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# Thermochemistry of Silicon-containing Compounds

Part 1.-Silicon-Halogen Compounds, an Evaluation

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Literature data on the heats of formation of silicon-halogen compounds have been collected and reviewed. The coverage includes all tetravalent monosilicon compounds containing Si-H-X, where X is a single halogen, as well as the subhalides  $SiX_n$ , where n = 1, 2 or 3. The data are critically evaluated from the standpoints of bond additivity and general chemical reactivity of the species involved as well as by detailed consideration of individual studies. Earlier compilations or reviews are discussed. A set of recommended values (with uncertainties) is proposed. For the divalent species,  $SiX_2$ , a self-consistent set of lone-pair stabilisation energies is obtained.

There is considerable current interest in the kinetics and mechanisms of reactions involving silicon-containing compounds. As well as a general review<sup>1</sup> a number of particular aspects have been surveyed very recently. These have included hydrogen-abstraction reactions,<sup>2</sup> molecular rearrangements<sup>3</sup> and reactions of silylene intermediates<sup>4</sup> and of the unsaturated silene (or sila-olefin) species.<sup>5, 6</sup> We have contributed to this field by measuring bond dissociation energies, particularly of Si—H bonds.<sup>7</sup> In order to gain a more fundamental understanding in this area it is highly desirable to have reliable knowledge of the thermodynamic properties of silicon-containing compounds, in particular their heats of formation.

However, many desirable data in this area are either missing or of an unreliable nature. This has been pointed out most recently by Bell et al.,<sup>8</sup> who attempted to remedy the situation by semi-empirical theoretical calculations. Unfortunately these workers did not, in all cases, base their calculations on the most recently published data. One of the principal data sources for heats and formation for silicon compounds has been the CATCH tables published by Pedley and Iseard.<sup>9</sup> This compilation, with its attempt at correlations of all data, has been extremely useful but has become increasingly out of date. An updated version for organosilicon compounds has been published by Pedley and Rylance,<sup>10</sup> but this does not include the purely inorganic compounds. The JANAF tables,  $1^{1a-d}$  until recently, were patchy in their coverage, as is the NBS compilation,<sup>12</sup> which suffers from the added disadvantage of lack of source references. It is for these reasons that we felt it was necessary to provide some critical evaluation of the existing data in this area. During the course of preparation of this work, the 1982 supplement of the JANAF tables was published.<sup>11e</sup> Although this considerably improves the coverage of data on silicon compounds, there are nevertheless important differences between it and our assessment. Thus this present evaluation does not lose its importance. In this paper we consider the silicon-halogen compounds. In the first part the stable tetravalent compounds are reviewed while in the second part the subhalides are covered. In later papers we plan to consider organosilicon molecules, although a recent group-additivity scheme<sup>13</sup> for these compounds is of considerable value.

# COMPOUNDS OF TETRAVALENT SILICON

## GENERAL CONSIDERATIONS AND ADDITIVITY RULES

It might be argued that a review of experimental values should not be contaminated by numbers deduced from, or estimated by use of, empirical laws, such as additivity schemes. However, we reject this view on the grounds that such laws may be shown to work quite well for series of substituted silanes, and therefore offer a useful criterion for assessment of data.

The law of bond additivity<sup>14</sup> states that, for a reaction such as

$$2L_2SiXY \rightleftharpoons L_2SiX_2 + L_2SiY_2$$

where L represents a fixed ligand and X and Y exchangeable ones, any thermodynamic change will be zero. The extent to which non-zero thermodynamic changes are observed represents a departure from this law. Such non-zero changes may be identified with combinations of bond-interaction terms in schemes such as those devised by Allen<sup>15</sup> and earlier by Zahn.<sup>16</sup> If a reaction obeys the law of bond additivity then the equilibrium constant will be given solely by symmetry numbers (so-called statistical redistribution): in the case of the above, for example,

$$K \text{ (bond additivity)} = \frac{[L_2 \text{Si}X_2][L_2 \text{Si}Y_2]}{[L_2 \text{Si}XY]^2} = \frac{1}{4}.$$

redistribution reaction	T/°C	K (obs.)	ref.	<i>K</i> (random) <sup>a</sup>	$\Delta G^{\circ}$ (intrinsic) <sup>b</sup> /kcal mol <sup>-1</sup>
$2Me_3SiH \rightleftharpoons Me_4Si + Me_2SiH_2$	124	0.43	23	0.375	-0.11
$2Me_{2}SiH_{2} \rightleftharpoons Me_{3}SiH + MeSiH_{3}$	124.5	0.66	23	0.444	-0.31
$2 \text{MeSiH}_2 \text{Cl} \rightleftharpoons \text{MeSiHCl}_2 + \text{MeSiH}_3$	100	0.476	25	0.333	-0.26
$2MeSiHCl_2 \rightleftharpoons MeSiCl_3 + MeSiH_2Cl$	100	0.041	25	0.333	+1.55
$2Me_2SiHCl \rightleftharpoons Me_2SiCl_2 + Me_2SiH_2$	100	0.098	25	0.25	+0.69
$2Me_3SiCl \rightleftharpoons Me_4Si + Me_2SiCl_2$	350	0.0135	26	0.375	+4.12
$2Me_2SiCl_2 \rightleftharpoons Me_3SiCl + MeSiCl_3$	350	0.0251	26	0.444	+3.56

 Table 1. Equilibrium constants and free-energy changes for some catalysed redistribution reactions

<sup>a</sup> K (random) may be identified with K (bond additivity), see text. <sup>b</sup> For definition, see text.

A number of equilibrium studies (with equilibrium brought about by use of suitable catalysts) have been reported by Moedritzer.<sup>17</sup> However, the departures are not large in energy terms. Some examples involving Me for H, Cl and H and Cl for Me redistribution are shown in table 1.\* Since the free-energy change associated with departure from statistical redistribution is not the true Gibbs free-energy change, we propose the term intrinsic free-energy change.<sup>18, 19</sup> Entropies (again intrinsic) obey bond additivity, if anything better than enthalpies of formation, and therefore it is reasonable to suppose that  $\Delta S^{\circ}(int) \approx 0$  for these reactions and that the intrinsic free-energy changes to a close approximation. Thus the

\* The energy units used in this paper are kcal  $mol^{-1}$  (1 cal = 4.184 J). This is because the bulk of data discussed are quoted thus.

