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A Critical Evaluation of Bond Energy/ Group Contribution Methods of Calculating the Heat of Formation: Development of a New Generalized Scheme. Part I. Alkanes*

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SUMMARY

Results of application of seven well-known bond energy/group contribution methods to the experimental data on heats of formation of 70 alkanes, including a few polymers, are reported. The earlier claims of accuracy of many of these schemes become untenable with the emergence of new data on nonanes and polymers, calling for more parameters to cope with the steric interaction energy in higher branched alkanes. A new general bond energy scheme is developed with low standard error of ± 0.28 kcal/mole which is close to the experimental uncertainty. Heats of formation of some polyolefin structures are predicted for the experimental verification in the future. The energy terms of the new scheme are transferable to other non-hydrocarbon organic compounds for which a general scheme is under way.

INTRODUCTION

The approximate constancy of bond energies in different molecular structures has given rise to many useful correlations for predicting heats of formation and other thermochemical and thermodynamic properties. The

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noncyclic alkanes C_nH_{2n+2} particularly provide a very favorable situation for the constancy and transferability of the C–C and C–H bond energies because of the nearly equivalent tetrahedral bond angles, uniformity of orbital hybridization, and the absence of any strong polarity effects. Many of such correlation methods for hydrocarbons were reviewed by Skinner and Pilcher [17] in 1963. Subsequently a few new methods have emerged as has also new data on higher alkanes and hydrocarbon polymers. The standard combustion data on ten branched nonanes obtained by Good [5], on well-characterized α -olefin polymers [8], and a few isomeric pentanes redetermined by Pilcher and Chadwick [14] afford a renewed test for the successfulness of various schemes in predicting the heats of atomization or formation in the ideal gas state. In this paper, seven existing bond energy/group contribution schemes, some previously recognized as very successful procedures, and a few new methods cited in standard work [7, 15], have been applied to 70 alkanes on which precise experimental data is available to date. A new simple bond energy scheme is developed to fit all alkanes within a standard error of ± 0.28 kcal/mole which is only slightly higher than the experimental uncertainty. The heats of formation of some substituted olefin polymers are predicted with the help of the new scheme, which may be shortly verified in an experimental program [9].

CALCULATION PROCEDURES AND RESULTS

The experimental values of $\Delta H_f^\circ(g)$ for most of the alkanes are taken from the API data tabulated in the form of heats of atomization, ΔH_a° , as given in Ref. 19, using the given values of the heats of atomization of carbon and hydrogen. The new combustion data [14] on n-pentane, isopentane and neopentane are adopted in place of the old values. The combustion data on 11 nonanes in the liquid state obtained by Good [5] are combined with the heats of vaporization of these compounds as given in the API tables. The latter values are mostly on the basis of predictions of the Greenshields-Rossini correlation scheme [6] as it has been established that the uncertainty in the heat of vaporization so calculated seldom differs from the experimental one using vapor pressure data. Heats of formation in the ideal gas state of the four hydrocarbon polymers were obtained from recent combustion data on these polymers which are well characterized in respect to partial crystallinity, using the "hypothetical" heat of vaporization calculated by the scheme of Tatevskii et al. [20] extended to polymers (10).

Sauders-Matthews-Hurd's Method [20]

The 11 group contribution parameters of the SMH method in terms of the heat of formation are, in kcal/mole: $-\text{CH}_3$, -10.05; $>\text{CH}_2$, -4.95; $>\text{CH}$ - (2nd carbon), -1.57; $>\text{CH}$ - (3rd or higher), -0.88; $>\text{C}$ < (2nd carbon), 0.85; $>\text{C}$ < (3rd or higher), 2.45; and the steric correction terms:

$>\text{CH}-\text{CH}<$, 0.75; $>\text{CH}-\text{C}\equiv$, 2.39; $>\text{CH}-\overset{|}{\text{C}}\text{H}-\text{CH}<$, 2.30; $\equiv\text{C}-\text{C}\equiv$, 4.61 and 0.88 for each $-\text{C}_2\text{H}_5$ side chain. The two additional steric terms recommended for this scheme from the present work, are: $[\text{C}_4\text{CC}_3] = 2.14$ and $[\text{C}_4\text{CC}_4] = 5.60$, as these improve the precision substantially.

Tatevskii's Scheme [20]

The following values of the nine parameters B_{ij} , of the scheme of Tatevskii, Benderskii, and Yarovoi (TBY), expressed as the heat of formation contribution (kcal/mole), were used for calculations: B_{12} , -12.54; B_{13} , -10.79; B_{14} , -10.03; B_{22} , -4.96; B_{23} , -2.58; B_{24} , -1.35; B_{33} , 0.98; B_{34} , 3.14; and B_{44} , 6.19. The two new parameters recommended from the present work are: $[\text{C}_4\text{CC}_3] = 1.94$ and $[\text{C}_4\text{CC}_4] = 5.35$. The numerical subscripts in the above terms indicate the type of sp^3 carbons forming the bond; primary (C_1), secondary (C_2), tertiary (C_3), etc., and (C), any type, the contributions from their associated C-H bonds being implied in the B_{ij} terms.

