Enthalpies of Formation of Organometallic Compounds with First-Order Index of the Molecule

Z. J. Chen[†] and S. B. Desu[*]

Department of Materials Science and Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Received October 30, 1992. Revised Manuscript Received January 22, 1993

On the basis of the concept of the first-order index of a molecule, the enthalpies of formation were calculated for $(C_nH_{2n+1})_i(C_mH_{2m+1})_jM$, $(i + j = 4)$ and $(C_nH_{2n+1})_i(C_mH_{2m+1})_jMH$, $(i + j = 3)$, M = Si, Ge, and Sn, in tetra- and trialkyl derivative forms for *m*, *n* varying from 1 to 10. The calculated data are in excellent agreement with the experimental data available. In these calculations only two parameters were required which were determined from experimental data of alkanes; others parameters involved were all obtained from the basic atomic quantum energy level structure and the electronegativities of atoms from standard tables. The method is also applicable to compounds with branched chains, the expansion and some calculated examples are given.

I. Introduction

The enthalpies of formation of chemical compounds are important parameters in chemical vapor deposition (CVD) and other types of thin-film processes. In the past, there have been several reports on the enthalpy of formation of polysilanes, disilane, trisilane, tetrasilane, dimethylsilane, etc.[1–5] In this work, we have studied the enthalpy of formation of complex organometallic compounds that commonly occur in many CVD processes. Enthalpy data are useful in the computer simulations of various CVD processes and in the calculations for equilibrium states of species in both the gaseous and condensed phase. In general, it is very difficult to experimentally determine enthalpies of formation of organic and organometallic compounds because of the limited number of $\Delta H_f{}^\circ{}_{298.15}$ values available. Theoretical calculations of heat of formation using quantum mechanical calculations are also complicated and may result in significant errors.[6–8] The calculated results of frequency at the HF/6-31G level have a 10% systematic error coming from the harmonic approximation. After rescaling the results for the heat of formation, there is still a 6–10% error arising from the truncation of the base function.[9–10]

To overcome these problems, additive processes are often used in order to calculate enthalpies of formation of organic and organometallic compounds.[11] Such methods are based on the structural similarity of molecules and the use of fixed values for given atomic groups or chemical bonds which are experimentally determined. However, since these calculations require the use of a considerable number of experimentally determined parameters, application to heteroorganic compounds is still complicated.

Consequently, a powerful additive method which uses a small number of experimental parameters to calculate enthalpies of formation for organic and organometallic compounds is desired. The first-order molecule bond index[12–14] is one such additive method which requires only two or three parameters that can be determined from experimental data. We use this method here to obtain enthalpies of formation of organometallic compounds of IVA elements (Si, Ge, Sn) in tetra- and trialkyl derivative forms. The results obtained agree closely with the available experimental data.[15,16] In this method only two parameters are determined from experimental data of alkanes; while the other parameters are all obtained from the basic atomic energy level structure and electronegativities of atoms listed in standard physical and chemical tables.

As a first step the physical basis for the first order index of a molecule is analyzed. Subsequently, the physical meaning and the method of calculation is discussed with special emphasis on the topological terms. A set of formulas for calculating the enthalpies of organometallic compounds of IVA elements (Si, Ge, Sn) in tetra- and trialkyl derivatives is then given. Finally, the method is expanded to include the compounds with branched chains and some examples were provided.

[†] On leave from Department of Physics, Nankai University, China.

[*] To whom all the correspondence should be addressed.

(1) Martin, J. G.; O'Neal, H. E.; Ring, M. A. *Int. J. Chem. Kinet.* **1990**, *22*, 613.

(2) Walsh, R. *Organometallics* **1988**, *7*, 75. Walsh, R. *Pure Appl. Chem.* **1986**, *59*, 169.

(3) O'Neal, H. E.; Ring, M. A. *Organometallics* **1988**, *7*, 1017.

(4) Ring, M. A.; O'Neal, H. E.; Hartmen, J. K. *Combust. Flame* **1987**, *68*, 43.

(5) Gordon, M. S.; Truang, T. N.; Bonderson, E. K. J. *J. Am. Chem. Soc.* **1986**, *108*, 1421.

(6) Dykstra, C. E. *Ab initio calculation of the structures and properties of molecules*; Elsevier Science: New York, 1988.

(7) Gaussian 88 user's guide and programmer's reference: Frisch, M. J.; Head-Gordon, M. Revision C Version, Sept 1988, Multiflow Computer, Inc., 175 N. Main St., Brandford, CT 06405.