conclusion from table 1 is that redistribution enthalpy changes are small in the cases reported and that bond additivity is quite a good approximation. This conclusion is supported by quite a few other cases listed by Moedritzer, although there are some significant departures [involving the substituent groups N(CH<sub>3</sub>)<sub>2</sub> and OCH<sub>3</sub>]. One particular case<sup>20</sup> for which experiments have been carried out but for which equilibrium constants have not been calculated is the Et for F redistribution resulting from reaction of  $SiF_4$  with  $SiEt_4$ . If it is assumed that the quoted product distributions represent close to final equilibrium, enthalpy changes derived for the redistribution reactions involved are again found to be small ( $< 1 \text{ kcal mol}^{-1}$ ). Even allowing for some uncertainty, this suggests that organofluorosilanes obey bond additivity quite well. This is an important result because the Si-F bond, being potentially the most polar bond formed by silicon, should give rise to the greatest electrostatic bond-bond interactions and therefore the greatest departures from additivity. It is certainly true that the fluoromethanes exhibit much greater departures from bond additivity than do the chloromethanes.<sup>21</sup> Purely halogen exchange processes are nearly statistical and thus conform to bond additivity very well.22

In terms of a criterion of assessment of consistency, therefore, bond additivity can be very useful. Small percentage errors in the determination of equilibrium constants lead to only small errors in  $\Delta H^{\circ}$  (usually *ca*. tenths of kcal mol<sup>-1</sup>) whereas small percentage errors in enthalpies of combustion, because these are large, can lead to errors in  $\Delta H_{\rm f}^{\circ}$  values which are large (*ca*. several kcal mol<sup>-1</sup>). Thus one may justify the use of this kind of consistency argument in assessment of combustion-derived (and other calorimetric) data. A similar approach, with allowance for small bond interaction terms, has been usefully exploited for boron compounds.<sup>27</sup>

#### EXPERIMENTAL DATA ON THE HALOGENOSILANES

### FLUOROSILANES

Tetrafluorosilane. The most recently measured value for  $\Delta H_{\rm f}^{\circ}({\rm SiF_4})^*$  is  $-386.0 \pm 0.2$  kcal mol<sup>-1</sup> by Wise *et al.*<sup>28</sup> using direct fluorine bomb combustion calorimetry. There appears no reason to doubt the reliability of this value and it has been adopted by both JANAF<sup>11 a, d</sup> and CATCH<sup>9</sup> as well as CODATA.<sup>29</sup>

Partially fluorinated silanes. Very little work has been reported on the partially fluorinated silanes, and early values listed by  $CATCH^9$  and the first JANAF tables<sup>11a</sup> are little more than guesses. Recently, however, values have been obtained by Farber and Srivastava<sup>30</sup> by mass-spectrometric study of the high-temperature hydrogenolysis equilibria:

$$SiF_4 + H_2 \rightleftharpoons SiF_3H + HF$$
$$SiF_3H + H_2 \rightleftharpoons SiF_2H_2 + HF$$
$$SiF_2H_2 + H_2 \rightleftharpoons SiFH_3 + HF.$$

Using a third-law approach  $\Delta H_f^\circ$  values were obtained for SiF<sub>3</sub>H, SiF<sub>2</sub>H<sub>2</sub> and SiF<sub>3</sub>H. These are listed in table 2 along with the old estimates and new JANAF estimates based on linear interpolation (bond additivity) between SiH<sub>4</sub> and SiF<sub>4</sub>. SiH<sub>4</sub> is an anchor point for the comparisons shown in table 2, and the value  $\Delta H_f^\circ(SiH_4) = +8.2 \pm 0.5$  kcal mol<sup>-1</sup> listed by JANAF,<sup>11d</sup> essentially the same as in CATCH,<sup>9</sup> would appear to be reliable.

In trying to assess the data for the partially fluorinated silanes we calculate that the Farber and Srivastava values give F for H disproportionation enthalpies of  $+14.9 \text{ kcal mol}^{-1} (\text{SiH}_3\text{F}), -8.0 \text{ kcal mol}^{-1} (\text{SiH}_2\text{F}_2) \text{ and } +7.8 \text{ kcal mol}^{-1} (\text{SiHF}_3).$ 

\* Unless otherwise stated, the notation  $\Delta H_t^o$  (compound) will be taken to refer to the gaseous state at 298.15 K throughout this paper.

	$\Delta H_{\rm f}^{\rm o}({\rm g}, 298 \ {\rm K})/{\rm kcal \ mol^{-1}}$			
compound	old values <sup>9, 11 a</sup>	Farber and Srivastava <sup>30</sup>	bond additivity (JANAF <sup>11d</sup> )	
SiH <sub>4</sub> <sup>a</sup>	+8.2	+8.2	+ 8.2	
SiH <sub>3</sub> F	$-105 \pm 5$	-99.4 + 2.0	90	
SiH <sub>2</sub> F <sub>2</sub>	$-194 \pm 10$	$-192.2\pm2.0$	- 189	
SiHF <sub>3</sub>	$-283\pm5$	$-293.0\pm2.0$	-287	
SiF <sub>4</sub> <sup>b</sup>	-386.0	$-386.0^{-1}$	-386.0	

Table 2. Entha	lpies of	formation	for th	e fluorinated	silanes
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<sup>*a*</sup> For reference purposes;  $\Delta H_{f}^{o}$  from ref. (9) and (11*d*). <sup>*b*</sup> For reference purposes;  $\Delta H_{f}^{o}$  from ref. (28) [also ref. (9) and (11*d*)].

In the light of the previous discussion these values appear numerically too high, and the alternation in sign seems particularly unlikely in view of the figures (and trend) for the analagous fluoromethanes,<sup>21</sup> viz. -12.3 kcal mol<sup>-1</sup> (CH<sub>3</sub>F), -6.8 kcal mol<sup>-1</sup> (CH<sub>2</sub>F<sub>2</sub>) and +1.0 kcal mol<sup>-1</sup> (CHF<sub>3</sub>). Thus we conclude that there is some unassessed source of error in the Farber and Srivastava data and that we must make do with the JANAF,<sup>11d</sup> *i.e.* bond additivity, values at the present time. It must, however, be recognised that the fluorosilane series are probably the most likely of the halogenosilanes to show deviations from bond additivity. In this case the deviations in  $\Delta H_{\rm f}^{\circ}$ may actually lie in the sense of less negative values (less exothermic compounds) since it is known that on long standing the partially fluorinated silanes tend to disproportionate and form SiH<sub>4</sub> and SiF<sub>4</sub>.<sup>31</sup> Our assessed error limits (table 5) allow for this possibility.

