

Thermochemistry of silicon-containing materials*

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Abstract: A brief survey is given of the thermochemistry of a number of silicon-containing substances that are of interest in modern technology. Among those discussed are: silicalite (SiO_2), silicon disulfide (SiS_2), the crystalline and vitreous forms of silicon diselenide (SiSe_v), silicon sesquiterelluride (Si_2Te_3), silicon nitride (Si_3N_4), and vanadium disilicide (VSi_2).

INTRODUCTION

Of all the elemental building blocks of today's 'high-tech' materials, silicon is, perhaps, the most ubiquitous. For example, it is found in the high-temperature silicides of furnace heating elements. The refractory behavior of molybdenum disilicide and an SiC-whisker-reinforced derivative [1] has led to their being considered for high-temperature aerospace applications. Resistance to deterioration of these silicides of Group-6 metals is attributed to the formation of a skin of SiO_2 that impedes further oxidation by the air. It is this very property that makes Si such a valuable starting material for the fabrication of integrated circuits because the oxide films isolate devices and act as insulators between conductors. Murarka [2] discussed the mechanism of the deposition of V on Si surfaces. Since the Si substrate always contains SiO_2 , vanadium silicide is formed with, possibly, some oxygen in solution. Deposition of tungsten on silicon has been suggested [3] as a means of forming gate and interconnection metallizations in electronic devices and integrated circuits. Silicon nitride, Si_3N_4 , is a key material with numerous practical applications. A proposed synthesis route to it involves the reaction of SiS_2 with NH_3 [4]. Glasses with SiS_2 as a component are excellent fast ion conductors [5].

This is indeed an eclectic, albeit truncated, list. Nevertheless, each application has in common with the others that the understanding of its mechanism of formation and operation can be enhanced through the application of fundamental thermodynamic reasoning. However, much of the basic thermodynamic information required for such analyses has, until recently, been unavailable or of marginal quality. Several years ago, we initiated an experimental and data evaluation program at the National Institute of Standards and Technology (NIST) to provide a reliable database for inorganic materials of importance in modern technologies. This paper presents a condensed outline of the progress made to date toward that objective to the extent that it concerns silicon-containing substances.

FLUORINE BOMB CALORIMETRY—A BRIEF OUTLINE

One theme will be common to the following discussions, namely, the use of fluorine bomb calorimetry to determine values of the standard molar enthalpy of formation $\Delta_f H_m^\circ$ of the silicon-containing compounds. For that reason, a short description of this technique now follows.

Traditionally, combustion or solution calorimetry have been used for the most reliable determinations of the massic energy or enthalpy of reaction and, thus, $\Delta_r H_m^\circ$. However, many of today's important materials are refractory and, as such, react incompletely or not at all with high-pressure oxygen in a combustion bomb or strong mineral acids in a solution calorimeter. This is particularly true for

* Lecture presented at the 15th International Conference on Chemical Thermodynamics, Porto, Portugal, 26 July–1 August 1998, pp. 1167–1306.

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silicon-based compounds which, normally, are responsive, at best, to strong HF(aq). In practical terms, the use of these techniques would leave the investigator with the labyrinthine analytical task of identifying and assaying a complicated mixture of reaction products. It was to circumvent such difficulties that the technique of fluorine bomb calorimetry was invented.

In generic terms, one can think of this method as being analogous to classical combustion calorimetry, but with fluorine substituted for oxygen. Thus, the energy of combustion of a sample is measured in an apparatus that, superficially perhaps, resembles a conventional calorimetric system. There are, however, several vital and significant innovations. Thus, the bomb is made of nickel or Monel, both of which resist corrosion by F₂ by forming a thin protective coating of NiF₂. Gaskets and other parts exposed to F₂ are made of gold, copper, lead, or nickel, and O-rings of Teflon. Almost all materials combine upon contact with F₂ to some extent at room temperature. For that reason, an apparatus was devised to separate F₂ from substances to be burned in the calorimeter until the end of the fore-rating period of an experiment. This device consists of a fluorine storage vessel connected to the combustion bomb [6] by means of a nickel line fitted with a remotely operable valve. Typically, the storage vessel is charged with F₂ to a pressure of approximately 1 MPa; at the end of the fore-rating period, the valve is opened, and F₂ expands into the combustion vessel where the sample ignites spontaneously or is made to do so by means of a fuse of sulfur or an electrical pulse passed through a fine wire. At the end of an experiment, the corrected temperature rise of the calorimetric system is calculated, and the products of combustion are analyzed.

