A topological index and its applications.
Part 3. Estimations of the enthalpies of formation of mixed halogen-substituted methanes, silanes and boron mixed halides

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Abstract

A new kind of topological index H_1, previously proposed, was used to correlate the enthalpies of formation of various mixed halides, for example mixed halogen-substituted methanes and silanes together with boron mixed halides. Good linear relations were found between the H_1 and corresponding $\Delta_f H^{\ominus}_{298}$ values, with relatively low standard deviations. Based on the linear equations obtained, the $\Delta_f H^{\ominus}_{298}$ values of the remaining sets of compounds, whose experimental data are not yet available, were estimated. Moreover, the ΔH value of the exchange reaction of boron trihalides was calculated for the first time.

INTRODUCTION

It is increasingly being realized that a set of graph invariants known as topological indices are powerful tools in the description of chemical phenomena [1]. These include the Randic indices [2], currently being greatly extended by Kier and Hall [3, 4], which are the most extensively used and have been applied successfully in the correlations and predictions of various properties of homologous families of compounds. But the majority of the studies have been mainly restricted to organic compounds. For inorganic compounds, especially those containing heavy metal atoms, the methods are less successful, even using the series of connectivity indices proposed by Kier and Hall [3, 4]. Hence, some modification is required for these cases. One approach is to incorporate more electronic information [5] into the vertexes and/or edges of a graph originally used to describe a molecule.

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TABLE 1

First ionization potentials and electron affinities of the atoms relevant to this study (in kJ mol^{-1})

	F	Cl	Br	I	H	C	Si	B
I	1681.0	1251.1	1139.9	1008.4	1312.0	1086.4	786.5	800.6
A	322.0	348.7	324.5	295.0	72.9	122.0	120.0	23.0

In our preceding articles [6, 7], a new topological index H_1 (eqn. (1)) was proposed by introduction of the term shown in eqn. (2), to describe the edges in more detail

$$H_1 = \left(\sum_i \frac{1}{\sqrt{p_i q_i} \, (1 + \Delta_i)} \right)^2 \tag{1}$$

where p_i and q_i are the branching degrees of the vertexes (that is the atoms in a molecule), which have similar meanings as those of Randic [2], and Δ_i is the term adopted to describe the ith edge in a graph, and can be written as

$$\Delta_i = \alpha[I_i(1) - A_i(1)] + (1 - \alpha)[I_i(2) - A_i(1)] \tag{2}$$

where $I_i(n)$ and $E_i(n)$, $n = 1, 2$, are the first ionization potentials and electronic affinities (in kJ mol^{-1}), respectively, for atoms 1 and 2 bridging the edge i. The values employed in our calculations are listed in Table 1. As can be seen, $\Delta_i \gg 1$, thus $1 + \Delta_i$ can be taken as Δ_i.

According to our simple bonding model, the first term $I_i(1) - E_i(2)$ in eqn. (2) represents donating bonding from the HOAO of atom 1 to the LUAO of atom 2; the second term $I_i(2) - E_i(1)$, however, represents the back-bonding from the HOAO of atom 2 to the LUAO of atom 1, which may be very important in some cases, e.g. the back-donation of the lone pair of fluorine to the vacant p-orbital of boron greatly increases the stability of BF$_3$. Therefore, in eqn. (2), the α term is considered as an adjustable parameter that reflects the difference in these two kinds of interactions. In the following calculations, however, we always take it to be 0.5 in order to avoid further need of empirical non-observables, which means that both kinds of interactions are taken to be equally important. This assumption may not always hold, but its practical application in the correlation of both NMR chemical shifts [7], for example, ^{95}Mo-NMR shifts in the series of MoO$_n$X$_{4-n}$ (X = S, Se) compounds, and Mössbauer isomer shifts [6], for example, ^{119}Sn shifts in the series of PcSnX and SnX$_n$Y$_m$ (X = halogen) compounds, has shown it to be quite valid.

In the present paper, we continue our exploration of the new topological index in the field of thermochemistry in the hope of finding quantitative

correlations. Although, as is well known, thermochemical data of compounds are vital to the understanding of both chemical thermodynamics and kinetics [8, 9], most of the data are not up-to-date; thus, many semi-empirical methods, including those using bond additivity and group additivity, have been introduced. In spite of the surprising success of the law of group additivity, it has serious disadvantages when applied to compounds with many very polar bonds, such as the fluorocarbons and chlorocarbons [10, 11]. However, our quantitative correlation analyses demonstrate that the new topological indices have remarkably good linear relations with the heats of formation of these types of compound. Based on these relations, the enthalpies of formation $\Delta_f H_{298}^{\ominus}$ of some mixed-halogenated compounds, whose thermochemical data are not at present available, have been estimated with reasonable accuracy.

