CHEMICAL ENGINEERING COMMUNICATIONS

ISSN: 0098-6445 (Print) 1563-5201 (Online) Journal homepage: https://www.tandfonline.com/loi/gcec20

ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS

K.G. JOBACK & R.C. REID

To cite this article: K.G. JOBACK & R.C. REID (1987) ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS, CHEMICAL ENGINEERING COMMUNICATIONS, 57:1-6, 233-243, DOI: 10.1080/00986448708960487

To link to this article: https://doi.org/10.1080/00986448708960487

Published online: 21 May 2007.

Submit your article to this journal

Article views: 2108

View related articles

Citing articles: 953 View citing articles

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=gcec20

Jiangsu Favored Ex. 1052

Chem. Eng. Comm. 1987, vol 57, pp. 233–243
Photocopying permitted by license only
© 1987 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

ESTIMATION OF PURE-COMPONENT PROPERTIES FROM GROUP-CONTRIBUTIONS

K.G. JOBACK and R.C. REID

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

(*Received February 5, 1987*)

Simple group-contribution methods are proposed to estimate eleven important physical properties of pure materials. A common set of structural groups was employed. High accuracy is not claimed, but the proposed methods are often as accurate as or more accurate than techniques in common use today.
KEYWORDS Viscosity critical properties ideal gas group contributions estimation methods

In principle, properties of pure components are determined by the architecture of the molecules as well as, in certain instances, state variables such as temperature and pressure. For those properties which are unique (e.g., the critical temperature) or are functions of temperature only (e.g., the ideal-gas heat capacity), molecular group-contribution methods have been widely employed to estimate numerical values. Many such methods are described elsewhere [Reid *et al.*, 1987].

It was our objective to develop a family of group-contribution estimation methods using a consistent set of molecular groups that would cover a wide variety of organic compounds. The properties selected are listed in Table I.

Many different estimation equations requiring group contributions were examined, and those selected are given in Table II. Note we have assumed no interaction *between* groups, and structurally-dependent parameters (Σ) are thereby determined simply by summing the number frequency of each group times its group contribution. Clearly this is only a first-order approximation, but it is our experience that there rarely exist sufficient data to obtain reliable contributions between so-called "next-nearest neighbors." Also, introducing group interactions often leads to a significantly more complex estimation method.

We selected 41 molecular groups to allow one to treat many diverse types of organic compounds. These groups are the same as used earlier by Lydersen [1955] with the omission of >Si< and >B-, but with the inclusion of =N-(ring). Multiple linear regression techniques were employed to determine the group contributions for each structurally-dependent parameter. The contributions are shown in Table III. To obtain optimum values, in the regression procedure, we minimized the sum of the absolute errors found from the estimated and

TABLE I

Properties estimated

Property	Symbol	Units	Comments
Normal boiling point	T_b	K	$P = 1$ atm
Normal freezing point	T_f	K	
Critical temperature	T_c	K	
Critical pressure	P_c	bar	
Critical volume	V_c	cm^3/mole	
Enthalpy of formation, ideal gas at 298 K	$\Delta H^0_{f,298}$	kJ/mole	
Gibbs energy of formation, ideal gas, unit fugacity, at 298 K	$\Delta G^0_{f,298}$	kJ/mole	
Heat capacity, ideal gas	C^0_p	J/mole K	Function of T
Enthalpy of vaporization, at T_b	ΔH_{vb}	kJ/mole	
Enthalpy of fusion,	ΔH_f	kJ/mole	
Liquid viscosity	η_L	N s/m^2	Function of T

experimental property values, Y_{est} and Y_{exp}, i.e.,

$$\text{Minimize the objective function: } \sum |Y_{est} - Y_{exp}| \tag{1}$$

Minimizing the *sum-of-squares* of the errors was not done as we found this procedure weighted outliers too heavily. Thus our method will lead to slightly higher errors for such outliers, but will provide an improved estimation procedure for the majority of compounds.