(8) Ho, P.; Coltrin, M. E.; Binkley, J. S.; Melius, C. F. *J. Phys. Chem.* **1985**, *89*, 4647–4658.

(9) Ho, P.; Coltrin, M. E. *J. Phys. Chem.* **1986**, *90*, 3399–3406.

(10) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1990**, *94*, 5120–5127.

(11) Benson, S. W. *Thermochemical Kinetics*; John Wiley & Sons: New York, 1976.

(12) Kier, L. B.; Hall, L. H. *J. Pharm. Sci.* **1981**, *70*, 583–589.

(13) Voronkov, M. G.; Klyuchnikov, V. A. *Dokl. Akad. Nauk SSSR* **1987**, *295*, 1405–1408.

(14) Voronkov, M. G.; Klyuchnikov, V. A. *Dokl. Akad. Nauk SSSR* **1988**, *303*, 128–131.

(15) Voronkov, M. G.; Klyuchnikov, V. A.; Korchagina, A. N.; et al. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1986**, 1976–1981.

(16) Klyuchnikov, V. A.; Danilova, T. F.; Voronkoe, M. G.; D'yakov, V. M. *Dokl. Akad. Nauk SSSR* **1985**, *281*, 1141–1145.

0897-4756/93/2805-0535$04.00/0

II. Theoretical Background

Let E_α be the energy of formation of an atom with a nucleus Z_α, formed from a free nucleus and electrons. E_α is equal to the sum of interaction energies between electrons and the nucleus and that between electrons. If E_t is the total energy of a molecule and ΔH is the energy of formation of a molecule from free atoms (i.e., the heat of formation or the enthalpy), then we can write

$$\Delta H = E_t - \sum_\alpha E_\alpha \tag{1}$$

where

$$E_\alpha = \frac{1}{2}\int_{V_\alpha}\frac{Z_\alpha \rho_{e\alpha}\,d\tau_1}{r_{1\alpha}} + \frac{1}{4}\int_{V_{\alpha 1}}\int_{V_{\alpha 2}}\frac{\rho_{12\alpha}\,d\tau_1\,d\tau_2}{r_{12}} \tag{2}$$

and

$$\begin{aligned} E_t = \sum_\alpha\left(\frac{1}{2}\int_{V_\alpha}\frac{Z_\alpha\rho_e\,d\tau_1}{r_{1\alpha}} + \frac{1}{4}\int_{V_{\alpha1}}\int_{V_{\alpha2}}\frac{\rho_{12}\,d\tau_1\,d\tau_2}{r_{12}}\right) + \\ \sum_{\alpha\neq\beta}\frac{1}{2}\left(\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \int_{V_\beta}\frac{Z_\alpha\rho_e\,d\tau_1}{r_{1\alpha}} + \right. \\ \left.\int_{V_\alpha}\frac{Z_\beta\rho_e\,d\tau_1}{r_{1\beta}} + \int_{V_{\alpha1}}\int_{V_{\beta2}}\frac{\rho_{12}\,d\tau_1\,d\tau_2}{r_{12}}\right) \end{aligned} \tag{3}$$

ρ_e is the density of negative charge, ρ_{12} is the probability density of finding two electrons in volumes $d\tau_1$ and $d\tau_2$, r_{12} is the distance between $d\tau_1$ and $d\tau_2$, $r_{\alpha\beta}$ is the distance between nuclei α and β in a molecule, V_α and V_β are the volumes of nuclei of α and β and the subscript α in $\rho_{e\alpha}$ and $\rho_{12\alpha}$ refers to the atomic state.

The enthalpy of formation of a molecule can be written as

$$\begin{aligned} \Delta H = \sum_\alpha\left(\frac{1}{2}\int_{V_\alpha}\frac{Z_\alpha\rho_e\,d\tau_1}{r_{1\alpha}} - \frac{1}{2}\int_{V_\alpha}\frac{Z_\alpha\rho_{ea}\,d\tau_1}{r_{1\alpha}} + \right. \\ \left.\frac{1}{4}\int_{V_{\alpha1}}\int_{V_{\alpha2}}\frac{\rho_{12}\,d\tau_1\,d\tau_2}{r_{12}} - \frac{1}{4}\int_{V_{\alpha1}}\int_{V_{\alpha2}}\frac{\rho_{12\alpha}\,d\tau_1\,d\tau_2}{r_{12}}\right) + \\ \sum_{\alpha\neq\beta}\frac{1}{2}\left(\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}} + \int_{V_\beta}\frac{Z_\alpha\rho_e\,d\tau_1}{r_{1\alpha}} + \right. \\ \left.\int_{V_\alpha}\frac{Z_\beta\rho_e\,d\tau_1}{r_{1\beta}} + \int_{V_{\alpha1}}\int_{V_{\beta2}}\frac{\rho_{12}\,d\tau_1\,d\tau_2}{r_{12}}\right) = \\ \Big(\sum_\alpha({}_\alpha\langle e|N\rangle_\alpha^{\text{molecule}} - {}_\alpha\langle e|N\rangle_\alpha^{\text{atom}}) + \\ \sum_\alpha({}_\alpha\langle e|e\rangle_\alpha^{\text{molecule}} - {}_\alpha\langle e|e\rangle_\alpha^{\text{atom}})\Big) + \\ \Big(\sum_{\alpha\neq\beta}({}_\alpha\langle N|N\rangle_\beta + {}_\beta\langle e|N\rangle_\alpha + {}_\alpha\langle e|N\rangle_\beta + {}_\alpha\langle e|e\rangle_\beta\Big) \end{aligned} \tag{4}$$

