15		290.8
C_5H_{10}	2-methyl-1-butene	4.503	4.567	4.514	70.134	304.30	470.00	467.60	38.50	37.30		288.3
C_5H_{10}	2-methyl-2-butene	4.800	4.750	4.560	70.134	311.71	481.00	475.39	39.10	35.15		290.8
C_6H_{12}	1-hexene	5.700	5.700	5.600	84.161	336.63	504.03	502.57		31.79		348.0
C_7H_{14}	1-heptene	6.700	6.700	6.600	98.188	366.79	537.29	536.08		28.59		403.0
C_8H_{16}	1-octene	7.700	7.700	7.600	112.215	394.44	566.70	565.59		25.96		458.0
C_3H_4	propadiene	2.200	2.400	2.040	40.065	238.70	393.00	393.14		51.57		152.2
C_4H_6	1,3-butadiene	3.400	3.400	3.200	54.090	268.74	425.00	425.79	43.30	44.11	221.0	216.0
C_6H_{10}	1,5-hexadiene*	5.400	5.400	5.200	82.144	332.60	507.00	499.97		33.78		326.0
$C_{10}H_{18}$	1,3-decadiene*	9.300	9.300	9.160	138.250	442.00	615.00	617.02		23.21		543.8
C_5H_8	cyclopentene	3.004	3.777	3.771	68.119	317.39	506.00	508.99		47.89		247.4
C_6H_{10}	cyclohexene	3.644	4.582	4.580	82.146	356.13	560.48	560.23		43.48		291.9
C_2H_2	acetylene	2.360	1.380	1.270	26.038	188.43	308.33	308.63	61.39	61.46	113.0	109.8
C_3H_4	propyne	2.860	2.230	2.270	40.065	249.95	402.38	402.67	56.28	56.38	164.0	164.8
C_4H_6	1-butyne*	3.860	3.230	3.270	54.092	281.23	463.70	439.70		47.34		219.8
C_4H_6	2-butyne*	3.860	3.230	3.270	54.092	300.12	488.70	469.23		47.34		219.8
C_5H_8	1-pentyne*	4.860	4.230	4.270	68.118	313.33	493.50	477.15		40.62		274.8
C_6H_6	benzene	3.252	4.086	4.032	78.114	353.24	562.16	562.16	48.98	49.01	259.0	261.7
C_7H_8	toluene	4.252	5.086	5.032	92.141	383.78	591.79	593.64	41.04	41.59	316.0	316.7
C_8H_{10}	ethylbenzene	5.252	6.086	6.032	106.167	409.34	617.20	617.47	36.00	36.12	374.0	371.7
C_8H_{10}	*o*-xylene	5.152	5.986	6.032	106.167	417.58	630.30	631.40	37.30	37.09	369.0	371.7
C_8H_{10}	*m*-xylene	5.452	6.186	6.032	106.167	412.27	617.05	618.99	35.35	35.19	376.0	371.7
C_8H_{10}	*p*-xylene	5.252	6.086	6.032	106.167	411.52	616.20	620.76	35.11	36.12	379.0	371.7
C_9H_{12}	propylbenzene	6.252	7.086	7.032	120.194	432.39	638.32	637.82	32.00	31.92	440.0	426.7
C_9H_{12}	isopropylbenzene	6.101	7.165	7.002	120.194	425.56	631.10	629.77	32.09	31.34		425.1
C_9H_{12}	1,2,3-trimethylbenzene	6.052	6.886	7.032	120.194	449.27	664.47	665.56	34.54	33.46		426.7
C_9H_{12}	1,2,4-trimethylbenzene	6.352	7.086	7.032	120.194	442.53	649.17	651.41	32.32	31.92		426.7
C_9H_{12}	1,3,5-trimethylbenzene	6.852	7.386	7.032	120.194	437.89	637.25	638.06	31.27	29.80		426.7
$C_{10}H_{14}$	butylbenzene	7.252	8.086	8.032	134.221	456.46	660.50	659.98	28.87	28.60	497.0	481.7
$C_{10}H_{14}$	isobutylbenzene*	7.101	8.165	8.002	134.221	445.94	650.00	646.64	30.50	28.13		480.1
$C_{10}H_{14}$	4-isopropyl-1-methylbenzene*	7.101	8.165	8.002	134.221	450.28	651.00	652.93	27.30	28.13		480.1
$C_{10}H_{14}$	1,4-diethylbenzene	7.252	8.086	8.032	134.221	456.94	657.88	660.68	28.03	28.60		481.7
$C_{10}H_{14}$	1,2,3,5-tetramethylbenzene*	7.452	8.086	8.032	134.221	471.20	679.00	678.74		28.60		481.7
$C_{10}H_{14}$	1,2,4,5-tetramethylbenzene	7.452	8.086	8.032	134.221	469.99	675.00	677.00	29.40	28.60		481.7
$C_{11}H_{16}$	pentamethylbenzene*	8.052	8.786	9.032	148.250	504.55	719.00	718.96		27.43		536.7
$C_{12}H_{18}$	hexamethylbenzene	8.652	9.486	10.032	162.280	536.60	758.00	756.88		26.33		591.7
$C_{10}H_8$	naphthalene	4.836	6.368	6.682	128.174	491.14	748.40	748.37	40.51	40.54	413.0	407.5
$C_{11}H_{10}$	1-methylnaphthalene	5.836	7.368	7.682	142.200	517.89	772.00	770.84		35.40		462.5
$C_{11}H_{10}$	2-methylnaphthalene	5.836	7.368	7.682	142.200	514.26	761.00	765.44		35.40		462.5
$C_{12}H_{10}$	biphenyl*	5.504	7.172	8.064	154.210	529.25	789.00	793.67	38.50	40.15	502.0	483.5
$C_{14}H_{10}$	phenanthrene	6.420	8.650	9.332	178.240	613.00	873.00	901.07		33.87	554.0	553.2
$C_{14}H_{10}$	anthracene	6.420	8.650	9.332	178.240	613.10	869.30	901.22		33.87	554.0	553.2
$C_{18}H_{14}$	*o*-terphenyl*	7.756	10.258	12.096	230.310	605.00	891.00	866.64	39.00	32.62		705.3
$C_{18}H_{14}$	*m*-terphenyl*	7.756	10.258	12.096	230.310	636.00	924.90	911.05	35.10	32.62		705.3
$C_{18}H_{14}$	*p*-terphenyl*	7.756	10.258	12.096	230.310	649.00	926.00	929.67	33.20	32.62		705.3
$C_{13}H_{12}$	diphenylmethane	7.504	9.172	9.064	168.240	538.20	770.00	774.51	28.60	28.92		538.5
C_9H_{10}	indane	4.752	6.006	6.338	118.178	451.12	684.90	688.83	39.50	41.07		388.6
CH_4O	methanol	5.000	1.284	1.290	32.040	337.85	512.64	512.72	80.92	80.94	118.0	110.9
C_2H_6O	ethanol	6.670	2.360	2.290	46.070	351.44	513.92	513.96	61.37	60.54	167.0	165.9
C_3H_8O	1-propanol	7.080	3.280	3.290	60.100	370.35	536.78	537.25	51.70	51.50	219.0	220.9
C_3H_8O	2-propanol	7.519	3.439	3.260	60.100	355.45	508.30	511.37	47.62	48.24	220.0	219.3
$C_4H_{10}O$	1-butanol	7.490	4.200	4.290	74.120	390.81	563.05	562.55	44.23	44.67	275.0	275.9
$C_4H_{10}O$	2-butanol	7.429	4.359	4.260	74.120	372.66	536.05	537.03	41.79	42.27	269.0	274.3
$C_4H_{10}O$	2-methyl-1-propanol	7.429	4.359	4.260	74.120	381.04	547.78	549.11	43.00	42.27	273.0	274.3
$C_4H_{10}O$	2-methyl-2-propanol	8.164	4.464	4.277	74.120	355.50	506.21	505.59	39.73	40.80	275.0	275.2
$C_5H_{12}O$	1-pentanol	7.900	5.120	5.290	88.150	411.13	588.15	587.41	39.09	39.38	326.0	330.9
$C_5H_{12}O$	3-methyl-1-butanol	8.142	5.146	5.174	88.150	405.20	579.40	576.49		39.07		324.6
$C_5H_{12}O$	2-methyl-2-butanol	7.877	5.251	5.191	88.150	375.50	545.00	536.73		37.87		325.5
$C_6H_{14}O$	1-hexanol	8.310	6.040	6.290	102.180	430.70	611.00	611.00	34.85	35.19	381.0	385.9
$C_6H_{14}O$	2-hexanol	8.249	6.199	6.260	102.180	408.15	586.20	579.62		33.75		384.3
$C_6H_{14}O$	4-methyl-1-pentanol	8.552	6.066	6.174	102.180	424.80	603.50	600.18		34.95		379.6
$C_6H_{14}O$	2-methyl-2-pentanol	8.287	6.171	6.191	102.180	394.20	559.50	559.44		34.00		380.5
$C_6H_{14}O$	4-methyl-2-pentanol	8.491	6.225	6.144	102.180	404.80	574.50	572.51		33.52		377.9
$C_7H_{16}O$	1-heptanol	8.720	6.960	7.290	116.200	449.76	633.00	633.68	31.63	31.79	435.0	440.9
$C_8H_{18}O$	1-octanol	9.130	7.880	8.290	130.233	468.31	652.50	655.49	28.60	28.98	490.0	495.9
$C_8H_{18}O$	2-octanol	9.069	8.039	8.260	130.233	452.00	637.00	633.27		28.02		494.3
$C_8H_{18}O$	4-methyl-3-heptanol	9.204	8.012	8.058	130.233	443.00	623.50	619.34		28.18		483.2
$C_8H_{18}O$	5-methyl-3-heptanol	9.204	8.012	8.058	130.233	445.00	621.20	622.14		28.18		483.2

Table V (Continued)