TABLE II

Estimation equations[1]

$T_b = 198.2 + \sum$	(2)
$T_f = 122.5 + \sum$	(3)
$T_c = T_b[0.584 + 0.965\sum - (\sum)^2]^{-1}$	(4)
$P_c = (0.113 + 0.0032n_A - \sum)^{-2}$	(5)
$V_c = 17.5 + \sum$	(6)
$\Delta H^0_{f,298} = 68.29 + \sum$	(7)
$\Delta G^0_{f,298} = 53.88 + \sum$	(8)
$C^0_p = \sum (a) - 37.93 + [\sum (b) + 0.210]T + [\sum (c) - 3.91 \times 10^{-4}]T^2 + [\sum (d) + 2.06 \times 10^{-7}]T^3$	(9)
$\Delta H_{vb} = 15.30 + \sum$	(10)
$\Delta H_f = -0.88 + \sum$	(11)
$\eta_L = MW \times \exp\{[\sum (\eta_A) - 597.82]/T + \sum (\eta_B) - 11.202\}$	(12)

[1] The notation $\sum$ signifies that, for the particular property of interest, one sums the product of the number of times a group appears in the compound and the group contributions in Table III. In cases where the property is a function of temperature, different $\sum(\ )$ terms are required.

TABLE III

Group contributions

	T_c	P_c	V_c
Non-ring increments			
—CH3	0.0141	−0.0012	65
—CH2—	0.0189	0	56
>CH—	0.0164	0.0020	41
>C<	0.0067	0.0043	27
=CH2	0.0113	−0.0028	56
=CH—	0.0129	−0.0006	46
=C<	0.0117	0.0011	38
=C=	0.0026	0.0028	36
≡CH	0.0027	−0.0008	46
≡C—	0.0020	0.0016	37
Ring increments			
—CH2—	0.0100	0.0025	48
>CH—	0.0122	0.0004	38
>C<	0.0042	0.0061	27
=CH—	0.0082	0.0011	41
=C<	0.0143	0.0008	32
Halogen increments			
—F	0.0111	−0.0057	27
—Cl	0.0105	−0.0049	58
—Br	0.0133	0.0057	71
—I	0.0068	−0.0034	97
Oxygen increments			
—OH (alcohol)	0.0741	0.0112	28
—OH (phenol)	0.0240	0.0184	−25
—O— (nonring)	0.0168	0.0015	18
—O— (ring)	0.0098	0.0048	13
>C=O (nonring)	0.0380	0.0031	62
>C=O (ring)	0.0284	0.0028	55
O=CH— (aldehyde)	0.0379	0.0030	82
—COOH (acid)	0.0791	0.0077	89
—COO— (ester)	0.0481	0.0005	82
=O (except as above)	0.0143	0.0101	36
Nitrogen increments			
—NH2	0.0243	0.0109	38
>NH (nonring)	0.0295	0.0077	35
>NH (ring)	0.0130	0.0114	29
>N— (nonring)	0.0169	0.0074	9
—N= (nonring)	0.0255	−0.0099	—
—N= (ring)	0.0085	0·0076	34
=NH	—	—	—
—CN	0.0496	−0.0101	91
—NO2	0.0437	0.0064	91
Sulfur increments			
—SH	0.0031	0.0084	63
—S— (nonring)	0.0119	0.0049	54
—S— (ring)	0.0019	0.0051	38

	T_b	T_f	$\Delta H^0_{f,298}$	$\Delta G^0_{f,298}$
Non-ring increments				
—CH3	23.58	−5.10	−76.45	−43.96
—CH2—	22.88	11.27	−20.64	8.42
>CH—	21.74	12.64	29.89	58.36

TABLE III (*contd.*)

