Enthalpies of Formation of Solid Silicon Dichalcogenides

M.S. Chandrasekharaiah[a] **and John L. Margrave**
Houston Advanced Research Center, Materials Science Research, The Woodlands, Texas 77381

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A critical review of the published thermodynamic data for solid SiS_2, $SiSe_2$ and Si_2Te_3 has been made. The most probable values for the enthalpies of formation of these three phases at 298.15 K have been evaluated and an estimate of the uncertainties is made.

Key words: dichalcogenides; enthalpy of formation; silicon; thermodynamic properties.

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1. Introduction

Among the three binary systems considered in this report, namely Si-S, Si-Se, and Si-Te, experimental data for the equilibrium phase diagram have been reported only for the Si-Te system.[1] The ditelluride phase ($SiTe_2$) is not an intermediate phase of this system. The only solid phase present in the equilibrium diagram is Si_2Te_3. On the other hand, both the SiS_2 and the $SiSe_2$ solids have been well characterized.[2–8] In this assessment, the presently available data are reviewed and the enthalpies of formation for the SiS_2(cr), $SiSe_2$(cr) and Si_2Te_3(cr) phases are critically evaluated.

The accuracy of any derived thermodynamic datum depends not only on the accuracy of the experimental values but also on the accuracy of the auxiliary data that are used in the calculation. In evaluating the formation enthalpies for these three compounds, the thermal functions for the four elements (Si, S, Se and Te) and the corresponding compounds form the important auxiliary data. A survey of the literature shows less than satisfactory agreement in these auxiliary data.

Sources of thermal functions for the elements are summarized in Table 1a. The NBS Tables[12], Glushko, Medvedev *et al.*[10a], and Hultgren *et al.*[9] give the thermal functions for all four elements, although only the Hultgren publication gives temperature dependent values. The JANAF Tables[11], Glushko, Gurvich *et al.*[10b], and Gurvich[13] gave values for silicon and sulfur only. Mills[2] and Gronvold *et al.*[19] presented recommended data for S, Se, and Te. Mills[2] used data for Si recommended by Hultgren[9].

Sources of thermal functions for the compounds are summarized in Table 1b. Only Mills[2] gave tabulations for the three compounds of interest here (SiS_2, $SiSe_2$, Si_2Te_3).

Table 2 lists the reported entropies of the elements; Tables 3a and 3b list the reported enthalpies of formation at 298.15 K for the gaseous elements and the pertinent compounds, respectively. It is difficult to decide which values of the auxiliary data are the most accurate. The scatter in recommended values of the enthalpies of formation of the compounds demonstrated in Table 3b is in large part due to the differences in elemental thermodynamic data from different sources, as shown in Tables 2 and 3a. In many cases, tabulations of auxiliary data do not give complete information on the source and evaluation of the data, and data from different sources are conflicting. In the Hultgren *et al.*[9] tabulation for all four elements, all sources of data are documented in complete detail, accuracy estimates are made and explained, and the data treatment is fully described. For these reasons, we have selected the thermal functions for the elements tabulated by Hultgren *et al.*[9] and the enthalpy values recommended here are based on that set of data. (Differences in the analysis due to the use of different values for the thermal functions are indicated wherever possible.)

2. The Enthalpy of formation of Si_2Te_3(cr)

The equilibrium phase diagram of the Si-Te system was studied in detail by Bailey[14] using thermal analysis and metallography. According to him, the Si_2Te_3 phase is formed by a peritectic reaction at 1165 ± 3 K and it is the only solid phase in this binary system. The works of Bailey[14], Exsteen *et al.*[15],

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[a] Presently at Chemical Research and Licensing, Pasadena, Texas.

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TABLE 1a. Sources of thermal functions with year of publication

Reference (Pub. Date)	Elements Si	 S	 Se	 Te
NBS Tables[12](1982)[a]	1965	1964	1964	1964
Glushko,Medvedev[10a](1966,1970)[a]	1970	1966	1966	1966
Hultgren[9](1973)	1965	1972	1972	1964
Mills[2] (1974)		1974	1974	1974
JANAF Tables[11](1985)	1967	1977		
Glushko,Gurvich[10b](1979)	1979[b]	1978[b]		
Gronvold *et al.*[19](1984)		1984	1984	1984
Gurvich[13](1989,1991)	1991[b]	1989[b]		

[a]Values given only at 298.15 K.

[b]In references 10 and 13, there is no difference between values for silicon. Either no reevaluation was made or no change in recommended values was made. For sulfur, values in the two publications were different.

TABLE 1b. Sources of thermal functions with year of publication

			COMPOUNDS							
Reference (Pub. Date)	SiS(cr)	SiS(g)	SiS_2(cr)	SiS_2(g)	SiSe(g)	$SiSe_2$(cr)	$SiSe_2$(g)	SiTe(g)	$SiTe_2$(g)	Si_2Te_3(cr)
NBS Tables[12](1982)[a]		1965	1965		1965	1965		1965		
Glushko,Medvedev[10a],[a](1970)		1970	1970		1970	1970	1970			
Mills[2](1974)	1974	1974	1974	1974	1974	1974	1974	1974	1974	1974
JANAF Tables[11](1985)		1971	1972							
Glushko,Gurvich[10b](1979)	1979	1979	1979	1979						
Gurvich[13](1991)	1991	1991	1991	1991						

TABLE 2. Reported entropies of the elements at 298.15 K[$J \cdot K^{-1} \cdot mol^{-1}$] and 1 bar

