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Bond Additivity Properties of Silicon Compounds

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A compilation and evaluation of combustion and heat of formation data and of entropy and heat capacity data for the ideal gas state at 298.17°K on silicon compounds has been made, and the thermodynamic bond additivity relations of some silicon–ligand bonds have been determined. These additivities may be used to estimate heat capacities and entropies of silicon compounds with an accuracy generally better than ±1 eu and to estimate silicon compound enthalpies of formation to an accuracy generally better than ±3 kcal/mole. It is noted that additivity relations hold surprisingly well for all silicon compounds with the exception of the alkylsilanes. This suggests that the data for the alkylsilanes are in error and that the current conclusion that the silicon–carbon bond energy appreciably decreases with increasing size of the alkyl ligand is also erroneous.

Introduction

It has been noted with particular regard to organic compounds that many molecular properties, including the thermodynamic properties, are additive functions of molecular constituency. Thus, empirical contributions (or additivities) of specific atoms, or bonds or groups of atoms composing a molecule, may be summed to provide estimates of certain molecular properties. A number of such additivity schemes have been developed.[1,2] Some of the applications emphasizing the desirability and potential value of these additivity schemes are: (1) additivity relations provide a means of tabulating vast quantities of data in a very concise and efficient manner; (2) gross errors in experimental data are revealed through comparisons of the experimental values with values estimated from additivity relations; and (3) additivity relations provide a mechanism for making reliable estimates of molecular properties in the absence of experimental data.

The use of bond additivity relations for the estimations of the entropy and heat of formation of ethyl alcohol at 298°K and in the ideal gas state at 1 atm is illustrated in Table I. Internal rotation symmetry of C_2H_5OH is $\sigma = 3$; symmetry correction $= -R \ln 3$; $S^\circ_{298} = 65.9$ eu. The experimental values are $\Delta H_f^\circ(C_2H_5OH) = -54.6$ kcal/mole; $S_f^\circ(C_2H_5OH) = 64.5$ eu.

TABLE I

Number and type of bonds	Additivities to ΔH_f°	Additivities to S_f°
5 (C–H)	5(−3.83 kcal/bond)	5(12.90)
1 (C–O)	−12.0 kcal/bond	−4.0
1 (O–H)	−27.0 kcal/bond	24.0
1 (C–C)	2.73 kcal/bond	−16.4
	$\Delta H_f^\circ = -55.4$ kcal/mole	$S^\circ_{298} = 68.1$ eu (uncor)

The bond additivities used above are those developed by Benson and Buss[1] and have been shown to be generally accurate to ±2 kcal/mole and ±1.0 eu/mole when applied to hydrocarbons and related compounds.

Compared to the extensive tabulations of thermodynamic data for organic compounds, relatively little information is available on silicon compounds. Data are scattered in the literature and have not been collected or systematically analyzed. In addition, all heat of formation data prior to 1962 are in error as a result of incorrect values assumed for the heat of formation of amorphous silica.[3]

The purpose of this paper has been to develop a much needed additivity scheme which may be used to estimate heats of formation, entropies, and heat capacities of silicon compounds in the ideal gas state at 298°K. To that end we have collected, correlated, and evaluated, in the manner of Benson and Buss,[1] the thermochemical data presently available on silicon compounds.

Discussion

Heat of formation, entropy, and heat capacity data for silicon compounds in the ideal gas state at 25° have been collected and analyzed. The data were found to be sufficiently accurate to develop a bond additivity scheme for the estimation of all three thermodynamic properties. The bond additivity values which have been deduced represent "best fits" to the data reported in the literature. These values are listed in Table II. It must be emphasized that bond additivity relations, by definition, neglect interactions between neighboring bonds (*i.e.*, ligands bonded to the same atom do not interact) and therefore are not capable of fitting all of the data exactly even if the data were free from errors. In the present instance, it is quite likely that the additivity values are generally more reliable than the thermodynamic data from which they have been derived.