	T_b	T_f	$\Delta H^0_{f,298}$	$\Delta G^0_{f,298}$
Non-ring increments (*contd.*)				
>C<	18.25	46.43	82.23	116.02
=CH2	18.18	−4.32	−9.63	3.77
=CH—	24.96	8.73	37.97	48.53
=C<	24.14	11.14	83.99	92.36
=C=	26.15	17.78	142.14	136.70
≡CH	9.20	−11.18	79.30	77.71
≡C—	27.38	64.32	115.51	109.82
Ring increments				
—CH2—	27.15	7.75	−26.80	−3.68
>CH—	21.78	19.88	8.67	40.99
>C<	21.32	60.15	79.72	87.88
=CH—	26.73	8.13	2.09	11.30
=C<	31.01	37.02	46.43	54.05
Halogen increments				
—F	−0.03	−15.78	−251.92	−247.19
—Cl	38.13	13.55	−71.55	−64.31
—Br	66.86	43.43	−29.48	−38.06
—I	93.84	41.69	21.06	5.74
Oxygen increments				
—OH (alcohol)	92.88	44.45	−208.04	−189.20
—OH (phenol)	76.34	82.83	−221.65	−197.37
—O— (nonring)	22.42	22.23	−132.22	−105.00
—O— (ring)	31.22	23.05	−138.16	−98.22
>C=O (nonring)	76.75	61.20	−133.22	−120.50
>C=O (ring)	94.97	75.97	−164.50	−126.27
O=CH— (aldehyde)	72.24	36.90	−162.03	−143.48
—COOH (acid)	169.09	155.50	−426.72	−387.87
—COO— (ester)	81.10	53.60	−337.92	−301.95
=O (except as above)	−10.50	2.08	−247.61	−250.83
Nitrogen increments				
—NH2	73.23	66.89	−22.02	14.07
>NH (nonring)	50.17	52.66	53.47	89.39
>NH (ring)	52.82	101.51	31.65	75.61
>N— (nonring)	11.74	48.84	123.34	163.16
—N= (nonring)	74.60	—	23.61	—
—N= (ring)	57.55	68.40	55.52	79.93
=NH	83.08	68.91	93.70	119.66
—CN	125.66	59.89	88.43	89.22
—NO2	152.54	127.24	−66.57	−16.83
Sulfur increments				
—SH	63.56	20.09	−17.33	−22.99
—S— (nonring)	68.78	34.40	41.87	33.12
—S— (ring)	52.10	79.93	39.10	27.76

	Ideal gas heat capacity (a)	(b)	(c)	(d)
Non-ring increments				
—CH3	1.95E+1	−8.08E−3	1.53E−4	−9.67E−8
—CH2—	−9.09E−1	9.50E−2	−5.44E−5	1.19E−8
>CH—	−2.30E+1	2.04E−1	−2.65E−4	1.20E−7
>C<	−6.62E+1	4.27E−1	−6.41E−4	3.01E−7
=CH2	2.36E+1	−3.81E−2	1.72E−4	−1.03E−7
=CH—	−8.00	1.05E−1	−9.63E−5	3.56E−8
=C<	−2.81E+1	2.08E−1	−3.06E−4	1.46E−7
=C=	2.74E+1	−5.57E−2	1.01E−4	−5.02E−8

TABLE III (*contd.*)