# CHLOROSILANES

*Tetrachlorosilane*. The experimental values for  $\Delta H_f^{\circ}(SiCl_4)$  are discussed in detail in JANAF.<sup>11 a, b</sup> The 1974 Supplement<sup>11 b</sup> adopts the value of  $-158.4\pm0.3$  kcal mol<sup>-1</sup> obtained by Gross et al.<sup>32</sup> by direct chlorination of silicon in a bomb calorimeter. These workers and the JANAF tables argue that this study is more reliable than several earlier investigations based on calorimetric studies of solution and hydrolysis reactions, largely because of uncertainties in the final state. To try to avoid these difficulties Schäfer and Heine<sup>33</sup> measured the heat of solution of SiCl<sub>4</sub> in aqueous HF containing silver fluoride. They obtained a value for  $\Delta H_{f}^{o}(SiCl_{4})$  of  $-156.7\pm0.4$  kcal mol<sup>-1</sup> (corrected by JANAF<sup>11a,b</sup> to  $-157.1\pm0.4$  kcal mol<sup>-1</sup>). However, because there may be uncertainties<sup>32</sup> associated with  $\Delta H_f^{\circ}(AgCl, c, 298 \text{ K})$ this value was not preferred.<sup>11b</sup> The reason for the discrepancy, which, although small, is outside the combined error limits, is however not proved and suggests that  $\Delta H_{f}^{o}(SiCl_{4})$  may not be so precisely known as is claimed.<sup>11b,32</sup> A recent value of  $-157.7 \pm 1.6$  kcal mol<sup>-1</sup> derived from high-temperature equilibration studies of SiCl<sub>4</sub>, SiHCl<sub>3</sub>, H<sub>2</sub> and HCl over solid silicon by Wolf and Teichmann<sup>34</sup> could agree with either earlier value and does not resolve the discrepancy. The CATCH tables also adopt a value of  $-158.4\pm0.2$  kcal mol<sup>-1</sup>. We recommend this value but with wider limits,  $viz. -158.4 \pm 1.3$  kcal mol<sup>-1</sup>, until more work has been carried out. None of this evidence appears to have been considered in the review by Bell et al.<sup>8</sup> who quote the CRC Handbook<sup>35</sup> value of -145.7 kcal mol<sup>-1</sup>. Unfortunately this is based on the 1952 NBS Circular 500<sup>36</sup> and so is considerably out of date.

Trichlorosilane. There is a considerable amount of experimental information on  $\Delta H_f^{\circ}(SiHCl_3)$ , most of which has been discussed by Farber and Srivastava<sup>37</sup> and some of which has been evaluated by JANAF 1982 supplement.<sup>11 e</sup> The early data based on oxygen bomb calorimetry,<sup>38</sup> solution (hydrolysis) calorimetry<sup>39</sup> and electron impact<sup>40</sup> has been shown to have large uncertainties.<sup>11 e, 37</sup> The early JANAF value,<sup>11 a</sup> the CATCH tables<sup>9</sup> and NBS Technical Note 270–3<sup>12</sup> were based on one or all of these and are therefore unreliable. All the recent values are essentially based on a high-temperature study of the gaseous equilibrium

$$SiCl_4 + H_2 \rightleftharpoons SiHCl_3 + HCl.$$

A computer evaluation of various experimental ratios in the high-temperature Si—H—Cl system led first Hunt and Sirtl<sup>41</sup> and later Sirtl *et al.*<sup>42</sup> to  $\Delta H_f^{\circ}(\text{SiHCl}_3) = -116.9 \pm 1 \text{ kcal mol}^{-1}$ . Farber and Srivastava<sup>37</sup> using a third-law method of evaluating equilibrium constants obtained  $\Delta H_f^{\circ}(\text{SiHCl}_3) = -119.3 \pm 1.5 \text{ kcal mol}^{-1}$ . Finally Wolf and Teichmann<sup>34</sup> obtained  $\Delta H_f^{\circ}(\text{SiHCl}_3) = -118.8 \pm 1.4 \text{ kcal mol}^{-1}$ . These results all depend on the value chosen for  $\Delta H_f^{\circ}(\text{SiCl}_4)$  and when placed on a common basis with the recommended value for this quantity (*vide supra*) they become  $-118.6 \pm 1.0$ ,<sup>41, 42</sup>  $-119.3 \pm 1.5^{37}$  and  $-119.5 \pm 1.4 \text{ kcal mol}^{-1, 34}$  respectively, *i.e.* in good agreement. Thus we recommend  $\Delta H_f^{\circ}(\text{SiHCl}_3) = -119.3 \pm 1.6 \text{ kcal mol}^{-1}$ , which incorporates the uncertainty in  $\Delta H_f^{\circ}(\text{SiCl}_4)$ .

Dichloro- and monochloro-silanes. The only experimental values for these heats of formation come from the mass-spectrometric study of the high-temperature gaseous equilibria  $SiHCI + H \rightarrow SiHCI + HCI$ 

$$S_1HCl_3 + H_2 \rightleftharpoons S_1H_2Cl_2 + HCl$$

$$SiH_2Cl_2 + H_2 \rightleftharpoons SiH_3Cl + HCl$$

by Farber and Srivastava.<sup>37</sup> Using the third-law approach  $\Delta H_{f}^{\circ}(g, 298 \text{ K})$  values were obtained for SiH<sub>2</sub>Cl<sub>2</sub> and SiH<sub>3</sub>Cl. These are listed in table 3 along with the old (unreliable) estimates from JANAF<sup>11 a</sup> and CATCH<sup>9</sup> and the values from other sources. For comparison purposes the data for SiH<sub>4</sub>, SiHCl<sub>3</sub> and SiCl<sub>4</sub> are also included. In assessing the data for the partially chlorinated silanes we calculate that the Farber and Srivastava<sup>37</sup> values give Cl for H disproportionation enthalpies of  $-2.3 \text{ kcal mol}^{-1}$  (SiH<sub>3</sub>Cl),  $-1.1 \text{ kcal mol}^{-1}$  (SiH<sub>2</sub>Cl<sub>2</sub>) and  $+4.9 \text{ kcal mol}^{-1}$  (SiHCl<sub>3</sub>). In the light of previous discussion and in contrast to the fluorosilanes, these values do appear to be sufficiently small to be considered reasonable. Indeed it is clear that individual values are all close to the bond-additivity figures. Linear interpolation (*i.e.* bond additivity) has been suggested before for this series by Seiter and Sirtl<sup>43</sup> (with quite reasonable values) and also by Lapidus *et al.*<sup>44</sup> (working generally with old and unreliable figures). Thus at the present time we recommend the Farber and Srivastava<sup>37</sup> values as being the most reliable.

Finally it should be noted that the theoretical calculations of Bell *et al.*<sup>8</sup> do not interpolate linearly between  $SiH_4$  and  $SiCl_4$  (even with an erroneous value). The departures from linearity suggest that the MOB I method<sup>8</sup> tends to over-estimate bond-interaction parameters.