Entropies and Heat Capacities.—The most reliable entropies and heat capacities of gaseous compounds are those obtained from spectroscopic and structural data employing the standard relations of statistical thermodynamics. All of the "observed" entropies

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[1] For general reviews of additivity relations as applied to thermodynamic properties see S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958), and ref 2.

[2] G. J. Janz, *Quart. Rev.* (London), **9**, 229 (1955).

[3] U. S. National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952, gives $\Delta H_f^\circ(SiO_2\ (aq)) = -201.5$ kcal/mole. Since that time, successively more negative values have been obtained, with the most recent determination [S. S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, **67**, 815 (1963)] giving $\Delta H_f^\circ(SiO_2(am)) = -215.9$ kcal/mole.

TABLE II

BOND ADDITIVITY RELATIONS FOR TETRAVALENT SILICON

Bonds	$\Delta H_f°$, kcal	$C_p°$, eu	$S°$, eu
Si–C	−6.0	3.00	13.84
Si–C_{vinyl}[a]	−17.9		
Si–C_{phenyl}[a]	−5.75		
Si–H	1.75	2.25	13.70
Si–Si	6.6	*d*	*d*
Si–Cl	−38.0	5.41	21.03
Si–Br	−24.5	5.80	23.80
Si–F	−96.0	4.89	18.30
Si–I	−7.0	6.00	26.50
Si–D		2.92	14.30
Si–O	−52.0	9.60	−1.24
Si–N[a,b,c,e]	−27.9		
C–H[c]	−3.83	1.74	12.90
C–C[c]	2.73	1.98	−16.40
C–O[c]	−12.0	2.70	−4.0
O–H[c]	−27.0	2.70	24.0
C_{vinyl}–H[c]	3.2	13.8	2.6
C_{phenyl}–H[c]	3.25	11.7	3.0

[a] The ligancies of C_{vinyl}, C_{phenyl}, and N are 4, 6, and 3, respectively. [b] Calculated from the heat of formation difference: $\Delta H_f°[(CH_3)_3SiCl(l)] - \Delta H_f°[(CH_3)_3SiN(C_2H_5)_2(l)] = 4.1 \pm 1.3$ kcal/mole. [c] See ref 1. [d] Use atom additivities of ref 1. [e] A. P. Claydon and C. T. Mortimer, *J. Chem. Soc.*, 3212 (1962).

TABLE III

ENTROPY AND HEAT CAPACITY DATA FOR SILICON COMPOUNDS (EU)

Compd	$S°^a$ (obsd)	$S°^b$ (calcd)	Δ(O–C)	$C_p°^a$ (obsd)	$C_p°^b$ (calcd)	Δ(O–C)	Ref
SiH_4	48.88	49.86	−0.98	10.22	9.00	1.22	*c*
H_3SiF	59.09	57.22	1.87	11.33	11.64	−0.31	*d*
H_3SiCl	62.98	59.95	3.03	12.02	12.16	−0.14	*d*
H_3SiBr	62.76	62.72	0.04	12.69	12.55	0.14	*e*
H_3SiI	64.54	65.42	−0.88	12.86	12.75	0.11	*d*
D_3SiF	59.89	59.02	0.87	13.15	13.65	−0.50	*d*
D_3SiCl	64.97	61.75	3.22	14.02	14.17	−0.15	*d*
D_3SiI	66.95	67.22	−0.27	15.00	14.76	0.24	*d*
H_2SiCl_2	67.83	68.07	−0.24	14.45	15.32	−0.87	*f*
H_2SiBr_2	73.92	73.61	0.31	15.68	16.10	−0.42	*c*
SiF_4	67.44	68.24	−0.80	17.56	17.56	0.00	*g*
$SiCl_4$	79.10	79.10	0.00	21.63	21.63	0.00	*g*
$SiBr_4$	90.22	90.22	0.00	23.21	23.21	0.00	*h*
$ClSiBr_3$	90.14	90.25	−0.11	22.78	22.81	−0.03	*h*
Cl_2SiBr_2	89.48	88.27	1.21	22.39	22.42	−0.03	*h*
Cl_3SiBr	83.52	84.71	−1.19	21.72	22.03	−0.31	*h*
$ISiBr_3$	96.58	95.72	0.86	23.39	24.40	−1.01	*i*
$Si(CH_3)_4$	85.79	85.79	0.00	33.50	32.88	0.62	*j*
$(CH_3)_3SiCl$	86.44	84.96	1.48	26.47	30.07	−3.60	*k*
$(CH_3)_2SiCl_2$	86.02	86.05	−0.03	26.17	27.26	−1.09	*l*
CH_3SiF	75.07	75.51	−0.44	22.73	22.89	−0.16	*m*
$[(CH_3)_3Si]_2O$	127.85	127.85	0.00	57.00	57.00	0.00	*n*