RESULTS

Linear relations between $\Delta_f H_{298}^{\ominus}$ and H_1 for mixed halogenated methanes

There have been a number of reviews of the data on $\Delta_f H_{298}^{\ominus}$ values of mixed halogenated hydrocarbons [12–15]. For the sake of completeness, we shall take the experimental values recommended by Kudchader and Kudchader [15], which are listed in column 3 of Tables 2–6. Based on eqns. (1) and (2), the H_1 values of each compound are computed and listed in column 2 of Tables 2–5. We have found four linear relations between $\Delta_f H_{298}^{\ominus}$ and H_1, as illustrated in Fig. 1 for mono-, di-, tri- and tetrahalogen-substituted methanes, respectively. The linear regression parameters are also listed in Tables 2–5.

It can be seen from Tables 2–5 that the linear relations obtained here are remarkably good, as seen from the fairly high correlation coefficients ($r > 0.99$) involved (Fig. 1). And it is interesting to note that the coefficients

TABLE 2

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of monohalogenated methanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.	Ref. 16
CH$_3$F	3.2051	−233.89	−324.47	−284.18
CH$_3$Cl	3.5923	−81.96	−79.37	−85.94
CH$_3$Br	3.6920	−37.74	−39.46	−35.52
CH$_3$I	3.8242	13.77	13.47	17.57

Regression equation: $\Delta_f H^{\ominus} = -1518.269 + 400.547 H_1 \times 10^6$; $r = 0.9998$; $s = 2.22$.

TABLE 3

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of dihalogenated methanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.	Ref. 16
CH_2F_2	3.1219	−452.71	−444.76	−493.38
CH_2Cl_2	3.9086	−95.40	−98.74	−93.80
CH_2Br_2	4.1180	−14.77	−6.69	−4.77
CH_2I_2	4.3993	117.57	116.94	113.43
CH_2FCl	3.5042	−264.43	−286.56	−300.91
CH_2FBr	3.6027		−233.26	−250.58
CH_2FI	3.7333		−175.85	−198.32
CH_2ClBr	4.0126		−53.01	−49.75
CH_2ClI	4.1503		7.51	8.79
CH_2BrI	4.2575		−54.62	−50.71

Regression equation: $\Delta_f H^{\ominus} = -1817.375 + 439.697 H_1 \times 10^6$; $r = 0.9993$; $s = 9.83$.

TABLE 4

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of trihalogenated methanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.	Ref. 16
CHF_3	3.0398	−697.05	−665.34	−710.94
$CHCl_3$	4.2383	−102.93	−122.67	−103.81
$CHBr_3$	4.5672	16.74	26.23	42.51
CHI_3	5.0146	210.87	228.82	213.93
CHF_2Cl	3.4173	−483.67	−494.46	−505.93
$CHFCl_2$	3.8168	−284.93	−313.55	−305.06
CHF_2Br	3.5145		−450.41	−459.78
CHF_2I	3.6435		−391.99	−401.24
$CHFClBr$	3.9195		−267.02	−258.95
$CHFClI$	4.0556		−205.39	
$CHFBr_2$	4.0237		−219.87	−208.61
$CHFBrI$	4.1615		−157.44	
$CHFI_2$	4.3017		−93.97	
$CHCl_2Br$	4.3466		−73.64	−53.93
$CHCl_2I$	4.4899		−8.79	
$CHClBr_2$	4.4562		−24.02	−7.78
$CHClBrI$	4.6013		41.66	
$CHClI_2$	4.7486		108.37	
$CHBr_2I$	4.7140		92.72	
$CHBrI_2$	4.8632		160.25	

Regression equation: $\Delta_f H^{\ominus} = -2041.780 + 452.797 H_1 \times 10^6$; $r = 0.9975$; $s = 26.19$.

