

THERMODYNAMICS OF SILICON COMPOUNDS (METHYLSILANES, CHLOROSILANES, METHYLCHLOROSILANES)

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SUMMARY

Methods are presented for the estimation of heats of formation, heat contents, and entropies of methyl and chlorine substituted silane.

INTRODUCTION

Calculations on the chemical equilibria and reaction heat effects for silicon compounds are hindered by lack of data. Although in recent years reaction heats and heats of formation have been measured¹⁻⁸, knowledge of thermodynamic properties is slender. Thermodynamic functions of simple compounds such as chlorosilanes can be calculated from structural and spectroscopic data⁹. For complicated molecules such as alkylchlorosilanes, this is more difficult because erroneous assignment of the lowest vibration frequencies and neglect of internal rotation contributions can give rise to large deviations.

A systematic approach is given by O'Neal and Ring¹ who propose a first order

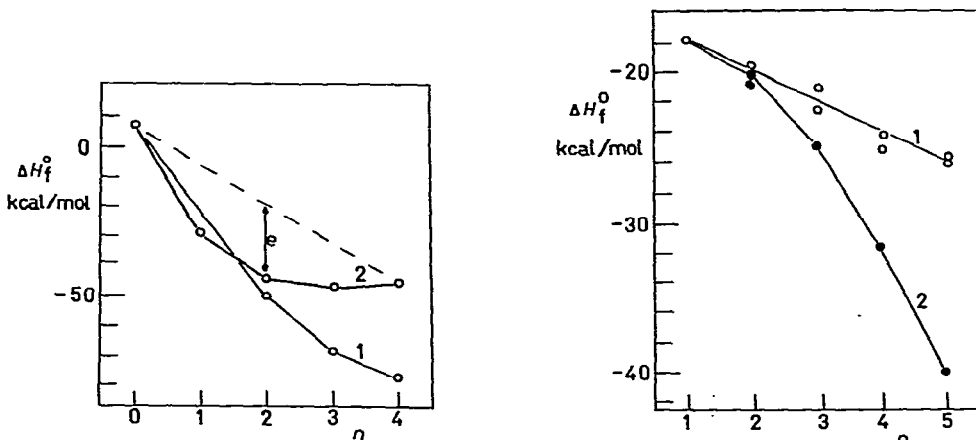


Fig. 1. Heat of formation of methyl- and ethylsilanes^{3,7}; curve 1: $\text{Me}_n\text{SiH}_{4-n}$ curve 2: $\text{Et}_n\text{SiH}_{4-n}$; e is the maximum deviation from linearity.

Fig. 2. Heat of formation of methyl and chlorine substituted methane¹⁴⁻¹⁶; curve 1: $\text{Cl}_n\text{CH}_{4-n}$ curve 2: $\text{Me}_n\text{CH}_{4-n}$.

bond-additivity method for silicon compounds. The principle is that a molar thermochemical quantity of a compound can be found by adding bond terms for all the bonds in the molecule, the terms being derived from available information. For a large number of compounds covered by their method, the results are satisfactory. For some compounds, however, substantial differences between calculated and experimental data are evident. The differences are largest for methyl- and ethylsilanes. This can be seen in Fig. 1 in which the heat of formation of methyl- and ethylsilanes is plotted against the number of alkyl groups. The deviation from a straight line, which one would expect in the case of additivity, is obvious. Errors up to 25 kcal per mole are found. From the curves in Fig. 2, in which the heats of formation of carbon compounds R_nCH_{4-n} ($R = Cl$ or CH_3) are shown, it is clear that although the deviation is smaller, simple additivity does not exist even here.

For the calculation of heat content, first order additivity leads to better estimations than in the case of heat of formation¹⁰. From a plot of heat content versus number of substituents, however, an appreciable deviation from linearity can be observed as Fig. 3 shows.