It can be seen that terms in the first pair of square brackets relate the paramters of a given atom in a particular atomic group. In other words, it arises from those electrons that are localized at a certain atom. Note that the summation is taken over all the atoms not including cross terms between atoms; consequently, it is related to the sum of paramters denoting the structure of each chemical bond. If we convert all the bonds comprising a molecule into a criterion bond and assign an index to it, then every bond can be assigned a bond index x_b, for example, the CH_2-CH_2 bond can be taken as a criterion and an index of unity can be assigned. The sum of all x_b is a parameter reflecting the dimensional aspect in the structure character of molecules. Using the concept of molecular connectivity[17,18] and taking into account that the species considered here have the cluster type terms only, the first square brackets in (4) are nothing but the first-order index of the molecule. The contribution of the first pair of square brackets in eq 4 therefore may be rewritten as

$$K^1X, \quad \text{where } {}^1X = \sum_i x_i \tag{5}$$

and K is the energy attributed to the standard bond or the energy of a bond whose bond index equals 1.

The second pair of square brackets in eq 4 relates to the delocalized electrons that penetrate among atoms of the molecule and so its value depends on the intermolecular topological geometry. We denote the term in the second pair of square brackets as topological geometry term G. Because the forces between atoms in molecules are short-range forces, appreciable only over distances of the order of 1–3 Å, those molecules with the same topological geometry and bond type will have the same topological energy term regardless of molecular dimension. Therefore, we may consider G as a constant for a particular group of compounds with the same geometry. For example, consider the compound $(C_mH_{2m+1})_i(C_nH_{2n+1})_jSi$ $(i + j = 4)$. When m, n are large, the G term will take same value regardless of the value of n and m. Thus we can rewrite (4) as

$$\Delta H = K^1X + G \tag{6}$$

In summary, the enthalpy of formation of organometallic compounds is contributed by two parties, one is related to the first-order index of molecule denoting the dimensional aspect of molecular structure, another is relted to the topological aspect of molecular structure.

III. First-Order Index of the Molecule and the Topological Geometry Term

In this section the detail will be given about the calculation of the first-order index and of the topological geometry term for molecules of organometallic compounds.

First-Order Index of Molecule. According to Kier and Hall[17,18] each bond within a molecule can be described by two δ^v values known as the vertex valence of the atomic or atom group. Each of these is connected with an atom or an atomic group located at the ends of the bond. Therefore for each bond of a molecule, the bond index x_b in eq 5 is computed according to

$$x_b = (\delta^v_i\delta^v_j)_b^{-1/2} \tag{7}$$

These bond indexes are summed over the entire molecule to give the first-order index of a molecule:

$${}^1X = \sum_i x_i = \sum_b m_b x_b = \sum_b m_b(\delta^v_i\delta^v_j)_b^{-1/2} \tag{8}$$

Here m_b is the number of bonds of type b, and the vertex valence δ^v_i is assigned to each atom (other than hydrogen) or atomic group in the molecule. Kier and Hall[17] computer δ^v_i for each atom as the sum of the valence elctrons participating in σ, π, and lone-pair orbitals on each atom minus the number participating in bonding with hydrogen.

---

(17) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Chemistry and Drug Research*; Academic: New York, 1976.

(18) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Structure–Activity Analysis*; Research Studies Press: 1986; p 18.