							T_c/K		P_c/bar		G_v	
formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	obsd	calcd	obsd	calcd	obsd	calcd
$C_8H_{18}O$	2-ethyl-1-hexanol	9.265	7.745	8.002	130.233	457.80	640.20	639.43		29.83		480.1
$C_9H_{20}O$	1-nonanol*	10.130	8.880	9.290	144.261	486.70	671.00	671.06		26.21		550.9
$C_{10}H_{22}O$	1-decanol*	11.130	9.880	10.290	158.290	506.10	687.00	688.29		23.93		605.9
$C_2H_6O_2$	ethylene glycol***	11.340	2.720	2.580	62.070	470.49	607.00	638.11		68.24		181.9
$C_6H_{12}O$	cyclohexanol***	7.840	5.114	5.144	100.160	434.30	625.00	621.18	37.50	44.83		322.9
C_3H_6O	2-propene-1-ol***	6.680	2.880	2.850	58.080	370.15	543.00	541.21		59.27		196.7
$C_{10}H_{20}O$	menthol***	8.819	8.789	9.114	156.270	489.50	694.00	688.56	46.04	28.90		541.3
C_6H_6O	phenol	4.782	3.986	4.018	94.110	455.02	694.20	694.26	61.30	61.22		261.0
C_7H_8O	*o*-cresol	5.442	4.886	5.018	108.140	464.19	697.60	697.10	50.05	51.92		316.0
C_7H_8O	*m*-cresol	5.982	5.086	5.018	108.140	475.49	705.80	705.47	45.60	48.81	316.0	316.0
C_7H_8O	*p*-cresol	5.782	4.986	5.018	108.140	475.13	704.60	708.05	51.50	50.33		316.0
$C_8H_{10}O$	*o*-ethylphenol	6.442	5.886	6.018	122.167	477.67	703.00	701.82		43.84		371.0
$C_8H_{10}O$	*m*-ethylphenol	6.982	6.086	6.018	122.167	491.57	718.80	714.45		41.56		371.0
$C_8H_{10}O$	*p*-ethylphenol	6.782	5.986	6.018	122.167	491.13	716.40	716.63		42.68		371.0
$C_8H_{10}O$	2,3-xylenol	6.342	5.786	6.018	122.167	490.07	722.80	721.54		45.06		371.0
$C_8H_{10}O$	2,4-xylenol	6.642	5.986	6.018	122.167	484.13	707.60	708.41		42.68		371.0
$C_8H_{10}O$	2,5-xylenol	6.642	5.986	6.018	122.167	484.33	706.90	708.70		42.68		371.0
$C_8H_{10}O$	2,6-xylenol	6.102	5.786	6.018	122.167	474.22	701.00	701.76		45.06		371.0
$C_8H_{10}O$	3,4-xylenol	6.882	5.986	6.018	122.167	500.15	729.80	728.35		42.68		371.0
$C_8H_{10}O$	3,5-xylenol	7.382	6.286	6.018	122.167	494.89	715.60	713.80		39.46		371.0
$C_{10}H_{14}O$	thymol*	8.491	8.065	7.988	150.221	505.70	718.00	715.21		32.15		479.3
C_2H_6O	dimethyl ether	2.870	2.710	2.363	46.068	248.30	400.00	399.88	53.70	50.89	190.0	170.0
C_3H_8O	ethyl methyl ether	3.870	3.710	3.363	60.095	280.60	437.80	438.59	44.30	43.35	221.0	224.9
$C_4H_{10}O$	diethyl ether	4.870	4.710	4.363	74.122	307.58	466.74	468.28	36.38	37.63	280.0	280.0
$C_4H_{10}O$	methyl propyl ether	4.870	4.710	4.363	74.122	311.72	476.25	474.58	38.01	37.63		280.0
$C_4H_{10}O$	isopropyl methyl ether	4.719	4.789	4.333	74.122	303.92	464.48	464.45	37.62	36.69		278.3
$C_5H_{12}O$	butyl methyl ether	5.870	5.710	5.363	88.149	343.31	512.78	510.61	33.71	33.20	329.0	334.9
$C_5H_{12}O$	*tert*-butyl methyl ether	5.364	5.814	5.350	88.149	328.30	497.10	493.92	34.30	32.26		334.2
$C_5H_{12}O$	ethyl propyl ether	5.870	5.710	5.363	88.149	336.36	500.23	500.27	33.70	33.20	339.0	334.9
$C_6H_{14}O$	methyl pentyl ether	6.870	6.710	6.363	102.176	372.00	546.53	541.86	30.42	29.68	392.0	389.9
$C_6H_{14}O$	dipropyl ether	6.870	6.710	6.363	102.176	363.23	530.60	529.08	30.28	29.68		389.9
$C_6H_{14}O$	diisopropyl ether	6.568	6.868	6.303	102.176	341.66	500.32	500.69	28.32	28.57	386.0	386.7
$C_8H_{18}O$	di-*tert*-butyl ether	7.850	8.918	8.337	130.230	380.38	550.00	543.96		23.49		498.5
$C_3H_8O_2$	dimethoxymethane	4.740	4.420	3.726	76.100	315.00	480.60	481.13	39.50	42.51	213.0	244.9
$C_4H_{10}O_2$	1,2-dimethoxyethane	5.740	5.420	4.726	90.120	358.00	536.00	534.00	38.70	36.85	271.0	299.9
$C_6H_{14}O_2$	1,1-diethoxyethane	7.195	7.233	6.524	118.170	375.40	527.00	543.37		30.34		398.8
C_4H_8O	ethyl vinyl ether	4.570	4.410	3.963	72.110	308.70	475.00	473.55	40.47	40.42		258.0
$C_5H_{10}O$	allyl ethyl ether*	5.470	5.310	4.923	86.130	340.80	518.00	511.47		36.36		310.8
C_7H_8O	methyl phenyl ether	5.122	5.796	5.395	108.135	426.80	645.60	645.80		39.77		336.7
$C_8H_{10}O$	ethyl phenyl ether	6.122	6.796	6.395	122.170	442.96	647.00	655.22	34.20	34.75		391.7
$C_{12}H_{10}O$	diphenyl ether	7.374	8.882	8.427	170.211	531.20	766.80	766.28		30.92		503.5
C_2H_4O	ethylene oxide	2.080	2.320	1.981	44.054	283.70	469.00	469.24	71.90	59.11	140.0	148.9
C_3H_6O	propylene oxide*	3.080	3.320	2.981	58.081	308.00	488.20	492.76	49.20	48.95	186.0	203.9
C_4H_8O	tetrahydrofuran	3.360	3.930	3.599	72.108	338.00	540.10	536.16	51.90	47.88	224.0	237.9
$C_5H_{10}O$	2-methyltetrahydrofuran	4.360	4.930	4.599	86.135	351.00	537.00	541.38	37.60	40.79	267.0	292.9
C_4H_4O	furan	2.968	3.434	3.051	68.080	304.50	490.20	488.87	55.00	54.75	218.0	207.8
C_5H_6O	2-methylfuran	3.968	4.434	4.051	82.100	338.00	527.00	526.87	47.20	45.65	247.0	262.8
$C_5H_4O_2$	furfural	4.218	4.534	4.553	96.090	434.90	670.00	673.32	58.90	51.67		290.4
$C_5H_{10}O$	tetrahydropyran	4.000	4.735	4.408	86.130	361.00	572.20	562.23	47.70	43.38	263.0	282.4
C_5H_8O	dihydropyran	3.804	4.485	4.134	84.120	359.00	561.70	562.17	45.60	45.98	268.0	267.4
$C_4H_8O_2$	dioxane	4.160	4.636	3.962	88.110	374.60	587.00	580.87	52.10	45.82	238.0	257.9
C_2H_4O	acetaldehyde*	3.800	2.250	2.070	44.053	294.00	461.00	460.44		61.33		153.8
C_3H_6O	propanal*	4.300	3.250	3.070	58.080	321.00	496.00	495.89	45.70	50.40	205.0	208.8
C_7H_6O	benzaldehyde	4.502	5.186	5.102	106.119	452.20	695.00	694.89	46.50	46.48		320.6
$C_6H_{12}O_3$	paraldehyde	7.320	7.545	6.516	132.160	397.50	563.00	574.00		31.63		398.4
C_3H_6O	acetone	4.300	3.250	3.070	58.080	329.20	508.10	508.56	47.00	50.40	209.0	208.8
C_4H_8O	2-butanone	4.800	4.250	4.070	72.107	352.74	536.78	537.96	42.07	42.70	267.0	263.8
$C_5H_{10}O$	2-pentanone	5.800	5.250	5.070	86.134	375.41	561.08	559.22	36.94	37.01	301.0	318.8
$C_5H_{10}O$	3-pentanone	5.300	5.250	5.070	86.134	375.11	561.46	565.19	37.29	37.01	336.0	318.8
$C_5H_{10}O$	3-methyl-2-butanone	4.952	5.196	4.954	86.134	367.48	553.40	558.34	38.50	37.61	310.0	312.5
$C_6H_{12}O$	2-hexanone	6.800	6.250	6.070	100.161	400.70	587.00	584.47	33.20	32.65		373.8
$C_6H_{12}O$	3-hexanone	6.300	6.250	6.070	100.161	396.60	582.82	584.44	33.20	32.65		373.8
$C_6H_{12}O$	4-methyl-2-pentanone	6.952	6.196	5.954	100.161	389.60	571.00	566.58	32.70	33.11		367.5
$C_7H_{14}O$	2-heptanone	7.800	7.250	7.070	114.188	424.20	611.50	607.17	34.36	29.20		428.8
$C_9H_{18}O$	5-nonanone	9.300	9.250	9.070	142.241	461.60	640.00	644.38		24.10		538.8
$C_6H_{10}O$	cyclohexanone	6.500	5.565	5.145	98.150	428.90	629.00	629.41	38.50	38.50		323.0
$C_4H_6O_3$	acetic anhydride	10.200	5.035	4.503	102.090	413.20	569.00	569.15	46.80	46.80		287.7
$C_2H_4O_2$	acetic acid	5.000	3.000	2.360	60.050	391.05	592.71	593.46	57.86	58.06	171.0	169.8
$C_3H_6O_2$	propanoic acid	6.400	4.000	3.360	74.080	414.50	602.20	609.54	41.20	47.95	222.0	224.8
$C_4H_8O_2$	butanoic acid	7.400	5.000	4.360	88.110	437.20	628.00	630.38	52.70	40.83	290.0	279.8
$C_4H_8O_2$	2-methylpropanoic acid	7.649	5.079	4.330	88.110	427.85	609.00	614.07	40.50	39.86	292.0	278.1
$C_5H_{10}O_2$	pentanoic acid	8.400	6.000	5.360	102.122	459.50	651.00	650.86		35.55		334.8
$C_5H_{10}O_2$	2-methylbutanoic acid	8.249	6.079	5.330	102.122	449.70	634.00	638.62		34.81		333.1
$C_2H_4O_2$	methyl formate	3.100	3.080	2.433	60.050	304.85	487.20	487.42	59.98	56.05	172.0	173.8
$C_3H_6O_2$	ethyl formate	4.100	4.080	3.433	74.080	327.50	508.50	508.66	47.40	46.58	229.0	228.8

Table V (Continued)

formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	T_c/K obsd	T_c/K calcd	P_c/bar obsd	P_c/bar calcd	G_v obsd	G_v calcd
$C_4H_8O_2$	propyl formate	5.100	5.080	4.433	88.110	354.05	538.00	536.01	40.60	39.84	285.0	283.8
$C_5H_{10}O_2$	isobutyl formate	5.949	6.159	5.422	102.130	371.40	551.00	551.43	38.80	34.09	352.0	338.2
$C_6H_{12}O_2$	pentyl formate	7.100	7.080	6.433	116.160	403.60	576.00	585.25	34.60	30.89		393.8
$C_6H_{12}O_2$	isopentyl formate	6.752	7.026	6.317	116.160	396.70	578.00	579.19		31.29		387.4
$C_3H_6O_2$	methyl acetate	4.400	4.080	3.433	74.080	330.40	506.80	509.07	46.90	46.58	228.0	228.8
$C_4H_8O_2$	ethyl acetate	5.400	5.080	4.433	88.110	350.30	523.20	526.58	38.30	39.84	286.0	283.8
$C_5H_{10}O_2$	propyl acetate	6.400	6.080	5.433	102.130	374.70	549.40	551.01	33.30	34.80	345.0	338.8
$C_6H_{12}O_2$	butyl acetate	7.400	7.080	6.433	116.160	399.25	579.00	575.66		30.89		393.8
$C_6H_{12}O_2$	isobutyl acetate	7.249	7.159	6.403	116.160	389.70	561.00	563.49	31.60	30.33		392.1
$C_7H_{14}O_2$	isopentyl acetate	8.052	8.026	7.317	130.187	415.70	599.00	592.35		28.09		442.4
$C_4H_8O_2$	methyl propanoate	5.400	5.080	4.433	88.110	352.80	530.60	530.34	40.04	39.84	282.0	283.8
$C_5H_{10}O_2$	ethyl propanoate	6.400	6.080	5.433	102.130	372.20	546.00	547.34	33.62	34.80	345.0	338.8
$C_6H_{12}O_2$	propyl propanoate	7.400	7.080	6.433	116.160	395.80	578.00	570.69		30.89		393.8
$C_7H_{14}O_2$	isobutyl propanoate	8.249	8.159	7.403	130.187	410.00	592.00	582.24		27.32		447.1
$C_8H_{16}O_2$	isopentyl propanoate	9.052	9.026	8.317	144.214	433.40	611.00	607.37		25.48		497.4
$C_5H_{10}O_2$	methyl butanoate	6.400	6.080	5.433	102.130	375.90	554.40	552.78	34.80	34.80	340.0	338.8
$C_5H_{10}O_2$	methyl isobutanoate	6.249	6.159	5.403	102.130	365.50	540.80	539.19	34.30	34.09	339.0	337.1
$C_6H_{12}O_2$	ethyl butanoate	7.400	7.080	6.433	116.160	394.70	566.00	569.10	30.60	30.89	421.0	393.8
$C_6H_{12}O_2$	ethyl isobutanoate	7.249	7.159	6.403	116.160	383.20	553.00	554.09	30.70	30.33	421.0	392.1
$C_7H_{14}O_2$	propyl butanoate	8.400	8.080	7.433	130.187	416.20	600.00	589.53		27.77		448.8
$C_7H_{14}O_2$	propyl isobutanoate	8.249	8.080	7.403	130.187	408.20	589.00	579.69		27.77		447.1
$C_8H_{16}O_2$	isobutyl butanoate	9.249	9.159	8.403	144.214	430.10	611.00	600.89		24.85		502.2
$C_8H_{16}O_2$	isobutyl isobutanoate	9.098	9.238	8.373	144.214	421.80	602.00	590.69		24.49		500.5
$C_9H_{18}O_2$	isopentyl butanoate	10.052	10.026	9.317	158.241	452.00	619.00	623.92		23.32		552.4
$C_6H_{12}O_2$	methyl pentanoate	7.400	7.080	6.433	116.160	400.50	567.00	577.46	31.90	30.89		393.8
$C_7H_{14}O_2$	ethyl pentanoate	8.400	8.080	7.433	130.187	419.20	570.00	593.78		27.77		448.8
$C_7H_{14}O_2$	ethyl isopentanoate	8.249	8.159	7.403	130.187	408.20	588.00	579.69		27.32		447.1
$C_8H_{16}O_2$	propyl isopentanoate	9.249	9.159	8.403	144.214	429.10	609.00	599.49		24.85		502.2
$C_9H_{18}O_2$	isobutyl isopentanoate	10.098	10.238	9.373	158.241	441.70	621.00	609.29		22.49		555.5
$C_{10}H_{20}O_2$	ethyl octanoate	11.400	11.080	10.433	172.268	481.70	659.00	652.81		21.31		613.8
$C_{11}H_{22}O_2$	ethyl nonanoate	12.400	12.080	11.433	186.295	500.20	674.00	669.58		19.74		668.8
$C_{13}H_{26}O_2$	methyl dodecanoate	14.400	14.080	13.433	214.350	540.00	712.00	707.22		17.29		778.8
$C_6H_{10}O_2$	ethyl crotonate*	7.000	6.680	5.993	114.140	411.00	599.00	597.14		33.40		396.6
$C_4H_6O_4$	dimethyl oxalate*	6.800	6.160	4.866	118.090	436.50	628.00	636.69	39.80	39.40		307.6
$C_8H_{14}O_4$	ethyl succinate	10.800	10.160	8.866	174.200	490.90	663.00	670.56		25.09		527.6
$C_8H_8O_3$	methyl salicylate	7.982	6.986	6.465	152.150	496.10	709.00	707.79		41.37		395.6
CH_5N	methylamine	2.700	1.420	1.580	31.057	266.83	430.70	432.09	74.20	71.31		126.9
C_2H_7N	ethylamine	3.700	2.420	2.580	45.083	289.70	456.00	455.00	56.20	57.44	182.0	181.9
C_3H_9N	propylamine	4.700	3.420	3.580	59.111	321.70	497.00	491.86	47.40	47.81		236.9
C_3H_9N	isopropylamine	4.549	3.499	3.550	59.111	305.60	471.80	469.04	45.40	46.31	221.0	235.2
$C_4H_{11}N$	butylamine	5.700	4.420	4.580	73.138	351.20	524.00	524.32	41.50	40.86		291.9
$C_4H_{11}N$	*sec*-butylamine	5.352	4.366	4.464	73.138	336.20	514.30	505.87	50.00	41.61		285.5
$C_4H_{11}N$	*tert*-butylamine	5.194	4.524	4.567	73.138	316.80	483.90	478.53	38.40	39.46	293.0	291.2
C_2H_7N	dimethylamine	3.500	2.420	2.580	45.083	280.03	437.22	442.37	53.40	57.44		181.9
$C_4H_{11}N$	diethylamine	5.500	4.420	4.580	73.138	329.05	496.60	493.49	37.10	40.86	301.0	291.9
$C_6H_{15}N$	dipropylamine	7.500	6.420	6.580	101.192	382.20	550.00	550.05	31.40	31.58		401.9
$C_6H_{15}N$	diisopropylamine	7.198	6.578	6.520	101.192	357.05	523.10	516.78	30.20	30.36		398.6
$C_8H_{19}N$	dibutylamine	9.500	8.420	8.580	129.246	432.75	607.50	602.26	31.10	25.71		511.9
$C_8H_{19}N$	diisobutylamine	9.198	8.578	8.520	129.246	412.84	584.40	577.23	32.00	24.91		508.6
C_3H_9N	trimethylamine	3.600	3.800	3.580	59.111	276.02	432.79	434.76	40.87	41.20	254.0	236.9
$C_6H_{15}N$	triethylamine	6.600	6.800	6.580	101.192	392.50	535.60	530.89	30.32	28.76	389.0	401.9
C_2H_3N	acetonitrile	4.000	2.580	2.450	41.052	354.80	545.50	552.57	48.30	48.28	173.0	174.7
C_3H_5N	propionitrile	5.000	3.580	3.450	55.080	370.29	564.40	561.95	41.80	41.79	229.0	229.7
C_4H_7N	butanenitrile	6.000	4.580	4.450	69.110	391.10	582.20	580.04	37.90	36.60		284.7
C_5H_9N	hexanenitrile	8.000	6.580	6.450	97.160	436.80	622.00	622.99	32.50	29.14		394.7
C_2H_5NO	acetamide*	5.000	2.670	2.650	59.068	495.16		751.45		66.51		185.7
CH_6N_2	methylhydrazine*	2.400	1.566	2.160	46.070	362.00	567.00	592.10	80.40	95.95	271.0	158.8
C_2H_7NO	ethanolamine*	4.600	3.130	2.943	61.083	443.57		679.91		55.79		201.8
C_4H_5N	pyrrole	3.168	2.984	3.268	67.090	403.00	639.80	643.00		65.33		219.7
C_4H_9N	pyrrolidine	3.560	3.480	3.816	71.120	359.64	368.60	567.13	56.10	56.15	249.0	249.9
$C_5H_6N_2$	2-methylpyrazine	4.252	4.434	4.848	94.120	410.00	634.30	634.19	50.10	52.33	283.0	306.6
$C_5H_{11}N$	piperidine	4.200	4.285	4.625	85.150	379.55	594.00	587.91	46.50	49.82		294.4
C_5H_5N	pyridine	3.252	3.760	3.940	79.101	388.41	620.00	618.13	56.30	55.98	254.0	256.7
C_6H_7N	2-methylpyridine	4.252	4.760	4.940	93.128	402.56	621.00	622.69	46.00	46.53		311.7
C_6H_7N	3-methylpyridine	4.252	4.760	4.940	93.128	417.29	645.00	645.47		46.53		311.7
C_6H_7N	4-methylpyridine	4.252	4.760	4.940	93.128	418.51	646.00	647.36	46.60	46.53		311.7
C_7H_9N	2,3-dimethylpyridine	5.152	5.660	5.940	107.155	434.41	655.40	656.84		40.92		366.7
C_7H_9N	2,4-dimethylpyridine	5.452	5.860	5.940	107.155	431.55	647.00	647.93		38.73		366.7
C_7H_9N	2,5-dimethylpyridine	5.252	5.760	5.940	107.155	430.16	644.20	648.87		39.80		366.7
C_7H_9N	2,6-dimethylpyridine	5.452	5.860	5.940	107.155	417.20	623.80	626.39		38.73		366.7
C_7H_9N	3,4-dimethylpyridine	5.152	5.660	5.940	107.155	452.28	683.80	683.87		40.92		366.7
C_7H_9N	3,5-dimethylpyridine	5.452	5.860	5.940	107.155	445.10	667.20	668.28		38.73		366.7
C_6H_7N	aniline	4.752	4.366	4.612	93.128	457.60	699.00	698.72	53.10	52.99	274.0	293.6
C_6H_9N	*o*-toluidine*	5.652	5.266	5.612	107.155	473.50	694.00	707.68	37.50	45.83		348.6
C_6H_9N	*m*-toluidine*	5.952	5.466	5.612	107.155	476.60	709.00	707.58	41.50	43.23		348.6

Table V (Continued)

formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	T_c/K		P_c/bar		G_v	
							obsd	calcd	obsd	calcd	obsd	calcd
C_6H_9N	*p*-toluidine*	5.752	5.366	5.576	107.155	473.70	667.00	706.39	23.80	44.50		346.7
C_6H_9N	*N*-methylaniline	5.752	5.366	5.612	107.155	469.40	701.00	699.98	52.00	44.50		348.6
$C_7H_{11}N$	*N*,*N*-dimethylaniline	6.752	6.586	6.612	121.182	467.30	687.00	682.27	36.30	36.29		403.6
$C_7H_{11}N$	*N*-ethylaniline	6.752	6.366	6.612	121.182	476.20	698.00	695.27		38.35		403.6
$C_7H_{11}N$	*N*,*N*-dimethyl-*o*-toluidine	7.652	7.486	7.612	135.209	467.30	668.00	670.65	31.20	32.78		458.6
$C_{12}H_{11}N$	diphenylamine	8.004	8.592	8.644	169.230	575.00	825.00	820.04	38.00	32.53		515.4
C_7H_5N	benzonitrile	5.052	5.416	5.482	103.123	464.30	699.40	703.73	42.20	42.21		341.5
C_8H_7N	*p*-tolunitrile	6.052	6.416	6.482	117.150	490.20	723.00	726.19		36.60		396.5
C_9H_7N	quinoline	4.836	6.042	6.590	129.160	510.78	782.00	778.29		44.46		402.5
C_9H_7N	isoquinoline	4.836	6.042	6.590	129.160	516.39	803.00	786.84		44.46		402.5
CH_3NO_2	nitromethane	3.700	3.000	2.420	61.040	374.34	588.00	587.93	58.70	59.02	173.0	173.1
C_3H_3NO	isooxazole	2.968	3.108	2.959	69.060	368.00	552.00	590.82		63.68		202.7
$C_3H_3N_2$	propanedinitrile*	7.000	4.160	3.900	66.062	491.50	710.00	714.10	36.00	40.37		254.5
$C_{12}H_{10}N_2$	azobenzene*	7.704	9.772	9.224	182.225	566.14	830.00	811.74	41.00	28.08		547.3
CH_4S	methanethiol	1.650	2.200	2.000	48.100	279.11	470.00	469.02	72.30	68.79	145.0	150.0
C_2H_6S	ethanethiol	2.650	3.200	3.000	62.130	308.20	499.00	499.90	54.90	55.07	207.0	205.0
$C_5H_{12}S$	isopentylmercaptan	5.302	6.146	5.884	104.216	393.00	604.00	592.12		34.90		363.6
C_2H_6S	2-thiapropane	2.760	3.200	3.000	62.127	310.48	503.00	501.79	55.30	55.06	201.0	205.0
C_3H_8S	2-thiabutane	3.760	4.200	4.000	76.160	339.80	533.00	532.77	42.60	45.89		260.0
$C_4H_{10}S$	3-thiapentane	4.760	5.200	5.000	90.180	365.25	557.00	557.60	39.60	39.33	318.0	315.0
$C_{10}H_{22}S$	diisopentyl sulfide	10.064	11.092	10.768	174.341	484.15	664.00	668.18		21.53		632.2
$C_4H_{10}S_2$	diethyl disulfide	5.520	6.400	6.000	122.246	427.13	642.00	640.29		38.35		370.0
$C_6H_{10}S$	diallyl sulfide	5.960	6.400	6.120	114.211	411.75	653.00	611.19		35.83		376.6
C_4H_4S	thiophene	2.628	3.854	3.258	84.140	357.15	579.40	579.72	56.90	57.47	219.0	219.2
C_4H_8S	tetrahydrothiophene	3.020	4.350	3.806	88.172	394.15	632.00	631.77		50.44		249.3
CH_3F	fluoromethane	2.378	1.682	1.230	34.033	194.74	317.80	318.77	58.80	65.81	113.0	107.6
CH_2F_2	difluoromethane	3.296	2.624	1.460	52.024	221.46	351.60	351.97	58.30	59.89	121.0	120.3
CHF_3	trifluoromethane	3.754	3.826	1.690	70.014	191.00	299.30	299.52	48.58	48.32	133.0	132.9
CF_4	perfluoromethane	3.752	5.288	1.920	88.005	145.13	227.60	227.60	37.40	37.39	140.0	145.6
C_2H_5F	fluoroethane	3.148	2.812	2.230	48.060	235.50	375.31	375.98	50.28	50.61		162.6
$C_2H_4F_2$	1,1-difluoroethane	3.836	3.884	2.460	66.050	248.20	386.70	388.32	45.00	44.61	181.0	175.3
$C_2H_3F_3$	1,1,1-trifluoroethane	4.064	5.216	2.690	84.050	225.60	346.30	350.74	37.60	36.48	194.0	187.9
C_2F_6	perfluoroethane	5.208	7.712	3.380	138.020	194.90	293.04	294.30		31.84	150.0	225.9
$C_3H_3F_5$	1,1,1,2,2-pentafluoropropane***	5.980	8.000	4.150	134.049	255.71	380.11	379.41	31.37	29.08	273.0	268.2
C_3F_8	perfluoropropane	6.664	10.136	4.840	188.020	236.50	345.10	345.91	26.80	27.19	299.0	306.2
C_4F_{10}	perfluorobutane	8.120	12.560	6.300	238.030	271.20	386.40	385.99	23.23	23.57	378.0	386.5
C_5HF_{11}	1-*H*-undecafluoropentane	9.348	13.652	7.530	270.045	318.20	444.00	443.87		23.03		454.1
C_5F_{12}	perfluoropentane	9.576	14.984	7.760	288.036	302.40	422.00	420.36	20.40	20.75		466.8
C_6HF_{13}	1-*H*-tridecafluorohexane	10.804	16.076	8.990	320.053	344.70	471.80	470.83		20.28		534.4
C_6F_{14}	perfluoro-2-methylpentane	11.376	15.958	9.104	338.044	330.81	453.00	448.46	18.20	21.72	550.0	540.7
C_6F_{14}	perfluoro-3-methylpentane	11.179	15.825	9.018	338.044	331.52	450.00	450.57	16.90	22.05		536.0
C_6F_{14}	perfluoro-2,3-dimethylbutane	11.720	18.222	8.988	338.044	332.93	463.00	449.37	18.70	17.02	525.0	534.3
C_6F_{14}	perfluorohexane	11.032	17.408	9.220	338.044	329.80	448.77	449.10	18.68	18.51	606.0	547.1
C_7F_{16}	perfluoroheptane	12.488	19.832	10.680	388.052	355.66	474.80	475.60	16.20	16.70	664.0	627.4
C_8F_{18}	perfluorooctane	13.944	22.256	12.140	438.060	376.70	502.00	495.67	16.60	15.20		707.7
C_9F_{20}	perfluorononane	15.400	24.680	13.600	488.068	398.50	524.00	516.85	15.60	13.94		788.0
$C_{10}F_{22}$	perfluorodecane	16.856	27.104	15.060	538.068	417.40	542.00	534.38	14.50	12.88		868.3
C_4F_8	perfluorocyclobutane	6.184	9.556	4.796	200.031	267.16	388.46	394.66	27.84	32.04	324.0	303.8
$C_8F_{16}O$	perfluoro-2-butyltetrahydrofuran	12.010	20.422	10.999	416.062	375.80	500.20	505.41	16.07	16.95	588.0	644.9
C_6HF_{11}	undecafluorocyclohexane	9.058	13.412	6.964	282.057	335.20	477.70	469.71		24.83		423.0
C_6F_{12}	perfluorocyclohexane	9.276	14.334	7.194	300.047	326.00	457.20	455.26	24.30	23.43		435.7
C_7F_{14}	perfluoromethylcyclohexane	9.934	17.218	8.654	350.055	349.50	486.80	483.26	23.30	19.56		516.0
$C_{10}F_{18}$	perfluorodecalin	11.568	21.946	11.530	462.081	415.00	566.00	561.21	15.20	16.46		674.1
C_2H_3F	fluoroethene***	2.598	2.602	1.835	46.050	201.00	327.90	326.58	52.40	53.58	144.0	140.9
$C_2H_2F_2$	1,1-difluoroethene***	2.936	3.664	2.019	64.040	187.45	302.90	301.25	44.60	47.02	154.0	151.0
C_2F_4	perfluoroethene	4.072	5.528	2.398	100.020	197.20	306.50	306.52	39.40	39.65	172.0	171.9
$C_3H_3F_3$	trifluoropropene***	4.304	5.556	3.290	96.052	244.00	376.20	376.90	38.00	37.77	211.0	220.9
C_6F_{12}	perfluorohex-1-ene	10.146	15.414	8.284	300.050	330.20	454.40	455.17		20.53		495.6
C_7F_{14}	perfluorohept-1-ene	11.602	17.838	9.744	350.050	354.20	478.20	478.78		18.33		575.9
C_6F_{10}	perfluorocyclohexene	8.374	12.572	6.600	292.050	325.20	461.80	460.83		25.91		403.0
C_6H_5F	fluorobenzene	3.824	4.913	4.262	96.104	357.88	560.09	560.10	45.51	45.75	269.0	274.4
$C_6H_2F_4$	1,2,3,4-tetrafluorobenzene	5.540	7.394	4.952	150.080	367.51	550.83	550.67	37.91	37.15	313.0	312.3
$C_6H_2F_4$	1,2,3,5-tetrafluorobenzene	5.540	7.394	4.952	150.080	357.61	535.21	535.83	37.47	37.15		312.3
$C_6H_2F_4$	1,2,4,5-tetrafluorobenzene	5.540	7.394	4.952	150.080	363.41	543.35	544.52	38.01	37.15		312.3
C_6HF_5	pentafluorobenzene	6.112	8.271	5.182	168.070	358.89	530.97	530.98	35.31	34.47	324.0	325.0
C_6F_6	perfluorobenzene	6.684	9.048	5.412	186.060	353.41	516.73	516.69	32.73	32.74	335.0	337.6
$C_7H_3F_5$	2,3,4,5,6-pentafluorotoluene	7.112	9.221	6.182	182.090	390.65	566.52	566.34	31.26	31.02	384.0	380.0
C_7F_8	perfluorotoluene	8.716	12.027	6.872	236.060	377.73	534.47	532.23	27.05	25.26	428.0	417.9
$C_{10}F_8$	perfluoronaphthalene	9.412	12.984	8.522	272.100	482.00	673.10	671.70		25.39		508.7
CH_3Cl	chloromethane	1.849	2.289	1.820	50.488	249.06	416.25	415.41	66.79	68.85	139.0	140.1
CH_2Cl_2	dichloromethane	2.512	3.658	2.640	84.933	313.00	510.00	510.02	60.80	62.50		185.2
$CHCl_3$	trichloromethane	2.989	5.107	3.460	119.378	334.32	536.40	536.39	54.70	53.54	276.0	230.3

Table V (Continued)

formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	T_c/K obsd	T_c/K calcd	P_c/bar obsd	P_c/bar calcd	G_v obsd	G_v calcd
CCl_4	tetrachloromethane	3.280	6.636	4.280	153.823	349.90	556.40	556.37	45.60	45.50	276.0	275.4
C_2H_5Cl	chloroethane	2.756	3.329	2.820	64.510	285.45	460.40	461.40	52.70	54.16		195.1
$C_2H_4Cl_2$	1,1-dichloroethane	3.326	4.738	3.640	98.960	330.50	523.00	524.80	50.70	49.79	236.0	240.2
$C_2H_4Cl_2$	1,2-dichloroethane	3.512	4.658	3.640	98.960	356.70	561.00	563.28	53.70	51.09	225.0	240.2
$C_2H_3Cl_3$	1,1,1-trichloroethane	3.710	6.227	4.460	133.400	347.24	545.00	545.21	43.00	43.74		285.3
$C_2H_3Cl_3$	1,1,2-trichloroethane*	4.082	6.067	4.460	133.400	386.70	606.00	600.90		45.61		285.3
$C_2H_2Cl_4$	1,1,2,2-tetrachloroethane*	4.652	7.476	5.280	167.850	419.40	626.00	642.01		40.79		330.4
C_2HCl_5	pentachloroethane	5.036	8.965	6.100	202.300	435.00	646.00	659.58		36.17		375.5
C_3H_7Cl	chloropropane	3.756	4.329	3.820	78.540	320.40	503.00	502.41	45.80	45.26		250.1
C_2H_3Cl	chloroethene*	2.343	3.029	2.460	62.499	259.78	432.00	425.74	56.70	59.66		175.3
C_2HCl_3	trichloroethene*	3.243	5.567	3.995	131.389	360.10	571.00	573.24	49.10	51.51		259.7
C_2Cl_4	tetrachloroethene	3.600	6.876	4.780	165.834	394.40	620.20	621.22		46.28		302.9
C_3H_5Cl	3-chloropropene	3.456	4.029	3.420	76.530	318.30	514.00	503.47		49.01		228.1
C_6H_5Cl	chlorobenzene	3.894	5.486	4.852	112.560	404.87	632.40	632.41	45.20	45.16	308.0	306.8
$C_6H_4Cl_2$	dichlorobenzene	4.536	6.886	5.672	147.000	452.00	729.00	693.97		40.93		351.9
CH_3Br	bromomethane	1.690	3.800	2.150	94.939	276.61	464.00	464.11		66.17		158.2
CH_2Br_2	dibromomethane	2.300	6.600	3.300	173.835	369.52	607.00	606.48	65.00	51.87		221.5
$CHBr_3$	tribromomethane	2.830	9.400	4.450	252.731	422.13	685.00	680.70	56.48	41.65		284.7
$C_2H_4Br_2$	1,2-dibromoethane*	3.300	7.600	4.300	187.862	404.70	583.00	643.12	71.50	44.42		276.5
C_6H_5Br	bromobenzene	3.894	6.886	5.182	157.010	429.21	670.00	670.42	45.20	43.71	324.0	325.0
CH_3I	iodomethane	1.690	5.068	2.620	141.939	315.70	528.00	529.70		64.42		184.1
C_2H_5I	iodoethane*	2.650	6.068	3.620	155.966	345.60	554.00	560.57		53.32		239.1
C_6H_5I	iodobenzene	3.894	8.154	5.652	204.010	461.60	721.00	721.02	45.20	42.86	351.0	350.8
CHF_2Cl	chlorodifluoromethane	3.639	4.253	2.280	86.469	232.40	369.30	365.64	49.71	51.15	166.0	165.4
$CHFCl_2$	dichlorofluoromethane	3.350	4.760	2.870	102.923	282.10	451.58	447.62	51.84	51.42	196.0	197.8
CCl_2F_2	dichlorodifluoromethane	3.796	5.962	3.100	120.914	245.20	384.95	384.06	41.36	42.52	217.0	210.5
	refrigerant 500	3.778	5.204	2.879	100.500	239.69	378.65	375.62	44.26	43.78	200.0	198.3
$CClF_3$	chlorotrifluoromethane	3.844	5.625	2.510	104.459	193.20	302.00	302.20	38.70	40.29	180.0	178.0
CCl_3F	trichlorofluoromethane	3.608	6.299	3.690	137.370	296.90	471.20	467.54	44.10	44.22	248.0	242.9
$C_2H_3ClF_2$	1-chloro-1,1-difluoroethane	4.086	5.553	3.280	100.500	263.40	409.60	409.26	43.32	39.56	231.0	220.4
C_2HClF_4	chloro-1,1,2,2-tetrafluoroethane***	5.002	6.717	3.740	136.480	263.00	399.90	399.11	37.20	39.58	244.0	245.7
C_2ClF_5	chloropentafluoroethane	5.230	8.049	3.970	154.470	235.20	353.20	354.97	32.29	33.17	252.0	258.3
$C_2Cl_2F_4$	1,1-dichlorotetrafluoroethane	5.112	8.386	4.560	170.920	277.00	418.60	419.24	33.00	34.24	294.0	290.8
$C_2Cl_2F_4$	1,2-dichlorotetrafluoroethane	5.252	8.386	4.560	170.920	276.20	418.90	416.63	32.60	34.24	294.0	290.8
$C_2Cl_3F_3$	1,2,2-trichlorotrifluoroethane	5.134	8.723	5.150	187.380	320.80	487.30	485.27	34.10	35.10	325.0	323.2
CCl_4F_2	tetrachloro-1,2-difluoroethane	5.016	9.060	5.740	203.830	366.00	551.00	555.22		35.79		355.7
C_2Cl_3F	chlorotrifluoroethene	4.024	5.865	2.999	116.470	245.30	379.00	381.78	40.50	42.04	212.0	204.9
C_2ClF_3	1-chloro-2,2-difluoroethene	3.479	4.893	2.804	98.480	254.60	400.60	402.44	44.60	47.18	197.0	194.2
C_6ClF_5	chloropentafluorobenzene	6.754	9.621	6.002	202.510	391.11	570.81	571.01	32.38	32.06	376.0	370.1
$C_6Cl_2F_4$	dichlorotetrafluorobenzene	6.824	10.194	6.592	218.970	430.90	626.00	628.22	53.20	31.35		402.5
$C_6Cl_3F_3$	1,3,5-trichlorotrifluorobenzene	6.894	10.767	7.182	235.420	471.52	684.80	686.49	32.70	30.63	448.0	435.0
$CBrF_3$	bromotrifluoromethane	3.544	7.016	2.840	148.910	215.26	340.20	339.61	39.70	40.20	176.0	196.2
CBr_2F_2	dibromodifluoromethane	3.516	8.744	3.760	209.820	298.00	471.30	470.53		39.15		246.8
$C_2Br_2F_4$	1,2-dibromotetrafluoroethane	4.852	11.168	5.220	259.830	320.40	487.80	488.01	33.93	31.70	341.0	327.1
$C_4Br_2F_8$	1,4-dibromooctafluorobutane	7.764	16.016	8.140	359.840	370.00	532.50	529.94	23.90	22.96		487.7
C_6BrF_5	bromopentafluorobenzene	6.754	11.021	6.332	246.960	410.00	601.00	598.59	30.40	30.84		388.2
CH_2ClBr_2	bromochloromethane	2.376	5.109	2.970	129.384	341.21	558.00	558.56	63.99	58.00		203.3
CCl_3Br	bromotrichloromethane	3.190	8.027	4.610	198.274	377.86	603.00	602.48	46.50	42.77		293.5
$CBrClF_2$	bromochlorodifluoromethane	3.566	7.353	4.430	165.365	269.00	426.88	424.12	42.54	41.31	246.0	283.6
$C_2Br_2ClF_3$	BrClFC–CBrF$_2$	4.804	11.505	5.220	276.280	366.00	560.70	558.13	36.10	31.98		327.1
$C_2H_2Cl_2O$	chloroacetyl chloride	4.626	4.988	3.710	112.943	379.15	581.00	580.78	51.10	52.53		244.0
C_3F_6O	perfluoroacetone***	7.508	8.962	4.450	166.020	245.70	357.14	353.55	28.40	29.70	329.0	284.7
C_3ClF_5O	chloropentafluoroacetone***	7.530	9.299	5.040	182.480	281.00	410.60	404.18	28.78	30.64		317.2
$C_2HF_3O_2$	trifluoroacetic acid***	7.064	6.216	3.050	114.020	346.00	491.30	502.08	32.58	37.50	204.0	207.7
C_2F_3N	trifluoroacetonitrile***	4.864	5.546	3.140	95.020	204.30	311.11	311.08	36.18	37.47	202.0	212.7
C_6HF_5O	pentafluorophenol	6.962	7.921	5.168	184.070	418.79	609.00	608.91	40.00	40.60	348.0	324.2
H_2	hydrogen (normal)**	2.520	0.246	0.455	2.020	20.38	33.20	33.20	12.97	12.97	65.0	65.0
H_2	hydrogen (equilibrium)**	2.571	0.249	0.437	2.020	20.28	32.98	32.98	12.93	12.93	64.0	64.0
HD	hydrogen deuteride**	2.575	0.499	0.418	3.020	22.14	36.00	36.00	14.80	14.80	63.0	63.0
D_2	deuterium**	2.366	0.680	0.364	4.030	23.45	38.40	38.40	16.60	16.60	60.0	60.0
D_2	deuterium (equilibrium)**	2.765	0.687	0.364	4.030	23.64	38.20	38.20	16.50	16.50	60.0	60.0
T_2	tritium**	3.129	1.120	0.300	6.320	25.04	40.00	40.00	18.03	18.03	56.5	56.5
^3He	helium-3**	183.630	5.678	0.582	3.000	3.19	3.31	3.31	1.14	1.14	72.0	72.0
^4He	helium-4**	-4.250	4.350	0.324	4.003	2.10	5.30	5.30	2.29	2.29	57.8	57.8
Ne	neon**	2.447	2.308	0.031	20.183	27.25	44.50	44.50	27.25	27.25	41.7	41.7
Ar	argon**	0.977	2.510	0.640	39.944	87.29	150.69	150.69	48.63	48.63	75.2	75.2
Kr	krypton**	0.890	3.958	0.949	83.700	120.85	209.40	209.40	55.01	55.01	92.2	92.2
Xe	xenon**	0.727	5.119	1.433	131.300	166.05	289.75	289.75	58.68	58.68	118.8	118.8
XeF_2	xenon difluoride	2.276	4.144	1.960	169.300	387.50	631.00	636.52	93.20	104.06	149.0	147.8
XeF_4	xenon tetrafluoride	3.652	6.288	2.420	207.290	388.90	612.00	611.64	70.40	66.91	188.0	173.1
Rn	radon**	0.251	6.100	1.450	222.000	211.40	376.99	376.99	75.25	75.25	119.7	119.7
air	air	2.222	2.375	0.831	28.970	78.85	132.45	129.77	37.72	37.77	88.3	85.7

Table V (Continued)

							T_c/K		P_c/bar		G_v	
formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	obsd	calcd	obsd	calcd	obsd	calcd
F_2	fluorine	1.376	2.144	0.460	37.997	85.01	144.30	144.38	52.15	56.02	66.0	65.3
Cl_2	chlorine	1.140	2.818	1.640	70.906	239.18	416.90	410.11	79.77	74.46	124.0	130.2
Br_2	bromine	1.140	5.600	2.300	159.808	331.93	588.00	569.14	103.00	62.07	127.0	166.5
IBr	iodine bromide	1.140	6.868	2.770	206.810	389.00	719.00	666.99		57.82	139.0	192.3
I_2	iodine	1.140	8.136	3.240	253.809	457.50	819.00	784.44		53.52		218.2
ClF_5	chlorine pentafluoride	4.010	6.769	1.970	130.440	260.00	416.00	404.82	52.70	37.35	233.0	148.3
ClO_3F	perchloryl fluoride	4.258	4.461	1.920	102.450	226.40	368.40	350.14	53.70	56.45	161.0	145.6
HF	hydrogen fluoride	3.688	1.197	0.450	20.010	293.00	461.00	460.34	64.80	53.86	69.0	64.7
HCl	hydrogen chloride	0.570	1.409	0.820	36.460	188.00	324.70	330.35	83.10	84.36	81.0	85.1
DCl	deuterium chloride	0.670	1.459	0.820	37.470	191.50	323.50	335.00		83.79		85.1
HBr	hydrogen bromide	0.570	2.800	1.150	80.910	206.77	363.20	363.34	85.50	85.67		103.2
DBr	deuterium bromide	0.670	2.850	1.150	81.920	208.00	362.00	363.87		84.76		103.2
HI	hydrogen iodide	0.570	4.068	1.620	127.910	237.60	424.00	417.51	83.10	80.78		129.1
DI	deuterium iodide	0.670	4.118	1.620	128.920	237.00	421.80	414.60		79.97		129.1
Rb	rubidium**	–2.760	8.000	3.837	85.470	974.00	2105.09	2105.09	18.54	18.54	251.0	251.0
Cs	cesium**	–2.807	13.105	4.764	132.910	958.00	2078.95	2078.95	12.20	12.20	302.0	302.0
O_2	oxygen**	1.149	2.025	0.600	31.999	90.19	154.58	154.58	50.42	50.42	73.0	73.0
O_3	ozone***	2.019	2.735	0.963	47.998	161.25	268.00	267.29	67.88	52.40	89.4	92.9
CO	carbon monoxide**	2.542	2.459	0.964	28.010	81.65	132.91	132.91	34.99	34.99	93.0	93.0
CO_2	carbon dioxide	2.400	1.920	0.980	44.010	185.90	304.10	304.07	73.75	73.67	94.0	93.9
$COCl_2$	phosgene***	2.940	4.278	2.710	98.920	281.00	455.00	451.54	56.70	58.01	190.0	189.0
OF_2	oxygen fluoride	2.246	2.854	0.823	54.000	128.40	215.00	211.13		55.77		85.3
H_2O	water**	0.870	–0.236	0.290	18.015	373.15	647.11	647.11	220.76	220.76	55.9	55.9
D_2O	heavy water***	1.070	–0.136	0.290	20.030	374.58	644.00	644.13	216.60	210.78	56.0	55.9
S	sulfur**	–0.276	0.357	2.146	32.060	717.80	1314.02	1314.02	182.02	182.02	158.0	158.0
H_2S	hydrogen sulfide	0.760	1.200	1.000	34.082	212.96	373.54	371.07	90.08	91.53	98.0	95.0
D_2S	deuterium sulfide	0.960	1.300	1.000	36.090	215.00	372.30	371.42		90.13		95.0
SO_2	sulfur dioxide	2.400	2.520	1.580	64.060	263.20	430.80	430.50	78.84	77.61	122.0	126.9
SO_3	sulfur trioxide	3.800	2.780	1.870	80.060	318.00	491.00	498.03	82.10	85.57	127.0	142.8
COS	carbonyl sulfide	1.660	2.460	1.690	60.076	223.00	375.00	374.59	63.49	75.01	135.0	132.9
CS_2	carbon disulfide	0.920	3.000	2.400	76.130	319.00	552.00	552.02	73.00	73.61	173.0	172.0
SF_5Cl	sulfur chloride pentafluoride	4.810	7.569	2.970	162.500	254.10	390.90	387.43		38.68		203.3
SF_4	sulfur tetrafluoride	3.152	5.488	1.920	108.050	232.70	364.00	371.46		43.32		145.6
SF_6	sulfur hexafluoride	4.928	7.232	2.380	146.050	209.60	318.69	318.65	37.59	37.50	198.0	170.9
Se	selenium**	0.681	0.886	0.435	78.960	1010.00	1766.00	1766.00	271.55	271.55	63.9	63.9
H_2Se	hydrogen selenide	0.400	2.700	1.500	80.980	231.90	411.00	410.67	89.20	89.88	120.0	122.5
D_2Se	deuterium selenide	0.600	2.800	1.505	82.990	233.00	412.40	408.88		87.88		122.8
SeF_6	selenium hexafluoride	4.528	9.132	2.880	192.950	227.00	345.50	348.59		33.42		198.4
$SeOCl_2$	selenium oxychloride***	2.540	6.178	3.430	165.870	300.40	506.00	489.03	70.90	55.09	235.0	228.6
TeF_6	tellurium hexafluoride	4.928	10.132	2.980	241.590	227.00	345.50	345.10		34.96		203.9
$TeCl_4$	tellurium tetrachloride	3.080	9.236	4.880	269.410	597.00	1000.00	955.12	85.60	45.76	310.0	308.4
Hg	mercury**	–4.979	3.600	0.055	200.590	629.88	1765.01	1765.01	150.99	150.99	43.0	43.0
$HgCl_2$	mercuric chloride	1.390	6.418	2.440	271.500	577.00	973.00	979.42		84.79	174.0	174.2
$HgBr_2$	mercuric bromide	1.390	9.200	3.100	360.400	595.00	1012.00	1009.98		61.63		210.5
HgI_2	mercuric iodide	1.390	11.736	4.040	454.400	627.00	1072.00	1064.29		50.78		262.2
B_2H_6	diborane	3.000	4.000	2.400	27.670	185.60	289.80	297.68	40.50	17.91		172.0
BF_3	boron trifluoride	3.564	5.216	1.890	67.810	172.00	260.80	271.20	49.90	29.43	115.0	143.9
BCl_3	boron trichloride	3.210	6.227	3.660	117.170	285.80	455.00	455.42	38.70	38.42	239.0	241.3
BBr_3	boron tribromide	3.210	10.400	4.650	250.520	364.00	581.00	580.03		34.64		295.7
BI_3	boron triiodide	3.210	14.204	6.060	391.520	483.00	773.00	769.65		31.08		373.3
$C_3H_9BO_3$	methyl borate	7.100	7.130	5.289	103.910	342.00	501.70	495.93	35.90	27.32		330.9
$AlCl_3$	aluminum trichloride	7.710	8.227	3.960	133.340	453.00	620.00	649.45	26.30	27.59	257.0	257.8
$AlBr_3$	aluminum tribromide	7.710	12.400	4.950	266.690	528.00	763.00	756.97	28.90	27.02	310.0	312.2
AlI_3	aluminum triiodide	7.710	16.204	6.360	407.690	655.00	983.00	939.04		25.47	408.0	389.8
$GaCl_3$	gallium trichloride	6.710	8.227	3.960	176.080	474.00	694.00	692.64		36.44	263.0	257.8
$GaBr_3$	gallium tribromide	6.710	12.400	4.950	309.430	552.00	806.70	806.61		31.36	303.0	312.2
GaI_3	gallium triiodide	6.710	16.204	6.360	450.430	613.00	951.00	895.75		28.14	395.0	389.8
N_2	nitrogen	2.500	2.520	1.800	28.013	77.35	126.09	126.09	33.94	33.94	139.0	139.0
N_2O	nitrous oxide***	1.850	1.960	1.770	44.010	184.67	309.60	308.01	72.40	71.98	97.0	137.3
NO	nitric oxide**	6.016	1.511	0.328	30.010	121.41	180.00	180.00	64.80	64.81	58.0	58.0
N_2O_4	dinitrogen tetraoxide	3.200	2.720	2.320	92.010	294.30	431.00	469.10	101.00	101.16	167.0	167.6
NF_3	nitrogen trifluoride***	2.664	4.016	1.270	71.000	144.40	234.00	234.11	45.30	45.69		109.8
$NClF_2$	nitrogen chloride difluoride***	2.546	4.353	1.860	87.460	207.00	337.50	336.92	64.30	49.98		142.3
HNF_2	difluoroamine	2.876	2.564	1.040	53.010	250.00	403.00	402.54		62.84		97.2
NH_4Cl	ammonium chloride	12.170	1.949	2.280	53.490	793.00	882.00	1064.44	16.35	88.04		165.4
NO_2F	nitryl fluoride	2.288	2.432	1.390	65.000	213.20	349.50	350.06		82.31		116.4
NOF_3	trifluoroamine oxide	2.664	3.916	1.560	87.000	186.00	303.00	301.55		58.07	147.0	125.8
NOCl	nitrosyl chloride***	2.112	2.424	1.690	65.460	267.70	440.00	442.27	91.20	83.23	139.0	132.9
NH_3	ammonia**	1.500	0.214	0.580	17.030	239.82	405.50	405.33	113.50	113.49	72.0	71.9
ND_3	nitrogen trideuteride***	1.800	0.314	0.580	20.050	242.10	405.60	404.54		119.30		71.9
N_2H_4	hydrazine	1.400	0.566	1.160	32.050	386.70	653.00	656.14	147.00	147.01		103.8
N_2F_4	tetrafluorohydrazine	3.952	5.888	2.080	104.010	199.00	309.00	310.34	37.00	37.31		154.4
N_2F_2	*cis*-difluorodiazine***	2.460	2.854	1.620	66.010	167.50	272.00	273.41		68.17		129.1
N_2F_2	*trans*-difluorodiazine***	2.660	3.004	1.620	66.010	161.70	260.00	262.19		63.71		129.1
C_2N_2	cyanogen	3.600	2.660	2.900	52.020	252.00	400.00	396.93	59.80	58.85		199.5