	Ideal gas heat capacity (a)	(b)	(c)	(d)
Non-ring increments (*contd.*)				
≡CH	2.45E + 1	−2.71E − 2	1.11E − 4	−6.78E − 8
≡C—	7.87	2.01E − 2	−8.33E − 6	1.39E − 9
Ring increments				
—CH2—	−6.03	8.54E − 2	−8.00E − 6	−1.80E − 8
>CH—	−2.05E + 1	1.62E − 1	−1.60E − 4	6.24E − 8
>C<	−9.09E + 1	5.57E − 1	−9.00E − 4	4.69E − 7
=CH—	−2.14	5.74E − 2	−1.64E − 6	−1.59E − 8
=C<	−8.25	1.01E − 1	−1.42E − 4	6.78E − 8
Halogen increments				
—F	2.65E + 1	−9.13E − 2	1.91E − 4	−1.03E − 7
—Cl	3.33E + 1	−9.63E − 2	1.87E − 4	−9.96E − 8
—Br	2.86E + 1	−6.49E − 2	1.36E − 4	−7.45E − 8
—I	3.21E + 1	−6.41E − 2	1.26E − 4	−6.87E − 8
Oxygen increments				
—OH (alcohol)	2.57E + 1	−6.91E − 2	1.77E − 4	−9.88E − 8
—OH (phenol)	−2.81	1.11E − 1	−1.16E − 4	4.94E − 8
—O— (nonring)	2.55E + 1	−6.32E − 2	1.11E − 4	−5.48E − 8
—O— (ring)	1.22E + 1	−1.26E − 2	6.03E − 5	−3.86E − 8
>C=O (nonring)	6.45	6.70E − 2	−3.57E − 5	2.86E − 9
>C=O (ring)	3.04E + 1	−8.29E − 2	2.36E − 4	−1.31E − 7
O=CH— (aldehyde)	3.09E + 1	−3.36E − 2	1.60E − 4	−9.88E − 8
—COOH (acid)	2.41E + 1	4.27E − 2	8.04E − 5	−6.87E − 8
—COO— (ester)	2.45E + 1	4.02E − 2	4.02E − 5	−4.52E − 8
=O (except as above)	6.82	1.96E − 2	1.27E − 5	−1.78E − 8
Nitrogen increments				
—NH2	2.69E + 1	−4.12E − 2	1.64E − 4	−9.76E − 8
>NH (nonring)	−1.21	7.62E − 2	−4.86E − 5	1.05E − 8
>NH (ring)	1.18E + 1	−2.30E − 2	1.07E − 4	−6.28E − 8
>N— (nonring)	−3.11E + 1	2.27E − 1	−3.20E − 4	1.46E − 7
—N= (nonring)	—	—	—	—
—N= (ring)	8.83	−3.84E − 3	4.35E − 5	−2.60E − 8
=NH	5.69	−4.12E − 3	1.28E − 4	−8.88E − 8
—CN	3.65E + 1	−7.33E − 2	1.84E − 4	−1.03E − 7
—NO2	2.59E + 1	−3.74E − 3	1.29E − 4	−8.88E − 8
Sulfur increments				
—SH	3.53E + 1	−7.58E − 2	1.85E − 4	−1.03E − 7
—S— (nonring)	1.96E + 1	−5.61E − 3	4.02E − 5	−2.76E − 8
—S— (ring)	1.67E + 1	4.81E − 3	2.77E − 5	−2.11E − 8

	ΔH_{vb}	ΔH_f	Liquid viscosity (η_A)	(η_B)
Non-ring increments				
—CH3	2.373	0.908	548.29	−1.719
—CH2—	2.226	2.590	94.16	−0.199
>CH—	1.691	0.749	−322.15	1.187
>C<	0.636	−1.460	−573.56	2.307
=CH2	1.724	−0.473	495.01	−1.539
=CH—	2.205	2.691	82.28	−0.242
=C<	2.138	3.063	—	—
=C=	2.661	4.720	—	—
≡CH	1.155	2.322	—	—
≡C—	3.302	4.151	—	—
Ring increments				
—CH2—	2.398	0.490	307.53	−0.798

TABLE III (*contd.*)

	ΔH_{vb}	ΔH_f	Liquid viscosity (η_A)	(η_B)
Ring increments (*contd.*)				
>CH—	1.942	3.243	−394.29	1.251
>C<	0.644	−1.373	—	—
=CH—	2.544	1.101	259.65	−0.702
=C<	3.059	2.394	−245.74	0.912
Halogen increments				
—F	−0.670	1.398	—	—
—Cl	4.532	2.515	625.45	−1.814
—Br	6.582	3.603	738.91	−2.038
—I	9.520	2.724	809.55	−2.224
Oxygen increments				
—OH (alcohol)	16.826	2.406	2173.72	−5.057
—OH (phenol)	12.499	4.490	3018.17	−7.314
—O— (nonring)	2.410	1.188	122.09	−0.386
—O— (ring)	4.682	5.879	440.24	−0.953
>C=O (nonring)	8.972	4.189	340.35	−0.350
>C=O (ring)	6.645	—	—	—
O=CH— (aldehyde)	9.093	3.197	740.92	−1.713
—COOH (acid)	19.537	11.051	1317.23	−2.578
—COO— (ester)	9.633	6.959	483.88	−0.966
=O (except as above)	5.909	3.624	675.24	−1.340
Nitrogen increments				
—NH2	10.788	3.515	—	—
>NH (nonring)	6.436	5.009	—	—
>NH (ring)	6.930	7.490	—	—
>H— (nonring)	1.896	4.703	—	—
—N= (nonring)	3.335	—	—	—
—N= (ring)	6.528	3.649	—	—
=NH	12.169	—	—	—
—CN	12.851	2.414	—	—
—NO2	16.738	9.679	—	—
Sulfur increments				
—SH	6.884	2.360	—	—
—S— (nonring)	6.817	4.130	—	—
—S— (ring)	5.984	1.557	—	—