[a] Calculated from spectroscopic data. [b] Calculated from bond additivities by the procedure illustrated in the Introduction, that is, by summing the additivity values of all of the bonds in the molecule with suitable symmetry corrections in the case of entropy. [c] A. P. Altshuller, *J. Chem. Phys.*, **23**, 761 (1955). [d] G. Nagarjan, *Bull. Soc. Chim. Belges*, **71**, 237 (1962). [e] D. W. Mayo, H. E. Opitz, and J. S. Peake, *J. Chem. Phys.*, **23**, 1344 (1955). [f] J. A. Hawkins and M. K. Wilson, *ibid.*, **21**, 360 (1953). [g] F. L. Voelz, A. G. Meister, and F. F. Cleveland, *ibid.*, **19**, 1084 (1951). [h] B. Schneider and J. Pliva, *Chem. Listy*, **48**, 336 (1954). [i] G. Nagarajan, *Current Sci.* (India), **30**, 377 (1961). [j] K. Shimizu and H. Murato, *J. Mol. Spectry.*, **5**, 44 (1960). [k] K. Shimizu and H. Murato, *Bull. Chem. Soc. Japan*, **32**, 1158 (1959). [l] K. Shimizu and H. Murato, *J. Mol. Spectry.*, **4**, 214 (1960). [m] R. L. Collins and J. R. Nielson, *J. Chem. Phys.*, **23**, 351 (1955). [n] D. W. Scott, S. S. Todd, J. F. Messerly, R. T. Moore, A. Osborne, W. T. Berg, and J. P. McCullough, *J. Phys. Chem.*, **65**, 1320 (1961).

TABLE IV

EXAMPLE DISCREPANCIES IN COMBUSTION DATA

Compd	ΔH_c, kcal	ΔH_c/monomer, kcal[a]	ref
$[(C_6H_5)_2SiO]_3$	4470	1490	*b*
	4812	1603	*c, d*
$[(C_6H_5)_2SiO]_4$	6380	1598	*b*
$[(CH_3)_2SiO]_3$	1397	466	*b*
	1407	469	*d*
	1435	475	*c*
$[(CH_3)_2SiO]_4$	1930	483	*b*
$[(CH_3)_2SiO]_5$	2394	479	*b*
$[(CH_3)_2SiO]_6$	2872	479	*b*
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	1727		*c*
	1751		*d, e*

[a] It is interesting to note that the heats of combustion per monomer unit of the methyl- and phenylsilicones are roughly constant. This can be rationalized on the basis of additivity relations as follows. Additivity relations imply that molecular property changes in disproportionation reactions are due only to symmetry changes. The polymerization reactions of silicic acids are reactions in which n(Si–OH) and n(SiO–H) bonds are broken and n(H–OH) and n(SiO–Si) bonds are formed. Written in terms of the bonds, the polymerization reactions are disproportionation reactions and therefore, assuming bond additivities, should have zero enthalpies: $2n(\text{SiO–H}) \rightarrow n(\text{H–O–H}) + n(\text{Si–O–Si})$ $\Delta H_R° = 0$. This implies that the heats of combustion of the unstable methyl- and phenylsilicic acids may be assumed to be the same as the heats of combustion of the monomer units of the resulting silicon polymers and that the instability of the silicic acids is a result of the positive entropy of polymerization. [b] K. B. Goldblum and L. S. Moody, *Ind. Eng. Chem.*, **47**, 847 (1955). [c] T. Tanaka, *J. Chem. Phys.*, **19**, 1330 (1951). [d] T. Tanaka, *ibid.*, **22**, 957 (1954). [e] T. Tanaka, *Bull. Chem. Soc. Japan*, **28**, 15 (1955).

and heat capacities (columns 2 and 5 of Table III) have been estimated in this way with the exception of that for silicon tetramethyl which is an experimental third-law value. The entropies and heat capacities "calculated" from the additivity values are shown in columns 3 and 6 of Table III.