TABLE 5

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of tetrahalogenated methanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.	Ref. 16
CF$_4$	2.9589	−974.96	−861.61	−920.15
CCl$_4$	4.5814	−95.81	−134.56	−102.97
CBr$_4$	5.0397	79.50	70.84	84.47
CI$_4$	5.6703	267.94	353.42	
CF$_3$Cl	3.3314	−707.93	−694.67	−716.34
CF$_3$Br	3.4274	−649.78	−651.62	−660.61
CF$_3$I	3.5548	−589.53	−594.55	−602.08
CF$_2$Cl$_2$	3.7260	−493.29	−517.85	−497.94
CFCl$_3$	4.1426	−284.93	−331.16	−296.27
CCl$_3$Br	4.6939	−38.91	−84.10	−42.80
CF$_2$ClBr	3.8275	−472.37		−463.96
CF$_2$ClI	3.9620	−412.08		−409.61
CF$_2$Br$_2$	3.9304	−426.22		−413.63
CF$_2$BrI	4.0667	−365.18		−363.51
CF$_2$I$_2$	4.2053	−303.05		−304.97
CFCl$_2$Br	4.2497	−283.17		−263.13
CFCl$_2$I	4.3913	−219.70		
CFClBr$_2$	4.3581	−234.60		−216.98
CFClBrI	4.5015	−170.33		
CFClI$_2$	4.6473	−104.98		
CFBr$_3$	4.4678	−185.43		−170.87
CFBr$_2$I	4.6131	−120.33		
CFBrI$_2$	4.7606	−54.22		
CFI$_3$	4.9105	12.93		
CCl$_3$I	4.8427	−17.41		
CCl$_2$Br$_2$	4.8078	−33.10		−3.60
CCl$_2$BrI	4.9584	34.43		
CCl$_2$I$_2$	5.1113	102.93		
CClBr$_3$	4.9230	18.58		−42.55
CClBr$_2$I	5.0754	86.86		
CClBrI$_2$	5.2301	156.19		
CClI$_3$	5.3872	226.56		
CBr$_3$I	5.1938	139.91		
CBr$_2$I$_2$	5.3503	210.04		
CBrI$_3$	5.5092	281.21		

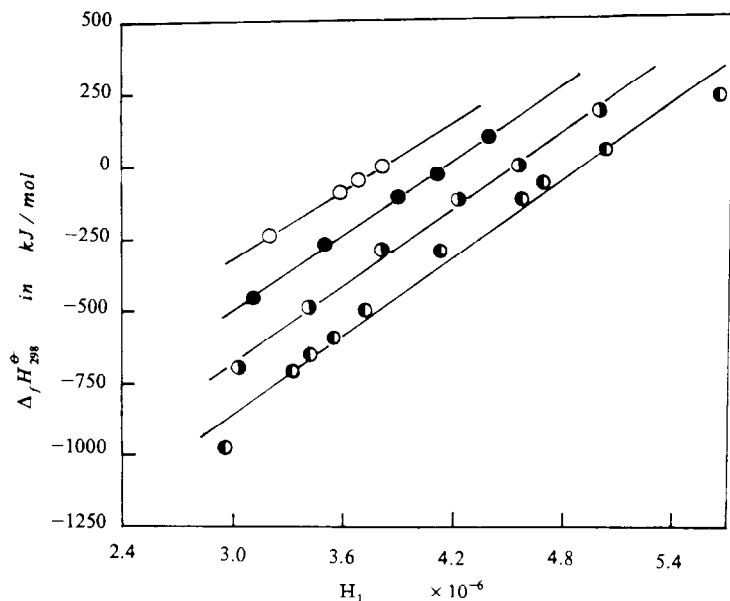Regression equation: $\Delta_f H^{\ominus} = -2187.491 + 448.111 H_1 \times 10^6$; $r = 0.9930$; $s = 48.70$.

Fig. 1. Plots of $\Delta_f H_{298}^{\ominus}$ vs. H_1 of various halogenated methanes: $\bigcirc$; mono-; $\bullet$, di-; $\mathbb{O}$, tri-; and $\mathbb{O}$, tetrahalogen-substituted methanes.

of each family of halomethanes follow the order: $r_{\mathrm{mono}} > r_{\mathrm{di}} > r_{\mathrm{tri}} > r_{\mathrm{tetra}}$, which may be caused by the increase in the number of the very polar carbon–halogen bonds in the series. Meanwhile, the standard deviations of the $\Delta_f H_{298}^{\ominus}$ values from those observed is lowest for the mono-substituted methanes, which is in the range of experimental uncertainty (Table 2); the deviations then increase slightly for the other three series, following the same order as that of the correlation coefficients (Tables 3–5).