The Somayajulu-Zwolinski Generalized Treatment [19]

The generalized SZ-method gives the following equation for computing the molar heats of atomization from which heats of formation are worked out:

$$E(\text{C}_n\text{H}_{2n+2}) = (2n + 2) E_0 + (n - 1) E_{\text{CC}} + 3n_1\delta_1 + 4n_2\delta_2 + 3n_3\delta_3 + 2(m - 2n_2 - 3n_3)\delta_4 + 1.s \quad (1)$$

where n = total number of carbon atoms in the alkane, n_1 , n_2 , n_3 , and n_4 , respectively, are the numbers of primary secondary, tertiary, and quaternary carbon atoms; and m , and 1 are special numbers representing, in a consolidate manner, the weighted sum of various steric interactions in an alkane structure for which the computational procedure is given. The seven parameters of the equation have the values, in kcal/mole: $E_0 = 99.395$ (the energy

of the C–H bond in methane); $E_{CC} = 85.42$ (the energy of the C–C bond in diamond); $\delta_1 = -1.06$; $\delta_2 = -0.95$; $\delta_3 = -0.84$; $\delta_4 = 0.02$; and $s = -0.22$.

Greenshields and Rossini's Scheme [6]

In this (GR) scheme the variation of $\Delta H_f^\circ(g)$ of an isomer from the corresponding *n*-alkane (for which the established standard values of the API are assumed) is given by the equation:

$$\Delta H_f^\circ(\text{isomer},g) - \Delta H_f^\circ(\text{n-alkane},g) = -0.469c_3 - 1.364c_4 + 1.139 \Delta P_3 + \frac{12.508\Delta\omega}{n(n-1)} + 1.978P_4'' + 5.19P_4' \quad (2)$$

where *n* is the total number of carbon atoms in the alkane; c_3 and c_4 are the numbers of tertiary and quaternary carbons; P_3 , the total number of pairs of carbon atoms, 3 bonds apart; ω , the Wiener number, the total quaternary carbon atoms separated by one carbon atom; and P_4'' , the number of pairs (quaternary + tertiary) separated by one carbon atom. The last two terms are the same as designated by $[C_4CC_4]$ and $[C_4CC_3]$ in the present paper. The method is not applied to normal alkanes since they form the basic data from which the isomeric variation is computed. It is also not applicable to polymers due to the lack of a satisfactory procedure [10] of calculating the Wiener number per repeat unit of a polymer.

Allen and Skinner's Procedure [1, 18]

The Allen's scheme alone does not seem to correlate well enough with higher, branched alkanes, but with Skinner's steric term [S] added to it, it becomes an extremely accurate procedure. The calculation of [S], however, requires a detailed examination of an alkane in respect of 21 types of gauche 1,4 steric interactions of hydrogens in the staggered position of the molecule and a factor such as the "angle-release mechanism" for the strained bonds, involving in all some 25 parameters. For certain alkanes such as 2,2,3,4- and 2,2,4,4-tetra methyl pentanes, Skinner was unable to calculate [S] due to the unrealistic proximity of the H...H atoms in the staggered configuration. We did not, therefore, attempt to extend this method for nonanes but have simply taken Skinner's application to 52 alkanes [17] based on his following equation:

$$\Delta H_a^\circ(C_nH_{2n+2},g) = -15.54 - 2.35n - b_3\tau - C_4\Delta + [S] \quad (3)$$

where b_3 = number of adjacent pairs of C_3-C_3 bonds, C_4 = number of adjacent trios of C_4-C_4 bonds, $\tau = 2.58$, $\Delta = -0.55$, and $[S]$ = steric repulsion energy calculated individually.

Overmars and Blinder's Method [13]

The four averaged, atomization energy terms of the OB scheme are: $E(C-C) = 83.645$, $E(C-H,p) = 98.590$, $E(C-H,s) = 98.164$, and $E(C-H,t) = 97.736$ kcal/mole. These are transformed to the heat of formation terms as: $(C-C) = 1.798$, $(C-H''') = -3.766$, $(C-H'') = -3.340$ and $(C-H') = -2.912$.

Verma and Doraiswamy's Procedure [21]

The group contribution terms recommended in this (VD) method are: $-CH_3$, -10.248 ; $>CH_2$, -4.941 ; $>CH-$, -1.287 ; $>C<$, 0.617 ; a side-chain with 2 or more C-atoms, 0.800 ; $>CH-CH-CH<$, -1.200 ; and 0.600 for a

pair of adjacent $>CH-$ and $>C<$. These terms as well as the heat of formation in kcal/mole at $298.15^\circ K$ were derived from their simplified linear relationship: $(\Delta H_f^\circ)_T = A + BT$.