Differences between "observed" and "calculated" values, Δ(O–C), are shown in columns 4 and 7. In general, the heat capacities and entropies obey bond additivity relations very well. The few exceptions are the normal and deuterated monochlorosilanes. Since the main contribution to the molecular partition function and therefore to the entropy comes from the molecular weight, comparison of the entropies of the monochlorosilanes with the entropies of the corresponding bromo- and/or the iodosilanes suggests that the literature values for the former are 3 eu units too high. It is impossible for monochlorosilane to have an entropy larger than monobromosilane.

Since the entropies and heat capacities tabulated in the literature for all of the methyl-containing compounds except silicon tetramethyl and hexamethyldisiloxane exclude contributions from the methyl torsional modes, it was necessary to add in estimated values for the contribution from the hindered rotations of the methyl groups to obtain the values listed in Table III. The corrections added were $0.5R$/methyl group to the heat capacity (*i.e.*, the free-rotor contribution) and 2.93 eu/methyl group to the entropies. The latter value was obtained from a calculation of the partition function for free rotation of the methyl

TABLE V

HEAT OF FORMATION DATA FOR SILICON COMPOUNDS (KCAL)

Compd	$-\Delta H_c$	ΔH_{vap}	$-\Delta H_f^{\circ a}$ (gas)	$-\Delta H_f^{\circ b}$ (calcd)	Δ(O–C)	Ref
$Si(OCH_3)_4$	700	8.3	297	302	5	*g*
	694		303		−1	*h*
$Si(OC_2H_5)_4$	1320	9.2	322	322	0	*g*
$Si(O\text{-}i\text{-}C_3H_7)_4$	1944	9.6	346	342	−4	*g*
$Si_2O(OCH_3)_6$	1056	14	540	557	17	*h*
$Si_3O_2(OCH_3)_8$	1399	18	803	802	−1	*i*
$(CH_3)_2Si(OC_2H_5)_2$	1119	8.1	199	196	−3	*i–k*
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	1751	10	215	216	1	*i–k*
$(CH_3)_2(SiOH)_2O$	940	15	330	330	0	*l*
$(CH_3)_2Si(OH)_2$	475	10	192	194	2	*i–l*
$(C_2H_5)_2Si(OH)_2$	782	12	208	202	−6	*i–k*
$(C_6H_5)_2Si(OH)_2$	1601	17	136	136	0	*i–l*
$Si_2O(CH_3)_6$	1344	8.3	258	212	−46[c]	*l*
	1401		201		11[d]	*h*
	1399		203		9[d]	*m*
$Si_3O_2(CH_3)_8$	1860	10	350	348	−2	*h*
	1861		351		−3	*m*
$Si_4O_3(CH_3)_{10}$	2411	12	405	487	82[c]	*l*
	2289		527		−40[c]	*h*
	2328		488		−1	*m*
$Si_5O_4(CH_3)_{12}$	2756	14	667	651	−16[d]	*h*
$Si_2(OCH_3)_6$	1150	12	448	447	−1	*h*
$HSiCl_3$	118	6.4	114	112	−2	*g*
$(CH_3)_2SiCl_2$[e]		8	106	111	5	*n*
$(C_6H_5)_2SiCl_2$[f]		14	50	55	5	*n*
$SiCl_4$		7	161	152	−9[d]	*o*
$SiCl_4$		7	152		0	*n*
SiF_4			384	384	0	*p*
$SiBr_4$		9	98	98	0	*t*
SiI_4		15	28	28	0	*t*
SiH_4 By decomposition to the elements			−7	−7	0	*q*
Si_2H_6			−17	−17	0	*q*
Si_3H_8			−26	−27	−1	*r*
$Si(CH_3)_4$	920	6	76	73	−3	*s*
$(CH_3)_3SiH$	766	6	67	51	−16[d]	*s*
$(CH_3)_2SiH_2$	624	5	48	32	−16[d]	*s*
$C_2H_5SiH_3$	644	5	28	18	−10[c]	*s*
$(C_2H_5)_2SiH_2$	915	7	43	41	−2	*s*
$(C_2H_5)_3SiH$	1272	8	46	66	20[c]	*s*
$Si(C_2H_5)_4$	1597	10	44	90	46[c]	*s*
$C_2H_3SiH_3$	603	5	1	1	0	*s*
$i\text{-}C_4H_9SiH_3$	964	7	31	28	−3	*s*
$n\text{-}C_4H_9SiH_3$	962	8	31	28	−2	*s*
$(CH_3)_2Si(i\text{-}C_3H_7)_2$	1594	10	47	90	43[c]	*s*