Two properties treated are functions of temperature, i.e., the ideal-gas heat capacity and the liquid viscosity. For the former, the temperature range is from 273 to about 1000 K while, for the latter, from a value of T_f to a reduced temperature of about 0.7.

It should be noted in Table II the *total* number of atoms, n_A, appears in the equation for critical pressure, and the compound molecular weight, MW, in the liquid viscosity formulation. Also, in the estimation of T_c, it is preferable to employ an experimental value of T_b, but, if this is not available, it may be approximated separately.

The data used in the development of all the methods were obtained from the literature. Critical property values, T_c, P_c, and V_c, were obtained from Ambrose [1978, 1979] and Reid *et al.* [1987]. Values for the thermodynamic properties, $\Delta H^0_{f,298}$, $\Delta G^0_{f,298}$, and C^0_p were obtained from Reid *et al.* and Stull *et al.* [1969]. Values for T_b, T_f, ΔH_{vb}, and ΔH_f were obtained from Reid *et al.* and Stull *et al.*

TABLE IV

Summations of group contributions for use in the example

Property	—Cl No. of groups	—Cl Group value	=CH— (ring) No. of groups	=CH— (ring) Group value	=C< (ring) No. of groups	=C< (ring) Group value	Σ
T_b	2	38.13	4	26.73	2	31.01	245.20
T_f	2	13.55	4	8.13	2	37.02	133.66
T_c	2	0.0105	4	0.0082	2	0.0143	0.0824
P_c	2	−0.0049	4	0.0011	2	0.0008	−0.0038
V_c	2	58	4	41	2	32	344
$\Delta H^0_{f,298}$	2	−71.55	4	2.09	2	46.43	−41.88
$\Delta G^0_{f,298}$	2	−64.31	4	11.30	2	54.05	24.68
C^0_p, Σ (a)	2	33.3	4	−2.14	2	−8.25	41.54
Σ (b)	2	-9.63×10^{-2}	4	5.74×10^{-2}	2	1.01×10^{-1}	0.239
Σ (c)	2	1.874×10^{-4}	4	-1.64×10^{-6}	2	-1.42×10^{-4}	8.42×10^{-5}
Σ (d)	2	-9.96×10^{-8}	4	-1.59×10^{-8}	2	6.78×10^{-8}	-1.27×10^{-7}
ΔH_{vb}	2	4.532	4	2.544	2	3.059	25.36
ΔH_f	2	2.515	4	1.101	2	2.394	14.22
η_L, Σ (η_A)	2	625.45	4	259.65	2	−245.74	1798.0
Σ (η_B)	2	−1.814	4	−0.702	2	0.912	−4.612