The procedure of Benson et al. [2] has been omitted in view of its limited accuracy, which was pointed out by the authors themselves, for C_9 -alkanes and beyond.

The New Bond Energy Scheme

In the development of the new scheme, the four basic terms 1) the sp^3 - sp^3 carbon-carbon bond, $C^3-C^3 = 0.45$ kcal/mole; 2) the carbon-primary hydrogen bond, $C^3-H''' = -3.48$ kcal/mole; 3) carbon-secondary hydrogen bond, $C^3-H'' = -2.68$ kcal/mole; and 4) carbon-tertiary hydrogen bond, $C^3-H' = -1.78$ kcal/mole are taken from the original scheme of Laidler [11] as recommended by Mackle and O'Hare [12] and Cox [4]. The sp^3 carbon is further discriminated, as in the Tatevskii's scheme, into primary, secondary, tertiary, and quaternary carbons designated as C_1 , C_2 , C_3 , and C_4 , the common superscript 3 indicating tetrahedral hybridization being eliminated. A further distinction was made as to whether C_3 and C_4 carbons are situated in the terminal position, or in the third 3rd or higher position from the nearest end of the longest extended chain, as is done in the SMH scheme. In order to fit in the experimental data of alkanes Nos. 53 and 54 in Table 2, it was further necessary to distinguish the tertiary carbon which is deeply situated (embedded) in the alkane, i.e.,

Table 1. Bond Energy Parameters of the New Scheme

No.	Bond	$\Delta H_f^\circ(g)$ term (kcal/mole)	Alkanes from which derived	Bond energy ^a (kcal/mole)	Remarks
1	C ³ -H ^{'''}	-3.48 ± 0.14	Simple n-alkanes, terminally branched	98.42	The basic C-C and C-H bonds of sp ³ -carbon of the Cox scheme [4], designated in this work as C ³
2	C ³ -H ^{''}	-2.68 ± 0.12	Methyl alkanes	97.62	
3	C ³ -H [']	-1.78 ± 0.10		96.72	
4	C ³ -C ³	0.45 ± 0.05		85.19	Primes indicate the number of identi- cal hydrogens; energy term per C-H bond; the numerical subscripts de- note primary, secondary, etc.
	(C ₁ -C ₁) (C ₁ -C ₂) (C ₁ -C ₃) (C ₁ -C ₄) (C ₂ -C ₂) (C ₂ -C ₃)				same as for C ³ -C ³ , above
5	(C ₃)-C ₂ ; (C ₃)*-C ₂	0.77 ± 0.11	10, 15, 16, 24, 25, 26	84.87	
6	C ₃ -C ₃	1.03	12	84.61	
7	C ₄ -C ₂	1.12 ± 0.19	11, 17, 27, 41	84.52	
8	(C ₄)-C ₂ ; (C ₄)*-C ₂	1.47 ± 0.28	20, 31, 34, 55	84.17	
9	(C ₃)-C ₃ (C ₃)-C ₃	1.86 ± 0.05	28, 32, 33, 46	83.78	

10	(C ₃)*-C ₃	2.60 ± 0.38	33, 54	83.04	(C)* indicates 3rd or higher position from any end, of either the main chain or branches.
11	C ₄ -C ₃	<u>2.77</u>	21	82.87	
12	(C ₄)-C ₃ (C ₄)-(C ₃) C ₄ -(C ₃)	3.56 ± 0.28	35, 37, 42, 45, 48 52, (50)	82.08	
13	(C ₃)*-C ₄	<u>5.78</u>	53	79.86	
14	C ₄ -C ₄ (C ₄)-C ₄ (C ₄)-(C ₄) (C ₄)*-C ₃ (C ₄)*-C ₄ (C ₄)*-(C ₃)* (C ₄)*-(C ₄)* [C ₃ CC ₃]	6.54 ± 0.59	39, 49	79.10	
		Unknown ^b			
		0.00 ± 0.21	19, 29, 68		Steric correction term for a vicinal pair of C ₃ ; not assignable to any particular bond
15	[C ₄ CC ₃]	1.74 ± 0.18	36, 43, 50		Steric correction term for vicinal C ₄ and C ₃
16	[C ₄ CC ₄]	5.26 ± 0.03	51, 69		Steric correction term for vicinal pair of C ₄

^aBased on NBS values of enthalpies of atomization of carbon and hydrogen as 171.29 and 52.10 kcal/mole, respectively [19].

^bThe alkanes involving these (anticipated) terms have not yet been isolated or their heats of combustion measured.