Reference (Pub. Date)	Si(cr)	S(cr)	S_2(g)	Se(cr)	Se_2(g)	Te(cr)	Te_2(g)
Glushko,Medvedev (1966,70)[10a]	18.83	31.92	228.14	42.13	252.07	49.50	268.18
Hultgren[9](1973)	18.83	31.8	228.18	41.97	249.37	49.50	268.3
Mills[2](1974)		31.88	228.14	42.26	243.62	49.50	258.97
Glushko,Gurvich[10b](1979)	18.810	32.054	228.164				
NBS Tables[12](1982)	18.83	31.80	228.18	42.442	252.0	49.71	268.14
Gronvold *et al.*[19](1984)		32.054	228.070	42.270	247.274	49.221	258.822
JANAF Tables[11](1985)	18.82	32.056	228.165				
Gurvich[13](1989,1991)	18.810	32.070	228.164				

Brebrick[16], and Davey and Baker[17] all confirm the presence of this phase with a narrow compositional homogeneity ($0.5945 \leq x_{Te} \leq 0.6050$) as the only solid phase of silicon and tellurium. O'Hare and coworkers have recently reported a measured value of $\Delta_f H°(Si_2Te_3,cr,298.15\ K)$ of $-(71 \pm 6)$ $kJ \cdot mol^{-1}$.[40] There are no additional reports on the binary phase diagram of Si-Te since the recent review by O'Hare[18].

The binary equilibrium diagram of Si-Te given by Massalski[1] is accepted. Si_2Te_3 is the only solid phase in this system. According to Ploog *et al.*,[20] this phase crystallizes in the trigonal space group P3lc with the lattice parameters a = 0.7430 nm, c = 1.3482 nm, and Z = 4. The two terminal solid solutions are almost pure silicon and tellurium. The red crystalline platelets that Weiss and Weiss[21] and Rau and Kannewurf[22] considered as solid $SiTe_2$ were probably mixtures of Si_2Te_3 and an amorphous eutectic phase. Ploog *et al.*[20] reported (without supporting data) that Si_2Te_3 melted congruently at 1162 K. Davey and Baker[17] were unable to confirm this observation. The uncertainties in temperatures are assigned by the present authors.

Polycrystalline, single-phase Si_2Te_3 can be prepared by heating the appropriate mixture of elemental silicon and tellurium in an evacuated silica ampoule to 1273 K. The resultant sample is then quenched and annealed below 1164 K for several hours. Large, single-crystal red platelets can be prepared by the vapor transport reaction of silicon and tellurium in a temperature gradient furnace[15,16]. Temperatures range from 1173 K at the silicon-rich side to 973 K at the tellurium-rich side. When heated, Si_2Te_3 decomposes rapidly to Si(cr), Te_2(g), and SiTe(g). It is unlikely that $SiTe_2$(g) is an equi-

TABLE 3a. Reported enthalpies of formation at 298.15 K(kJ·mol^{-1})

Reference (Pub. Date)	Si(g)	S(g)	S_2(g)	Se(g)	Se_2(g)	Te(g)	Te_2(g)
NBS Tables[12](1982)	455.6	278.805	128.37	227.07	146.0	196.73	168.2
Glushko,Medvedev (1966,70)[10a]	452.0	272.9	127.5				
Hultgren[9](1973)	455.6		129.03			196.271	168.36
Mills[2](1974)		279.1	128.7	235.4	139.3	211.7	160.4
JANAF Tables[11](1985)	450	276.98	128.6				
Glushko,Gurvich[10b](1979)	450.00	277.030	128.6				
Gronvold[19]		277.106	128.491	237.609	144.139	209.451	163.176
Gurvich[13](1989,1991)	450.0	277.180	128.6				

TABLE 3b. Reported enthalpies of formation at 298.15 K (kJ·mol^{-1})

		Compounds								
Reviews	SiS(cr)	SiS(g)	SiS_2(cr)	SiS_2(g)	SiSe(g)	$SiSe_2$(cr)	$SiSe_2$(g)	SiTe(g)	$SiTe_2$(g)	Si_2Te_3(cr)
Glushko,Medvedev[10a] (1966,70)		103.3	−207.5							
Mills[2](1974)	−160.7	116.7	−213.4	79.5	202.9	−146.4	164.4	219.7	216.3	−77.4
Glushko,Gurvich[10b] (1979)	−168.877	108.055	−287.00	7.023						
NBS Tables[12] (1982)		112.47	−207.1		99.50	−29		129.66		
JANAF Tables[11] (1985)		105.96	−213.384							
Gurvich[13] (1989,1991)	−98.629	108.205	−245.861	48.162						
Individual Evaluations										
O'Hare[18]					199	−80±42 (Third law) −84±48 (Second law)				−80±15
Chandrasekharaiah			−235	30		−208±41				−65±10

librium species. Exsteen *et al.*[15] reported an ion of this mass, but Bailey[14] failed to observe this species in his mass spectrometric study.

Mills[2] recommended $\Delta_f H°(Si_2Te_3,cr,298.15\ K) = -77.4 \pm 20.9$ kJ·mol^{-1}. He deduced this value from the dissociation pressure measurements by Exsteen *et al.*[15] and Brebrick[16], coupled with the thermal functions then available[2]. O'Hare[18] reevaluated $\Delta_f H°(Si_2Te_3,cr,298.15\ K)$ using the same two experimental sources and the thermal functions listed in Table 4. O'Hare[18] calculated both third law and second law derivations. His results are summarized in Table 4. He concluded that the true value probably lies in the vicinity of −80±15 kJ·mol^{-1}.