First, however, before serious calorimetric experiments are begun, much effort is usually expended on the analytical characterization of the substance. This procedure can be quite protracted [7] when a nonstoichiometric composition is possible, because, in that case, major element analyses are required. All substances to be studied by fluorine bomb calorimetry are identified by their X-ray diffraction patterns, and analyses for trace metals, C, H, O and N, are also performed.

Many elements and compounds burn in F₂ to form only gaseous fluorides in their highest oxidation states:



others form solids:



or a liquid and a gas:



Usually, it is possible to identify the gaseous products by F.t.i.r. and the solids by X-ray powder diffraction. Occasionally, gravimetric analyses for one of the elements are reported when a single fluoride has formed, as in reaction [2].

In any case, it is essential to characterize as fully as possible the initial chemical state of the substance and the identities of the products. Indeed, those requirements are imposed by the first law of thermodynamics.

For more complete treatises on fluorine bomb calorimetry, the reader is referred to works by Hubbard [8], Leonidov & Medvedev [9], Hubbard *et al.* [10], and Leonidov & O'Hare [11].

CASE HISTORIES OF THE THERMOCHEMISTRY OF SOME INORGANIC COMPOUNDS OF SILICON

Silicon chalcogenides in general

There are few analogies between the chalcogenides of silicon. In (silicon + sulfur) there is but one well-documented compound, namely, the crystalline disulfide, SiS₂. There appears to be no corresponding vitreous or amorphous modification. Although arguments have been put forward for its existence, there is still no convincing evidence that SiS(s) has ever been isolated.

In (silicon + selenium), there is but one crystalline phase, namely, the diselenide. It has a limited range of homogeneity. Vitreous SiSe_ν has been prepared, where ν seems to have a maximum value of approximately 1.94, but never 2 [12].

Efforts to synthesize silicon telluride were reported almost 50 years ago, but it was shown [13] only as recently as 1965 that the product obtained by heating Si and Te in a sealed tube, and that had been variously described as SiTe and SiTe₂ was, in fact Si₂Te₃. It is now known that the sesquite telluride is the only intermediate compound in the (silicon + tellurium) phase diagram.

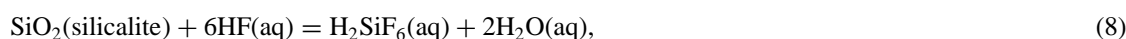
Silicon dioxide (silicalite)

A serious disadvantage of α -quartz as a reference material in silicate thermochemistry is its reluctance to dissolve in HF(aq) at $T \approx 298.15$ K, which results in calorimetric experiments that extend over several hours, with the concomitant probable loss of accuracy of the measurements. It was for that reason that Johnson *et al.* [14] proposed that a new polymorph of SiO₂ be adopted as a reference material. Silicalite is topologically related to certain zeolites with which it shares their caged structures. It has the distinct advantage over α -quartz that it dissolves rapidly in HF(aq) at $T = 298.15$ K.

Measurements of the energy of the reaction:



by fluorine bomb calorimetry yielded $\Delta_f H_m^\circ$ (SiO₂, silicalite). Solution calorimetric studies of the reaction:



combined with the result from fluorine bomb calorimetry, gave $\Delta_f H_m(\text{H}_2\text{SiF}_6, \text{aq})$. Now, recalling the currently accepted reference reaction:



one can, by using the well-established $\Delta_f H_m$ (SiO₂, α -quartz) and $\Delta_f H_m(\text{H}_2\text{O}, \text{aq})$, along with $\Delta_f H_m(\text{H}_2\text{SiF}_6, \text{aq})$ from reaction [8], derive $\Delta_f H_m^\circ = -(138.22 \pm 1.36)$ kJ/mol for reaction [9]. This result is significantly more negative than previous determinations at $T = 298.15$ K, and explains why the reference reaction of α -quartz with HF(aq) is not suitable at this temperature.