Table I. Values of δ^v_i for Some Atoms or Atomic Groups

1. CH_3 0.5	5. Si 0.4	9. SiH 0.3
2. CH_2 1.0	6. Ge 0.14286	10. GeH 0.10714
3. CH 1.5	7. Sn 0.08695	11. SnH 0.06522
4. C 2.0	8. Pb 0.05128	12. PbH 0.03846

Table II. Reciprocal of Bond Indexes of Some Chemical Bonds, $1/x_b = (\delta^v_i\delta^v_j)^{1/2}$

C–C	2.0				
C–CH	1.732	CH–CH	1.5		
C–CH_2	1.414	CH–CH_2	1.2247	CH_2–CH_2	1.0
C–CH_3	1.0	CH–CH_3	0.8660	CH_2–CH_3	0.7071
Si–C	0.89442	SiH–C	0.77459		
Si–CH	0.77460	SiH–CH	0.67082		
Si–CH_2	0.63245	SiH–CH_2	0.54772		
Si–CH_3	0.44721	SiH–CH_3	0.38730		
Ge–C	0.53452	GeH–C	0.46291		
Ge–CH	0.46291	GeH–CH	0.40089		
Ge–CH_2	0.37796	GeH–CH_2	0.32733		
Ge–CH_3	0.267	GeH–CH_3	0.23145		
Sn–C	0.41703	SnH–C	0.36116		
Sn–CH	0.36115	SnH–CH	0.31277		
Sn–CH_2	0.29488	SnH–CH_2	0.25537		
Sn–CH_3	0.20851	SnH–CH_3	0.18058		
Pb–C	0.32026	PbH–C	0.27735		
Pb–CH	0.27735	PbH–CH	0.24019		
Pb–CH_2	0.22645	PbH–CH_2	0.19612		
Pb–CH_3	0.16013	PbH–CH_3	0.13868		

If Z^v is the total number of valence electrons, we can write δ^v as

$$\delta^v_i = Z^v_i - h_i = \sigma_i + p_i + n_i - h_i \tag{9}$$

where h_i is the number of bonded hydrogens on atom i and σ_i, p_i, and n_i are the numbers of σ, p orbital, and of lone-pair electrons, respectively. Thus, the values of δ^v_i depend on the atomic number, its valence (hybrid) state and the number of bonded hydrogen atoms. A more satisfactory definition was suggested in ref 18 for δ^v_i as

$$\delta^v = \frac{Z_v - h}{Z - Z_v} = \frac{\sigma_i + p_i + n_i - h_i}{\text{no. of core electrons}} \tag{10}$$

where Z is the atomic number of the atom. Consequently for any bond A_i–A_j connecting atom i and atom j the bond index is computed as

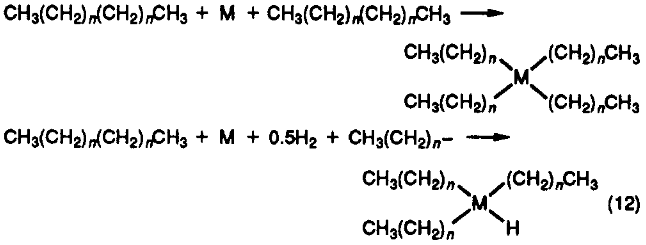
$$x_b = (\delta^v_i\delta^v_j)_b^{-1/2} = \left(\frac{(Z - Z_v)_i(Z - Z_v)_j}{(Z_v - h)_i(Z_v - h)_j}\right)^{1/2} \tag{11}$$

where A_i and A_j stand for atom or atomic group, Z is the overall number of electrons in an atom or in a group, Z_v is the number of valence electrons in an atom or in a group, and h is the number of atoms of hydrogen bonded to the atoms under consideration. The values of δ^v_i for some atoms or groups are listed in Table I.

The bond indexes can be computed according to eq 11. The values of bond indexes of the bond appearing in compounds under consideration are listed in Table II.

The first-order index of the molecule ^1X is computed according to eq 8. The summation is carried out over all the bonds within the molecule. If we apply these calculations to normal alkanes, the K in eq 5 means the homologous difference, i.e., the change in enthalpy caused by the addition of one CH_2– group to a polymethylene chain. This value is obtained from the standard table, here chosen as −20.66 kJ/mol.