The present evaluation uses the measured values of both Exsteen *et al.*[15] and Brebrick[16] to derive the enthalpy of formation of the Si_2Te_3 phase. Exsteen *et al.*[15] derived the following expression for the partial pressure of Te_2(g) in equilibrium with a mixture of Si_2Te_3(cr) and Si(cr) between 775 and 950 K based on their Knudsen cell mass spectrometric measurements:

$$\lg P_{Te2}/\text{atm} = -(11.1 \pm 0.4 \times 10^3\ (K/T) + (7.9 \pm 0.5). \quad (1)$$

The experimentally measured pressure data were not reported. Hence, for the reaction:

$$Si_2Te_3(cr) = 2\ Si(cr) + 3/2\ Te_2(g) \quad (2)$$

the Gibbs energy change is given by $\Delta_r G°/\text{kJ·mol}^{-1} = 318.8 - 0.227\ T/K$ and the enthalpy change (at the mean temperature of 854 K) is 318.8 ± 11.5 kJ·mol^{-1}. Using the thermal functions listed in Table 4 (under "this work"), the enthalpy of formation of Si_2Te_3(cr) based on the different measurements is calculated according to both second and third law methods. The results are given in Table 4.

Brebrick[16] used optical density measurements between 875 and 1165 K to measure the partial pressures of Te_2(g) for reaction (1) and obtained:

$$\text{Log}\ P_{Te2}/\text{atm} = -10152(K/T) + 7.5634. \quad (3)$$

The corresponding values for the Gibbs energy change of reaction (1) $\Delta_r G° = 291.6 - 0.2172(T/K)$ kJ·mol^{-1}. Combining this result with the thermal functions listed in Table 4 (under "this work") and applying both second and third law methods, the resulting calculated values of the enthalpy of formation are given in Table 4. The table shows that these values are about 12–15 kJ·mol^{-1} smaller than the corresponding values calculated by O'Hare using different thermal functions.

Generally the $\Delta_f H°(298.15\ K)$ values evaluated by the third law procedure are considered more reliable than those calculated using the second law method. However, this assumption is true only if the necessary thermal functions for all the

TABLE 4. Evaluations of enthalpy of formation of Si_2Te_3 (cr): $\Delta_fH°(Si_2Te_3,cr,298.15\ K)$ (kJ·mol^{-1})

Evaluation	O'Hare[18]		This work	
	Thermal functions used:		Thermal functions used:	
	Si(cr)	Glushko,Gurvich [10b]	Si(cr)	Hultgren[9]
	Te_2(g)	Gronvold[19]	Te_2(g)	Hultgren[9]
	Si_2Te_3(cr)	Mills[2]	Si_2Te_3(cr)	Mills[2]
Experimental source:	Brebrick[16]	Exsteen[15]	Brebrick[16]	Exsteen[15]
Third Law	−71 ± 10	−89 ± 17	−57 ± 10	−80 ± 10
Second Law	−69 ± 10	−93 ±	−65 ± 10	−86 ± 10
Recommended value:	−80 ± 15	−65 ± 10		

species are known accurately and experimental equilibrium constant values are available. No experimentally obtained individual equilibrium data were reported for either the measurements of Exsteen and coworkers[15] or those of Brebrick[16]. Only least-squares-analyzed expressions for the partial pressures of Te_2(g) are given. Under these circumstances, the enthalpy values derived by the second law method are as reliable as those based on the third law.

Of the two investigations, the measurements of Exsteen *et al.*[15] extended over only a 175 K temperature interval, while those of Brebrick[16] spanned nearly 300 K. In addition, no details about the handling of the hygroscopic Si_2Te_3(cr) sample were given by Exsteen *et al*[15]. Brebrick[16] not only used a dry box for all sample handling but also kept the silica tube containing the sample free from any residual moisture. In contrast, Exsteen *et al.*[15] used the ion current integration method to convert the measured ion currents to partial pressures. When there is more than one vapor species effusing from the orifice, this method of calibration has serious limitations. Hence the Knudsen mass spectrometric data will give less reliable pressure information. Furthermore, Brebrick[16] measured the equilibrium pressures of Te_2(g) over liquid tellurium using the same apparatus and calibrated his optical density conversion to pressure using the vapor pressure of pure liquid tellurium. His results are in excellent agreement with the corresponding values assessed by Hultgren, *et al.*[9] Therefore, in our opinion the partial pressure of Te_2 obtained by Brebrick[16] should be given greater weight. Thus, $\Delta_fH°(Si_2Te_3,cr,298.15\ K) = -65\pm10$ kJ·mol^{-1} is recommended. This value is in good agreement with the recent measurements of O'Hare *et al.*[40]

3. Enthalpy of Formation of $SiSe_2$(cr)

Silicon diselenide can be prepared directly by heating a mixture of silicon and selenium in an inert gas atmosphere. Hillel and Cueilleron[3] also prepared it by heating a mixture of silica and boron selenide to 1173 K. $SiSe_2$ crystallizes in an orthorhombic habit with the space group Ibam and has the lattice parameters $a = 0.968\pm0.001$ nm, $b = 0.6003\pm0.0019$ nm, and $c = 0.581\pm0.001$nm.[23] No detailed phase diagram work has been reported. Hansen and Anderko[24] indicate the possible existence of SiSe(cr).