Silicon disulfide (SiS₂)

Prepared by the reaction of SiO₂ with Al₂S₃ followed by sublimation, SiS₂ is extremely sensitive to H₂O(g) and O₂(g), which possibly explains the large spread in values of $\Delta_f H_m^\circ$ (SiS₂), from -200 kJ/mol to -329 kJ/mol, found in the literature and discussed in detail elsewhere [15]. In exploratory tests, SiS₂ reacted spontaneously and completely with F₂ in a fluorine bomb calorimeter, and this provided a route to an unequivocal value for $\Delta_f H_m^\circ$ (SiS₂). Experimentally, the biggest challenge was to protect the sulfide from contamination. For that reason, it was handled exclusively in a glovebox with a recirculating atmosphere of high-purity nitrogen. F.t.-Raman spectroscopy was used to characterize the SiS₂. Absence of peaks due to Si–O bonds was taken as a criterion of purity. Carbon and nitrogen, if present, would presumably have been combined in the starting materials as refractory carbides and nitrides and would not have sublimed with the SiS₂; hydrogen would most likely have been present as H₂S and been eliminated in the preliminary heating of SiO₂ and Al₂S₃ under low pressure.

On the basis of the measured massic energy of the reaction:



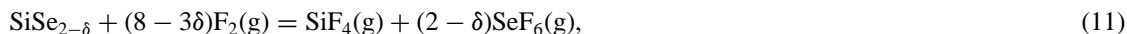
$\Delta_f H_m^\circ$ (SiS₂, cr, 298.15 K) was determined to be $-(254.6 \pm 2.9)$ kJ/mol [15]. Surprisingly, this was closer to the results obtained by third-law treatments of high-temperature equilibrium measurements than by solution calorimetry. In general, high-temperature techniques are more forgiving of impurities than reaction calorimetry.

Silicon selenides (SiSe_{2-δ})

Like silicon disulfide, literature values for $\Delta_f H_m$ of silicon diselenide at $T = 298.15$ K were, at one time, in stark disagreement: -30 kJ/mol and $-(84 \pm 48)$ kJ/mol [16]. Here again, a major problem is preservation of the integrity of the substance. Crystalline silicon diselenide has a range of stoichiometry, but the vitreous modification cannot be prepared with $n(\text{Se})/n(\text{Si}) = 2$, and seems to have a maximum value of

$n(\text{Se})/n(\text{Si})$ in the vicinity of 1.94. An important similarity shared by the disulfide and diselenide of silicon is that they both react spontaneously and completely with F_2 .

Measurements of the massic energy of combustion at $T = 298.15 \text{ K}$:



gave $\Delta_f H_m^\circ(\text{SiSe}_2, \text{cr}) = -(178.4 \pm 1.3) \text{ kJ/mol}$ [16], which is very different from the earlier values; $\Delta_f H_m^\circ(\text{SiSe}_{1.94}, \text{cr}) = -(176.7 \pm 4.5) \text{ kJ/mol}$; and $\Delta_f H_m^\circ(\text{SiSe}_{1.94}, \text{vit}) = -(170.2 \pm 2.4) \text{ kJ/mol}$. These results lead to the enthalpy of transition:



$\Delta_{\text{trs}} H_m^\circ = -(5.6 \pm 2.2) \text{ kJ/mol}$, which is similar to that for the analogous transition $\text{SiO}_2(\text{glass}) = \text{SiO}_2(\alpha\text{-quartz})$.

Silicon sesquitelluride (Si_2Te_3)

Although the solid compounds SiTe and SiTe_2 have been claimed, and even had their enthalpies of formation determined, the preponderance of recent evidence supports the existence of just the sesquitelluride, Si_2Te_3 , in (silicon + tellurium). This compound can be nonstoichiometric; the range of x in $\text{Si}_2\text{Te}_{3-x}$ has been given as 0.07, or even larger by some authors.

Calorimetric grade Si_2Te_3 was synthesized from a mixture of high-purity Si and Te, with $n(\text{Te})/n(\text{Si}) = 1.5$, and the product was purified by vapor transport. Because of the likelihood of nonstoichiometry, analyses of the sample were performed for Si, Te, O, and trace metals. The volatility of Si_2Te_3 at high temperatures precluded analyses for trace C, H and N. Since those elements were present to a negligible extent in the original Si and Te, it was assumed that they could safely be ignored in the telluride product. In summary, the analyses gave $n(\text{Te})/n(\text{Si}) = (1.503 \pm 0.007)$; thus, the sample was taken to have the exact Si_2Te_3 composition.