Table V (Continued)

							T_c/K		P_c/bar		G_v	
formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	obsd	calcd	obsd	calcd	obsd	calcd
HCN	hydrogen cyanide	4.800	1.455	1.670	27.026	299.00	456.79	456.00	53.90	60.60	139.0	131.8
P	phosphorus**	0.087			30.970	553.00	994.00	994.00		59.21		128.0
PH_3	phosphine	1.000	1.700	1.600	34.000	185.41	324.50	319.77	65.40	65.01		128.0
PD_3	phosphorus trideuteride	1.300	1.840	1.600	37.020	187.00	323.60	318.56		64.97		128.0
PH_4Cl	phosphonium chloride	13.320	3.609	3.300	70.460	246.00	322.30	325.87	73.70	52.85	130.0	221.5
PF_3	phosphorus trifluoride	3.064	4.916	2.290	87.970	178.00	271.20	284.92	43.30	41.84		165.9
PCl_3	phosphorus trichloride	2.710	5.927	4.060	137.330	349.10	563.00	565.13		48.74	264.0	263.3
PCl_5	phosphorus pentachloride	3.600	8.745	5.700	208.240	433.00	646.00	682.02		38.84		353.5
PBr_3	phosphorus tribromide	2.710	10.100	5.050	270.690	446.10	711.00	722.16		39.39	300.0	317.7
PF_2Cl	phosphorus chloride difluoride	2.946	5.253	2.880	104.420	225.90	362.40	362.93	45.20	44.83		198.4
$PFCl_2$	phosphorus dichloride fluoride	2.828	5.590	3.470	120.880	287.00	463.00	462.83	49.60	47.08		230.8
$P_3N_3F_6$	phosphonitrilic fluoride trimer	8.004	12.597	7.920	248.930	324.00	461.00	462.07		24.52		475.6
$P_4N_4F_8$	phosphonitrilic fluoride tetramer	10.672	16.796	10.560	331.910	363.00	496.40	496.71		19.41		620.8
$P_5N_5F_{10}$	phosphonitrilic fluoride pentamer	13.340	20.995	13.200	414.890	392.50	524.00	519.81		16.05		766.0
PSF_3	thiophosphoryl trifluoride	3.074	6.116	3.290	120.030	220.90	346.00	353.48	38.20	40.52		220.9
PSF_2Cl	thiophosphoryl chloride difluoride	2.956	6.453	3.880	136.480	279.00	439.20	448.10	41.40	42.25		253.4
As	arsenic**	−0.803	1.065	−0.091	74.920	888.00	1673.02	1673.02	222.95	222.95	35.0	35.0
AsH_3	arsine	1.000	1.500	1.400	77.950	218.00	373.10	375.97		169.57		117.0
AsD_3	arsenic deuteride	1.300	1.650	1.400	80.970	220.00	372.10	374.78		159.77		117.0
$AsCl_3$	arsenic trichloride	2.710	5.727	3.860	181.280	403.00	654.00	652.38		67.95	252.0	252.3
$SbCl_3$	antimony trichloride	2.460	5.727	4.260	228.110	493.40	794.00	805.39		85.51	272.0	274.3
$SbBr_3$	antimony tribromide	2.460	9.900	5.250	361.460	553.00	904.00	902.67		54.45	300.0	328.7
SbI_3	antimony triiodide	2.460	13.704	6.660	502.460	674.00	1102.00	1100.18		42.56		406.3
$BiCl_3$	bismuth chloride	2.210	5.727	3.960	315.340	720.00	1179.00	1185.42	120.00	118.21	261.0	257.8
$BiBr_3$	bismuth bromide	2.210	9.900	4.950	448.690	726.00	1220.00	1195.30		67.60	301.0	312.2
SiH_4	silane	1.500	2.400	2.100	32.120	161.00	269.70	272.11	48.40	41.35		155.5
$SiCH_6$	methylsilane	2.500	3.400	3.100	46.147	215.60	352.50	351.45		37.63		210.5
SiC_4H_{12}	tetramethylsilane	5.500	6.400	6.100	88.230	299.80	448.64	449.63	28.21	27.68	362.0	375.5
SiC_8H_{20}	tetraethylsilane	9.500	10.400	10.100	144.330	427.90	603.70	595.51	26.02	19.95		595.5
CH_5SiCl	chloromethylsilane	3.070	4.809	3.920	80.590	280.00	517.80	448.10		39.64		255.6
CH_4SiCl_2	dichlorodimethylsilane	4.640	7.218	5.740	129.060	343.45	520.40	525.91	34.90	33.25	350.0	355.7
C_3H_9SiCl	chlorotrimethylsilane	5.070	6.809	5.920	108.640	333.15	497.80	504.73	32.00	30.81	366.0	365.6
SiH_3CCl_3	trichloromethylsilane	4.210	7.627	5.560	149.480	338.80	517.00	524.65	32.80	35.13	348.0	345.8
$SiCl_3C_2H_5$	trichloroethylsilane	5.210	8.627	6.560	163.510	371.55	560.00	561.02	33.30	31.22	403.0	400.8
$C_4H_{10}SiCl_2$	dichlorodiethylsilane	6.640	9.218	7.740	157.120	403.60	595.80	590.60	30.60	26.78	455.0	465.7
$Si_2C_6H_{18}O$	hexamethyldisiloxane	9.870	11.510	10.563	162.380	372.70	516.60	515.82	19.10	18.78	629.0	621.0
$Si_3C_8H_{24}O_2$	octamethyltrisiloxane	13.470	16.620	15.026	236.540	425.00	562.90	562.06		14.10		866.4
$Si_4C_{10}H_{30}O_3$	decamethyltetrasiloxane	17.070	21.730	19.489	310.690	465.00	599.40	594.25		11.27		1111.9
$Si_5Cl_{12}H_{36}O_4$	dodecamethylpentasiloxane	20.670	26.840	23.952	384.850	502.00	629.00	624.60	9.45	9.38		1357.3
$Si_6C_{14}H_{42}O_5$	tetradecamethylhexasiloxane	24.270	31.950	28.415	459.000	536.00	653.20	652.74	8.04	8.03		1602.8
$Si_7C_{16}H_{48}O_6$	hexadecamethylheptasiloxane	27.870	37.060	32.878	533.160	561.00	671.80	671.26	6.77	7.02		1848.3
$Si_8C_{18}H_{54}O_7$	octadecamethyloctasiloxane	31.470	42.170	37.341	607.310	584.00	688.90	688.57	6.24	6.23		2093.7
$Si_2Cl_{12}H_{30}O$	hexaethyldisiloxane	10.470	17.510	16.563	246.540	504.00	693.00	691.58		13.36		950.9
$Si_4C_{20}H_{50}O_3$	decaethyltetrasiloxane	14.470	31.730	29.489	450.960	598.00	788.00	782.63		8.00		1661.9
$Si_5C_{24}H_{60}O_4$	dodecaethylpentasiloxane	16.470	38.840	35.952	553.170	633.00	823.00	813.09		6.66		2017.3
$Si_4C_8H_{24}O_4$	octamethylcyclotetrasiloxane	14.400	20.440	17.852	296.620	448.00	586.50	586.73	13.24	12.06		1021.8
$Si_5C_{10}H_{30}O_5$	decamethylcyclopentasiloxane	18.000	25.550	22.315	370.780	483.00	593.00	612.63		9.92		1267.3
$Si_3C_{12}H_{30}O_3$	hexaethylcyclotrisiloxane	16.800	21.330	19.389	306.630	520.00	673.00	666.05		11.52		1106.4
$Si_4C_{16}H_{40}O_4$	octaethylcyclotetrasiloxane	22.400	28.440	25.852	408.840	569.00	698.00	700.31		8.93		1461.8
SiF_4	silicon tetrafluoride	4.252	6.688	3.020	104.080	187.00	259.00	289.25	37.20	30.39		206.1
$SiCl_4$	silicon tetrachloride	3.780	8.036	5.380	169.900	330.80	508.10	518.37	35.93	36.58		335.9
$SiBr_4$	silicon tetrabromide	3.780	13.600	6.700	367.520	503.00	795.70	788.21		31.56		408.5
SiI_4	silicon tetraiodide	3.780	18.672	8.580	535.700	560.50	944.00	878.31		25.78		511.9
$SiHCl_3$	trichlorosilane	3.210	6.627	4.560	135.450	306.00	479.00	487.60		40.15	268.0	290.8
$SiHBr_3$	tribromosilane	3.210	10.800	5.550	268.810	382.00	610.00	608.71		34.79	305.0	345.2
$TiCl_4$	titanium tetrachloride	3.480	7.436	5.380	189.710	409.60	638.00	647.43	46.60	46.51	339.0	335.9
$TiBr_4$	titanium tetrabromide	3.480	13.000	6.700	367.520	503.00	795.70	795.06		34.22	391.0	408.5
TiI_4	titanium tetraiodide	3.480	18.072	8.580	555.520	650.00	1040.00	1027.42		28.39	505.0	511.9
$ZrCl_4$	zirconium tetrachloride	16.280	7.436	5.080	233.030	604.00	778.00	777.13	57.70	57.14	319.0	319.4
$ZrBr_4$	zirconium tetrabromide	16.280	13.000	6.400	410.840	630.00	805.00	810.59		38.26	424.0	392.0
ZrI_4	zirconium tetraiodide	16.280	18.072	8.280	598.840	704.00	960.00	905.80		30.61	530.0	495.4
$HfCl_4$	hafnium tetrachloride	22.280	9.236	5.480	320.300	590.00	725.70	726.68	54.20	54.41	314.0	341.4
$HfBr_4$	hafnium tetrabromide	22.280	14.800	6.800	498.110	595.00	746.00	732.84		36.71	415.0	414.0
HfI_4	hafnium tetraiodide	22.280	19.872	8.680	686.110	690.00	916.00	849.85		29.41	528.0	517.4
$GeCl_4$	germanium tetrachloride	4.280	8.836	5.280	214.400	359.70	553.20	555.97	38.61	39.29	330.0	330.4
$GeBr_4$	germanium tetrabromide	4.280	14.400	6.600	392.210	459.50	710.23	710.23	30.37	30.37	403.0	403.0
GeI_4	germanium tetraiodide	4.280	19.472	8.480	580.210	650.00	973.00	1004.68		25.83	500.0	506.4
$SnCl_4$	tin tetrachloride	4.280	10.136	5.680	260.500	387.30	591.90	598.63	37.50	37.67	351.0	352.4
$SnBr_4$	tin tetrabromide	4.280	15.700	7.000	438.310	478.00	744.00	738.83		29.01	417.0	425.0
SnI_4	tin tetraiodide	4.280	20.772	8.880	626.310	637.50	968.00	985.36		24.72	531.0	528.4
VOCl	vanadium oxychloride	3.270	3.869	3.310	102.390	400.00	636.00	636.23		69.54	171.0	222.0
$NbCl_5$	niobium pentachloride	4.850	8.845	6.300	270.170	527.20	803.50	803.03	48.80	49.43	397.0	386.5