Topological Geometry Term. It has been suggested[9] that the topological geometry term G in eq 6 can be calculated using an ideal reactions such as



$$CH_3(CH_2)_n(CH_2)_nCH_3 + M + CH_3(CH_2)_n(CH_2)_nCH_3 \longrightarrow [CH_3(CH_2)_n]_2M[(CH_2)_nCH_3]_2$$

$$CH_3(CH_2)_n(CH_2)_nCH_3 + M + 0.5H_2 + CH_3(CH_2)_n\text{–} \longrightarrow [CH_3(CH_2)_n]_2M(H)(CH_2)_nCH_3 \tag{12}$$

or

$$2CH_3(CH_2)_{2n}CH_3 + M \rightarrow [CH_3(CH_2)_n]_4\,M + \Delta g_1 \tag{13}$$

$$1.5CH_3(CH_2)_{2n}CH_3 + M + 0.5H_2 \rightarrow [CH_3(CH_2)_n]_3MH + \Delta g_2 \tag{14}$$

Thus the interrelation among the three topological geometry terms of $[CH_3(CH_2)_n]_4M$, $[CH_3(CH_2)_n]_3MH$, and $CH_3(CH_2)_{2n}CH_3$ compounds can be given as

$$G[CH_3(CH_2)_n]_4M = 2G[CH_3(CH_2)_{2n}CH_3] + \Delta g_1 \tag{15}$$

$$G[CH_3(CH_2)_n]_3MH = 1.5G[CH_3(CH_2)_{2n}CH_3] + \Delta g_2 \tag{16}$$

The value $G[CH_3(CH_2)_{2n}CH_3]$ is determined from experimental data on n-alkanes and equals −46.56 kJ/mol.

The Δg_1 and Δg_2 in (15) and (16) are the changes in the topological geometry term due to the replacement of $-CH_2-$ by a heteroatom M or MH in the alkane molecule. To calculate the value of Δ_g, we use the assumption suggested by ref 19 that the electrons and the electronegativities of the heteroatoms M or MH carry responsibility for the changes: where a = 2 for tetralkyl and 1.5 for trialkyl

$$\Delta g_1 = a[K_c - K_m]K - \frac{\sum E_m}{\sum E_c}K - 2l_dK + l_fK$$

$$\Delta g_2 = a[K_c - K_{mh}]K - \frac{\sum E_{mh}}{\sum E_c}K - 2l_dK + l_fK \tag{17}$$

derivatives, and K_c, K_m and K_{mh} are the electronegativities of carbon, M, and MH atoms. E_c, E_m, and E_{mh} are the conventional energies of all the electrons involved respectively in the carbon, heteroatom M, or MH. They are calculated as the sum of the principal (n) and the secondary (l) quantum numbers of all the electrons. $\sum E_{mh}$ was calculated with allowance for the electron of the hydrogen atom. As an example, consider the value of $\sum_{Ge}$: the electronic configuration (nl^i) of Ge is $1s^22s^2p^63s^2p^6d^{10}4s^2p^2$, so $\sum_{Ge} = \sum(n + l)i = 122$. Some of the values of K_c, K_m, K_{mh}, $\sum E_m$, $\sum E_c$, and $\sum E_{mh}$ for various groups of atoms are listed in Table III. $2l_dK$ and l_fK are for elements having electron in sublevels d and f.

In summary, the heat of formations is calculated from eq 6, wherein the indexes ^1X are calculated according to (8), K is quoted from data of alkanes, the geometry term G are calculated by the formulas (15) and (16), and Δg are obtained from (17). The related values appearing in the calculation of δ^v and ^1X are listed in Tables I and II, and

---

(19) Kupchik, J. *Quant. Struct. Act. Relat.* **1985**, *4*, 123–128.

Table III. Electronegativity K_A and Conventional Energy Σ_A of Atom(s)

atom(s)	K_A	Σ_A	atom(s)	K_A	Σ_A
CH_3	2.21	15	Sn	1.59	224
CH_2	2.24	14	SiH	2.03	39
CH	2.31	13	GeH	1.93	123
C	2.46	12	SnH	1.88	225
Si	1.89	38	H	2.17	1
Ge	1.69	122			

Table IV. Heats of Formation of $(C_mH_{2m+1})_i(C_nH_{2n+1})Si$

molecular formula	index order	Δg, kJ/mol	geom, kJ/mol	enthalpy, kJ/mol	
				calcd	exptl
$(C_1H_3)_4Si$	8.944 27	47.883	−45.237	−231	−229 ± 3
$(C_1H_3)_1(C_2H_5)_3Si$	11.222 13	43.383	−49.737	−282	−281 ± 5
$(C_1H_3)_2(C_2H_5)_2Si$	10.462 84	44.883	−48.237	−264	−263 ± 5
$(C_1H_3)_3(C_2H_5)_1Si$	9.703 56	46.383	−46.737	−247	
$(C_1H_3)_1(C_3H_7)_3Si$	14.222 13	43.383	−49.737	−344	−343 ± 5
$(C_1H_3)_2(C_3H_7)_2Si$	12.462 84	44.883	−48.237	−306	−306 ± 5
$(C_2H_5)_4Si$	11.981 41	41.883	−51.237	−299	−297 ± 5
$(C_2H_5)_1(C_3H_7)_3Si$	14.981 41	41.883	−51.237	−361	−360 ± 5
$(C_2H_5)_2(C_3H_7)_2Si$	13.981 41	41.883	−51.237	−340	−341 ± 5
$(C_2H_5)_3(C_3H_7)_1Si$	12.981 41	41.883	−51.237	−320	−319 ± 5
$(C_3H_7)_4Si$	15.981 41	41.883	−51.237	−382	−378 ± 5
$(C_3H_7)_1(C_4H_9)_3Si$	18.981 41	41.883	−51.237	−444	−444 ± 7
$(C_3H_7)_2(C_4H_9)_2Si$	17.981 41	41.883	−51.237	−423	−423 ± 6