Fluorination of Si_2Te_3 in the calorimeter proceeds as follows:



The molar enthalpy change of reaction [13], combined with values of $\Delta_f H_m^\circ$ for SiF_4 and TeF_6 yields $\Delta_f H_m^\circ(\text{Si}_2\text{Te}_3, \text{cr}, 298.15 \text{ K}) = -(71 \pm 6) \text{ kJ/mol}$ [7]. This result is in reasonable accord with those deduced from Knudsen-effusion, mass-spectrometric studies, $-(89 \pm 19) \text{ kJ/mol}$, and decomposition pressures measured as a function of T by means of observations of optical density, $-(72 \pm 5) \text{ kJ/mol}$.

Silicides of group 6 metals

New values of the standard molar enthalpies of formation of the molybdenum and tungsten silicides have been determined recently. According to the phase diagrams, molybdenum has three silicides of intermediate composition: MoSi_2 , Mo_3Si , and Mo_5Si_3 . Tungsten has but two: WSi_2 and W_5Si_3 . Although the existence of W_3Si has been postulated, it has not been isolated. All five compounds have ranges of composition. Their reactions with F_2 have been studied by bomb calorimetry, on the basis of which the enthalpy of formation values collected together in Table 1 have been determined.

Table 1 Standard molar enthalpies of formation of molybdenum and tungsten silicides ($p^\circ = 0.1 \text{ MPa}$, $T = 298.15 \text{ K}$)

	$\Delta_f H / (\text{kJ/mol})$	Ref.
$\text{MoSi}_{2.067}$	$-(140.5 \pm 4.2)$	[17]
Mo_3Si	$-(125.2 \pm 5.8)$	[18]
Mo_5Si_3	$-(314.3 \pm 8.3)$	[19]
$\text{WSi}_{2.060}$	$-(80.4 \pm 4.7)$	[20]
W_5Si_3	$-(126 \pm 18)$	[21]

Silicon nitride (Si₃N₄)

Silicon nitride is one of the preeminent engineering materials of the present day. Because of its stability, especially at operational extremes, it is being used, for example, in automobile engines, gas turbines, thin film technology, as a high-temperature lubricant, and in coatings and fuel cells. Although many physical and chemical characteristics of this material are well known, its thermodynamic properties are by no means well established. A recent critical survey by Gurvich *et al.* [22] lists values of $\Delta_f H_m^\circ$ that range from $-(621 \pm 80)$ kJ/mol to $-(842 \pm 3)$ kJ/mol. There is also much interest in the enthalpy difference between the α - and β -modifications of Si₃N₄; estimates range all the way from 30 kJ/mol to negligible.

We have recently described [23] a fluorine bomb investigation of well-characterized specimens of the α - and β -forms of the nitride. The combustion reaction in the calorimeter is straightforward:



This reaction does not take place spontaneously, but a few mg of powdered rhombohedral sulfur added to the Si₃N₄ is a convenient fuse (the spontaneous reaction of S with F₂ to form SF₆ is sufficient to cause ignition). Examination of the reaction products by F.t.i.r. showed only SiF₄, SF₆, and, in high-pressure scans, CF₄ from the carbon impurity. As with other nitrides, no NF₃ was detected.

The following results at $T = 298.15$ K have been reported in a brief communication [23]: $\Delta_f H_m^\circ$ (Si₃N₄, α) = $-(828.9 \pm 3.4)$ kJ/mol and $\Delta_f H_m^\circ$ (Si₃N₄, β) = $-(827.8 \pm 2.5)$ kJ/mol. These values agree with some deduced from earlier high-temperature studies. They also indicate that the enthalpy difference between the α - and β -modifications is small.

Vanadium disilicide

Because of their importance in the electronics industry, the vanadium silicides have been studied by a number of authors. In his recent review, Schlesinger [24] listed four determinations of $\Delta_f H_m^\circ$ (VSi₂) at $T = 298.15$ K with results that lie between -314 kJ/mol and -112 kJ/mol, and he recommended -120.6 kJ/mol as the most probable. Since fluorine bomb calorimetry has been successful in studies of inorganic silicides, we recently embarked on a systematic study of three of them, namely, VSi₂, V₃Si, and V₅Si₃. Here we report our findings for VSi₂.

All the vanadium silicides are attacked by F₂; thus, a two-compartment bomb-and-tank apparatus was required for this work. In trial experiments, we were unable to force VSi₂ to react to completion; accordingly, tungsten foil was used as an auxiliary 'fuel' as a means to approach that objective. Nevertheless, small quantities of VF₃ were always formed. It is clear, on the basis of the present and earlier investigations, that compounds of vanadium, in reacting with F₂ seem, inevitably, to form a little VF₃ in addition to VF₅.