Table V (Continued)

							T_c/K		P_c/bar		G_v	
formula	compound[a]	N_t	N_p	N_v	MW	T_b/K	obsd	calcd	obsd	calcd	obsd	calcd
$NbBr_5$	niobium pentabromide	4.850	15.800	7.950	492.430	634.80	1010.00	966.93		32.21	469.0	477.2
$TaCl_5$	tantalum pentachloride	4.850	10.545	6.500	358.210	512.50	767.00	780.64		48.34	402.0	397.5
$TaBr_5$	tantalum pentabromide	4.850	17.500	8.150	580.470	622.00	974.00	947.43		31.48	461.0	488.2
MoF_6	molybdenum hexafluoride	4.628	8.432	4.280	209.930	307.00	473.00	470.24	47.50	41.67	226.0	275.4
$MoCl_5$	molybdenum pentachloride	3.350	9.045	7.000	273.210	541.00	850.00	858.43		48.10	369.0	425.0
WF_6	tungsten hexafluoride	4.628	10.332	3.380	297.840	290.00	444.00	444.20	43.40	41.65	233.0	225.9
WCl_6	tungsten hexachloride	3.920	12.354	6.920	396.570	619.90	923.00	967.58		40.45	422.0	420.6
$WOCl_4$	tungsten oxide tetrachloride	3.780	10.196	5.570	341.660	500.70	782.00	784.60		48.90	338.0	346.3
Re_2O_7	rhenium oxide	8.000	13.020	7.030	298.200	723.00	942.00	1031.18		27.69	206.0	426.6
$ReOCl_4$	rhenium oxide tetrachloride	3.780	10.496	6.070	344.010	496.15	781.00	777.47		46.80	362.0	373.8
UF_6	uranium hexafluoride	4.628	10.632	3.780	352.020	329.00	505.80	503.94	46.60	46.83	250.0	247.9

[a] (*) The values listed as observed for this compound may not be experimental and reliable. (**) The critical indices for this compound are the observed ones. (***) (1) Ethylene glycol: the –OH groups of this compound are treated as the ethanolic –OH group. (2) Cyclohexanol: the –OH group in this compound is treated as the methanolic –OH group. (3) 2-Propene-1-ol: the –OH group of this compound is treated as the propanolic –OH group. (4) Methanol: Counting from the side chain, the alcohol in this compound has a chain length of eight. Therefore, the –OH group of this compound is treated as the octanolic –OH group. (5) 1,1,1,2,2-Pentafluoropropane: the $-CF_3$ is treated as in the perfluoro compounds. The $-CF_2$ group is treated as in the normal compounds. (6) Fluoroethene: $=CHF$ in this compound is treated as in perfluoro compounds. (7) 1,1-Difluoroethene: the $=CF_2$ group in this compound is treated as in perfluoro compounds. (8) Trifluoropropene: the compound is assumed to be 3,3,3-trifluoropropene. The $-CF_3$ group is then treated as in perfluoro compounds. (9) Chloro-1,1,2,2-tetrachloroethane: this compound is treated as a perhalogenated compound. (10) Perfluoroacetone and chloropentafluoroacetone are treated as perhalogenated compounds. (11) Trifluoroacetic acid: according to the notes provided by Kudchdker, Alani, and Zwolinski (*4*), this compound contained traces of water as impurity, producing a difference of 15 kPa between the bubble point and the dew point. We treated the $-CF_3$ group in this compound as in normal compounds. (12) Trifluoroacetonitrile: the CF_3 group in this compound is treated as normal and the –CN group as in cyanogen, hydrogen cyanide, etc. (13) Ozone: it is treated as consisting of two =O and –O– groups. (14) Phosgene: it is treated as consisting of >C=, =O, and two –Cl groups. (15) Heavy water: the critical indices of water are used in the calculation of the critical indices for this compound. (16) Selenium oxychloride: the estimated critical temperature for this compound in literature is 730 K. This value appears be incorrect. (17) Nitrous oxide: the critical indices for this compound are calculated assuming the molecule to be consisting of ≡N, =N=, and =O groups. (18) Nitrogen trifluoride and nitrogen chloride difluoride: nitrogen atom in these compounds is treated as the nitrogen atom of the tertiary amines. (19) Nitrogen trideuteride: the experimental critical indices for ammonia are used in the calculation of the critical indices for this compound. (20) *cis*-Difluorodiazine, *trans*-difluorodiazine, and nitrosyl chloride: for nitrogen in these compounds, the critical indices of =N– (general) are used. In the case of *trans*-difluorodiazine, the trans alkene correction is also applied.

timate the critical constants for all the higher members in any homologous series using Kreglewski's equations. In the case of critical temperature, estimated values are obtained by averaging the critical temperatures predicted by eq 11 and 12. The experimental critical temperatures of normal alkanes are compared with the predicted values in Table IV. The procedure of Kreglewski applies from butane to all alkanes of higher carbon number. Kreglewski's procedure, however, yields poor results for the lower members. However, by combining the procedures of Lydersen and Ambrose with those of Kreglewski as shown above, we were able to generate the critical constants of several homologous series of compounds (*18*, *19*). According to eq 8 P_c tends to zero as N tends to infinity. It is instructive, therefore, to assume that $P_c = 0$ at the infinite critical temperature of 960 K for the homologous series of compounds.

Special Corrections

For treating molecules such as the branched alkanes, we also need to make corrections for branching as well for steric interactions. For $\sum\Delta_t$ of alkanes Ambrose used the equation

$$\sum\Delta_t = 1.242 + 0.138N - 0.043N_3 - 0.120N_4 - 0.023\Delta P \tag{15}$$

where ΔP is the difference between the Platt number of the isomer and the normal alkane. Platt number is the total number of pairs of carbon atoms three bonds apart (*20*). Better results are, however, obtained by replacing the parameter ΔP by N_g, the number of C–C–C–C structural features in the gauche position as in *gauche*-butane. In general, for N_i we write

$$N_i = n_i(-CH_3)N_1 + n_i(>CH_2)N_2 + n_i(>CH-)N_3 + n_i(>C<)N_4 + n_i(C-C-C-C)N_g \tag{16}$$

In order to make the present scheme consistent with the approach to normal alkanes we have deliberately set the n_i values of both $-CH_3$ and $>CH_2$ groups equal to 1.000 and obtained the values for other constants of eq 16 by linear regression. This is equivalent to transforming eq 16 into eq 17 as suggested by Ambrose in his comments on this paper:

$$N_i = N + \Delta n_i(>CH-)N_3 + \Delta n_i(>C<)N_4 + n_i(C-C-C-C)N_g \tag{17}$$

where

$$\Delta n_i(>CH-) = 1 - n_i(>CH-)$$

$$\Delta n_i(>C<) = 1 - n_i(>C<)$$

It is more expedient to use eq 17 than eq 16 in the case of alkanes.

According to Ambrose, eq 3 and 5 are not satisfactory for alkanols, perfluoroalkanes, etc. He has, therefore, modified his procedures for the calculation of the group contributions, Δ_i, in these compounds. Both Δ_t and Δ_p of the –OH group of the alkanols is expressed as a function of the carbon number in the case of primary alkanols or the effective carbon number in the case of the branched alkanols. We have found that the n_t of the ethanolic –OH group has a value of 4.67, and it decreases to a value of 1.13 in 1-octanol and remains constant for the higher alkanols. Similarly, n_p has a value of 0.36 in ethanol, but it decreases through other alkanols to a value of –0.12 in 1-octanol. For normal alkanols, we have

$$n_t = 4.67 - 0.59(N - 2) \tag{18}$$

$$n_p = 0.36 - 0.08(N - 2) \tag{19}$$

where N takes the values from 2 to 8 only. Above the carbon number 8, the values of the indices are those of 1-octanol only. For branched alkanols, the –OH group has the indices of the alkanol of the longest chain length present in it. Thus in 2-ethyl-1-hexanol, the –OH group has the indices of the hexanolic

-OH group. No such change is noticed in the n_v of the alkanols. Methanol forms an exception, and its -OH group has indices close to that of 1-propanol. It is interesting to point out that the limiting values of the -OH group of the alkanols are close to the indices of the -OH group of water. The values of the indices of the -OH group in water are $n_t = 0.87$, $n_p = -0.236$, and $n_v = 0.29$. In branched alkanols, we are also required to make a correction for C-C-C-O structural features in the gauche position. This correction is substantial for the critical temperature index n_t. Data are scarce for the evaluation of this correction for n_p. Alternatively, one may treat the branched alkanols on the basis of their effective carbon numbers as proposed by Ambrose.

No such variation has been found for the indices of the other groups with the carbon number. In the case of ketones corrections became necessary for the structural feature C—C—C═O. A correction was also applied for the structural feature C-C-COOH in acids. In alkenes, the trans isomer required a correction. The trans isomers of other compounds also seem to require a similar correction. Several other corrections were included in Table I. The C-C-Si-O correction is not applicable to the cyclic siloxanes.