[a] Calculated from combustion data. [b] Calculated from the summation of bond additivity values as illustrated in the Introduction. [c] Data incompatible with bond additives. [d] Data bordering on limits of experimental error. [e] Based on a heat of formation of $(CH_3)_2Si(OH)_2$ of −196 kcal/mole and the observed heat of hydrolysis of $(CH_3)_2SiCl_2$. [f] Based on a heat of formation of $(C_6H_5)_2Si(OH)_2$ of −136 kcal/mole and the observed heat of hydrolysis of $(C_6H_5)_2SiCl_2$. [g] H. Reuther, *Chem. Tech.* (Berlin), **2,** 331 (1950). [h] T. Tanaka, *J. Chem. Phys.*, **22,** 1268 (1954). [i] T. Tanaka, *ibid.*, **19,** 1330 (1951). [j] T. Tanaka, *ibid.*, **22,** 957 (1954). [k] T. Tanaka, *Bull. Chem. Soc. Japan*, **28,** 15 (1955). [l] K. B. Goldblum and L. S. Moody, *Ind. Eng. Chem.*, **47,** 847 (1955). [m] T. Tanaka, *Technol. Rept. Osaka Univ.*, **8,** 437 (1958). [n] M. A. Ring, H. E. O'Neal, A. H. Kadhim, and F. Jappe, *J. Organometal. Chem.* (Amsterdam), in press. [o] A. E. Beezer and C. T. Mortimer, *J. Chem. Soc.*, 2727 (1964). [p] S. S. Wise, U. S. Atomic Energy Commission Report ANL 6472, 1962, p 71. [q] S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65,** 779 (1961). [r] S. R. Gunn and L. G. Green, *ibid.*, **68,** 946 (1964). [s] S. Tannenbaum, S. Kaye, and G. F. Lewenz, *J. Am. Chem. Soc.*, **75,** 3753 (1953). [t] See ref 3.

group, Q_f = 3.71, and from the tabulated entropy corrections for a hindered rotor with a barrier potential of 1400 cal/mole.[4] This is the barrier to methyl rotation in tetramethylsilane.[5]

The most probable explanation for errors in the value of the entropy or the heat capacity obtained from spectroscopic data lies in incorrect vibrational assignments.

Enthalpy.—Additivity relations are not so readily applied to estimates of enthalpies of formation. If extensive and accurate experimental data are available, as in the case of the hydrocarbons, *group* additivity relations can be derived which are capable of estimating heats of formation with accuracies exceeding those of the data.[1] In cases where data are accurate but not extensive, *bond* additivity relations must

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(4) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 446.