The calorimetric reaction proceeded as follows:



Corrections were applied for the hypothetical fluorination of VF₃ to VF₅ [25].

The result for $\Delta_f H_m^\circ$ (VSi₂), $-(135 \pm 2)$ kJ/mol, is in fair agreement with two determinations from combustion calorimetry, but disagrees significantly with values from studies of high-temperature phase-equilibria, e.m.f. measurements, and high-temperature solution calorimetry. Sources of the disagreement have not yet been found.

REFERENCES

- 1 S. Bose, R. J. Hecht, *J. Mater. Sci.* **27**, 2749 (1992).
- 2 S. P. Murarka. *Silicides for VLSI Applications*. Academic Press, New York (1983).
- 3 S. P. Murarka, M. C. Peckerar. *Electronic Materials, Science and Technology*. Academic Press, New York (1989).
- 4 P. E. D. Morgan, E. A. Pugar, *J. Am. Ceram. Soc.* **68**, 699 (1985).
- 5 S. W. Martin, H. K. Patel, F. Borsa, D. Torgeson. *Solid State Ionics* **53-56**, 1141 (1992).
- 6 R. L. Nuttall, S. Wise, W. N. Hubbard. *Rev. Sci. Instrum.* **32**, 1402 (1961).

- 7 P. A. G. O'Hare, G. A. Hope, C. M. Beck III. *J. Chem. Thermodyn.* **25**, 919 (1993).
- 8 W. N. Hubbard. *Experimental Thermochemistry* (H. A. Skinner, ed.) Vol. II. Interscience Publishers, New York (1962).
- 9 V. Ya. Leonidov, V. A. Medvedev. *Ftornaya Kalorimetriya*. Izd. Nauka, Moscow (1978).
- 10 W. N. Hubbard, G. K. Johnson, V. Ya. Leonidov. *Experimental Chemical Thermodynamics*, Vol. 1: *Combustion Calorimetry* (S. Sunner, M. Månsson, eds) Pergamon Press, New York (1979).
- 11 V. Ya. Leonidov, P. A. G. O'Hare. *Pure Appl. Chem.* **64**, 103 (1992).
- 12 I. Tomaszkiwicz, S. Susman, K. J. Volin, P. A. G. O'Hare, *J. Chem. Thermodyn.* **26**, 1081 (1994).
- 13 J. Vennik, R. Callaerts. *C. R. Séances Acad. Sci.* **260**, 496 (1965).
- 14 G. K. Johnson, I. R. Tasker, D. A. Howell, J. V. Smith, *J. Chem. Thermodyn.* **19**, 617 (1987).
- 15 I. Tomaszkiwicz, G. A. Hope, P. A. G. O'Hare, *J. Chem. Thermodyn.* **29**, 1031 (1997).
- 16 I. Tomaszkiwicz, S. Susman, K. J. Volin, P. A. G. O'Hare, *J. Chem. Thermodyn.* **26**, 1081 (1994).
- 17 P. A. G. O'Hare, *J. Chem. Thermodyn.* **25**, 1333 (1993).
- 18 I. Tomaszkiwicz, G. A. Hope, C. M. Beck III, P. A. G. O'Hare. *J. Chem. Thermodyn.* **28**, 29 (1996).
- 19 I. Tomaszkiwicz, G. A. Hope, C. M. Beck III, P. A. G. O'Hare. *J. Chem. Thermodyn.* **29**, 87 (1997).
- 20 P. A. G. O'Hare, *J. Chem. Thermodyn.* **24**, 1323 (1992).
- 21 I. Tomaszkiwicz, G. A. Hope, C. M. Beck III, P. A. G. O'Hare. *J. Chem. Thermodyn.* **27**, 585 (1995).
- 22 L. V. Gurvich, I. V. Veyts, C. B. Alcock. *Thermodynamic Properties of Individual Substances*, Vol. 2. Hemisphere Publishing, New York (1991).
- 23 P. A. G. O'Hare, I. Tomaszkiwicz, H. J. Seifert. *J. Mater. Res.* **12**, 3203 (1997).
- 24 M. E. Schlesinger. *Chem. Rev.* **90**, 607 (1990).
- 25 G. K. Johnson. Argonne National Laboratory, unpublished results.