Table V

molecular formula	X_b	ΔX	enthalpy, kJ/mol		error, %
			calcd	exptl	
$(n\text{-}C_4H_9)_3SiH$	15.719	0.0	340	341 ± 7	0.3
$((CH_3)_3C)_3SiH$	12.873	2.846	399		
$((CH_3)_2CHCH_2)_3SiH$	14.463	1.256	366		
$(C_2H_5)CH(CH_3))_3SiH$	14.628	1.091	363	355 ± 6	2.3

Table VI

molecular formula	X_b	ΔX	enthalpy, kJ/mol		error, %
			calcd	exptl	
$(n\text{-}C_5H_{11})_3SiH$	18.719	0.0	402	402 ± 7	0.2
$((CH_3)_3CCH_2-)_3SiH$	16.596	2.123	446.6		
$((CH_3)_2CHCH_2CH_2-)_3SiH$	17.848	0.871	420.8		
$((CH_3)_2CH-CH(CH_3)-)_3SiH$	16.856	1.863	441.3		
$((C_2H_5)C(CH_3)_2-)_3SiH$	16.237	2.482	454.1		
$((C_2H_5)CH(CH_3)CH_2-)_3SiH$	18.078	0.641	416	413 ± 7	0.7
$((C_2H_5)CH_2CH(CH_3)-)_3SiH$	17.626	1.093	425.4		
$((C_2H_5)_2CH-)_3SiH$	17.856	0.8634	420.6		

Table VII

molecular formula	X_b	ΔX	enthalpy, kJ/mol		error, %
			calcd	exptl	
$CH_3(n\text{-}C_3H_7)_2SiH$	11.062	0.0	243	240 ± 6	1.25
$CH_3(i\text{-}C_3H_7)_2SiH$	10.182	0.8800	261	255 ± 6	2.4

the values of electronegativities and conventional energies of atom(s) are listed in Table III.

Table VIII

molecular formula	X_b	ΔX	enthalpy, kJ/mol		error, %
			calcd	exptl	
$CH_3(n\text{-}C_4H_9)_2SiH$	13.06	0.0	284	283 ± 6	0.35
$((CH_3)_3C)_2SiHCH_3$	11.164	1.896	323		
$((CH_3)_2CHCH_2)_2SiHCH_3$	12.484	0.576	296	296 ± 7	0.07
$(C_2H_5)CH(CH_3))_2SiHCH_3$	12.334	0.726	299.3		

Table IX

molecular formula	X_b	ΔX	enthalpy, kJ/mol		error, %
			calcd	exptl	
$C_2H_5(n\text{-}C_3H_7)_2SiH$	11.719	0.0	258	259 ± 6	0.4
$C_2H_5(i\text{-}C_3H_7)_2SiH$	10.837	0.8820	276	270 ± 6	2.3

Table X

molecular formula	X_b	ΔX	enthalpy, kJ/mol		error, %
			calcd	exptl	
$C_2H_5(n\text{-}C_4H_9)_2SiH$	13.719	0.0	299	301 ± 6	0.7
$((CH_3)_3C)_2SiHC_2H_5$	11.819	1.900	338		
$((CH_3)_2CHCH_2)_2SiHC_2H_5$	13.233	0.486	309		
$(C_2H_5)CH(CH_3))_2SiHC_2H_5$	12.992	0.727	314	315 ± 6	0.2