^cFor a single valued bond energy term, the largest observed uncertainty is assigned; namely, that of the C₄-C₄ bond.

third or higher from any end, from that of the main extended chain or its branches, separately as $(C_3)^*$ and to assign higher energy terms to its bonds with C_3 or C_4 . At least two more such parameters are anticipated for $(C_4)^*$, the exact values of which must await future experimental data.

The bond energy terms of the new scheme are presented in Table 1. These terms represent the averages derived from relevant hydrocarbons also shown in Table 1, bearing serial numbers as per Table 2. Some economy of parameters can be achieved in the scheme without any appreciable increase in the over-all standard error. Thus, parameters $C_3-C_3 = 1.03$ and $C_4-C_3 = 2.77$ admitted in the scheme just for one single alkane of each type (Nos. 12 and 21 in Table 2) can be replaced by the closer terms: $(C_3)-C_3 = 1.78$ and $(C_4)-C_3 = 3.56$, respectively. This yields a 14-parameter scheme, having a precision of ± 0.31 kcal/mole, better than any of the existing methods for alkanes except the Allen-Skinner scheme, but requiring elaborate examination of an alkane structure as mentioned before. The parameter $(C_3)^*-C_4 = 5.78$, for an embedded tertiary carbon, is also a single-source value derived from 2,2-dimethyl-3-ethyl pentane, $\Delta H_f^\circ(1)$ exptl + ΔH_V° from GR scheme. At least the experimental heat of vaporization of this alkane was needed for the confirmation of this term underlined in Table 1, as also are the former two.

The result of uniform application of all eight schemes to 70 alkanes is presented in Table 2 in the form of the absolute error Δ , which is $[\Delta H_f^\circ(g)$, observed - $\Delta H_f^\circ(g)$, calculated]. At the end of Table 2 are given the average error $(\Sigma \pm \Delta_i)/N$ (disregarding sign) and the standard error $(\Sigma \Delta_i^2/N)^{1/2}$. The experimental $\Delta H_f^\circ(g)$ of 2,3-dimethyl pentane shows a uniform disagreement with all the important schemes, the experimental value being on an average 0.9 kcal more negative, and it is likely that the value may be incorrect.

DISCUSSION

A comparison of the predicting ability of the various schemes is made in Table 3. The first five schemes are generally considered as very successful for alkanes, but their former claims of a precision to the tune of the experimental uncertainty (± 0.3 kcal/mole) are not maintained by the new experimental data on branched nonanes [5] and long-chain polymers [8]. Methods 1 and 2 in Table 2 were found deficient merely in respect of two steric terms; namely, the vicinal interaction of a pair of quaternary (C_4) carbons separated by one C, or C_4 and C_3 one carbon apart in the chain. This steric factor was duly recognized by the scheme of Greenshields and

Rossini. When these steric correction terms were numerically worked out separately and incorporated in Tatevskii's scheme and the Saunders-Matthews-Hurd's scheme, their precision was improved dramatically, as may be seen from Table 3. The calculated terms for the two schemes so modified are given in the previous section, and the estimates of error affected by this introduction are parenthesized in Table 2. Methods 3 and 4 have good precision considering the substantial economy achieved in the number of basic parameters they employ, but the calculation of structural features and numbers associated with them is rather laborious and complicated; for instance, the m and l of the SZ scheme or the Platt and Wiener numbers of the GR scheme. Also, a few more basic parameters may still be wanting in these schemes in order to cope with the higher-order steric interactions in more branched higher alkanes than are presently available experimentally. The easy applicability of Methods 1 and 2, and also of the general scheme developed in this work, fully justifies the larger number of basic parameters.

A poorer precision of ± 1.35 kcal/mole now shown by the method of Overmars and Blinder has dismissed their earlier claim [13] that only four parameters properly averaged by least-square procedure brought about an over-all agreement of ± 0.58 kcal/mole "comparable with more elaborate schemes." Clearly more than four parameters are needed to deal with the steric interaction energies in alkanes. The standard error as high as ± 2.8 kcal/mole given by the Verma-Doraiswamy procedure invokes comments. The results are wide and inaccurate at least for the one temperature (298°K) tested here, and linear extension of such values to other temperatures on the basis of an oversimplification of the C_p - T relationship suggested by them is misleading. These authors tested their parameters on only three alkanes out of over 40 on which experimental data up to 1500°K were readily available from the API tables.