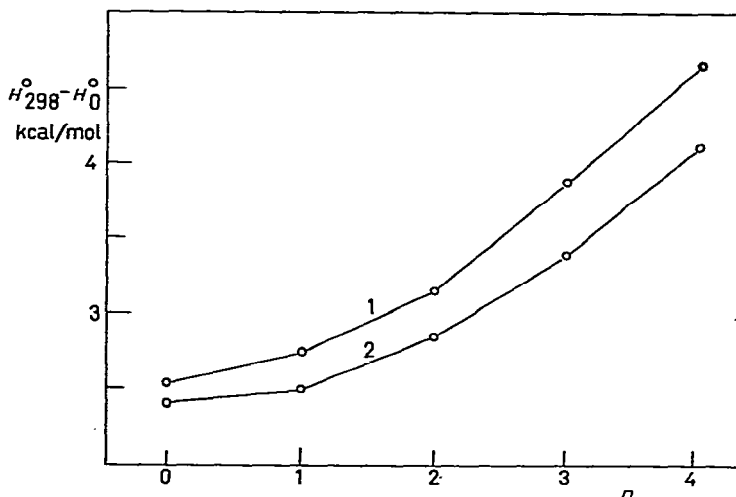
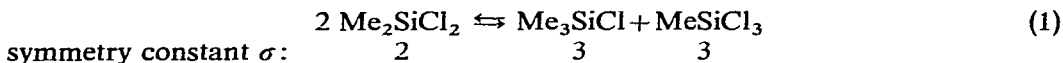


Fig. 3. Heat content of chlorosilanes (curve 1: Cl_nSiH_{4-n}) and chloromethanes (curve 2: Cl_nCH_{4-n}) from ref. 15.

Linearity is also absent in the case of entropy calculations (Fig. 6, curves 2 and 5). With application of symmetry corrections the agreement is improved (curves 1 and 4), but is still not satisfactory. If equilibrium constants of rearrangement reactions are calculated from data obtained by such an additivity method, subtle differences in free enthalpy remain unobserved. Only the entropy difference arising from symmetry factors is visible. The disproportionation equilibrium of dimethyldichlorosilane for instance has on the left and right hand side an equal number of methyl groups and chlorine atoms. Their group contributions thus compensate each other, so the equilibrium constant would only contain the symmetry factors:



$$K = \frac{p(\text{Me}_3\text{SiCl}) \cdot p(\text{MeSiCl}_3)}{p^2(\text{Me}_2\text{SiCl}_2)} = 0.44 \quad (2)$$

Experiments^{11,12}, however, show a slightly temperature-dependant equilibrium constant which is about 20 to 30 times smaller. The same kind of discrepancy is observed for the redistribution reactions of methylchlorosilanes carried out by Moedritzer and Van Wazer¹³. This paper is an attempt to overcome some of the errors involved in the bond-additivity methods. Methods for estimation of heats of formation, heat content, and entropy for all the methylchlorosilanes are given.

1. ESTIMATION OF THE HEAT OF FORMATION

The deviations mentioned above are of course caused by the influence which substituents have on the bond energy of the other ligands; it has previously been suggested for methylchlorosilanes that with increasing number of chlorine atoms in the molecule the silicon-chlorine bond energy increases by about 2 kcal per mole² for each additional chlorine atom. Most probably all the ligands in silanes have such a second order influence.

A procedure for including mutual influences in molecules with a tetravalent central atom is described below.

Method of calculation

A thermochemical quantity for a molecule of type X_nAY_{4-n} is assumed to comprise the sum of n bond terms for the A-X bonds, $(4-n)$ bond terms for the A-Y bonds, and a mutual influence term of the X and Y ligands:

$$Q(X_nAY_{4-n}) = n \cdot a(\text{A-X}) + (4-n) \cdot a(\text{A-Y}) + n \cdot (4-n) \cdot i(\text{X,Y}) \quad (3)$$

The primary factors $a(\text{A-X})$ and $a(\text{A-Y})$ form the linear part of the quantity Q and can be derived from the molecules AX_4 and AY_4 respectively. The mutual influence of n X atoms and $(4-n)$ Y atoms (or groups) is then assumed to be proportional to the number of X atoms and the number of Y atoms. The total influence part is equal to $n \cdot (4-n) \cdot i(\text{X,Y})$ in which $i(\text{X,Y})$ is the contribution of one X atom influencing one Y atom and vice versa. In a system with three different substituents (H, CH₃ and Cl) 6 out of the 15 possible values must be known for calculation of the others.