IV. Calculation of the First-Order Index, Topological Terms, and the Enthalpy

On the basis of the methods outlined in section III, we developed and coded software to calculate the enthalpies using the concept of first-order index and topological terms. The calculated values of enthalpies of formation for $(C_mH_{2m+1})_i(C_nH_{2n+1})_jM$ ($i + j = 4$) and $(C_mH_{2m+1})_i(C_nH_{2n+1})_jMH$ ($i + j = 3$); here M = (Si, Ge, Sn) are available with the software code upon request, and compared with the experimental data available in Table IV. The information given in Table IV on arbitrarily chosen saturated organometallic compounds indicates that the concepts of first-order index and topological term are very useful for calculation of the enthalpies of formation for long organic and organometallic compounds. This method can replace the complex procedure used by Bernstein[20] and Allen.[21] The disagreement between experimental and calculated $\Delta H_f{}^\circ{}_{298.15}$ values are of the order of 1–4 kJ mol^{-1} and well within the limits of accuracy of measurements. Statistical analysis was performed on the experimental data of 12 available $(C_mH_{2m+1})_i(C_nH_{2n+1})_jSi$ ($i + j = 4$) samples. The results indicated a standard deviation $s = 1.1183$ (kJ/mol), and correlation coefficient $r = 0.991$. For $(C_mH_{2m+1})_i(C_nH_{2n+1})_jSiH$ ($i + j = 3$) the results for $n = 20$ samples available were $s = 1.835$ (kJ/mol) and $r = 0.998$. It is worthy to note that only two parameters are required which are determined from experimental data of alkanes; other parameters involved are all taken from the basic atomic quantum energy level structure and the electronegativities of atoms from standard tables for all of the more than 3267 species of different organometallic compounds. The method can also be applied to unsaturated radicals and other coordination species which are often important in materials processing technologies but are generally poorly known. The results for some i-type species with branched chains are given in next section.

V. Heats of Formation for Some Branched Compounds

The concept and method outlined above can also be applied to branched compounds. In this case the molecular bond index is determined as a sum of ${}^1X_n$ and ΔX, where ${}^1X_n$ is calculted by formula (8) for normal compound (no branching), and ΔX is th value of the difference in ${}^1X$ between a branched and the normal one, both of these are calculated by eq (8):

$$\Delta X = {}^1X_n - {}^1X_b \qquad (18)$$

ΔX is a measure of the degree of skeletal branching. The value of ΔH increases with number of atoms and increase with skeletal branching, whereas the value of ${}^1X_b$ increases with number of atoms but decreases with branching. Using this as a first-order approximation, we take the sum of

$$X = {}^1X_n + \Delta X \qquad (19)$$

as the molecular index of compounds in formula 6 and

---

[20] Bernstein, H. J. *J. Chem. Phys.* **1952**, *20*, 263.

[21] Allen, T. H. *J. Chem. Phys.* **1959**, *31*, 1039.

Table XI

molecular formula	X_b	ΔX	enthalpy, kJ/mol calcd	enthalpy, kJ/mol exptl	error, %
$C_2H_5(n\text{-}C_5H_{11})_2SiH$	15.719	0.0	340	340 ● 6	0.0
$((CH_3)_3CCH_2\text{-})_2SiHC_2H_5$	14.303	1.416	370.0		
$((CH_3)_2CHCH_2CH_2\text{-})_2SiHC_2H_5$	15.138	0.5810	352.8		
$((CH_3)_2CH\text{-}CH(CH_3)\text{-})_2SiHC_2H_5$	14.477	1.242	366.4		
$((C_2H_5)C(CH_3)_2\text{-})_2SiHC_2H_5$	14.064	1.673	374.96		
$((C_2H_5)CH(CH_3)CH_2\text{-})_2SiHC_2H_5$	15.291	0.428	349.6		
$((C_2H_5)CH_2CH(CH_3)\text{-})_2SiHC_2H_5$	10.747	4.972	443.5		
$((C_2H_5)_2CH\text{-})_2SiHC_2H_5$	15.143	0.576	353	358 ● 7	1.5

maintain the value of K and formula for G in formula 6 unchanged. This expansion allows the formula to be applicable to both normal and branched compounds.

Seven different compounds have been considered: $(i\text{-}C_4H_9)_3SiH$, $(i\text{-}C_5H_{11})_3SiH$, $CH_3(i\text{-}C_3H_7)_2SiH$, $CH_3(i\text{-}C_4H_9)_2SiH$, $C_2H_5(i\text{-}C_3H_7)SiH$, $C_2H_5(i\text{-}C_4H_9)_2SiH$, and $C_2H_5(i\text{-}C_5H_{11})SiH$. Each of these have several possible structures with same number of atoms but different chemical skeletal branching. For each of the possible compounds the molecular index can be determined by formulas 19, 18, and 8, the topological geometry term G is determined in the same way as in section III. The results of calculation and the comparison with the experimental[15,16] are given bellow. The statistical analysis for the data of branched compounds available experimentally show good agreement between the calculated and experimental data; for $n = 7$, a sample standard deviation $s = 6.096$ kJ/mol that approaches the typical experimental error in the data; a correlation coefficient of $r = 0.987$ was obtained.

