Thermodynamic Properties of Gaseous Silicon Monotelluride and the Bond Dissociation Enthalpy D°_m(SiTe) at $T \to 0$

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Statistical-thermodynamic calculations have been combined with the results of high-temperature Knudsen-effusion studies of the vaporization of Si_2Te_3 to calculate the thermodynamic properties of SiTe(g) from $T \to 0$ to $T = 2000$ K. The dissociation enthalpy D°_m(SiTe, $T \to 0$) is (448 ± 8) kJ·mol^{-1}; its value is discussed vis-à-vis the other silicon monochalcogenides.

Key words: Silicon monotelluride; thermodynamic properties; enthalpy of formation; Gibbs free energy of formation; entropy; enthalpy; heat capacity; dissociation enthalpy.

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1. Introduction

For efficient technological applications of Si_2Te_3 (see Ref. 1, for example) it is desirable to understand the thermodynamics of its behavior not only at low temperatures, the topic with which our recently described measurements[1] of the standard molar enthalpy of formation $\Delta_f H^\circ_m$ at $T = 298.15$ K were mostly concerned, but also at high temperatures. According to Exsteen *et al.*,[2] vaporization of Si_2Te_3 occurs as follows (no value of x was given):

$$Si_2Te_3(cr) = (2-x)Si(cr) + \tfrac{1}{2}(3-x)Te_2(g) + x\,SiTe(g). \quad (1)$$

Thus, in addition to the well-established thermodynamic functions of Si(cr)[3] and Te_2(g),[4] the same quantities, with comparable accuracy, are also required for SiTe(g). At present, those are available only in approximate form, at just a few temperatures, computed on the basis of estimated spectroscopic constants. Thanks to a recent extensive rotational analysis by Gopal and coworkers[5] of the $A\,^1\Pi$–$X\,^1\Sigma^+$ band system of the emission spectrum of $Si^{130}Te$, the missing spectroscopic information has become available and it is now possible, by means of the well-known formulae of statistical mechanics, to calculate the thermodynamic properties of SiTe(g) as a function of temperature with the desired high level of reliability.

2. Calculations

Because Gopal *et al.*[5] determined spectroscopic constants for $Si^{130}Te$ only, their results were modified by us to refer to SiTe formed from Te of normal isotopic composition, the material encountered in everyday chemical reactions. We used the formulae given by Herzberg,[6] and first calculated the factor $\rho = \mu(Si^{130}Te) = 0.99839$, where μ denotes the reduced mass of the molecule on the basis of the molar masses of the elements: 28.0855 g·mol^{-1} for Si,[7] 127.60 g·mol^{-1} for Te of normal isotopic composition,[7] and 129.9062 g·mol^{-1} for ^{130}Te.[8] The following relations from Herzberg[6] were adopted in the present study: $\omega_e(SiTe) = \omega_e(Si^{130}Te)/\rho$; $\omega_e x_e(SiTe) = \omega_e x_e(Si^{130}Te)/\rho^2$; $B_e(SiTe) = B_e(Si^{130}Te)/\rho^2$; $\alpha_e(SiTe) = \alpha_e(Si^{130}Te)/\rho^3$; and $D_e(SiTe) = D_e(Si^{130}Te)/\rho^4$. The resulting adjusted spectroscopic constants (the Gopal *et al.* values for $Si^{130}Te$ are in parentheses) were: $\omega_e = 481.44$ cm^{-1} (480.66 cm^{-1}); $\omega_e x_e = 1.3471$ cm^{-1} (1.3428 cm^{-1}); $B_e = 0.14212$ cm^{-1} (0.141661 cm^{-1}); $\alpha_e = 0.5353 \cdot 10^{-3}$ $(0.5327 \cdot 10^{-3})$; and $D_e = 0.49 \cdot 10^{-7}$ $(0.49 \cdot 10^{-7})$. The symmetry number and the ground-state degeneracy of SiTe were each taken to be 1. Values of the physical constants are those recommended by CODATA,[9] with $R = 8.31451$ J·K^{-1}·mol^{-1}.

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3. Results

Table 1 gives the thermodynamic functions computed with the JANAF program[3] by treating SiTe(g) as an anharmonic oscillator, non-rigid rotor. A state sum program was used in which the contributions to the thermal functions of all vibration-rotation levels up to the dissociation limit ($\approx$ 37450 cm^{-1}) were included, as was done in the JANAF[3] tables for such molecules as H_2, D_2, HD, and N_2. Exploratory calculations showed that at $T \leqslant 2000$ K the effect on the results was negligible when the lowest excited state ($^1\Pi$) was included. Therefore, the quantities in Table 1 were determined solely on the basis of the ground ($^1\Sigma^+$) electronic state. Also included in the table are values of the standard molar enthalpy of formation, $\Delta_f H^\circ_m(T)$, and the standard Gibbs free energy of formation, $\Delta_f G^\circ_m(T)$. Those quantities have as their bases $\Delta_f H^\circ_m(298.15\ \mathrm{K})$, the derivation of which will be discussed in the next section. Thermodynamic functions X in columns 2 through 5 of Table 1 are believed to be uncertain by no more than $\pm 0.002\,X$, and both $\Delta_f H^\circ_m/10^3\cdot R\cdot K$ and $\Delta_f G^\circ_m/10^3\cdot R\cdot K$ are estimated to be uncertain by approximately ± 0.2.