The solution calorimetric measurements by Gabriel and Alvarez-Tostado[4] are the only calorimetric studies available at present. Mills[2] recalculated the enthalpy of formation of $SiSe_2$ from their data using values current in 1974 for the enthalpy of formation of SiO_2(cr) and obtained: $\Delta_fH°(SiSe_2,cr,298.15\ K) = -63\pm63$ kJ·mol^{-1}. Mills recommended, however, an estimated value of -143 ± 41 kJ·mol^{-1} for this enthalpy without giving any reason for his choice.

Emons and Theisen[25] reported the only other related measurement. They measured the total weight loss of the Knudsen effusion cell containing a mixture of $SiSe_2$(cr) and Si(cr). Assuming that all the observed weight loss was due to the effusion of the SiSe(g) species only, they derived the pressure values of SiSe(g) for the reaction:

$$1/2\ Si(cr)+1/2\ SiSe_2(cr) = SiSe(g). \tag{4}$$

No individual pressure data, but rather a least-squares-fitted expression for the partial pressure of SiSe(g), were given. From this, the Gibbs energy change for reaction (4) for the temperature range of $870 \leq T/K \leq 1076$ was calculated as: $\Delta_rG°/\ kJ\cdot mol^{-1} = 234.2-0.167T/K$.

In the absence of thermal functions for the solid silicon diselenide, O'Hare[18] assumed them to be similar to those of SiS_2(cr) at 1000 K and calculated a value of $\Delta_rH° = 239\pm10$ kJ·mol^{-1} for reaction (4) at 298.15 K. Combining this value with the estimated value of $\Delta_fH°(SiSe,g,298.15\ K) = 199\pm25$ kJ·mol^{-1} and using third law methods, he calculated $\Delta_fH°(SiSe_2,cr,298.15\ K) = -80\pm42$ kJ·mol^{-1}. (See Table 5.) Since O'Hare's review there have been no additional definitive experimental studies that could justify modification of the enthalpy value, and therefore only a few relevant comments can be made regarding the accuracy of the enthalpy of formation of $SiSe_2$(cr).

The pressure values of SiSe(g) obtained by Emons and Theisen[25] have significant uncertainties because of the nature of the experimental procedure. The equilibrium vapor composition was assumed to be solely SiSe(g) without any mass spectrometric or other evidence. The more serious limitation is their assumption of a cosine distribution of the effusing species. The works of Grimley *et al.*[26] and Ward *et al.*[27] demonstrated the fallacy of this assumption, especially for the total weight loss method. These factors introduce a rather indeterminate uncertainty in their pressure values and hence in the calculated enthalpy data.

Mills[2] lists three reports for the dissociation energies of SiSe(g). Two of them are spectroscopic data[28,29] and the other

TABLE 5. Evaluations of enthalpy of formation of $SiSe_2$(cr): $-\Delta_f H°(SiSe_2,cr,298.15\ K)$ (kJ·mol^{-1})

Evaluations	O'Hare[18]		This work		
	Thermal functions used:		Thermal functions used:		
	SiSe(g)	Mills[2]	Hultgren[9]	NBS Tables[12]	Se Gronvold[19]
	Se(g)	Gronvold[19]			Si JANAF[11]
$\Delta_f H°$(SiSe,g,298.15 K)	199 ± 21		135 ± 27	156 ± 27	
$\Delta_f H°(SiSe_2$,cr,298.15 K)					
Third Law	80 ± 42			208 ± 41	166 ± 38
157 ± 13					
Second Law	86 ± 48				

Both evaluations used the experimental measurements of Emons and Thiesen[25] and assumed for the reaction: 1/2 $SiSe_2$(cr) + 1/2 Si(cr) = SiSe(g), $\Delta_r H° = 239 \pm 10$ kJ·mol^{-1} [18]

is the value derived from the Knudsen effusion mass spectrometric measurement of the reaction[30]:

$$1/2\ Te_2(g) + SiSe(g) = 1/2\ Se_2(g) + SiTe(g) \qquad (5)$$

Mills selected a value derived from the mass spectrometric measurements of the equilibrium constant for reaction (5) of $D°$(SiSe,g,298.15 K) = 488 ± 25 kJ·mol^{-1}, but gave no reason for this choice. We feel that this choice of the dissociation energy of SiSe is an inferior one.

The accuracy of the equilibrium constants for reaction (5) deduced from the mass spectrometric data depends not only on the accuracy of simultaneously measured parameters such as the ion currents of all species, the temperature and the temperature uniformity, but also on the accuracy of estimating the ionization cross-sections and the multiplier gains for all species. The latter are species dependent and cannot be corrected through any calibration. These quantities are estimated, at best, to a factor of two accuracy. Further, the evaluation of the dissociation of SiSe(g) from the measured equilibrium constants involves the enthalpies of formation of all the other three species in equation (5). Thus the uncertainty in the dissociation energy of SiSe(g) obtained from the mass spectroscopic data will be large and difficult to estimate accurately. In addition, no actual experimentally determined data were given, but only the calculated value for the dissociation energy. Thus the dissociation energy of SiSe(g) calculated from the mass spectrometric data is less reliable than the corresponding value obtained from the spectroscopic measurements. The two spectroscopic data listed in references 28 and 29 are in excellent agreement and should be preferred.