TABLE V

Results from the example calculations

Compound: *p*-dichlorobenzene

Summation of group contributions from Table IV

Property	Eq. used	Estimated value	Experimental value
T_b	(2)	443.4 K	447.3 K
T_f	(3)	256 K	326 K
T_c	(4)[1]	681 K	685 K
P_c	(5)[2]	41.5 bar	39.0 bar
V_c	(6)	362 cm^3/mole	372 cm^3/mole
$\Delta H^0_{f,298}$	(7)	26.41 kJ/mole	23.01 kJ/mole
$\Delta G^0_{f,298}$	(8)	78.56 kJ/mole	77.15 kJ/mole
C^0_p(298)	(9)	112.3 J/mole K	113.9 J/mole K
(400)		139.2 J/mole K	143.3 J/mole K
(800)		206.8 J/mole K	210.7 J/mole K
(1000)		224.6 J/mole K	228.0 J/mole K
ΔH_{vb}	(10)	40.66 kJ/mole	38.79 kJ/mole
ΔH_f	(11)	13.3 kJ/mole	18.16 kJ/mole
η_L(333.8)	(12)[3]	7.26×10^{-4} N s/m^2	7.22×10^{-4} N s/m^2
(374.4)		4.92×10^{-4} N s/m^2	4.95×10^{-4} N s/m^2
(403.1)		3.91×10^{-4} N s/m^2	3.98×10^{-4} N s/m^2
(423.3)		3.40×10^{-4} N s/m^2	3.48×10^{-4} N s/m^2

[1] The experimental value of T_b (447 K) was employed in Eq. (4). If T_b had itself been estimated, a value of 443 K would have been obtained leading to a value for T_c of 675 K. In this case, the results are not too different. In other situations, large errors were found when using the estimated value of T_b.

[2] $n_A = 12$

[3] $MW = 147.0$ g/mole

TABLE VI

Statistical summary of regression testing

Property	No. of compounds used	Average absolute error	Standard deviation	Average per cent error
T_b	438	12.9 K	17.9 K	3.6
T_f	388	22.6 K	24.7 K	11.2
T_c	409	4.8 K	6.9 K	0.8
P_c	392	2.1 bar	3.2 bar	5.2
V_c	310	7.5 cm^3/mole	13.2 cm^3/mole	2.3
$\Delta H^0_{f,298}$	378	8.4 kJ/mole	18.0 kJ/mole	—
$\Delta G^0_{f,298}$	328	8.4 kJ/mole	18.3 kJ/mole	—
ΔH_{vb}	368	1.27 kJ/mole	1.79 kJ/mole	3.9
ΔH_f	155	2.0 kJ/mole	2.8 kJ/mole	39.

Values for η_L as a function of temperature were obtained from Orrick [1973] and Friend and Hargreaves [1945].

EXAMPLES AND DISCUSSION

To illustrate our proposed technique, we have estimated the values of each of the eleven properties in Table I using *p*-dichlorobenzene as an example substance. In Table IV, we show the group contribution summations for each property using the group values from Table III. In Table V, we summarize the results and compare them with experimental values.

In Table VI, we show an overall statistical summary of our regression results; a more detailed breakdown is given elsewhere [Joback, 1984].

Estimations of the normal boiling point and, in particular, the normal freezing point are not accurate and should be considered as only very approximate. There is a strong dependence of the actual conformation of the molecule on T_f as shown, for example, in the large difference found for T_f between, say, cis- and trans-isomers. To illustrate, the difference in T_f between cis- and trans-1,2-

TABLE VII

Comparison of critical property estimation techniques

	Lydersen [1955]		Ambrose [1978, 1979]		Klincewicz [1984]		Proposed	
	AAE[1]	AAPE[2]	AAE	AAPE	AAE	AAPE	AAE	AAPE
T_c	8.1	1.4	4.3	0.7	7.5	1.3	4.8	0.8
P_c	3.3	8.9	1.8	4.6	3.0	7.8	2.1	5.2
V_c	10.0	3.1	8.5	2.8	8.9	2.9	7.5	2.3

[1] AAE = average absolute error.
[2] AAPE = average absolute percent error.
Average absolute errors have units of kelvins for T_c, bars for P_c, and cm^3/mole for V_c.

TABLE VIII

Comparison of enthalpy of formation estimation techniques

	Average absolute error, kJ/mole	Standard deviation kJ/mole
Benson *et al.* [1969]	4.6	5.4
Verma-Doraiswamy [1965]	10.5	13.4
Andersen, Beyer, and Watson [1944]	9.2	10.5
Franklin [1949]	18.8	27.2
Proposed	9.2	9.2

dimethylcyclopentane is about 64 K. Since our procedure does not differentiate between cis- and trans-isomers, the regression yields some medium value.