The treatment for the halogenated alkanes is, however, complicated. In these compounds, corrections for interactions between certain pairs of adjacent bonds became necessary. For example, in the series of molecules CH_3F, CH_2F_2, CHF_3, CF_4, C_2F_6, C_3F_8, n-C_4F_{10}, i-C_4F_{10}, the molecular index N_i is calculated as follows:

$$N_i(CH_3F) = n_i(C) + n_i(F) + 3n_i(HF)$$

$$N_i(CH_2F_2) = n_i(C) + 2n_i(F) + 4n_i(HF)$$

$$N_i(CHF_3) = n_i(C) + 3n_i(F) + 3n_i(HF)$$

$$N_i(CF_4) = n_i(C) + 4n_i(F)$$

$$N_i(C_2F_6) = 2n_i(C) + 6n_i(F) + 4n_i(FC)$$

$$N_i(C_3F_8) = 3n_i(C) + 8n_i(F) + 8n_i(FC)$$

$$N_i(n\text{-}C_4F_{10}) = 4n_i(C) + 10n_i(F) + 12n_i(FC)$$

$$N_i(i\text{-}C_4F_{10}) = 4n_i(C) + 10n_i(F) + 9n_i(FC)$$

In the above expressions, we have

$n_i(C)$ = the group index of the appropriate carbon atom

$n_i(F)$ = the index of a fluorine atom

$n_i(HF)$ =
the group index of a pair of adjacent CH and CF bonds

$n_i(FC)$ =
the group index of a pair of adjacent FC and CC bonds

It may be noted that the $-CF_3$ group gives rise to three nonbonded FC interactions but we applied corrections for only two such nonbonded interactions. The correction for the nonbonded FC interaction was applied to perfluoro compounds only. In perhalogenated compounds, the same correction is applied whether the nonbonded halogen atom is F or not. The FC nonbonded interaction has different values in ring compounds and in alkenes. They have also been listed in Table I.

We have extended the present treatment to various classes of inorganic compounds. The valence state does not seem to have an appreciable effect on the critical indices. This is particularly true in the case of critical pressure and critical volume.

Besides steric and nonbonded interactions, resonance also seems to play an important role in the determination of the critical properties. According to Pauling (*21*), nitrous oxide can have six resonance structures. We calculated the critical indices of the nitrous oxide on the basis that it is constituted by ≡N, ≡N═, and ═O. We treated ozone as consisting of two ═O groups and one -O- group. Both Lydersen and Ambrose assumed the critical indices of H atom to be 0 in their schemes. The same assumption is made in the current scheme. We have, however, found that in compounds such as hydrogen fluoride, hydrogen cyanide, phosphonium chloride, ammonium chloride, etc. good results are obtained only if we assume that the H atom also contributes toward the critical indices. The experimental values for ammonium chloride appear to be unreliable. Judging from the value of 3.0 for its n_t, we feel that the resonance structures which make the H atom partially ionic are important. We have further found that the critical indices of -CN are about the same in hydrogen cyanide, cyanogen, benzonitrile, *p*-tolunitrile, and perfluoroacetonitrile. According to Ambrose, the experimental basis for the -CN increments is doubtful. The critical constants of perfluoroacetonitrile determined by Mousa, Kay, and Kreglewski (*22*) are quite reliable. Among the old determinations, the critical constants of cyanogen are somewhat reliable but those of hydrogen cyanide, benzonitrile, and *p*-tolunitrile are doubtful. Even then the agreement is quite remarkable when the -CN group in these five compounds is assumed to behave in the same manner. Perhaps the explanation may be sought in the phenomenon of resonance in these compounds. In treating dinitrogen tetroxide, we assumed that it is constituted by two N(V) groups and four ═O groups. We are, however, at a loss to estimate the critical indices of molecules such as CO, NO, and CS.

Results and Discussion

Extensive comparisons between experiment and prediction have already been made by both Lydersen and Ambrose. However, because of extensive revision made of the group indices, we have tested once again the above procedures with respect to about 600 compounds for which the critical constants are now available (*2*, *4*, *23*, *24*). Equation 16 was tested by using the critical temperatures and critical pressures for 51 alkanes in the range C_1 to C_{10} and critical volumes of 40 alkanes in the range C_1 to C_8. Our procedures for alkanols and halogenated compounds are somewhat simpler to use than the procedures developed by Ambrose. Nonbonded interactions play a significant role in the determination of the critical temperature. Their effect is slightly less in the case of critical pressure. They do not seem to have appreciable effect on critical volume. They were found to be inapplicable when the central atom is N. The nonbonded corrections were not applied to inorganic halides.

The critical constants estimated by the procedures described in this paper have been compared with the experimental values for about 600 compounds in Table V. In presenting the results in Table V, we tagged some compounds with asterisks. For those compounds tagged with one asterisk, the values tabulated as observed may be unreliable and need not be based on experiment as discussed by Ambrose (*23*). For compounds tagged with two asterisks, the molecular indices are the experimental ones and are not based on the group indices listed. For compounds tagged with three asterisks, the molecular indices were calculated as explained in the footnote.

We have graded the results using the scheme shown in Table VI. The number of compounds making grades A through F are listed in Table VII. The grades are excellent for the hydrocarbons and are relatively poor for the other classes of compounds. In general, the results are most satisfactory in the case of critical temperature. The uncertainty is somewhat

Table VI. Scheme for Grading the Results of the Estimation Procedures

grade	rel % dev in T_c	rel % dev in P_c and V_c
A	≤0.25	≤1.00
B	>0.25 and ≤0.75	>1.00 and ≤3.00
C	>0.75 and ≤1.50	>3.00 and ≤5.00
D	>1.50 and ≤3.00	>5.00 and ≤10.00
E	>3.00 and ≤5.00	>10.00 and ≤20.00
F	>5.00	>20.00

Table VII. Number of Compounds Making Grades A through F for Various Classes of Compounds

class of compounds		no.	A	B	C	D	E	F
hydrocarbons	T_c	129	83	33	9	1	2	1
	P_c	105	42	46	8	5	4	0
	V_c	72	25	30	16	1	0	0
oxygen compds	T_c	131	52	49	15	13	1	1
	P_c	79	26	22	10	9	10	2
	V_c	57	22	16	4	12	3	0
nitrogen compds	T_c	51	15	20	9	4	1	2
	P_c	37	13	5	4	3	7	5
	V_c	14	5	2	2	3	1	1
sulfur compds	T_c	11	7	2	0	1	0	1
	P_c	6	4	0	1	1	0	0
	V_c	5	3	1	1	0	0	0
halogen compds	T_c	102	52	24	17	6	2	1
	P_c	83	18	22	12	17	10	4
	V_c	55	15	20	9	7	4	0
inorganic compds	T_c	150	54	27	26	18	14	11
	P_c	76	23	19	7	6	9	12
	V_c	81	31	17	11	11	6	5
all classes	T_c	574	263	155	76	12	10	6
	P_c	386	126	114	42	41	40	23
	V_c	284	101	86	43	34	14	6

higher in the case of critical pressure and critical volume. For compounds of high molecular weight, this procedure estimates somewhat higher pressures and one has to resort to Kreglewski procedure as explained elsewhere in the text. It is instructive to point out here that compounds tagged with two asterisks are not included in this analysis.

It is quite remarkable that very few compounds made the grades D, E, and F in all three categories. From this we conclude that the present methods are quite satisfactory for the estimation of critical properties of various classes of compounds. These procedures apply also to mixtures. This has been shown with reference to air and refrigerant 500. Air is treated as a mixture of 78 mol % N_2, 21 mol % O_2, and 1 mol % Ar. Refrigerant 500 is a mixture of 39.4 mol % 1,1-difluoroethane and 61.6 mol % difluorodichloromethane.

We have compared in Table VIII the results obtained on the basis of eq 12 with those obtained by Ambrose (*9*) for the critical temperatures of some halogenated methanes. The absolute average error is greatly reduced by the present method of estimation. The results clearly indicate the importance of the nonbonded interactions.

Acknowledgment

My thanks are due Dr. K. N. Marsh and other members of the Thermodynamics Research Center for their kind interest in this work.

Table VIII. Comparison of Estimation Procedures for Halogenated Methanes

	ΔT_c/K	
compound	lit.[a]	this method
fluoromethane	−2.9	−1.0
difluoromethane	−7.0	−0.4
trifluoromethane	−2.9	−0.2
perfluoromethane	0.5	0.0
chloromethane	−7.0	0.0
dichloromethane	−8.0	0.0
trichloromethane	0.0	0.8
carbon tetrachloride	−3.0	0.0
bromomethane	1.8	−0.1
iodomethane	0.5	0.1
bromotrifluoromethane	0.2	0.6
chlorotrifluoromethane	−3.2	−0.2
dichlorodifluoromethane	−2.4	0.9
bromochlorodifluoromethane	2.0	2.8
dibromodifluoromethane	0.5	0.8
trichlorofluoromethane	2.2	3.7
chlorodifluoromethane	−2.3	3.7
dichlorofluoromethane	0.6	4.0
abs av dev	2.6	1.1

[a] Literature values are those estimated by Ambrose (*9*). $\Delta T_c = T_c(\text{obsd}) - T_c(\text{est})$.

Literature Cited

(1) Somayajulu, G. R. *J. Chem. Eng. Data* **1986**, *31*, 438.
(2) Kobe, K. A.; Lynn, R. E. *Chem. Rev.* **1953**, *52*, 117.
(3) Partington, J. R. *An Advanced Treatise on Physical Chemistry*; Longmans, Green and Co.: London, 1949.
(4) Kudchadker, A. P.; Alani, G. H.; Zwolinski, B. J. *Chem. Rev.* **1968**, *68*, 659.
(5) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
(6) Dykyj, J. *Kriticke Veliciny Cistich Latok A Zmesi*; Slovenske Vydavatelstvo Technickej Literatury: Bratislava, 1967.
(7) Lydersen, A. L. *Estimation of Critical Properties of Organic Compounds*; University of Wisconsin: Madison, WI, 1955. *Coll. Eng., Eng. Expt. Stn. Repr. 3*.
(8) Ambrose, D.; Broderick, B. E.; Townsend, R. *J. Appl. Chem. Biotechnol.* **1974**, *24*, 359.
(9) Ambrose, D. *NPL Report Chemistry 92*; National Physical Laboratory: Teddington, Middlesex, UK, 1978.
(10) Ambrose, D. *NPL Report Chemistry 98*, National Physical Laboratory; Teddington, Middlesex, UK, 1979.
(11) Kreglewski, A. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1961**, *9*, 163.
(12) Kreglewski, A.; Zwolinski, B. J. *Rocz. Chem.* **1966**, *35*, 1041, 1059.
(13) Kreglewski, A.; Zwolinski, B. J. *J. Phys. Chem.* **1961**, *65*, 1050.
(14) Riedel, L. *Z. Electrochem.* **1949**, *53*, 222.
(15) Riedel, L. *Chem. Ing. Tech.* **1952**, *24*, 353.
(16) Riedel, L. *Chem. Ing. Tech.* **1954**, *26*, 259.
(17) Riedel, L. *Chem. Ing. Tech.* **1963**, *35*, 433.
(18) *TRC Thermodynamic Tables—Hydrocarbons*; Thermodynamics Research Center, Texas A&M University: College Station, Texas, 1986.
(19) *TRC Thermodynamic Tables—Nonhydrocarbons*; Thermodynamics Research Center, Texas A&M University; College Station, Texas, 1986.
(20) Platt, J. R. *J. Chem. Phys.* **1947**, *15*, 419.
(21) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(22) Mousa, A. F. N.; Kay, W. B.; Kreglewski, A. *J. Chem. Thermodyn.* **1972**, *4*, 301.
(23) Mathews, J. F. *Chem. Rev.* **1972**, *72*, 71.
(24) Ambrose, D. *NPL Report Chemistry 107*, National Physical Laboratory: Teddington, Middlesex, UK, 1979.

Received for review November 30, 1987. Revised August 9, 1988. Accepted October 12, 1988. This research is financially supported by the Thermodynamics Research Center.