In the new scheme as many as 16 parameters were necessary to achieve a precision of ± 0.28 kcal/mole, close to the experimental uncertainty. To make these parameters transferable to substituted hydrocarbons and other organic compounds, the total steric energy in a molecule (though primarily from nonbonded interactions) must be split up and assigned bondwise rather than to a few interlocked parameters such as those of Schemes 2 to 4 which are applicable to alkanes only. Another advantage of such bondwise energy assignment is that it gives a relative picture of bond strengths in a molecule and indicates at least approximately which of the relevant atoms would be more labile than others and which bond more susceptible in a chemical reaction. Although empirically assigned, these well correlated

Table 2. Heats of Formation (Ideal Gas, 298.15°K) of 70 Alkanes: Calculations by Various Schemes

No.	Compound	$\Delta H_f^\circ(\text{g})$ obsd kcal/ mole	Error Δ , $\Delta H_f^\circ(\text{g})$, obsd - $\Delta H_f^\circ(\text{g})$, calcd [†] for various correlation-schemes														This work	
			SMH	TBY	SZ	GR	AS	OB	VD	10	11	12	calcd	Δ				
1	2	3	4	5	6	7	8	9	10	11	12	calcd	Δ					
1	Ethane	-20.24	-0.14	0.00	-	-	-	0.57	0.26	-	0.26	-	20.43	0.19				
2	Propane	-24.82	0.23	0.26	0.39	-	0.35	0.87	0.62	-	0.62	-	25.34	0.52				
3	n-Butane	-30.15	0.15	0.11	-0.02	-	-0.05	0.42	0.23	-	0.23	-	30.25	0.15				
4	2-Methylpropane	-32.15	-0.43	0.22	0.08	0.65	-0.02	-0.73	0.12	-	0.12	-	31.75	-0.40				
5	n-Pentane	-35.16 ^a	-0.21	0.16	-0.11	-	0.03	0.24	0.16	-	0.16	-	35.16	0.00				
6	2-Methylbutane	-36.84 ^a	-0.14	-0.14	-0.17	0.12	-0.11	-0.54	0.13	-	0.13	-	36.66	-0.18				
7	2,2-Dimethylpropane	-40.27 ^a	-0.92	-0.15	0.50	0.87	0.30	-2.30	0.11	-	0.11	-	39.96	-0.31				
8	n-Hexane	-39.96	-0.06	0.00	0.01	-	0.00	0.37	0.30	-	0.30	-	40.07	0.11				
9	2-Methylpentane	-41.66	-0.04	0.00	-0.07	0.02	0.00	-0.47	0.25	-	0.25	-	41.57	-0.09				
10	3-Methylpentane	-41.02	-0.09	0.01	0.08	-0.06	0.01	0.17	-1.01	-	-1.01	-	40.93	-0.09				
11	2,2-Dimethylbutane	-44.35	-0.05	-0.37	0.07	-0.11	0.01	-1.46	0.97	-	0.97	-	44.20	-0.15				
12	2,3-Dimethylbutane	-42.49	0.10	-0.31	0.20	-0.22	0.03	-0.45	1.08	-	1.08	-	42.49	(0.00)				
13	n-Heptane	-44.89	-0.04	0.03	0.00	-	0.00	0.33	0.31	-	0.31	-	44.98	0.09				
14	2-Methylhexane	-46.60	-0.03	0.02	-0.09	-0.05	-0.01	-0.53	0.25	-	0.25	-	46.48	-0.12				
15	3-Methylhexane	-45.97	-0.09	0.03	0.06	0.05	0.00	0.11	-1.02	-	-1.02	-	45.84	-0.13				
16	3-Ethylpentane	-45.34	-0.34	0.02	0.20	0.13	0.14	0.73	0.71	-	0.71	-	45.52	0.18				
17	2,2-Dimethylpentane	-49.28	-0.03	-0.35	-0.07	-0.06	0.00	-1.51	0.98	-	0.98	-	49.11	-0.17				
18	2,3-Dimethylpentane	-47.63	-0.78	-1.12	-0.90	-1.09	-0.75	-0.70	0.88	-	0.88	-	46.33	-1.30				