Checking of this method can be carried out on hydrocarbons for which suf-

TABLE I

CONTRIBUTION TO ENTHALPY OF FORMATION OF CARBON COMPOUNDS OF TYPE X_nCY_{4-n} AT 25°

Bond terms (kcal/mole)		Influence terms (kcal/mole)	
$a(\text{C-H})$	- 4.472	$i(\text{H, CH}_3)$	+ 0.994
$a(\text{C-Cl})$	- 6.375	$i(\text{H, Cl})$	- 0.176
$a(\text{C-CH}_3)$	- 9.925	$i(\text{H, C}_2\text{H}_5)$	+ 0.325
$a(\text{C-C}_2\text{H}_5)$	- 13.678	$i(\text{CH}_3, \text{C}_2\text{H}_5)$	- 0.241
		$i(\text{Cl, CH}_3)$	- 2.283

ficient literature data are available. In Table 1 the values of group contributions and influence terms are given for some methane derivatives. For calculation of the data of Table 1, the heats of formation of 9 compounds were needed. The heats of formation of the other hydrocarbons are computed by use of these terms, and are compared with known literature data in Table 2. The compounds for which the difference

TABLE 2

COMPARISON OF LITERATURE AND CALCULATED VALUES OF ENTHALPY OF FORMATION AT 25° FOR SOME CARBON COMPOUNDS (kcal/mole)

Compound	Name	ΔH_f° (lit.)	Ref.	ΔH_f° (calcd.)	Error
CH ₄	Methane	-17.89	14	-17.89	
CH ₃ Cl	Methyl chloride	-20.66	15	-20.66	
CH ₂ Cl ₂	Dichloromethane	-22.4	15	-22.77	-0.37
CHCl ₃	Trichloromethane	-25.0	15	-24.40	+0.60
CCl ₄	Carbon tetrachloride	-25.50	16	-25.50	
Me ₂ CCl	2-Chloro-2-methylpropane	-43.0	17	-43.0	
Me ₄ C	Neopentane	-39.70	17	-39.70	
Me ₃ CH	Isobutane	-31.5	17	-31.27	+0.23
Me ₂ CH ₂	Propane	-24.8	17	-24.8	
MeCH ₃	Ethane	-20.24	14	-20.36	-0.12
MeCH ₂ Cl	Ethyl chloride	-25.1	16	-26.12	-1.02
MeCHCl ₂	1,1-Dichloroethane	-29.1	16	-31.25	-2.15
Et ₂ CH ₂	n-Pentane	-35.0	18	-35.0	
Et ₃ CH	3-Ethylpentane	-45.34	18	-44.53	+0.81
MeEtCH ₂	n-Butane	-30.15	16	-30.15	
Me ₂ EtCH	Isopentane	-36.92	18	-36.17	+0.75
Me ₃ EtC	2,2-Dimethylbutane	-44.35	18	-44.18	+0.17
Me ₂ Et ₂ C	3,3-Dimethylpentane	-48.17	16	-48.17	
MeEt ₃ C	3-Methyl-3-ethylpentane	-51.38	16	-51.68	-0.30
MeEt ₂ CH	3-Methylpentane	-41.02	18	-40.59	-0.57

between literature and calculated value in column 6 is not given have been used for calculation of the group contributions. For the other compounds covered by the contribution terms of Table 1, no comparison is possible because of the lack of literature data. The errors (average 0.64 kcal) are small except for 1,1-dichloroethane. It

TABLE 3

CONTRIBUTION TO ENTHALPY OF FORMATION OF SILICON COMPOUNDS OF TYPE X_nSiY_{4-n} AT 25°

Bond terms	(Kcal/mole)	Influence terms	(Kcal/mole)
a(Si-H)	+ 1.9	i(H, Cl)	-0.6
a(Si-Cl)	-39.6	i(H, CH ₃)	+0.1
a(Si-CH ₃)	-20.0	i(Cl, CH ₃)	-2.0

should, however, be emphasized that the success of the method, which is in principle curve fitting, depends upon the availability of enough accurate experimental data.

TABLE 4
 HEAT OF FORMATION OF SILANE DERIVATIVES AT 25° (KCAL/MOLE)

Compound	ΔH_f° (lit.)	Ref.	ΔH_f° (calcd.)
SiH ₄	+7.3 +7.8	3 21	+7.6
SiH ₃ Cl			-35.7
SiH ₂ Cl ₂			-77.8
SiHCl ₃	-117.4	4	-118.7
SiCl ₄	-163.2	5	-158.4
	-153.7	6	
MeSiCl ₃	-150.5 ± 10	6	-144.8
Me ₂ SiCl ₂	-108.4	2	-127.2
	-104.8 ± 5	6	
Me ₃ SiCl	-80 ± 4.5	6	-105.6
	-84.7 ± 0.9	5	
Me ₄ Si	-77	7	-80.0
Me ₃ SiH	-67	7	-57.8
Me ₂ SiH ₂	-49	7	-35.8
MeSiH ₃			-14.0
Me ₂ SiHCl			-82.1
MeSiH ₂ Cl			-58.8
MeSiHCl ₂			-102.4