From the two spectroscopic data sources for the dissociation energy of SiSe(g)[28,29], we estimate a value of $D°$(SiSe,g,298.15 K) = 527±25 kJ·mol^{-1}. We assume O'Hare's value for the enthalpy of the reaction (4) to be preferred; i.e., $\Delta_r H° = 239 \pm 10$ kJ·mol^{-1}. Combining these values with thermal functions from different sources listed in Table 5, the resulting values of $\Delta_f H°$(SiSe,g,298.15 K) are derived and listed. The values of the enthalpy of formation of $SiSe_2$(cr) are calculated in each case and all values are compared in Table 5. For consistency, the value calculated using the enthalpy values of Hultgren *et al.*[9] is recommended here: $\Delta_f H°(SiSe_2,cr,298.15\ K) = -208 \pm 41$ kJ·mol^{-1}.

The recommended value is significantly different from those calculated by either O'Hare or Mills. This may be primarily due to the difference in selected values for the SiSe(g) dissociation energy. Another important contribution may be the difference in the values of the thermal functions used.

4. Enthalpy of Formation of SiS_2(cr)

The equilibrium diagram for the Si-S system has not been investigated in detail. Two solid phases, namely SiS and SiS_2, have been prepared and some of their properties have been reported.[17,19-23] Both Mills and Gurvich include values of the enthalpy of formation of SiS(cr), but it is not clear that SiS(cr) is an equilibrium phase at ambient temperature. Most of the reported preparations of SiS(cr) refer to the amorphous phase. Two crystalline forms of SiS_2 have been reported. The orthorhombic phase (oI12;space group Ibam) has the lattice parameters a = 0.9583 nm, b = 0.5614 nm, and c = 0.5547 nm[23]. The GeS_2-type tetragonal phase (tI12,space group I42d) has the lattice parameters a = 0.5420 nm, and c = 0.8718 nm[23]. No information about the phase transition between them has been reported. The melting temperature of SiS_2(cr) was reported as 1363 ± 50 K by Tiede and Thimann[31].

The disulfide is prepared directly by heating an appropriate mixture of the two elements under an inert gas atmosphere. It has also been prepared by heating a mixture of aluminum sulfide and silica[8]. The sample, thus prepared, is purified, usually by vacuum sublimation at 1375 K. The monosulfide is prepared by heating the SiS_2 with excess silicon and then quenching the vapors of SiS. The resultant product is amorphous to x-ray diffraction examination. The yellow form is probably the pure SiS while the other forms (red and black), are probably SiS with varying amounts of SiS_2 and Si[5]. These silicon sulfides are rather hygroscopic.

Although this paper is concerned primarily with solid silicon disulfide, a brief discussion of the enthalpy of formation of SiS(g) is necessary in order to examine critically the enthalpy of formation data of SiS_2(cr). Mills[2] recommended a value of $D°$(SiS,g,0 K) = 613 ± 12.4 kJ·mol^{-1} based on his survey of the equilibrium study by Rosenquist and Tungesvik[28] and the spectroscopic analyses by Gaydon[32], Lagerquist *et al.*[29], and Robinson and Barrow[33]. Later, Huber and Hertzberg[34] selected a similar value (619.4 kJ·mol^{-1}) without assigning any uncertainty. O'Hare[18] in his critical assessment accepted the value recommended by Mills[7]. Recently, Gurvich *et al.*[13] reexamined all the available data and recommended $D°(\text{SiS,g,0 K}) = 613.7\pm2.4$ kJ·mol^{-1}. These authors considered the more detailed spectroscopic analyses by Harris *et al.*[35], and recalculated the thermal functions for the SiS(g) molecule using more refined molecular constants for the different electronic states. Their revised energy levels for the different electronic states differ from those listed in JANAF Tables[11]. They attribute the discrepancies to the difference in the energy values for the different electronic states of the molecule. The value given by Gurvich *et al.*[13] is accepted in this evaluation.

To calculate the enthalpy change for reaction (6) at 298.15 K,

$$\text{SiS(g)} = \text{Si(g)}+\text{S(g)} \qquad (6)$$

we combine $D°(\text{SiS,g,0})$ with $[H°(298.15)-H°(0)]$ for SiS(g) from Gurvich *et al.*[13]. Using elemental thermal functions from the NBS tables[12], we calculate $\Delta_rH° = 618.98 \pm 2.6$ kJ·mol^{-1}. Using values given in the JANAF tables[11], we obtain $\Delta_fH°(\text{SiS,g,298.15 K}) = 108\pm8.4$ kJ·mol^{-1}. Comparatively, the corresponding value given in the JANAF tables is 106 ± 12.6 kJ·mol^{-1}.

Berezovskii *et al.*[36] measured the heat capacity of orthorhombic SiS_2(cr) from 5.4 to 305 K with an adiabatic calorimeter. The accuracy of the measurement was estimated to be 0.2–0.3% at $T > 20$ K and about 1% at $T < 20$ K. $S°(\text{SiS}_2\text{,cr,298.15 K}) = 76.86\pm0.25$ J·K^{-1}mol^{-1}, $H°(298.15\text{ K})-H°(0) = 11.18\pm0.04$ kJ·mol^{-1}, and $C_p°(298.15\text{ K}) = 61.63\pm0.20$ J·K^{-1}mol^{-1} are calculated from the heat capacity data.

Four evaluations report the enthalpy of formation of SiS_2(cr) [2,11,13,18]. Although all utilized the same set of calorimetric and high temperature equilibrium data, the calculated values are quite different. Table 6 summarizes these results and demonstrates the difficulty in arriving at an unambiguous evaluation for the enthalpy of formation of SiS_2.