(5) K. Shimizu and H. Murato, *J. Mol. Spectry.*, **5**, 44 (1960).

suffice with expected accuracies of ±2 kcal/mole. With silicon compounds, data are neither extensive nor accurate. As an illustration of the accuracies in available combustion data on silicon compounds, the combustion results for various silicic acid polymers obtained in different laboratories or at different times in the same laboratory are shown in Table IV. One can see that, although experimental precisions for these data were often of the order of 2–5 kcal/mole, absolute variations of 20–40 kcal/mole in identical compounds are not uncommon. Indeed, for $[(C_6H_5)_2SiO]_3$, the reported values differ by 342 kcal/mole. The reasons for such large errors are many. Incomplete combustion is common in silicon compounds, and accurate corrections for uncombusted silicon and carbon and for formation of silicon carbide are difficult to make. Often polymeric residues are formed whose compositions are uncertain. Sample purity, always a most important criterion in combustion experiments, is also often a source of appreciable error since silicon compounds are not easily obtained in highly pure form.

One might hope that most combustion data will be accurate to ±5 kcal/mole; however, larger errors are not to be considered impossible or even unusual, especially in the high molecular weight compounds.

Table V gives combustion and heat of formation data for various silicon compounds. Heats of formation in the condensed phase were calculated from the combustion data using $\Delta H_f^\circ(H_2O(l)) = -68.32$ kcal/mole, $\Delta H_f^\circ(CO_2(g)) = -94.05$ kcal/mole, and $\Delta H_f^\circ(SiO_2(am)) = -215.9$ kcal/mole. Heats of formation in the vapor phase were obtained using heat of vaporization data when available or estimated using a Trouton's constant of $\Delta S_{vap} = 22$ eu. Errors in the heats of vaporization should not exceed 2 kcal/mole.

The following compounds were selected as standards for the indicated bond additivities: $Si(OC_2H_5)_4$ for Si–O; SiH_4 for Si–H; $(C_6H_5)_2Si(OH)_2$ for $Si–C_{phenyl}$; and Si_2H_6 for Si–Si. The most reasonable values for Si–Cl and for Si–C were chosen on the basis of all of the available data.

In column 6 of Table V are tabulated the differences between experimentally observed heats of formation (column 4) and calculated heats of formation (column 5) using our bond additivities. In general, the agreement is quite acceptable. With the exception of the alkylsilanes Δ(O–C), values seldom exceed ±4 kcal/mole and have an average value of about ±3 kcal/mole. In almost all cases the differences are well within experimental error. In the two cases where the largest differences are observed ($Si_2O(CH_3)_6$ and $Si_4O_3(CH_3)_{10}$) there are additional data in the table which give better fits. This again illustrates the large experimental errors which often attend silicon compound combustion experiments.

The most glaring differences between observed and calculated heats of formation are found with the alkylsilanes (Table V). In this series four compounds fit the bond additivity assumption rather well, but bond additivities clearly suggest gross errors in the combustion data for triethylsilane, tetraethylsilane, and dimethyldi-*n*-propylsilane. Although the Δ(O–C) values for di- and trimethylsilane and ethylsilane are sizable, they are not wholly outside the bounds of reasonable experimental error. It is curious to note that these data have been the basis for the assertion that the silicon–carbon bond energies decrease appreciably with increasing size of the alkyl ligand. The quoted values range from $E(Si–CH_3)$ of 74 kcal to $E(Si–C_4H_9)$ of 56 kcal.[6] It would be difficult to rationalize such Si–C bond energy variations on any kind of reasonable bonding theory. Indeed, if such variations were real, one could hardly expect to find such small Δ(O–C) values for diethylsilanediol and diisopropyldiethoxysilane. Also, if such large energy differences were real, one would expect to observe a systematic increase in Si–C bond distances with increasing size of the alkyl ligand. Within experimental error, no such variations exist.[7] It should be noted that combustion experiments on silane placed the heat of formation of silane between −7 and −14 kcal/mole. However, decomposition studies have definitely shown that silane is unstable relative to its elements and gives a heat of formation of about +7 kcal/mole. It may be that accurate combustion results on silanes or other unoxygenated silicon compounds are particularly difficult to obtain and that systematic errors tending toward greater predicted stabilities are inherent in such data. Additional data on these compounds are needed. Fluorine combustion experiments would be particularly valuable.

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[6] S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).

[7] E. A. V. Ebsworth, "Volatile Silicon Compounds," The Macmillan Co., New York, N. Y., 1963.