#### BROMOSILANES

Tetrabromosilane. Based on a measurement of the heat of solution of SiBr<sub>4</sub> in aqueous HF containing silver fluoride, Schäfer and Heine<sup>33</sup> have obtained a value for  $\Delta H_f^{\circ}(\text{SiBr}_4, 1)$ , which in conjunction with vaporisation data is evaluated by  $JANAF^{11e}$  to give  $\Delta H_f^{\circ}(\text{SiBr}_4, \text{g}) = -99.3 \pm 4.0 \text{ kcal mol}^{-1}$ . The error limits seem a little pessimistic in the light of the  $\pm 1.1 \text{ kcal mol}^{-1}$  uncertainty in the Schäfer and

			ΔΠ <sub>Γ</sub> (g, 270 N)	/ AC41 11101		
compound	old values <sup>9, 11 a</sup>	Hunt and Sirtl <sup>41</sup>	Bell et al. <sup>8</sup>	Farber and Srivastava <sup>37</sup>	JANAF <sup>11 e</sup>	bond additivity
SiH a	+8.2	+ 7.3	+ 8.3	+ 8.2	+ 8.2	+8.2
SiH.C	- 48	- 34.043	- 38.0	$-32.4\pm2.5$	$-33.9\pm 2$	-33.5
SiH	- 80 - 80	$-75.0^{43}$	- 79.8	$-75.3\pm2.0$	$-76.6\pm3$	-75.1
SiHCL	-115.2(-119.6)	-116.9	-115.3	$-119.3\pm1.5$	$-118.6\pm1$	-116.8
SiCla	-158.4(-157.1)	- 156.7	-145.7	-158.4	- 158.4	- 158.4

Table 3. Enthalpies of formation for the chlorinated silanes

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Heine<sup>32</sup> measurement. We suggest  $\pm 2.0$  kcal mol<sup>-1</sup> as more reasonable. The *CATCH* tables quote  $\Delta H_{\rm f}^{\circ}({\rm SiBr}_4, {\rm g}) = -95.5$  kcal mol<sup>-1</sup> but this value is a weighted mean incorporating a hydrolysis study by Wolf *et al.*<sup>45</sup> which is judged by *JANAF*<sup>11*e*</sup> to be unreliable. We therefore recommend  $\Delta H_{\rm f}^{\circ}({\rm SiBr}_4, {\rm g}) = -99.3 \pm 2.0$  kcal mol<sup>-1</sup>.

Partially brominated silanes. These have again only been investigated by Farber and Srivastava<sup>46</sup> using the mass-spectrometric method to study the high-temperature gas equilibria  $SiBr + H \rightarrow SiHBr + HBr$ 

$$\operatorname{SiHBr}_3 + \operatorname{H}_2 \rightleftharpoons \operatorname{SiHBr}_3 + \operatorname{HBr}_3$$
  
 $\operatorname{SiHBr}_3 + \operatorname{H}_2 \rightleftharpoons \operatorname{SiH}_2 \operatorname{Br}_2 + \operatorname{HBr}_3$ 

$$SiH_2Br_2 + H_2 \rightleftharpoons SiH_3Br + HBr.$$

Using the third-law approach  $\Delta H_{f}^{\circ}(g, 298 \text{ K})$  values have been obtained for SiHBr<sub>3</sub>, SiH<sub>2</sub>Br<sub>2</sub> and SiH<sub>3</sub>Br and these are listed in table 4. The *CATCH* tables list only a value for  $\Delta H_{f}^{\circ}(\text{SiHBr}_{3})$  based on a hydrolysis study,<sup>45</sup> again judged to be unreliable in *JANAF*.<sup>11*e*</sup> In assessing these data for the partially brominated silanes we calculate Br for H disproportionation enthalpies of  $-4.3 \text{ kcal mol}^{-1}(\text{SiH}_{3}\text{Br}), -1.4 \text{ kcal mol}^{-1}(\text{SiH}_{2}\text{Br}_{2})$  and  $+2.5 \text{ kcal mol}^{-1}(\text{SiHBr}_{3})$ . Once again these small values do not seem unreasonable, and individual values are close to bond additivity, the latter having been adopted by *JANAF*<sup>11*e*</sup> following Hunt and Sirtl.<sup>47</sup> We would again therefore recommend the Farber and Srivastava values, with error limits increased to allow for uncertainties in  $\Delta H_{f}^{\circ}(\text{SiBr}_{4})$ .

Table 4. Enthalpies of formation for the brominated silanes

	$\Delta H_{\rm f}^{\rm o}({\rm g}, 298 \ {\rm K})/{\rm kcal} \ {\rm mol}^{-1}$		
compound	Farber and Srivastava <sup>46</sup>	bond additivity (JANAF <sup>11e</sup> )	
SiH <sub>4</sub> <sup>a</sup>	8.2	+8.2	
SiH <sub>3</sub> Br	$-15.3\pm0.5$	-18.7	
SiH <sub>2</sub> Br <sub>2</sub>	$-43.2\pm1.5$	-45.6	
SiHBr	$-72.5 \pm 1.0$	-72.4	
SiBr4 <sup>b</sup>	-99.3	-99.3	

<sup>a</sup> For reference purposes: see table 2. <sup>b</sup> For reference purposes: see text for discussion.

# IODOSILANES

Tetraiodosilane. The JANAF tables<sup>11 d, e</sup> contain a detailed discussion of experimental results pertinent to  $\Delta H_{f}^{\circ}(SiI_{4})$  and adopt a value of  $-26.4\pm4.0$  kcal mol<sup>-1</sup>. An evaluation of the same data by Kokovin and Thieme<sup>48</sup> led them to a value of -28.6 kcal mol<sup>-1</sup>. The latter do not discuss the data in the detailed manner of JANAF but the main difference appears to be that JANAF discounts the calorimetric hydrolysis study of Wolf,<sup>49</sup> whereas the other authors do not. It is clear that more work is needed to refine this value but in the light of the uncertainties associated with the hydrolysis reactions we recommend the JANAF value. The CATCH tables<sup>9</sup> quote  $-28.4\pm2.2$  kcal mol<sup>-1</sup>, but this is not based on all the known data and so must be disregarded.

Partially iodinated silanes. No experimental data exist for these and so following the previous discussion and also  $JANAF^{11e}$  we adopt bond-additivity interpolation between the known  $\Delta H_{\rm f}^{\rm o}$  values for SiH<sub>4</sub> and SiI<sub>4</sub>. This yields  $\Delta H_{\rm f}^{\rm o}$  values of

-0.5 kcal mol<sup>-1</sup> (SiH<sub>3</sub>I), -9.1 kcal mol<sup>-1</sup> (SiH<sub>2</sub>I<sub>2</sub>) and -17.8 kcal mol<sup>-1</sup> (SiHI<sub>3</sub>). Kokovin and Thieme<sup>48</sup> have similarly applied additivity but produce slightly differing values because of their different choice for  $\Delta H_f^o(SiI_4)$ .