The earliest calorimetric measurement by Sabatier[7] determined the enthalpy of the hydrolysis of SiS_2(cr), reaction (7).

$$\text{SiS}_2\text{(cr)}+2\text{H}_2\text{0(l)}=\text{SiO}_2\text{(pp.)}+2\text{H}_2\text{S(g)} \qquad (7)$$

Sabatier assumed that the SiO_2(cr) formed (product?, precipitated?) remained in fine suspension without any interaction with the solution, and that all the H_2S(g) formed left the solution phase completely. In spite of these questionable assumptions, the enthalpy of formation of SiS_2(cr) evaluated from his results is not very different from other calorimetric data (cf Table 2).

Gabriel and Alvarez-Tostado[4] reported $\Delta_rH°(298.15\text{ K}) = -193$ kJ·mol^{-1} for reaction (8).

$$\text{SiS}_2\text{(cr)}+6\text{NaOH(aq)} = \text{Na}_2\text{SiO}_3\text{(aq)} + 3\text{H}_2\text{O} + 2\text{Na}_2\text{S(aq)} \qquad (8)$$

Combining their data with the recent values for $\Delta_fH°(\text{Na}_2\text{SiO}_3\text{,aq})$, $\Delta_fH°(\text{Na}_2\text{S,aq})$, $\Delta_fH°(\text{NaOH,aq})$ and $\Delta_fH°(\text{H}_2\text{O,l})$, all at 298.15 K, results in a value of $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -(329\pm20)$ kJ·mol^{-1}. O'Hare[18] regards this value with some reservation because of their method of synthesis of the SiS_2(cr) and handling of the hygroscopic samples.

Rocquet and Ancey-Moret[8] measured calorimetrically the enthalpy changes of the following two reactions in aqueous HF (18.7 mass per cent solution).

$$\text{SiO}_2\text{(cr)}+6\text{HF(aq)} = \text{H}_2\text{SiF}_6\text{(aq)}+2\text{H}_2\text{O(l)} \qquad \Delta_rH°(298.15\text{ K}) = -136.9\text{ kJ·mol}^{-1} \qquad (9)$$

$$\text{SiS}_2\text{(cr)}+6\text{HF(aq)} = \text{H}_2\text{SiF}_6\text{(aq)}+2\text{H}_2\text{S(g)} \qquad \Delta_rH°(298.15\text{ K}) = -304.6\text{ kJ·mol}^{-1} \qquad (10)$$

The precision and accuracy of their enthalpy measurements are satisfactory, as can be verified by their enthalpy data for reaction (9). Their value is in good agreement with modern determinations. However, their sample purity seems to be unsatisfactory. The samples were probably contaminated with silica, which affected the enthalpy values of reaction (10). The sulfur contents were rather low indicating significant oxygen contamination. O'Hare[18] estimated a value of $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -213 \pm 10$ kJ·mol^{-1} from their results, using the auxiliary data from the NBS tables[12].

O'Hare[18] quotes another calorimetric measurement by Ivanova[37] of the heat of solution of SiS_2(cr) in 3 mol/kg NaOH(aq). In the absence of any details about the measurements, sample characterization, etc., O'Hare[18] stated that no reliabile estimate could be made regarding their value of $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -300$ kJ·mol^{-1}.

The most recent calorimetric study of SiS_2(cr) has been by Matskevich and Gorsh[38] who also measured the enthalpy of solution of SiS_2(cr) in NaOH(aq). According to O'Hare[18] more details were given in this study. Using their measured enthalpy of solution and other auxiliary data reported in the NBS Tables[12], O'Hare[18] calculated $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -308\pm10$ kJ·mol^{-1}. Gurvich *et al.*,[13] however, evaluated $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -287.4\pm9.6$ kJ·mol^{-1} using the same experimental data. It is difficult to explain these differences.

Drowart and Colin[30], Emons and Theisen[25], Fruehan and Turkdogan[6] and Byerley and Teo[39] reported results of their high temperature vaporization studies of SiS_2(cr).

Based on an unpublished report by Drowart and Colin[30] on the decomposition reaction:

$$\text{SiS}_2\text{(cr)} = \text{SiS(g)}+1/2\ S_2\text{(g)} \qquad (11)$$

Mills[2] quoted $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -240\pm25$ kJ·mol^{-1}. O'Hare[18] estimated a value of $\Delta_fH°(\text{SiS}_2\text{,cr,298.15 K}) = -249\pm25$ kJ·mol^{-1} from the same experimental data. No details are available to explain this discrepancy. However, the Knudsen mass spectrometric measurements of the equilibrium constants require accurate values for ionization cross sections and the multiplier factors for all the gaseous species. In addition, the calculated $\Delta_fH°(\text{SiS}_2\text{,cr})$ value depends very

TABLE 6. Enthalpy of formation of silicon disulfide $-\Delta_fH°(SiS_2,cr,298.15\ K)$ kJ·mol^{-1}

Evaluation		Mills[2]	O'Hare[18]	Gurvich[13]	JANAF[11]	Experimental reference
Method						
Heat of hydrolysis						
$SiS_2(cr)+2H_2O(l)=SiO_2(pp.)+2H_2S(g)$		219±8	200	210		7
$SiS_2(cr)+6NaOH(aq)=Na_2SiO_3(aq)+2Na_2S(aq)+3H_2O(l)$			304	329±20	268	4
Enthalpy of solution						
$SiS_2(cr)+6HF(aq)=H_2SiF_6(aq)+2H_2S$		210±13	213±10	213	213.8±13	8
Enthalpy of reaction						
$SiS_2(cr)+6NaOH(aq)=Na_2SiO_3(aq)+2Na_2S(aq)+3H_2O(l)$			308±10	287±9.6		37
Mass spectrometry						
$SiS_2(cr)+Si(cr)=2SiS(g)$		220±21	233±14	238	207.4	6
Mass spectrometry						
$SiS_2(cr)=SiS(g)+0.5\ S_2(g)$		240±25	249±25			30
Knudsen effusion, total wt. loss						
$SiS_2(cr)+Si(cr)=2SiS(g)$	Third Law	–	255±22	277±20	250.4	25
	Second Law		210±14		207.4	25
	Third Law	258±11	269±30			39
	Second Law	256±31	267±30			39

heavily on the corresponding enthalpy data for SiS(g) and $S_2(g)$.