For the critical constants, other group-contribution methods have been proposed, [Lydersen, 1955; Ambrose, 1978, 1979; Klincewicz, 1982]. In Table VII we show a limited comparison between the results of the proposed method and those currently in use. The statistics for the earlier methods were obtained from Klincewicz [1982]. It is seen that the Ambrose method is somewhat more accurate than the proposed method for T_c and P_c, but it is also more complex and less readily implemented in computer-based estimation programs. For V_c, the proposed method yielded the least error.

For the standard enthalpy of formation at 298 K, the proposed method was compared to other group-contribution techniques now in use, and the results are shown in Table VIII. In this comparison, a sample of 29 compounds was used. The proposed method showed an average absolute error which is somewhat larger than Benson *et al.*'s [1969] method and about equal to that from the Verma-Doraiswamy [1965] technique. However, with Benson *et al.*'s method containing over 250 groups and 25 corrections for rings and next-nearest neighbors, we feel that a major advantage of our proposed method lies in its simplicity and accuracy only slightly less than significantly more complicated methods.

There are few other group-contribution methods to estimate the standard Gibbs energy of formation at 298 K. When we compared our procedure to that of van Krevelen and Chermin [1951, 1952] using a sample of 43 compounds, the

TABLE IX

Comparison of heat capacity estimation techniques

	Average absolute error, J/mole K	Standard deviation J/mole K
Benson *et al.* [1969]	4.6	6.7
Rihani-Doraiswamy [1965]	13.4	19.2
Thinh *et al.* [1976]	4.6	6.7
Proposed	5.9	8.4

TABLE X

Comparison of viscosity estimation techniques

	Average absolute percent error	Standard deviation
Thomas [1946]	20	24
Orrick [1973]	16	14
van Velzen *et al.* [1972]	15	23
Morris [1964]	15	15
Proposed	18	20

proposed technique yielded an average absolute error of 4.6 kJ/mole and a standard deviation of 6.7 kJ/mole. The van Krevelen and Chermin method gave an absolute average error of 13.0 kJ/mole and a standard deviation of 17.2 kJ/mole. The proposed method does not require a separate correction for symmetry number or for multiple optical isomers. While the accuracy of the proposed method is reasonable, the use of it to calculate chemical equilibrium constants may lead to large errors due to the exponentiation required to determine K.

For the ideal-gas heat capacity, we present a comparison between the proposed method and those of Benson *et al.* [1969], Rihani-Doraiswamy [1965], and Thinh *et al.* [1976] in Table IX. A sample of 28 compounds was employed and C_p^0 values at 298 and 800 K were used. The methods of Benson *et al.* and Thinh *et al.* both yielded lower errors than the proposed method, however, Benson's technique provides values of the heat capacity only at discreet temperatures while the Thinh *et al.* procedure is applicable only to hydrocarbons.

There are no group-contribution methods for the enthalpy of vaporization at the normal boiling point or for the enthalpy of fusion with which to compare the proposed method. Clearly, as shown in Table VI, the accuracy in estimating ΔH_f is poor; again, as with T_f, the value is sensitive to the exact conformation of the molecule. For ΔH_{vb}, errors are not particularly large, but if reliable values of T_b, T_c, and P_c are available, it is more accurate to estimate ΔH_{vb} from corresponding-states correlations [Reid *et al.*, 1987].

For the liquid viscosity we present a comparison between the proposed method and those of Thomas [1946], Orrick [1973], van Velzen *et al.* [1972], and Morris [1964] in Table X. A sample of 36 compounds was employed and η_L values at 3 to 5 temperatures were used. All methods yielded large errors.

REFERENCES

Ambrose, D., "Correlation and Estimation of Vapor–Liquid Critical Properties: I. Critical Temperatures of Organic Compounds," National Physical Laboratory, Teddington, NPL Rep. Chem. **92**, 1978, corrected 1980.

Ambrose, D., "Correlation and Estimation of Vapor–Liquid Critical Properties: II. Critical Pressures and Volumes of Organic Compounds," National Physical Laboratory, Teddington, NPL Rep. **98**, 1979.