# SUMMARY

Table 5 shows a summary of the recommended values discussed in this section.

compound	$\Delta H_{\rm f}^{\sf o}$	compound	$\Delta H_{ m f}^{ m o}$
SiH <sub>3</sub> F	$-90 \pm 10$	SiH <sub>3</sub> Cl	$-32.4 \pm 2.5$
SiH <sub>2</sub> F <sub>2</sub>	-189 ± 8	SiH <sub>2</sub> Cl <sub>2</sub>	-75.3 ± 2.0
SiHF <sub>3</sub>	$-287 \pm 5$	SiHCl <sub>3</sub>	$-119.3 \pm 1.6$
SiF <sub>4</sub>	$-386.0 \pm 0.2$	SiCl <sub>4</sub>	$-158.4 \pm 1.3$
SiH <sub>3</sub> Br SiH <sub>2</sub> Br <sub>2</sub> SiHBr <sub>3</sub> SiBr <sub>4</sub>	$-15.3 \pm 2.1 -43.2 \pm 2.5 -72.5 \pm 2.2 -99.3 \pm 2.0$	SiH <sub>3</sub> I SiH <sub>2</sub> I <sub>2</sub> SiHI <sub>3</sub> SiI <sub>4</sub>	$-0.5 \pm 2.0 -9.1 \pm 3.0 -17.8 \pm 3.0 -26.4 \pm 4.0$

Table 5. Summary of recommended heats of formation (in kcal mol<sup>-1</sup>)

# FREE RADICALS AND COMPOUNDS OF TRI-, DI- AND MONO-VALENT STATES OF SILICON

### GENERAL CONSIDERATIONS

Whereas in the saturated tetravalent compounds the idea of a constant bond energy term (implicit in the law of bond additivity) works quite well, it cannot be presumed that the breaking of bonds in a compound  $SiX_4$ , by successive removal of atoms X, should occur with a constant increment. This is because in the intermediates,  $SiX_n$ (n = 1, 2, 3), the bonding involves atomic orbitals of differing energies with differing degrees of mixing, as well as differing effects of electron-electron repulsion. Although not expressed in this way, it has been known for a very long time that elements showing more than one common valency tend to favour one or the other in particular compound formation.<sup>50</sup> Different average bond energies in compounds of the type  $MX_n, MX_{n-2}$  are commonly found. Occasionally the sequential dissociation energies are quite close to the average, such as with CH4,51 but this is the exception rather than the rule. Possibly because of their similarity to organic compounds this was assumed to be the situation for silicon compounds<sup>11a</sup> before many real data became available. It still appears to colour the discussion of  $\Delta H_f^o(SiX_n)$  in JANAF.<sup>11e</sup> Since it is now known to be far from the truth,<sup>7</sup> the use of average bond energies to derive  $\Delta H_f^o(SiX_n)$ cannot be accepted.

The assessments of the heats of formation of these species fall quite naturally into three groups. First and most reliably established are  $\Delta H_f^{\circ}(SiX_2)$ . This is because the SiX<sub>2</sub> species are readily observed to participate in high-temperature equilibria of the type

 $Si + SiX_4 \rightleftharpoons 2SiX_2$ 

for which equilibrium constants have been measured and from them thermodynamic data obtained.  $SiX_2$  molecules have been observed by more than one technique and these equilibria have been studied by several groups, with good concordance.  $SiX_2$  molecules are also usually the most abundant species present. Thus these equilibria appear reliably established despite the fact that similar disproportionation equilibria involving  $SiX_3$  are (*vide infra*) much more open to question.

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Secondly and much more controversial are the values for  $\Delta H_{\rm f}^{\circ}({\rm SiX}_3)$ . The controversy arises because values from two different general approaches are in substantial disagreement. On the one hand are equilibrium studies of the reaction

$$SiX_2 + SiX_4 \rightleftharpoons 2SiX_3$$

leading to equilibrium constants and thereby thermodynamic data, whilst on the other are kinetic studies leading to  $D(X_3Si-H)$  and thereby  $\Delta H_f^o(SiX_3)$ , by use of  $\Delta H_f^o(SiHX_3)$ . These different methods give quite different values for  $\Delta H_f^o(SiX_3)$ . Because of this disagreement a further general argument in the terms of chemical reactivity is presented here. This is based on a consideration of the alternative decomposition pathways open to the disilane, Si<sub>2</sub>X<sub>6</sub>, viz.

$$\operatorname{Si}_2 X_6 \to 2\operatorname{Si} X_3$$
 (1)

$$\operatorname{Si}_{2}X_{6} \xrightarrow{\sim} \operatorname{Si}X_{2} + \operatorname{Si}X_{4}.$$
 (2)

The enthalpy change for process (1) is the bond dissociation energy  $D(X_3Si-SiX_3)$ . Although values are not known with precision, for the cases  $X \equiv Cl$  or F it is unlikely that these are less than  $D(Me_3Si-SiMe_3) = 80$  kcal mol<sup>-1.52</sup> This is because the more electronegative substituents invariably increase bond strengths.<sup>7, 53</sup> An upper limit for the enthalpy change for process (2) is provided by the activation energy  $E_2$ .  $\Delta H_2$  will be less than  $E_2$  since there will be a reverse (insertion) barrier. Process (2) is the most commonly observed thermal decomposition pathway for disilanes<sup>1, 54</sup> and so activation energies are relatively easy to obtain. For  $X \equiv Cl$ ,  $E_2 = 49.2 \pm 0.3$  kcal mol<sup>-1.53</sup> and for  $X \equiv F$  the value is *ca.* 47 kcal mol<sup>-1.55</sup> For the metathesis process

$$SiX_2 + SiX_4 \rightleftharpoons 2SiX_3$$
 (3)

the enthalpy change  $\Delta H_3^{\circ}$  is related to those of processes (1) and (2) via  $\Delta H_3^{\circ} = \Delta H_1^{\circ} - \Delta H_2^{\circ}$ . Thus from the figures given  $\Delta H_3^{\circ}$  must be at least 30 kcal mol<sup>-1</sup> for both the cases  $X \equiv Cl$ , F. Therefore any data suggesting a substantially lower figure for  $\Delta H_3^{\circ}$  are in conflict with this body of information derived from chemical reactivity considerations. This is unfortunately the case with the high-temperature Knudsen cell studies of Farber and Srivastava<sup>56-58</sup> for the equilibrium reaction (3) from which were obtained  $\Delta H_3^{\circ}$  (298 K) values of 7.8 kcal mol<sup>-1</sup> (X  $\equiv$  F),<sup>56</sup> 12.3 kcal mol<sup>-1</sup> (X  $\equiv$  Cl)<sup>57</sup> and 13.7 kcal mol<sup>-1</sup> (X  $\equiv$  Br).<sup>58</sup> We therefore feel that the equilibrium studies of reaction (3) are in error. We do not know why these experiments should give the wrong result but we note that in the equilibrium mixtures the SiX<sub>3</sub> species is always much less abundant than SiX<sub>2</sub> and therefore more prone to error in its determination.