Fruehan and Turkdogan[6] studied the reaction:

$$SiS_2(cr) + Si(cr) = 2\ SiS(g) \qquad (12)$$

with a Knudsen effusion mass spectrometer at 1000–1686K as a part of their desulfidation of steels investigation. No vapor pressure values are given, only $\Delta_rH°(1100K) = 428$ kJ·mol^{-1}. The enthalpy of formation of $SiS_2(cr)$ calculated from this information by different authors varies from −220±20 kJ·mol^{-1} to−238 kJ·mol^{-1}. Combining $\Delta_rH°(1100K) = 428$ kJ·mol^{-1} with the $\Delta_fH°(SiS,g,298.15\ K)$ = 108±8.4 kJ·mol^{-1} and using thermal functions from Gurvich *et al.*[13], one obtains $\Delta_fH°(SiS_2,cr,298.15\ K) = -233\pm14$ kJ·mol^{-1}.

At 1150 K, Fruehan and Turkdogan[6] observed SiS^+ as the principal vapor species with about 1 percent of S_2^+ and about 0.1 percent of SiS_2^+. From the limited experimental data presented, it is difficult to decide whether these authors achieved true Knudsen effusion equilibrium conditions in their partial pressure measurement, because the plot of $\ln(I^+_{SiS}T)$ against $1/T$ for SiS^+ (Fig. 10, Ref. 6) shows a definite trend with the orifice size. For example, at 1075K, *IT* for the cell with an orifice of 0.05 cm is nearly five times smaller than the corresponding value for the cell with an orifice of 0.025 cm. The reaction enthalpy value they report is more likely to be the reaction enthalpy of activation than the true change in the enthalpy.

Emons and Theisen[25] also studied the vaporization of a mixture of solid silicon and solid silicon disulfide from 894 K to 1076 K. They used the total mass loss of a silica Knudsen effusion cell as a method of obtaining the partial pressure of SiS(g) in equilibrium. The mass spectrometric results of Fruehan and Turkdogan[6] supported their assumption that all the mass loss was due to the effusion of SiS(g), but they had to assume a cosine distribution of the effusing vapors. It has been established that even for an ideal, knife-edge orifice, this condition is seldom obeyed. The effect of their assumption on the measured partial pressures and hence the enthalpy change is difficult to evaluate. No individual pressures or the weight losses were given. Only an expression for the pressure of SiS as a function of temperature was given. From their expression for the pressure, the following equation is derived for the Gibbs energy of reaction (15): $\Delta_rG/°kJ\cdot mol^{-1} = 395.2-0.2646\ T/K$ Combining this value with other auxiliary thermodynamic quantities from the JANAF tables gives : $\Delta_fH°(SiS_2,cr,298.15\ K) = -(249\pm25)\ kJ\cdot mol^{-1}$.

The Knudsen effusion measurement of reaction (12) by Byerley and Teo[39] is the other high-temperature study of interest. These authors recorded the mass loss rates of a silica Knudsen cell containing an equimolar mixture of $SiS_2(cr)$ and Si(cr) between 963 and 1161 K. Assuming all the observed mass loss of the Knudsen cell assembly was solely due to the effusion of SiS(g), they calculated the equilibrium constant of reaction (12). Using the thermal functions given by Glushko *et al.*[10], O'Hare[18] estimated $\Delta_fH°(SiS_2,cr,298.15\ K) = -(258\pm21)$ kJ·mol^{-1} from their equilibrium data. If, however, the thermal functions given in the JANAF tables[11] are used, one obtains $\Delta_fH°(SiS_2,cr,298.15\ K) = -(233\pm20)$ kJ·mol^{-1}.

The precision of the Byerley and Teo measurements[39] is good, but the accuracy of the derived data is affected by a few systematic errors. It was necessary to assume that the effusate from the orifice obeyed the cosine distribution, a condition not always obeyed even by an ideal, knife-edge orifice[27], much less by the cylindrical orifice they used. This is always an important limiting factor in determining the vapor pressures using the total mass loss procedure. Furthermore, measured mass losses were of the entire Knudsen cell, sample, and the outer container, not just of the sample. The silica cell with the sample was surrounded by a graphite cell. Even the lid with the orifice was held in place with a graphite gasket and a graphite cap. Therefore, interaction of the sulfide sample, especially the SiS(g), with the graphite to form volatile (carbon+sulfur) species was likely. Without a mass spectrometric study, the extent of this interaction is difficult to estimate. The authors reported that they did not obtain reproducible results with resublimed SiS_2(cr) and Si(cr) samples. They attributed the irreproducibility of the measurements to the "polymeric nature of the resublimed SiS_2." It is not clear why purified SiS_2(cr) should become polymeric while the thermally decomposed amorphous SiS did not produce polymeric SiS_2(cr). Finally, Byerley and Teo used a sample prepared from thermally decomposed amorphous SiS. The characterization of their sample was rather cursory. The statement that the residue after the run gave the same x-ray diffraction pattern as the starting sample does not show the phase purity of their sample. Any undecomposed, amorphous SiS(cr) would have gone undetected by x-ray diffraction and would have seriously affected the accuracy of their vapor pressure results. Further, an examination of the data in Table 1 of their paper leaves doubt as to whether the pressures were for true equilibrium. For example, at 1150 ± 3 K, they give $Kp = 100.4 \times 10^{-5}$ to 108.4×10^{-5} for a cell with orifice of 0.159 cm and $Kp = 143.2 \times 10^{-5}$ to 153.3×10^{-5} for a cell with orifice of 0.111 cm, a difference of 40 percent. With true equilibrium, such descrepancies should not be observed.