Although it has been shown [13] that the bond additivity scheme corrected by the neighbouring bond interactions can be successfully applied to the halomethanes, because the experimental $\Delta_f H_{298}^{\ominus}$ data for mixed halomethanes are very scattered, it seems impossible to obtain the basic parameters required. Thus, in this respect our topological approach may have some advantages. Accordingly, the $\Delta_f H_{298}^{\ominus}$ values for the complete sets of di-, tri- and tetra- mixed-halogen-substituted methanes were estimated using the linear equations obtained. By comparison with calculated values [16], good agreements were observed for each set.

Linear relations between $\Delta_f H_{298}^{\ominus}$ and H_I values for mixed halogenated silanes

Even fewer thermochemical data are available for silicon-containing compounds [17–19]. Here we report for the first time the topological

TABLE 6

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of monohalogenated silanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.
H$_3$SiF	4.2678	−354.80	−352.84
H$_3$SiCl	4.8807	−135.56	−134.26
H$_3$SiBr	5.0470	−64.02	−74.98
H$_3$SiI	5.2730	−2.09	5.61

Regression equation: $\Delta_f H^\ominus = -1874.850 + 356.623 H_1 \times 10^6$; $r = 0.9987$; $s = 9.62$.

studies on the heats of formation for various halogen-substituted silanes. The H_1, $\Delta_f H^\ominus_{obs}$ and $\Delta_f H^\ominus_{calc}$ values for mono-, di-, tri- and tetra- halogenated silanes are listed in Tables 6–9, respectively. Linear regression analyses show that there are good correlations between $\Delta_f H^\ominus_{298}$ values and the topological index H_1, with correlation coefficients as high as 0.99 for each set (Fig. 2). For mono-, di- and trihalogenated silanes, the standard deviations are in the range of the experimental uncertainty, with the exception of the tetrahalosilanes whose standard deviation is rather high for some unknown reason.

The enthalpies of formation of unknown sets of di-, tri- and tetrahalosilanes were estimated according to the linear equations obtained above (Tables 7–9). Due to the lack of both experimental and theoretical values for these compounds, comparison and thus further evaluation of the method cannot be made at present.

TABLE 7

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of dihalogenated silanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.
SiH$_2$F$_2$	4.1407	−790.78 ± 33.47	−782.62
SiH$_2$Cl$_2$	5.3900	−315.06 ± 8.37	−325.85
SiH$_2$Br$_2$	5.7420	−180.75 ± 10.46	−197.07
SiH$_2$I$_2$	6.2286	−38.07 ± 12.55	−19.12
SiH$_2$FCl	4.7447		−561.74
SiH$_2$FBr	4.9087		−501.79
SiH$_2$FI	5.1316		−420.28
SiH$_2$ClBr	5.5644		−261.96
SiH$_2$ClI	5.8016		−175.27
SiH$_2$BrI	5.9828		−108.99

Regression equation: $\Delta_f H^\ominus = -2296.870 + 365.694 H_1 \times 10^6$; $r = 0.9987$; $s = 20.13$.

TABLE 8

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of trihalogenated silanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.
SiHF$_3$	4.0155	−1200.81 ± 20.92	−1188.17
SiHCl$_3$	5.9241	−499.15 ± 6.69	−518.44
SiHBr$_3$	6.4817	−303.34 ± 9.20	−322.80
SiHI$_3$	7.2638	−74.48 ± 12.55	−48.37
SiHF$_2$Cl	4.6106		−979.35
SiHFCl$_2$	5.2468		−756.09
SiHF$_2$Br	4.7723		−922.61
SiHF$_2$I	4.9921		−845.50
SiHFClBr	5.4192		−695.63
SiHFClI	5.6532		−613.50
SiHFBr$_2$	5.5943		−634.17
SiHFBrI	5.8321		−550.74
SiHFI$_2$	6.0748		−465.55
SiHCl$_2$Br	6.1072		−454.22
SiHCl$_2$I	6.3556		−367.06
SiHClBr$_2$	6.2931		−388.99
SiHClBrI	6.5451		−300.54
SiHClI$_2$	6.8021		−210.37
SiHBr$_2$I	6.7375		−233.05
SiHBrI$_2$	6.9981		−141.59

Regression equation: $\Delta_f H^{\ominus} = -2597.180 + 350.891 H_1 \times 10^6$; $r = 0.9989$; $s = 28.20$.