 TABLE 5
 REARRANGEMENT EQUILIBRIA: COMPARISON OF MEASURED AND ESTIMATED FREE ENTHALPY CHANGE

Equilibrium	Ref.	Temp. (°K)	Press. (atm.)	ΔG° (exp.) (kcal)	ΔG° (calcd.) (kcal)	Error
A,1	12	573	49	2.39	5.20	2.81
2	11	623		4.56	5.26	0.70
3	12	648		5.01	5.30	0.29
4	11	693		4.66	5.34	0.68
5	19	768	1	4.64	5.44	0.80
B,1	12	573	53	5.19 ± 0.2	4.23	0.96
2	12	648	81	5.99 ± 0.47	4.35	1.64
3	12	723	86	5.95	4.51	1.44
C	12	723	100	5.32 ± 1.68	5.87	0.55
D	13	373		1.75 ± 0.11	2.43	0.68
E	13	373		2.22 ± 0.26	2.15	0.07
F	13	373		12.12 ± 0.52	12.53	0.41
G	13	373		1.43 ± 0.94	2.29	0.86
H	13	373		14.27 ± 1.09	11.74	2.53
J	13	373		4.01 ± 0.52	3.65	0.37

Incidental deviations in any group contribution method need not therefore be wholly ascribed to the method, but can also be caused by errors in the experimental values.

Application of the given method to silanes therefore looks promising, though the results are to be used with the reservations which apply to the experimental data underlying the calculations.

Best fits for the contributions to the enthalpy of formation of methyl and chlorine substituted silanes are given in Table 3. The bond terms have been derived from literature data given in column 2 of Table 4. The influence terms have been chosen mainly on the basis of a number of known equilibrium constants listed in Table 5. The free enthalpy change of rearrangement reactions can be shown to contain only influence terms, heat content, and entropy. The bond terms, being additive, are not involved. The free enthalpy change of reaction (1), for example, can be represented as:

$$\Delta G_{298}^0 = \Delta H_f^0(\text{Me}_3\text{SiCl}) + \Delta H_f^0(\text{MeSiCl}_3) - 2 \Delta H_f^0(\text{Me}_2\text{SiCl}_2) - T \cdot \Delta S_{298}^0 \quad (4)$$

Introduction of equation (3) in which Q can be ΔH_f^0 leads to:

$$\Delta G_{298}^0 = -2i(\text{Me, Cl}) - T \cdot \Delta S_{298}^0 \quad (5)$$

TABLE 6

HEAT CONTENT OF METHYLCHLOROSILANES AT VARIOUS TEMPERATURES (KCAL/MOLE)

Compound	T=400°K			T=500°K			T=600°K			
	$H_f^0 - H_{298}^0$	Ref.	$H_f^0 - H_{298}^0$ (calcd.)	Diff.	$H_f^0 - H_{298}^0$ (lit.)	$H_f^0 - H_{298}^0$ (calcd.)	Diff.	$H_f^0 - H_{298}^0$ (lit.)	$H_f^0 - H_{298}^0$ (calcd.)	Diff.
SiH ₄	1.149	15	1.185	0.036	2.473	2.574	0.101	3.969	4.159	0.190
SiH ₃ Cl	1.364	15	1.364		2.904	2.904		4.604	4.604	
SiH ₂ Cl ₂	1.632	15	1.639	0.007	3.422	3.420	0.002	5.349	5.333	0.016
SiHCl ₃	1.945	15	1.952	0.007	4.011	4.011		6.180	6.171	0.009
SiCl ₄	2.284	15	2.284		4.644	4.644	0.001	7.070	7.070	
MeSiCl ₃	2.649	15	2.662	0.013	5.504	5.576	0.072	8.555	8.678	0.123
Me ₂ SiCl ₂		16	3.045			6.520			10.302	
Me ₃ SiCl	3.436	16	3.436		7.480	7.480		11.95	11.950	
Me ₄ Si	3.722	15	3.838	0.116	8.048	8.461	0.413	12.95	13.629	0.679
Me ₃ SiH			3.151			6.942			11.190	
Me ₂ SiH ₂			2.474			5.443			8.783	
MeSiH ₃			1.815			3.980			6.428	
MeSiHCl ₂			2.340			4.966			7.811	
MeSiH ₂ Cl			2.047			4.412			7.028	
Me ₂ SiHCl			2.738			5.939			9.479	

Equation (5) can be used for other temperatures by introducing the heat content and appropriate entropy of reactants and products, as discussed in paragraphs 2 and 3. In Table 5 a number of rearrangement equilibria is listed with the experimental and from Tables 3, 6 and 7 calculated free enthalpy change.