19	2,4-Dimethylpentane	-48.29	0.00	0.02	-0.16	-0.08	-0.01	-1.38	0.22	-47.98	0.31
20	3,3-Dimethylpentane	-48.18	-0.53	-0.33	-0.37	-0.62	-0.02	-0.39	2.08	-47.74	-0.44
21	2,2,3-Trimethylbutane	-48.96	0.47	-0.43	-0.45	-0.34	-0.40	-0.33	2.35	-48.96	(0.00)
22	n-Octane	-49.82	-0.02	0.06	-0.01	-	0.00	0.28	0.32	-49.89	0.07
23	3-Methylheptane	-51.50	0.02	0.08	-0.07	-0.08	0.02	-0.55	0.30	-51.39	-0.11
24	3-Methylheptane	-50.82	0.01	0.13	0.14	0.12	0.07	-0.13	-1.01	-50.75	-0.07
25	4-Methylheptane	-50.69	0.14	0.26	0.27	0.47	0.20	0.26	1.11	-50.75	0.06
26	3-Ethylhexane	-50.40	-0.43	-0.08	0.08	0.30	0.01	0.55	0.60	-50.43	0.03
27	2,2-Dimethylhexane	-53.71	0.51	0.19	0.43	0.38	0.51	-1.05	1.51	-54.02	0.31
28	2,3-Dimethylhexane	-51.13	0.67	0.34	0.53	0.48	0.52	0.67	2.32	-51.24	0.11
29	2,3-Dimethylhexane	-52.44	0.11	0.21	0.14	0.09	0.05	-0.64	1.01	-52.25	-0.19
30	2,5-Dimethylhexane	-53.21	0.03	0.07	-0.15	-0.21	0.01	-1.41	0.24	-52.89	0.32
31	3,3-Dimethylhexane	-52.61	-0.01	0.19	-0.12	0.09	0.47	-0.05	2.59	-52.65	0.04
32	3,4-Dimethylhexane	-50.91	0.20	-0.07	0.27	0.01	0.31	0.89	2.54	-50.92	0.01
33	2-Methyl-3-ethylpentane	-50.48	0.44	0.36	0.70	0.67	0.16	1.32	2.17	-50.10	-0.38
34	3-Methyl-3-ethylpentane	-51.28	0.34	0.32	0.04	-0.29	0.41	1.28	3.12	-51.63	0.33
35	2,2,3-Trimethylpentane	-52.61	0.23	0.25	0.39	0.32	0.35	0.90	3.64	-52.76	0.15
36	2,2,4-Trimethylpentane	-53.57	2.35	2.03	-0.01	-0.37	-	-0.06	3.28	-53.78	0.21
37	2,3,3-Trimethylpentane	-51.73	0.20	0.66	0.35	0.28	0.27	1.78	4.52	-52.06	0.33
38	2,3,4-Trimethylpentane	-51.97	0.00	0.02	0.39	0.10	-0.21	0.68	4.33	-51.73	-0.24
39	2,2,3,3-Tetramethylbutane	-53.99	0.00	0.00	-0.98	-0.19	-0.59	1.23	6.26	-53.40	-0.59
40	n-Nonane	-54.71 ^b	0.03	0.10	0.02	-	0.01	0.24	0.37	-54.80	0.09
41	2,2-Dimethylheptane	-58.92 ^b	0.23	-0.06	0.15	0.08	-	-1.39	1.22	-58.93	0.01
42	2,2,3-Trimethylhexane	-57.75 ^b	0.04	0.07	0.12	-0.10	-	0.63	3.44	-57.67	-0.08
43	2,2,4-Trimethylhexane	-58.03 ^b	2.15	1.90	-0.03	0.10	-	0.35	3.76	-58.05	0.02
44	2,2,5-Trimethylhexane	-60.54 ^b	0.33	0.02	0.17	0.17	-	2.16	1.25	-60.43	-0.11

(continued)

Table 2 (continued)

No.	Compound	$\Delta H_f^\circ(g)$ obsd kcal/ mole	Error Δ , $\Delta H_f^\circ(g)$, obsd - $\Delta H_f^\circ(g)$, calcd lfor various correlation-schemes												This work	
			SMH	TBY	SZ	GR	AS	OB	VD	10	11	12	calcd	Δ		
1	2	3	4	5	6	7	8	9	10	11	12	calcd	Δ			
45	2,3,3-Trimethylhexane	-57.47 ^b	-0.59	-0.12	-0.34	-0.39	-	0.91	3.72	-	0.91	-	56.97	-0.50		
46	2,3,5-Trimethylhexane	-57.99 ^b	0.48	0.14	0.17	-0.04	-	-0.47	2.05	-	-0.47	-	57.65	-0.34		
47	2,4,4-Trimethylhexane	-57.31 ^b	1.96	2.15	-0.26	0.25	-	1.07	4.38	-	1.07	-	57.32	0.01		
48	3,3,4-Trimethylhexane	-56.36 ^b	-0.17	0.36	0.05	0.03	-	2.02	4.83	-	2.02	-	56.65	0.29		
49	2,2,3,3-Tetramethylpentane	-56.70	0.64	1.15	-0.17	0.54	0.39	3.38	8.50	-	3.38	-	57.29	0.59		
50	2,2,3,4-Tetramethylpentane	-56.64	2.12	1.70	0.05	-0.23	-	2.59	6.20	-	2.59	-	56.42	-0.22		
51	2,2,4,4-Tetramethylpentane	-57.83	5.72	5.05	0.26	1.74	-	2.25	7.37	-	2.25	-	57.80	-0.03		
52	2,3,3,4-Tetramethylpentane	-56.46	-0.25	0.48	-0.13	0.30	-0.41	2.77	5.79	-	2.77	-	56.38	-0.04		
53	2,2-Dimethyl-3-ethylpentane	-55.13 ^b	1.78	1.82	2.09	1.59	-	3.25	5.26	-	3.25	-	55.13	0.00		
54	2,4-Dimethyl-3-ethylpentane	-54.30 ^b	0.24	1.82	2.21	1.68	-	3.22	5.04	-	3.22	-	54.68	0.38		
55	3,3-Diethylpentane	-55.44	0.35	0.12	-0.59	-0.61	-0.11	2.09	3.11	-	2.09	-	55.52	0.08		
56	n-Decane	-59.67	0.03	0.13	-0.02	-	0.01	0.19	0.35	-	0.19	-	59.71	0.10		
57	n-Undecane	-64.60	0.05	0.16	-0.03	-	0.01	0.15	0.37	-	0.15	-	64.62	0.02		
58	n-Dodecane	-69.52	0.08	0.20	-0.03	-	0.02	0.11	0.39	-	0.11	-	69.53	0.01		
59	n-Tridecane	-74.45 ^c	0.10	0.23	-0.04	-	0.02	0.06	0.40	-	0.06	-	74.44	-0.01		