The third group concerns  $\Delta H_{\rm f}^{\circ}({\rm SiX})$ . Here, rather than specific controversy, is general uncertainty. Most precise of the determinations are again those based on high-temperature equilibria of the type

$$Si + SiX_{2} \rightleftharpoons 2SiX_{2}$$

However, SiX is by no means the most abundant species and in view of the doubts concerning SiX<sub>3</sub>, the measurements involving SiX must be open to some question. Apart from these the other general source of data is that on D(Si-X) derived from Birge-Sponer extrapolations of vibrational progressions in spectroscopic studies of SiX. D(Si-X) is, of course, related to  $\Delta H_f^o(\text{SiX})$  via  $\Delta H_f^o(\text{Si})$  and  $\Delta H_f^o(X)$ , which are well established, but for the SiX species the spectroscopy-based values usually have large uncertainties of  $ca. \pm 10$  kcal mol<sup>-1</sup> because of the difficulties of extrapolation. Thus there appears no very reliable set of figures for these species. However, for

completeness, they are included in the present evaluation. Note that the resulting recommended D(Si-X) values do not form a very consistent sequence as the halogen X varies. Dissociation energies for these and other diatomic species have been fitted recently to a general hyperbolic equation by Cherkesov.<sup>59</sup> If valid, this indicates errors in some of the values.

#### EXPERIMENTAL DATA ON SILICON SUBHALIDES

# SILICON SUBFLUORIDES, $SiF_n$

 $SiF_3$ . There is considerable disagreement concerning  $\Delta H_f^o(SiF_3)$ . The latest  $JANAF^{11d,e}$  value is  $-259.4\pm4$  kcal mol<sup>-1</sup>, which is essentially that obtained by Farber and Srivastava<sup>56</sup> from their high-temperature equilibration studies. Wang et al.<sup>60</sup> quote a value of -235 kcal mol<sup>-1</sup> from dissociative electron attachment measurements, but given no error limits. JANAF<sup>11d, e</sup> states, quoting an article by Franklin,<sup>61</sup> that this figure may be in error by 15 kcal mol<sup>-1</sup> or more because of the assumption of a constant fraction of active vibrations (in the energised negative ion). While this may be the case in general, there appears to be no reference to the  $SiF_a$ ion in Franklin's article and so the origin of this figure is rather mysterious. Earlier studies by Margrave and coworkers<sup>62</sup> based on positive ion appearance potentials gave -235+20 kcal mol<sup>-1</sup>. CATCH<sup>9</sup> evaluates Margrave's data to give  $-227 \pm 14$  kcal mol<sup>-1</sup>. Using the kinetic iodination technique developed by Benson and coworkers<sup>63</sup> we have obtained  $D(F_3Si-H) = 100.1 \pm 1.2 \text{ kcal mol}^{-1.7, 64}$  Used in combination with the value for  $\Delta H_{c}^{o}(SiHF_{3})$  recommended in this paper, this gives  $\Delta H_{\rm f}^{\rm o}({\rm SiF}_3) = -239 \pm 5 \, \rm kcal \, mol^{-1}$ . This is more reliable than our earlier derived figures  $(-235^{64} \text{ and } -245 \text{ kcal mol}^{-17})$  since the latter were not based on a critical assessment of  $\Delta H_{t}^{o}(SiHF_{3})$ . For the reasons already given we reject the Farber and Srivastava result.<sup>56</sup> The figure based on our dissociation energy measurement would appear the best available.

 $SiF_2$ . In contrast to  $\Delta H_f^{\circ}(SiF_3)$ ,  $\Delta H_f^{\circ}(SiF_2)$  seems well established. In spite of the difficulties with the results of the mass-spectrometric effusion method for SiX<sub>3</sub> it appears likely that the gaseous equilibrium

$$Si + SiF_4 \rightleftharpoons 2SiF_2$$

can be established at high temperatures and reliably studied. Thus Farber and Srivastava<sup>56</sup> have obtained by a third-law analysis  $\Delta H_f^{\circ}(SiF_2) = -140.6 \pm 0.3$  kcal mol<sup>-1</sup>. Apart from an earlier less precise study,<sup>65</sup> other values include -139.0 kcal mol<sup>-1</sup> from a transpiration study<sup>66</sup> and  $-140.5 \pm 3$  kcal mol<sup>-1</sup> from another effusion mass-spectrometer study of the reaction of CaF<sub>2</sub> with silicon.<sup>67</sup> JANAF<sup>11d, e</sup> quotes  $-140.5 \pm 3$  kcal mol<sup>-1</sup> and CATCH<sup>9</sup> quotes  $-140.8 \pm 1.1$  kcal mol<sup>-1</sup>. We take the Farber and Srivastava<sup>56</sup> value to be correct, though with widened error limits to allow for uncertainties in ionisation cross-sections.

SiF.  $\Delta H_f^o(SiF)$  is available from mass-spectrometric effusion studies of the gaseous equilibrium Si + SiF  $\rightarrow 2SiF$ 

$$Si + SiF_2 \rightleftharpoons 2SiF.$$

Ehlert and Margrave<sup>67</sup> obtained  $\Delta H_{f}^{\circ}(\text{SiF}) = -4.6 \pm 3 \text{ kcal mol}^{-1}$ , a value essentially adopted by both JANAF<sup>11a, e</sup> and CATCH<sup>9</sup> whilst, more recently, from the same system Farber and Srivastava<sup>56</sup> obtained  $-5.8 \pm 0.5 \text{ kcal mol}^{-1}$ . In view of the problems of this method for SiF<sub>3</sub> we have reservations about this value. However, spectroscopic studies of  $D_{0}^{\circ}(\text{Si}-\text{F})$  yield rather scattered results corresponding to values for  $\Delta H_{f}^{\circ}(\text{SiF})$  of  $+1,^{68} + 11^{69}$  and  $+16^{70}$  kcal mol<sup>-1</sup>. We recommend with

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caution, but no great confidence, a value of  $-5\pm 6 \text{ kcal mol}^{-1}$  corresponding to  $D_0^{\circ}(\text{Si}-\text{F}) = 131\pm 6 \text{ kcal mol}^{-1}$ .