It can be shown easily that introduction of the experimentally obtained heat of formation of the methylsilanes⁷ leads to very large deviations in the free enthalpy change of the rearrangements. This gives support to the opinion that the observed change of the silicon carbon bond energy with the type of ligands is partially or completely due to experimental errors¹.

2. ESTIMATION OF HEAT CONTENT

Molecular constants can be obtained from infrared and Raman spectroscopy and from electron diffraction. Calculation of thermodynamic functions then becomes possible⁹. From Fig. 3 it was seen that a rough estimate of the heat content, $H_T^0 - H_0^0$ can be obtained for the compounds X_nAY_{4-n} if the data for the extremes AX_4 and

TABLE 7

ENTROPY OF SILANE DERIVATIVES (e. u.)

Compound	T = 298°K				T = 400°K				T = 500°K		T = 600°K	
	S° (lit.)	Ref.	S° (calcd.)	Error	S° (lit.)	Ref.	S° (calcd.)	Error	S° (lit.)	S° (calcd.)	S° (lit.)	S° (calcd.)
SiH ₄	48.89	15	48.89		52.09	15	52.09		55.04	55.04	57.76	57.76
SiH ₃ Cl	59.86	15	60.13	0.27	63.80	15	64.18	0.38	67.23	67.70	70.33	70.85
SiH ₂ Cl ₂	68.30	15	68.47	0.17	73.19	15	73.36	0.17	77.18	77.47	80.69	81.04
SiHCl ₃	75.00	15	74.85	0.15	80.49	15	80.58	0.09	85.09	85.26	89.05	89.26
SiCl ₄	79.07	15	79.07		85.65	15	85.65		90.91	90.91	95.33	95.33
MeSiCl ₃	83.90	15	83.54	0.36	91.52	15	91.28	0.24	97.88	97.63	103.44	103.17
Me ₂ SiCl ₂	86.02	1	85.99	0.03			94.88			102.33		109.00
Me ₃ SiCl	86.44	20	86.78	0.34	95.90	20	96.83	0.93	104.60	105.36	112.50	113.16
Me ₄ Si	85.79	1	85.79		96.99	15	96.99		106.62	106.62	115.55	115.55
Me ₃ SiH			79.34				88.54			96.50		103.87
Me ₂ SiH ₂			71.12				78.32			84.62		90.44
MeSiH ₃			61.13				66.33			70.95		75.22
MeSiHCl ₂			78.65				85.54			91.31		96.43
MeSiH ₂ Cl			71.28				77.33			82.53		87.22
Me ₂ SiHCl			80.15				88.19			95.06		101.31

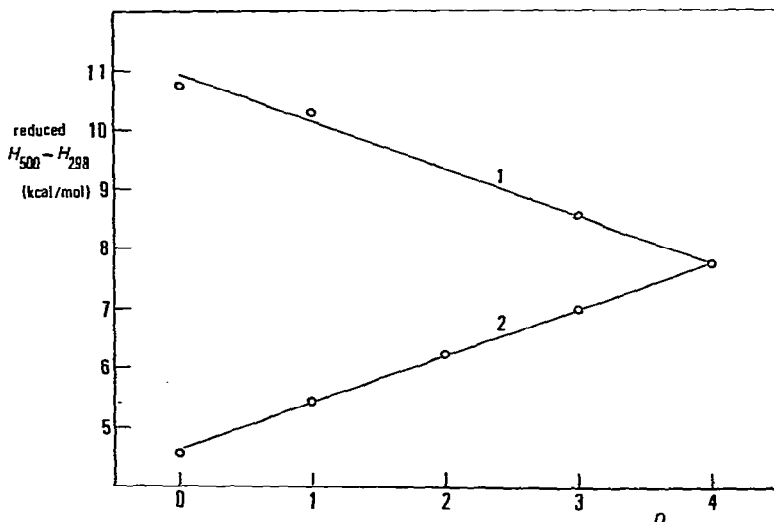


Fig. 4. Heat content reduced for molecular weight; curve 1: methylchlorosilanes ($Me_{4-n}SiCl_n$), curve 2: chlorosilanes (Cl_nSiH_{4-n}).