Linear relations between $\Delta_f H^{\ominus}_{298}$ and H$_1$ values for boron mixed halides

Thermochemical data of boron mixed halides are of importance in the quantitative understanding of both the thermodynamics of adduct formation and the mechanisms of halogen redistribution [20]. But of the complete set of mixed halides, only a few can be separated from their mixtures. Therefore, a theoretical evaluation of their $\Delta_f H^{\ominus}_{298}$ values is necessary.

The six available $\Delta_f H^{\ominus}_{298}$ values for boron trihalides, together with H_1 values for the complete set of boron mixed halides are compiled in Table 10. Correlation analysis yields an excellent linear relation between $\Delta_f H^{\ominus}_{298}$ and H_1 values with a correlation coefficient r of 0.9994 (Fig. 3), which lends us confidence to estimate the unknown enthalpies of formation for the remaining halides. The estimated values are listed in column 4 of Table 10. Based on these values, the ΔH values of the exchange reactions [20], for example

$$BCl_3(g) + BBr_3(g) \rightarrow BCl_2Br(g) + BClBr_2(g) \qquad (3)$$

TABLE 9

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of tetrahalogenated silanes

Compound	$H_1(\times 10^{-6})$	Obs.	Calc.
SiF$_4$	3.8922	−1615.02 ± 0.84	−1589.21
SiCl$_4$	6.4836	−662.75 + 5.44	−708.23
SiBr$_4$	7.2663	−415.47 ± 8.37	−442.21
SiI$_4$	8.3785	−110.46 ± 16.74	−64.10
SiF$_3$Cl	4.4784		−1389.88
SiF$_3$Br	4.6378		−1335.74
SiF$_3$I	4.8545		−1262.06
SiF$_2$Cl$_2$	5.1058		−1176.67
SiFCl$_3$	5.7742		−949.43
SiCl$_3$Br	6.6752		−643.12
SiF$_2$ClBr	5.2758		−1118.84
SiF$_2$ClI	5.5068		−1040.31
SiF$_2$Br$_2$	5.4487		−1060.10
SiF$_2$BrI	5.6833		−980.31
SiF$_2$I$_2$	5.9230		−898.85
SiFCl$_2$Br	5.9549		−887.97
SiFClBr$_2$	6.1385		−825.59
SiFClBrI	6.3874		−740.94
SiFClI$_2$	6.6413		−654.63
SiFBr$_3$	6.3248		−762.24
SiFBr$_2$I	6.5775		−676.34
SiFI$_3$	7.0976		−499.53
SiCl$_2$I	6.9347		−554.92
SiCl$_2$Br$_2$	6.8694		−577.10
SiCl$_2$BrI	7.1326		−487.64
SiCl$_2$I$_2$	7.4008		−396.48
SiClBr$_3$	7.0664		−510.11
SiClBr$_2$I	7.3333		−419.36
SiClBrI$_2$	7.6052		−326.94
SiClI$_3$	7.8821		−232.84
SiBr$_3$I	7.5369		−350.20
SiBr$_2$I$_2$	7.8125		−256.52
SiBrI$_3$	8.0930		−161.13

Regression equation: $\Delta_f H^{\ominus} = -2912.344 + 339.946 H_1 \times 10^6$; $r = 0.9978$; $s = 52.93$.