Two reports[25,39] gave $\Delta_f H°(SiS_2,cr)$ values calculated from the studies of reaction (11).

$$SiS_2(cr) = SiS(g)+1/2\ S_2(g) \qquad (11)$$

The reliability of the enthalpy changes assessed from these two investigations is not very good. Both Emons and Theisen[25] and Byerley and Teo[39] measured the mass losses of Knudsen cells containing solid SiS_2. In reaction (11), two vapors were in equilibrium but only one total mass loss was obtained. To calculate the individual partial pressures of SiS(g) and S_2(g), the exact gas phase composition at each temperature must be known. No such information was given in either of the papers. It is difficult to understand how the authors calculated the equilibrium constants and hence obtained the enthalpy of formation of SiS_2(cr). Presumably they assumed $p(SiS) = 2p(S_2)$ and $Kp = p(S_2)^{3/2}$.

As seen in Table 6, the results for $\Delta_f H°(SiS_2,cr,298.15\ K)$ exhibit a large scatter. Those from solution calorimetry vary from $-200\ kJ\cdot mol^{-1}$ to $-329\ kJ\cdot mol^{-1}$ while those from high temperature studies show a spread of -220 to $-277\ kJ\cdot mol^{-1}$. In none of the calorimetric studies have the impurity contents of the SiS_2(cr) samples been determined. Although impurity contents would affect significantly the accuracy of the calorimetric data, the major impurity would be oxygen. The effect of non-volatile impurities such as SiO_2 on vapor pressure data may be less severe. As described above, both the mass spectrometric method and the total mass loss method also suffer from severe limitations for the determination of the enthalpy data. At present, it is difficult to recommend a $\Delta_f H°(SiS_2,cr)$ value without a large deviation. Our best estimate for this quantity is $\Delta_f H°(SiS_2,cr,\ 298.15\ K) = -235 \pm 30\ kJ\cdot mol^{-1}$.

The enthalpy value given in the JANAF tables $\Delta_f H°(SiS_2,cr,298.15\ K) = -213.384 \pm 20.9\ kJ\cdot mol^{-1}$ was based on the assumption that the calorimetric results by Rocquet and Ancey-Moret[8] were accurate. As already mentioned, the probable oxygen contamination of their SiS_2 samples makes their results less reliable. The presently available calorimetric data fall into two groups, namely one around $-200\ kJ\cdot mol^{-1}$ and another around $-300\ kJ\cdot mol^{-1}$. We feel that the true value of the enthalpy of formation of SiS_2(cr) is more negative than the $-213\ kJ\cdot mol^{-1}$ given in the JANAF tables.

5. Conclusions

Si-Te system:

There is no stable solid silicon ditelluride. Si_2Te_3(cr) is the only solid phase of this system. Phase diagram studies as well as high temperature vaporization studies have confirmed the trigonal (P3lc) structure of Si_2Te_3. $\Delta_f H°(Si_2Te_3,cr,\ 298.15\ K)$ values have been calculated from the high-temperature studies of the equilibrium reaction:

$$Si_2Te_3(cr) = 2\ Si(cr)+3/2\ Te_2(g)$$

The recommended value is $\Delta_f H°(Si_2Te_3,cr,\ 298.15\ K) = -65 \pm 10\ kJ\cdot mol^{-1}$.

Si-Se system:

Silicon diselenide ($SiSe_2$) crystallizes in an orthorhombic habit with the space group Ibam and can be prepared by the direct reaction of silicon and selenium in an inert atmosphere. Emons and Theisen[25] studied the reaction:

$$1/2\ Si(cr)+1/2\ SiSe_2(cr) = SiSe(g).$$

Combining their experimental values of vapor pressures with other auxiliary thermodynamic data gives a recommended value of $\Delta_f H°(SiSe_2,cr,\ 298.15\ K) = -208 \pm 57\ kJ\cdot mol^{-1}$.

Si-S system:

Two crystalline forms of silicon disulfide have been characterized: orthorhombic and tetragonal. Tetragonal SiS_2, the high temperature form, melts congruently at 1363±50K. It can be prepared by direct combination of silicon and sulfur.

There are five solution-calorimetric studies and four high-temperature vaporization investigations reported for SiS_2(cr). The scatter in the enthalpy of formation data calculated from these sources is very large, a situation which cannot be explained with the presently available information. Our best estimate for the enthalpy of formation of silicon disulfide is $\Delta_f H°(SiS_2,cr,\ 298.15\ K) = -(235 \pm 30)\ kJ\cdot mol^{-1}$

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