### SILICON SUBCHLORIDES, $SiCl_n$

 $SiCl_3$ . There is considerable disagreement concerning  $\Delta H_f^{\circ}(SiCl_3)$ . The JANAF value<sup>11 a</sup> has been updated<sup>11 e</sup> to  $-93.3 \pm 4$  kcal mol<sup>-1</sup>, essentially the value obtained by Farber and Srivastava from the earlier quoted mass-spectral study,<sup>57</sup> but with increased error limits. These error limits do not cover the several other studies regarded by JANAF<sup>11e</sup> as much less definitive. Amongst these other studies was one from our laboratory concerned with measurement of  $D(Cl_3Si-H)^{71}$  by the kinetic iodination technique.<sup>63</sup> This yielded a value of  $91.3 \pm 1.5$  kcal mol<sup>-1</sup> for the bond strength which was in agreement with electron impact measurements of Steele et al.<sup>72</sup>  $(93 \pm 4 \text{ kcal mol}^{-1})$  and infrared chemiluminescence measurements by Jonathan et al.  $(90\pm 5 \text{ kcal mol}^{-1})^{73}$  although more precise. Taken in conjunction with the value for  $\Delta H_{f}^{o}(SiHCl_{3})$  recommended in this paper these bond-strength studies lead to  $\Delta H_{f}^{o}(SiCl_{3}) = -80.1 \pm 2.2^{71} - 78 \pm 4^{72}$  and  $-81 \pm 5^{73}$  kcal mol<sup>-1</sup>, respectively. Our earlier value for  $\Delta H_{f}^{\circ}(SiCl_{3})$  of -76 kcal mol<sup>-17,71</sup> is to be disregarded because it was not based on a critical assessment of  $\Delta H_{\rm f}^{\rm o}({\rm SiHCl}_3)$ . Other kinetic studies<sup>74-76</sup> of SiCl<sub>3</sub> radical reactions do not lead to very definitive values for either  $D(SiCl_3-H)$  or  $\Delta H_{f}^{o}(SiCl_{a})$ . Studies of negative-ion formation via dissociative electron attachment by Margrave and coworkers<sup>77, 78</sup> give  $\Delta H_f^{\circ}(SiCl_3) = -81$  kcal mol<sup>-1</sup>. The uncertainty is not stated. Correction relative to the quoted value for  $\Delta H_{f}^{o}(SiCl_{4})$  recommended in this paper would imply a value of -82 kcal mol<sup>-1</sup>. For the reasons already given we reject the Farber and Srivastava<sup>57</sup> value (and therefore  $JANAF^{11e}$ ) and recommend  $-80 \pm 2$  kcal mol<sup>-1</sup>. Several other studies report results pertaining to  $\Delta H_{\rm f}^{\rm o}({\rm SiCl}_3)$  but these either do not quote their sources in sufficient detail to assess<sup>79,80</sup> or make, in our view, unwarranted assumptions.81,82

SiCl<sub>2</sub>. There is general agreement concerning  $\Delta H_{\rm f}^{\circ}({\rm SiCl_2})$ . The most recent JANAF assessment<sup>11 e</sup> quoted  $-40.3 \pm 0.8$  kcal mol<sup>-1</sup>, which covers six independent studies of the equilibrium Si(a) + SiCl<sub>2</sub>(a)  $\Rightarrow 2SiCl<sub>1</sub>(a)$ 

$$Si(c) + SiCl_4(g) \rightleftharpoons 2SiCl_2(g)$$

and one of the same process but with silicon in the gaseous state. In four of these studies with good second- and third-law consistency the third-law values differ by no more than 0.8 kcal mol<sup>-1</sup>. It appears that  $\Delta H_{\rm f}^{\rm o}({\rm SiCl}_2)$  is well established and we recommend the above value. The *CATCH* tables merely quote the earlier *JANAF* value.<sup>11 a</sup>

SiCl. From mass-spectral studies of the equilibrium

$$Si(g) + SiCl_2(g) \rightleftharpoons 2SiCl(g)$$

Farber and Srivastava<sup>57</sup> obtained  $\Delta H_{f}^{\circ}(SiCl) = 47.1 \pm 0.6$  kcal mol<sup>-1</sup>. JANAF<sup>11e</sup> have adjusted this to  $47.4 \pm 1.6$  kcal mol<sup>-1</sup>, increasing the error limits to reflect less optimism about ion cross-sections. In view of the problems with SiCl<sub>3</sub> we have reservations about this value. Apart from this the only other values (including that quoted by CATCH) derive from extrapolations of spectroscopic data to give the related  $D_{0}^{\circ}(Si-Cl)$ . The values for the latter correspond to  $\Delta H_{f}^{\circ}(SiCl)$  values of 43,<sup>83</sup> 32<sup>69</sup> and 33 kcal mol<sup>-170</sup> all with high uncertainties. We recommend, with caution but no great confidence, a value of  $37 \pm 10$  kcal mol<sup>-1</sup> corresponding to  $D_{0}^{\circ}(Si-Cl) = 99 \pm 10$  kcal mol<sup>-1</sup>.

#### SILICON SUBBROMIDES, $SiBr_n$

 $SiBr_3$ . The only experimental value for  $\Delta H_f^{\circ}(SiBr_3)$  is that of Farber and Srivastava<sup>58</sup> of  $-48.0 \pm 0.5$  kcal mol<sup>-1</sup>. It is tempting therefore to recommend this. However, in view of the problems with SiF<sub>3</sub> and SiCl<sub>3</sub> we make an estimate based on  $D(Br_3Si-H) = 87 \pm 5$  kcal mol<sup>-1</sup>, a value consistent with substituent trends in Si-H bond strengths.<sup>7</sup> This bond strength combined with the recommended  $\Delta H_f^{\circ}(SiBr_3) = -38 \pm 6$  kcal mol<sup>-1</sup>. Once again in view of the discussion we prefer this latter value. Clearly more work is needed to refine this.

SiBr<sub>2</sub>. There is no great dispute regarding  $\Delta H_{\rm f}^{\circ}({\rm SiBr}_2)$ . JANAF<sup>11e</sup> recommends  $-12.5 \pm 4.0$  kcal mol<sup>-1</sup> and the CATCH tables  $-11.1 \pm 0.8$  kcal mol<sup>-1</sup>, based on the same two flow studies<sup>66, 84</sup> of the equilibrium

$$Si(c) + SiBr_4(g) \rightleftharpoons 2SiBr_9(g)$$
.

Farber and Srivastava<sup>58</sup> obtain  $\Delta H_{f}^{o}(SiBr_{2}) = -10.5 \pm 2.0$  kcal mol<sup>-1</sup> from their hightemperature study of the same equilibrium. Farber and Srivastava suggest that the other authors<sup>66, 84</sup> failed to account for the possible presence of SiBr<sub>3</sub> and this, in part, accounts for the small discrepancy. However, we doubt the presence of SiBr<sub>3</sub> and so take a weighted average of  $-11.0 \pm 2.0$  kcal mol<sup>-1</sup> as the recommended value.

SiBr. From mass-spectral studies of the equilibrium

## $Si(c) + SiBr_2(g) \rightleftharpoons 2SiBr(g)$

Farber and Srivastava<sup>58</sup> obtained  $\Delta H_f^{\circ}(SiBr) = 46.5 \pm 2.4$  kcal mol<sup>-1</sup>. In view of the problems of this method for SiBr<sub>3</sub> we have reservations about this value. JANAF<sup>11e</sup> recommends  $56.2 \pm 11$  kcal mol<sup>-1</sup> while CATCH<sup>9</sup> quote an NBS<sup>12</sup> figure of  $50 \pm 1$  kcal mol<sup>-1</sup>. These compilations are based on one or more of the several extrapolations of spectroscopic data for  $D_0^{\circ}(Si-Br)$  which correspond to  $\Delta H_f^{\circ}(SiBr) = 47 (\pm 11)^{85}$  and  $53 (\pm 12)^{.69} JANAF^{11e}$  corrects one of the extrapolations for ionic bonding. A theoretical treatment<sup>86</sup> and another compilation<sup>87</sup> quote values corresponding to 49 kcal mol<sup>-1</sup>. We recommend, with caution but no great confidence, a value of  $47 \pm 10$  kcal mol<sup>-1</sup>, corresponding to  $D_0^{\circ}(Si-Br) = 87 \pm 10$  kcal mol<sup>-1</sup>.