AY_4 are known, with errors up to 0.5 kcal at 25°. A much better approximation can be made by plotting $H^0(T_1) - H^0(T_2) + \frac{3}{2} R \cdot (T_1 - T_2) \cdot \ln M$ versus n ; M being the molecular weight. In Fig. 4 this is done for $T_1 = 500^\circ \text{K}$ and $T_2 = 298^\circ \text{K}$. The lines in the graph are straight to show incidental deviations. Deviation from linearity is caused by non-linear terms in the thermodynamic function which limit the accuracy of the method. From Table 6 it follows that the errors in heat content data thus obtained are sufficiently small for the data to be useful in thermodynamic calculations. It thus becomes possible to express the heat content of a compound in terms of group contributions (ϕ), which after summation have to be corrected for molecular weight:

$$(H^0(T_1) - H^0(T_2))(X_nAY_{4-n}) = n \cdot \phi(A-X)(T_1, T_2) + (4-n) \cdot \phi(A-Y)(T_1, T_2) - \frac{3}{2} R \cdot (T_1 - T_2) \cdot \ln M \quad (6)$$

The values for ϕ used in Table 6 have been chosen to fit the known experimental data.

3. ESTIMATION OF ENTROPY

Additivity relations have been applied successfully to entropy calculations¹⁰. A correction for symmetry has to be included to reach an accuracy of about 1 e.u. In the system under discussion, accuracy can be further improved if the same method

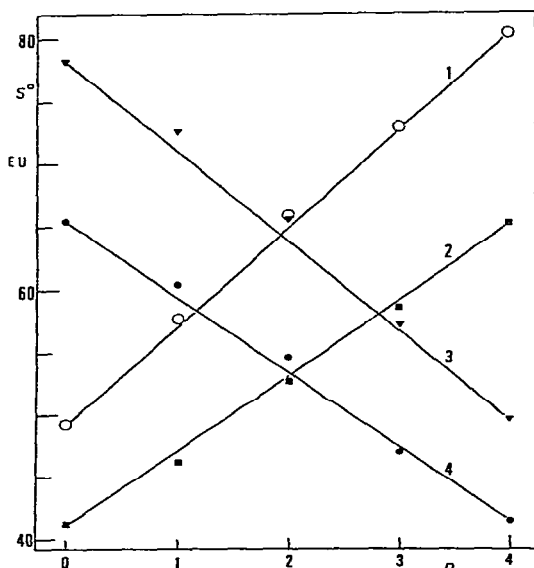


Fig. 5. Reduced entropy for chloromethanes (curves 1 and 2: $C_nH_{4-n}Cl_n$) and methyl derivatives of methane (curve 3 and 4: H_nCMe_{4-n}); curves 1 and 3: reduced for symmetry, curves 2 and 4: reduced for symmetry and molecular weight.

is applied which has been used to calculate the heat content. The entropy equation from statistical thermodynamics (see *e.g.* ref. 9) contains a molecular weight term ($\frac{3}{2} R \cdot \ln M$) and a symmetry correction term ($-R \cdot \ln \sigma$) amongst other terms. If the entropy value of compounds of the type X_nAY_{4-n} is reduced with respect to molecular

weight and symmetry, an almost linear relation is obtained:

$$S_T^0(X_nAY_{4-n}) = n \cdot \phi'(A-X)_T + (4-n) \cdot \phi'(A-Y)_T - R \cdot \ln \sigma + \frac{3}{2} R \cdot \ln M \quad (7)$$

The reduced entropy bond terms $\phi'(A-X)$ and $\phi'(A-Y)$ are additive, as is illustrated for some carbon compounds in Fig. 5, curves 2 and 4. For comparison, entropy reduced only for symmetry is plotted in curves 1 and 3. The dots are in both cases sufficiently represented by straight lines; the fit of the lower lines (2 and 4), however, is somewhat better. In Fig. 6 the entropy of some silanes is plotted in curves 2 and 5.