60	n-Tetradecane	-79.38 ^c	0.12	0.26	-0.05	-	0.02	0.01	0.41	-79.35	-0.03
61	n-Pentadecane	-84.31 ^c	0.14	0.29	-0.06	-	0.02	-0.04	0.42	-84.26	-0.05
62	n-Hexadecane	-89.23	0.17	0.33	-0.06	-	0.00	-0.07	0.44	-89.17	-0.06
63	n-Heptadecane	-94.15 ^c	0.20	0.37	-0.06	-	0.04	-0.11	0.46	-94.08	-0.07
64	n-Octadecane	-99.08 ^c	0.22	0.40	-0.07	-	0.04	-0.16	0.47	-98.99	-0.09
65	n-Nonadecane	-104.00 ^c	0.25	0.44	-0.07	-	0.05	-0.20	0.49	-103.90	-0.10
66	n-Eicosane	-108.93 ^c	0.27	0.57	-0.08	-	0.05	-0.24	0.50	-108.81	-0.12
<u>Polymers</u>											
67	Polyethylene	-9.89	0.01	0.03	-0.05	-	-	-0.13	0.00	-9.82	-0.07
68	Polypropylene	-15.55	0.33	0.40	0.43	-	-	-0.05	0.54	-15.59	0.04
69	Polyisobutylene	-17.11	<u>5.49</u>	<u>5.65</u>	0.21	-	-	4.97	7.72	-17.14	0.03
70	Poly(1-butene)	-19.50	0.45	0.78	0.84	-	-	-0.88	1.93	-20.18	0.68
	Average error		±0.51	±0.52	±0.26	±0.36	±0.15	±0.92	±1.95		±0.18
	Standard error		±1.14	±1.11	±0.47	±0.54	±0.24	±1.35	±2.87		±0.28
			(±0.36) ^d	(±0.44) ^d							(±0.31) ^e

^aNew values adopted; Ref. 14.

^bNew data of Good [5] as ΔH_f° (liquid) combined with ΔH_f° calculated by GR procedure [6].

^cValues based on extrapolated heats of combustion: E. J. Prosen and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **34**, 263 (1945).

^dStandard error recalculated using the slightly modified scheme affecting the values underlined in the column above.

^eThe new scheme with 14 parameters.

Table 3. Comparison of Bond Energy/Group Contribution Schemes Applied to 70 Alkanes

No.	Method	Standard error	No. of parameters	No. of alkanes tested	Applicability and remarks
1	Saunders-Matthews-Hurd [16] slightly modified	± 1.14 ± 0.36	11 13	70 (49) ^d 70	Alkanes (including polymers); modified with two new steric terms
2	Tatevskii et al. [20] slightly modified	± 1.11 ± 0.44	9 11	70 (49) ^d 70	Alkanes (including polymers); parameters not transferable to other compounds; modified with two new steric terms
3	Somayajulu and Zwolinski [19]	± 0.47	7 ^a	70 (54) ^d	Alkanes (including polymers), a very systematic procedure for calculating steric interactions; a few more parameters are still necessary for completeness
4	Greenshields and Rossini [6]	± 0.54	6	47 ^b (32) ^d	Alkanes only; not yet applicable to polymers for want of a procedure to work out the "Wiener" number per repeat unit

5	Allen and Skinner [1, 18]	± 0.24	+ up to 25 for individual molecules	4 (general)	52 ^c (37) ^d	Extremely precise but the steric term [S] cannot be calculated for some molecules; procedure laborious
6	Overmars and Blunder [13]	± 1.35		4	70 (52) ^d	Unsatisfactory; parameters inadequate in number; applicability general
7	Verma and Doraiswamy [21]	± 2.87		7	70 (3) ^d	Unsatisfactory; poor parameterization due to the attempt of establishing a linear ΔH_f° T relationship; original parameters taken from SMH method
8	This work	± 0.28		16 (+2 yet unknown)	70	Applicability: general; four basic parameters taken from Cox [4]
		± 0.31		14		

^aActually 6, as explained by the authors [19].