1. $(i\text{-}C_4H_9)_3SiH$

There are three possible compounds: $((CH_3)_3C)_3SiH$, $((CH_3)_2CHCH_2)_3SiH$, and $(C_2H_5)CH(CH_3))_3SiH$. The index of normal species $(n\text{-}C_4H_9)_3SiH$ is 15.719 (Table V).

2. $(i\text{-}C_5H_{11})_3SiH$

There are seven possible compounds: $((CH_3)_3CCH_2\text{-})_3SiH$, $((CH_3)_2CHCH_2CH_2\text{-})_3SiH$, $((CH_3)_2CHCH(CH_3)\text{-})_3SiH$, $((C_2H_5)C(CH_3)_2\text{-})_3SiH$, $((C_2H_5)CH(CH_3)CH_2\text{-})_3SiH$, $((C_2H_5)CH_2CH(CH_3)\text{-})_3SiH$, and $((C_2H_5)_2CH\text{-})_3SiH$. The index of normal species $(n\text{-}C_5H_{11})_3SiH$ is 18.719 (Table VI).

3. $CH_3(i\text{-}C_3H_7)_2SiH$

There is only one possible compound. The index of $CH_3(n\text{-}C_3H_7)_2SiH$ is 11.062 (Table VII).

4. $CH_3(i\text{-}C_4H_9)_2SiH$

There are three possible compounds: $((CH_3)_3C)_2SiHCH_3$, $((CH_3)_2CHCH_2)_2SiHCH_3$, and $((C_2H_5)CH(CH_3))_2SiHCH_3$. The index of $CH_3(n\text{-}C_4H_9)_2SiH$ is 13.06 (Table VIII).

5. $C_2H_5(i\text{-}C_3H_7)_2SiH$

There is only one possible compound. The index of $C_2H_5(n\text{-}C_3H_7)_2SiH$ is 11.719 (Table IX).

6. $C_2H_5(i\text{-}C_4H_9)_2SiH$

There are three possible compounds: $((CH_3)_3C)_2SiHC_2H_5$, $((CH_3)_2CHCH_2)_2SiHC_2H_5$, and $((C_2H_5)CH(CH_3))_2SiHC_2H_5$. The index of $C_2H_5(n\text{-}C_4H_9)_2SiH$ is 13.719 (Table X).

7. $C_2H_5(i\text{-}C_5H_{11})_2SiH$

There are seven possible compounds: $((CH_3)_3CCH_2\text{-})_2SiHC_2H_5$, $((CH_3)_2CHCH_2CH_2\text{-})_2SiHC_2H_5$, $((CH_3)_2CHCH(CH_3)\text{-})_2SiHC_2H_5$, $((C_2H_5)C(CH_3)_2\text{-})_2SiHC_2H_5$, $((C_2H_5)CH(CH_3)CH_2\text{-})_2SiHC_2H_5$, $((C_2H_5)CH_2CH(CH_3)\text{-})_2SiHC_2H_5$, and $((C_2H_5)_2CH\text{-})_2SiHC_2H_5$. The index of $C_2H_5(n\text{-}C_5H_{11})_2SiH$ is 15.719 (Table XI).

Glossary

a	=2 for tetralkyl and 1.5 for trialkyl derivatives in (17)
G	topological geometry term in (6)
$G(CH_3(CH_2)_nCH_3)$	the topological geometry term for $(CH_3(CH_2)_nCH_3)$ in (15) and (16)
Δg	change of the topological geometry term due to replacement of CH_2– by M or MH in the alkane molecule in (17)
ΔH	enthalpies of formation in (1), (4), and (6)
K	energy attributed to the standard bond or the energy of a bond whose bond index equals 1. In this work it has been chosen as −20.666 kJ/mol in (5), (6), and (17)
K_c, K_m, K_{mh}	electronegativities of carbon, M, and MH in (17)
l_d, l_f	quantum number in sublevels d and f in (17)
Σ_c, Σ_m Σ_{mh}	conventional energies of all the electrons entering respectively into the carbon, heteroatom M and MH in (17)
x_b	bond index in (5), (7), (8), and (11) and Table II
^1X	first-order index of molecule in (5), (6), (8), and (11).
ΔX	the difference in ^1X between a branched compounds and the corresponding normal one in (18) and (19).
δ^v	the vertex valence of the atom or atomic group, in (7)–(11) and Table I