# SILICON SUBIODIDES, $SiI_n$

 $SiI_3$ . There is no experimental value for  $\Delta H_f^{\circ}(SiI_3)$ , although  $JANAF^{11e}$  quotes a value of  $8.4 \pm 15$  kcal mol<sup>-1</sup> based on the dubious assumption of a constant Si—I bond energy in SiI<sub>4</sub>. If on the contrary we assume  $D(I_3Si-H) = 84 \pm 5$  kcal mol<sup>-1</sup>, a value extrapolated from the known Si—H bond-weakening effect of an iodine substituent,<sup>88</sup> and which is consistent with general substituent trends,<sup>7,89</sup> this leads to  $\Delta H_f^{\circ}(SiI_3) = +14 \pm 6$  kcal mol<sup>-1</sup> when combined with the recommended  $\Delta H_f^{\circ}(SiH_3)$  of this paper. Again we recommend this value (although the JANAF figure with its uncertainty encompasses it) whilst recognising the need for further work.

 $SiI_2$ . JANAF<sup>11e</sup> quote  $\Delta H_f^o(SiI_2) = 22.1 \pm 2 \text{ kcal mol}^{-1}$  based on two different high-temperature equilibrium studies.<sup>66, 90</sup> As with the other divalent silicon species we accept this as essentially reliable. The CATCH value of 19.3 kcal mol}^{-1} is based on only one of these studies.<sup>66</sup>

SiI. From spectroscopic studies and a linear Birge–Sponer extrapolation Billingsley<sup>91</sup> obtained  $D_0^{\circ}(\text{Si}-\text{I}) = 69.8 \text{ kcal mol}^{-1}$ , a value which corresponds to  $\Delta H_f^{\circ}(\text{SiI}) = 62.5 \text{ kcal mol}^{-1}$ . JANAF have corrected this to  $75 \pm 10 \text{ kcal mol}^{-1}$  by allowance for ionic character in the bond. However, such corrections do not appear to reconcile data for the other SiX species and so must be questionable. A theoretical<sup>86</sup>

and empirical<sup>92</sup> procedure produce values corresponding to  $\Delta H_{\rm f}^{\circ}({\rm SiI}) = 60$  and  $67 \pm 10$  kcal mol<sup>-1</sup>. We recommend, again with caution and no great confidence, a value of  $62 \pm 10$  kcal mol<sup>-1</sup> corresponding to  $D_0^{\circ}({\rm Si-I}) = 70 \pm 10$  kcal mol<sup>-1</sup>.

#### SUMMARY

Table 6 shows a summary of the recommended values discussed in this section.

compound	$\Delta H_{ m f}^{ m o}$	compound	$\Delta H_{ m f}^{m o}$
SiF <sub>3</sub>	$-239\pm 5$	SiCl <sub>3</sub>	$-80 \pm 2$
SiF <sub>2</sub>	$-141 \pm 2$	SiCl,	-40.3+0.8
SiF	$-5\pm 6$	SiCl	$37\pm10$
SiBr <sub>3</sub>	$-38 \pm 6$	SiI <sub>3</sub>	$14 \pm 6$
SiBr <sub>2</sub>	$-11\pm 2$	Sil,	$22 \pm 2$
SiBr	$47 \pm 10$	Sil	$62 \pm 10$

Table 6. Summary of recommended heats of formation (in kcal mol<sup>-1</sup>)

# DISCUSSION

The major objective of this paper is a review and evaluation of heats of formation of the individual silanes. These have already been discussed in the previous sections. One important use to which heat of formation data is often put is the derivation of bond-dissociation energies. Such derivations were carried out by Bell *et al.*<sup>8</sup> but, as we have pointed out, since their heat of formation data were in a number of cases out of date, their derived bond-dissociation energies are, therefore, also unreliable. We have also published a number of bond-dissociation-energy values.<sup>7</sup> Since many of them were direct (Si—H) in the sense that they did not depend on ancillary silane heats of formation, these are unaffected by the present discussion. However, the silicon-halogen (Si—X) bond-dissociation energies were indirect and so in some cases our earlier proposed values<sup>7</sup> need amendment.

The new values based on the heats of formation contained in this paper are shown in table 7. Only the first and second consecutive Si - X dissociation energies are shown, as the third and fourth are too uncertain to justify discussion.

One feature is worth singling out for comment. It is quite clear that, despite the uncertainties, in all cases the second dissociation energy is considerably less than the first. As has been discussed by us elsewhere<sup>7</sup> this is evidence of the operation of a lone-pair stabilisation effect in the SiX<sub>2</sub> species, akin to the inert-pair effect. The magnitude of this effect can be represented by the difference between first and second dissociation energies and is also listed in table 7. The monotonic trend in this effect from SiF<sub>2</sub> to SiI<sub>2</sub> adds some confidence to the data and suggests that the error limits may have been drawn too conservatively. Previously,7 without the benefit of a critical evaluation, we had obtained figures suggesting SiCl<sub>2</sub> to be more stabilised than SiF<sub>2</sub>. Clearly from the present figures this is not so. These stabilisation energies for SiX<sub>2</sub> are all greater than the value of 26 kcal mol<sup>-1</sup> for SiH<sub>2</sub>. This can be understood in terms of deshielding. The more electronegative halogen substituents attract the bonding electrons further away from the silicon nucleus, thus increasing the attraction of the nucleus for the (largely s-type) lone-pair electrons. This explanation, although probably oversimplified, also accounts for the maximum effect being observed in  $SiF_2$ and for the trend with halogen substitution.

bond	D	bond	D
SiF <sub>3</sub> —F SiF <sub>3</sub> —F	$166 \pm 5$ 117 + 5	SiCl <sub>3</sub> —Cl SiCl <sub>4</sub> —Cl	$107 \pm 2$ 69 + 2
difference	$49 \pm 10$	difference	$38 \pm 4$
SiBr <sub>3</sub> —Br SiBr <sub>2</sub> —Br	$\begin{array}{c} 88\pm 6\\ 54\pm 6\end{array}$	SiI <sub>3</sub> —I SiI <sub>2</sub> —I	$\begin{array}{c} 66\pm7\\ 34\pm6 \end{array}$
difference	$34 \pm 12$	difference	32 <u>+</u> 13

**Table 7.** First and second bond-dissociation energies (in kcal mol<sup>-1</sup>) in SiX<sub>4</sub>

I thank Dr M. Chase (Dow Chemical Co.) for advance, pre-publication copies of the latest JANAF thermochemical tables on silicon halides and Dr M. Farber for helpful correspondence.

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