Andersen, J.W., Beyer, G.H., and Watson, K.M., "Thermodynamic Properties of Organic Compounds. Estimation from Group Contributions," *Natl. Pet. News, Tech. Sec.* **36**: R476 (July 5, 1944).

Benson, S.W., Cruickshank, F.R., Golden, D.M., Haugen, G.R., O'Neal, H.E., Rogers, A.S., Shaw, R., and Walsh, R., "Additivity Rules for the Estimation of Thermochemical Properties," *Chem. Rev.* **69**, 279 (1969).

Franklin, J.L., "Prediction of Heat and Free Energies of Organic Compounds," *Ind. Eng. Chem.* **41**, 1070 (1949).

Friend, J.N., and Hargreaves, W.D., "Viscosity and the Hydrogen Bond—Hydroxyl and Ortho Effects," *Phil. Mag.* **36**, 731 (1945).

Joback, K.G., "A Unified Approach to Physical Property Estimation Using Multivariate Statistical Techniques," S.M. Thesis, Chem. Eng., Mass. Inst. of Tech., Cambridge, MA, 1984.

Klincewicz, K.M., "Prediction of Critical Temperatures, Pressures, and Volumes of Organic Compounds from Molecular Structure," S.M. Thesis, Chem. Eng., Mass. Inst. of Tech., Cambridge, MA, 1982; *AIChE J.* **30**, 137 (1984).

Lydersen, A.L., "Estimation of Critical Properties of Organic Compounds," Univ. Coll. Exp. Stn., Rept., Madison, WI, April, 1955.

Morris, P.S., "Estimation of Liquid Viscosity from Structure," M.S. Thesis, Department of Chemical Engineering, Polytechnic Institute of Brooklyn, Brooklyn, N.Y., 1964.

Orrick, C., "Estimation of Viscosity for Organic Compounds," M.S. Thesis, Department of Chemical Engineering, Oklahoma State University, Stillwater, OK, 1973; Private communication, J.H. Erbar, 1975.

Reid, R.C., Prausnitz, J.M., and Poling, B.E., *The Properties of Gases and Liquids*, McGraw-Hill Book Co., New York, 4th ed., 1987.

Rihani, D.N., and Doraiswamy, L.K., "Estimation of Heat Capacity of Organic Compounds from Group Contributions," *Ind. Eng. Chem. Fundam.* **4**, 17 (1965).

Stull, D.R., Westrum, E.F., and Sinke, G.C., *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons Inc., New York (1969).

Thinh, T.-P., and Trong, T.K., "Estimation of Standard Heats of Formation ΔH_{fT}^*, Standard Entropies of Formation ΔS_{fT}^*, Standard Free Energies of Formation ΔF_{fT}^* and Absolute Entropies S_T^* of Hydrocarbons from Group Contributions: An Accurate Approach," *Can. J. Chem. Eng.* **54**, 344 (1976).

Thomas, L.H., "The Dependence of the Viscosities of Liquids on Reduced Temperature, and a Relation between Viscosity, Density, and Chemical Constitution," *J. Chem. Soc.*, 573, (1946).

van Krevelen, S.W., and Chermin, H.A.G., "Estimation of the Free Enthalpy (Gibbs Free Energy) of Formation of Organic Compounds from Group Contributions," *Chem. Eng. Sci.* **1**, 66 (1951).

van Krevelen, S.W., and Chermin, H.A.G., "Erratum: Estimation of the Free Enthalpy (Gibbs Free Energy) of Formation of Organic Compounds from Group Contributions," *ibid.*, **1**, 238 (1952).

van Velzen, D., Cardozo, R.L., and Langenkamp, H., "A Liquid Viscosity-Temperature-Chemical Constitution Relation for Organic Compounds," *Ind. Eng. Chem. Fundam.* **11**, 20 (1972).

Verma, K.K., and Doraiswamy, L.K., "Estimation of Heats of Formation of Organic Compounds," *Ind. Eng. Chem. Fundam.* **4**, 389 (1965).