^b19 n-alkanes and 4 polymers excluded.

^cExcluding polymers and most nonanes.

^dTested by the originator.

Table 4. Predicted Heats of Formation of Some Polyolefins in the Condensed Amorphous State

No.	Polymer	Repeating structure	Predicted enthalpies (kcal/monomole)	
			$\Delta H_f^\circ(g)$ (hypothetical) ^a	$\Delta H_f^\circ(c)$ (condensed state) ^b
1	Poly(2-butene) (C ₄ H ₈) _n	$\begin{array}{c} \text{C} \\ \\ \dots\text{C}-\text{C}- \\ \\ \text{C} \end{array}$	-19.82 ± 0.24	-24.76 ± 0.39
2	Poly(3-methyl-1-butene) (C ₅ H ₁₀) _n	$\begin{array}{c} \dots\text{C}-\text{C}- \\ \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \end{array}$	-24.76 ± 0.45	-30.44 ± 0.54
3	Poly(1-pentene) (C ₅ H ₁₀) _n	$\begin{array}{c} \dots\text{C}-\text{C}- \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \\ \\ \text{C} \end{array}$	-25.09 ± 0.24	-30.90 ± 0.39

4	Poly(2-methyl-1-butene) (C ₅ H ₁₀) _n	$\begin{array}{c} \text{C} \\ \\ \dots \text{C}-\text{C}- \\ \\ \text{C} \\ \\ \text{C} \end{array}$	-21.03 ± 0.36	5.21	-26.24 ± 0.47
5	Poly(4-methyl-1-pentene) (C ₆ H ₁₂) _n	$\begin{array}{c} \dots \text{C}-\text{C}- \\ \\ \text{C} \\ \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \end{array}$	-31.50 ± 0.24	6.58	-38.08 ± 0.39
6	Poly(3,3-dimethyl-1-butene) (C ₆ H ₁₂) _n	$\begin{array}{c} \dots \text{C}-\text{C}- \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	-29.79 ± 0.64	6.29	-36.08 ± 0.71

(continued)

Table 4. (continued)

No.	Polymer	Repeating structure	Predicted enthalpies (kcal/monomole)		
			ΔH_f° (g)	ΔH_v° (hypothetical) ^a	ΔH_f° (c) (condensed state) ^b
7	Poly(3-hexene) or "Polydiazopropane" (C ₆ H ₁₂) _n	\dots C—C— C C C C	-27.52 ± 0.45	7.46	-34.98 ± 0.54
8	Poly(2-ethyl-1-butene) (C ₆ H ₁₂) _n	C C \dots C—C— C C	-24.92 ± 0.36	6.46	-31.38 ± 0.47

9 Poly(4,4-dimethyl-1-pentene) (C ₇ H ₁₄) _n	$\begin{array}{c} \dots \text{C}-\text{C}- \\ \\ \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	-37.30 ± 0.36	7.34	-44.64 ± 0.47
10 Poly(2-methyl-3-ethyl-1-pentene) (C ₈ H ₁₆) _n	$\begin{array}{c} \dots \text{C}-\text{C}- \\ \\ \text{C} \\ \\ \text{C} \\ / \backslash \\ \text{C} \quad \text{C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	-32.31 ± 0.32	8.79	-41.10 ± 0.44

^aCalculated by the TBY scheme since the API-adopted GR scheme is not yet applicable to polymers [10]; the estimated uncertainty for this scheme is ± 0.30 .

^bCondensed, amorphous state of polymer above glass transition, equivalent to the liquid state [10].

bond energy terms show close parallelism with the actual dissociation energies of the bonds; for instance, the dissociation energies of the C_i-C_j bond in methyl-substituted ethanes compared by Somayajulu and Zwolinski [19] bear a good relationship with our C-C bond energies in Table 1, Column 5. The bond energy terms formulated for alkanes in this paper form a part of a general scheme for organic compounds to be published in subsequent papers. The temperature coefficient of at least some of the bond energy terms will also be possible, based on a more exact $C_p^\circ - T$ relationship [7].

Polymers [10, 3]

The scheme is applied to some polyolefins structures that may become available experimentally in well characterized physical states. These are given in Table 4.

It appears that Polymers 4, 7, 8, and 10 in Table 4 should involve high steric hindrance as evidenced by their less negative heats of formation predicted from the alkane analysis. The polymerization of the corresponding 2-alkylalkenes may not be as facile as other α -olefins which polymerize readily by Ziegler-Natta catalysts. This inference is, however, based on energy (not free energy) considerations.

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