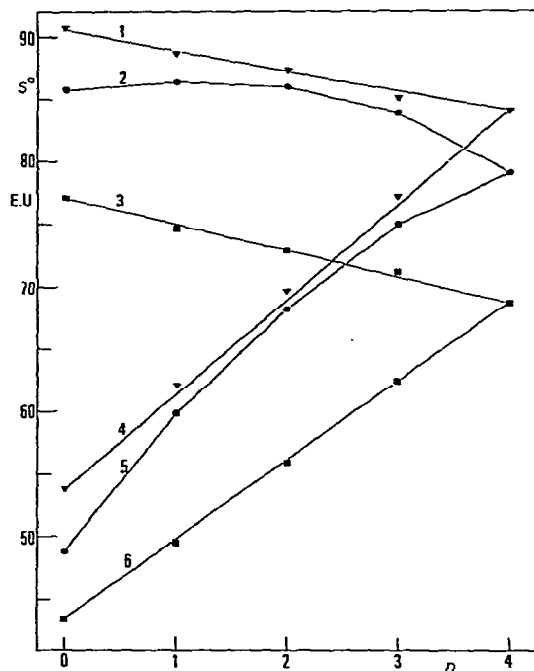


Fig. 6. Entropy of methylchlorosilanes (curves 1, 2, 3: $\text{Me}_{4-n}\text{SiCl}_n$) and chlorosilanes (curves 4, 5, 6: $\text{Cl}_n\text{SiH}_{4-n}$); curves 2 and 5: entropy, curves 1 and 4: entropy reduced for symmetry, curves 3 and 6: entropy reduced for symmetry and molecular weight.

The symmetry reduced entropy is given by the straight lines 1 and 4, while 3 and 6 represent entropy reduced for the molecular weight term as well as for symmetry. The spread of the points is smallest in the lines 3 and 6.

With this method the entropy of other silane derivatives has been calculated based on the values for SiH_4 , SiCl_4 and $\text{Si}(\text{CH}_3)_4$. The results are listed in Table 7. Where possible, comparison is made with data obtained by fundamental calculation. The average error is as small as 0.22 e.u. at 25°C, and 0.40 e.u. at 600°K.

Only one entropy value of an ethyl-containing silane is now needed to obtain data for all other ethyl-containing silanes.

4. APPLICATION TO REACTION HEATS

With the obtained thermochemical data, the heat effect of a direct synthesis of methylchlorosilanes may now be calculated. In Table 8 the experimental results

TABLE 8

REACTION HEAT OF THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES AT 270°

Run	Composition of the condensate (wt. %)						Reaction heat ^b	
	Me ₂ SiCl ₂	MeSiCl ₃	Me ₃ SiCl	MeSiHCl ₂	SiCl ₄	CH ₃ Cl ^a	Exp. ^c	Calcd.
1	62.8	17.4	2.6	6.9	2.0	8.2	-97.6	-82.9
2	41.8	38.0	0.0	13.0	0.0	7.2	-99.4	-84.9
3	29.1	34.0	0.0	31.0	0.0	5.9	-83.3	-76.7

^a Unconverted. ^b In kcal/atom Si. ^c From ref. 8.

of Habal and Klumpar⁸ for the heat of reaction at 270° are compared with values calculated from Tables 4 and 6. It can be concluded that the (negative) values in the literature, on which the estimates for the heats of formation of methylchlorosilanes are based are somewhat too small.

CONCLUSION

For the methyl- and chloro-substituted silanes, estimates are given for heats of formation, heat content, and entropy. The data are based on experimental values gathered from literature. The method of estimation of heat of formation introduces an influence term arising from the presence of different substituents. The agreement is better than with neglect of the inductive effects as is done in first-order bond additivity methods.

Heat content and entropy can also be estimated with higher accuracy than is possible with the existing methods. This is realized by reducing these quantities for molecular weight and, in the case of entropy, also for symmetry. The reduced bond terms have been shown to be additive with excellent agreement with experimental data.

With respect to the absolute value of the estimated heat of formation data some doubt remains. A systematic error affecting predicted reaction heats may be present. It might turn out that one or two of the additive bond terms need be some kcal more negative than those derived from the literature. This would not affect the influence terms. In spite of absence of corrections with respect to fugacities these influence terms give good agreement with experimental values for the free enthalpy difference in disproportionations.

Measurement of heats of formation from combustion and hydrolysis experiments is very complicated, because of the difficulties in the determination of the composition of the products. Measurement of the heat effects in synthesis of chlorosilanes, methylchlorosilanes, and ethylchlorosilanes might help to give the required accuracy.

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