can be calculated as -2.406 kJ mol^{-1}. As is well known, the reaction is entropically favourable, so the negative ΔH derives an automatically negative ΔG value for the reaction, which means that the reaction is thermodynamically favoured. Further analyses of the thermodynamics and kinetics of the reaction are then feasible.
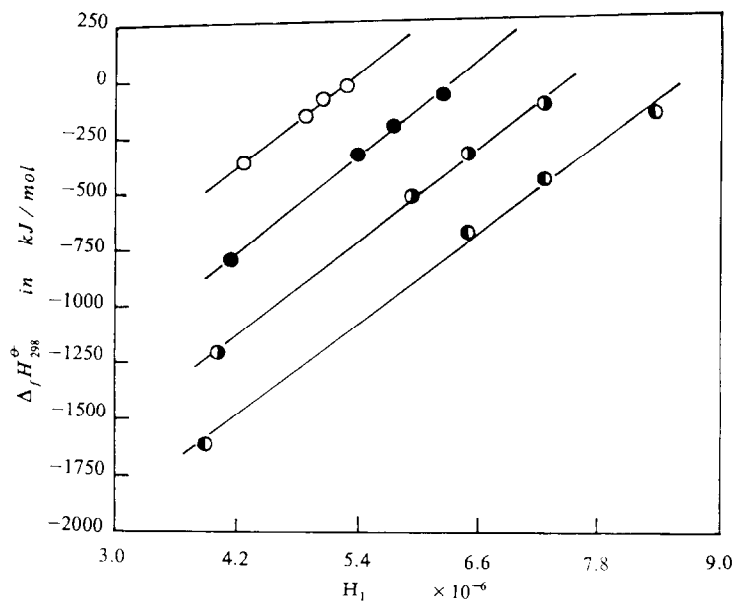
Fig. 2. Plots of $\Delta_f H_{298}^{\ominus}$ vs. H_1 of various halogenated silanes: $\bigcirc$, mono-; $\bullet$, di-; $\mathbb{O}$, tri-; and $\mathbb{O}$, tetrahalogen-substituted silanes.

TABLE 10

Topological indices H_1, and observed and calculated enthalpies of formation (kJ mol^{-1}) of boron mixed halides

Compound	$H_1(\times 10^{-6})$	Obs. [21]	Calc.
BF$_3$	2.624	−1137.00	−1114.58
BCl$_3$	4.242	−403.76	−411.71
BBr$_3$	4.717	−205.64	−205.23
BI$_3$	5.383	71.13	84.35
BClF$_2$	3.120	−890.36	−898.97
BCl$_2$F	3.659	−645.17	−664.67
BF$_2$Br	3.254		−840.82
BF$_2$I	3.435		−762.16
BFClI	3.999		−517.10
BFClBr	3.804		−601.83
BFBrI	4.151		−451.08
BCl$_2$Br	4.397		−344.18
BCl$_2$I	4.607		−252.92
BClBr$_2$	4.556		−275.10
BClI$_2$	4.988		−87.40
BClBrI	4.769		−182.55
BBr$_2$I	4.934		−110.88
BBrI$_2$	5.156		−14.39

Regression equation: $\Delta_f H^{\ominus} = -2254.415 + 434.433 H_1 \times 10^6$; $r = 0.9994$; $s = 17.28$.
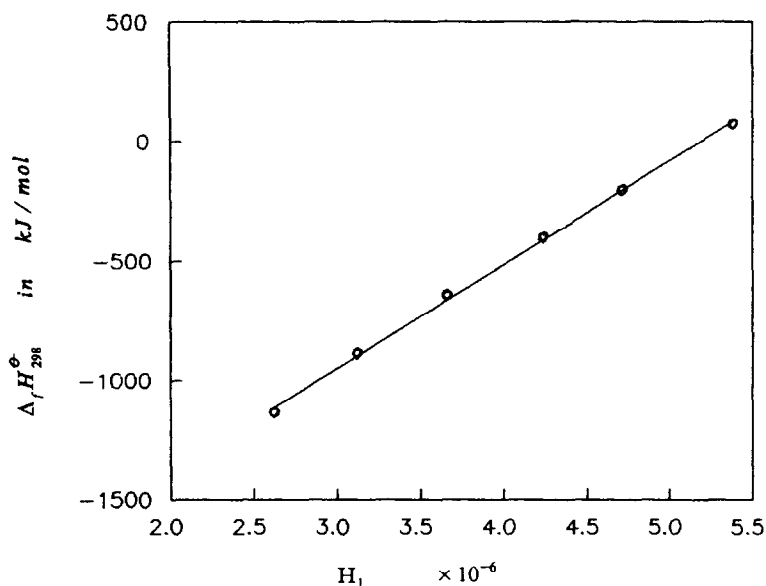
Fig. 3. Plot of $\Delta_f H_{298}^{\ominus}$ vs. H_1 of boron mixed halides.

CONCLUSIONS

In summary, our topological index H_1 has proved to be quite simple and effective in correlations with the enthalpies of formation for mixed halogenated methanes and silanes, as well as for boron mixed halides. The method is a useful tool for the estimation of unknown $\Delta_f H_{298}^{\ominus}$ values with reasonably good accuracy. Further exploration of its applications are in progress.

ACKNOWLEDGEMENTS

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