4. Discussion

There are differences between the quantities in columns 2 to 5 of Table 1 and those reported by previous investigators, none of whom had access to detailed spectroscopic information on SiTe. Brebrick's[10] values, which he listed at five temperatures only, are quite close to ours and tend to deviate from them by approximately one per cent. This seems to be due, almost entirely, to his use of $r_e = 0.251$ nm, somewhat greater than the $r_e = 0.22697$ nm implicit in the measurements of Gopal *et al.* There is similar disagreement with the results of Kelley and King,[11] calculated on the basis of an estimated moment of inertia.

Unlike the conflicting partial pressures, $p(\mathrm{Te_2})$, reported by Exsteen *et al.*[2] and Brebrick[10] for the dissociation of Si_2Te_3 according to:

$$\mathrm{Si_2Te_3(cr) = 2Si(cr) + (3/2)Te_2(g)}, \tag{2}$$

their results for $p(\mathrm{SiTe})$ in the reaction:

$$\mathrm{Si(cr) + \tfrac{1}{2}Te_2(g) = SiTe(g)} \tag{3}$$

are in good agreement. For temperatures between 775 K and 950 K, Exsteen *et al.* gave the relation:

$$\lg[p(\mathrm{SiTe})/0.1\ \mathrm{MPa}] = -(12.1\pm0.3)\cdot10^3\cdot(\mathrm{K}/T) + (8.3\pm0.4), \tag{4}$$

and Brebrick, for $873 \leqslant (T/\mathrm{K}) \leqslant 1213$, reported:

$$\lg[p(\mathrm{SiTe})/0.1\ \mathrm{MPa}] = -12.31\cdot10^3\cdot(\mathrm{K}/T) + 8.176. \tag{5}$$

The dimensionless constant on the right-hand side of Eq. (5) has been modified by us to take into account the new thermodynamic functions for SiTe(g) and the most up-to-date values[4] for Te_2(g). Exsteen *et al.* and Brebrick did not list experimental pressures at individual temperatures. Accordingly, we have calculated the molar enthalpy change $\Delta_r H^\circ_m\langle T\rangle$ and the molar Gibbs free energy change $\Delta_r G^\circ_m\langle T\rangle$ of reaction (3) from Eqs. (4) and (5) at the mean temperature $\langle T\rangle$ of each investigation, and used the second- and third-law methods to deduce the enthalpy of the reaction at T = 298.15 K. Auxiliary thermodynamic quantities were taken from Ref. 4 for Te_2(g); from Ref. 3 for Si(cr); and from Table 1 for SiTe(g).

Results are summarized in Table 2. The mean of the four derived $\Delta_r H^\circ_m$s, weighted as the inverse of the squares of the uncertainties, is $\langle\Delta_r H^\circ_m\rangle = (124.9\pm1.6)$ $\mathrm{kJ\cdot mol^{-1}}$. At the bottom of Table 2 is a Hess cycle that leads to $D^\circ_m(\mathrm{SiTe})$, the standard molar dissociation enthalpy of SiTe($^1\Sigma^+$) at $T \rightarrow 0$, where the Si(g) and Te(g) products are each taken to be in their $^3P_2$ ground-state configurations.

In his assessment of the thermochemistry of SiTe, Mills[12] listed D°_ms that ranged from 540 $\mathrm{kJ\cdot mol^{-1}}$ to 430 $\mathrm{kJ\cdot mol^{-1}}$, the higher values from extrapolations of spectroscopic information, and the lower, which he favored, from the vaporization studies we have just analyzed. Lakshminarayana and Gopal[13] discussed $D^\circ_m(\mathrm{SiTe})$. In summary, they gave 550 $\mathrm{kJ\cdot mol^{-1}}$ (the linear Birge-Sponer extrapolation of ω_0) as the upper limit; estimated 479 $\mathrm{kJ\cdot mol^{-1}}$ by comparing $D^\circ_m(\mathrm{Si}\text{–}X)$ for X = O, S, Se, and Te; and regarded Huber and Herzberg's[14] selection of the thermochemical value of 443 $\mathrm{kJ\cdot mol^{-1}}$ as "somewhat low."

As we have seen, second- and third-law treatments of the results of studies[2,10] of the high-temperature vaporization of Si_2Te_3 yield four values of $\Delta_f H^\circ_m(\mathrm{SiTe, g, 298.15\ K})$ that are in excellent agreement. Those, in turn, lead to $D^\circ_m(\mathrm{SiTe})$ that is close to Huber and Herzberg's[14] choice. It is clear that $D^\circ_m(\mathrm{SiTe})$ from thermochemistry is now known with an accuracy of at least ±10 $\mathrm{kJ\cdot mol^{-1}}$. Any diminution of the uncertainty attached to $\Delta_f H^\circ_m(\mathrm{Si, g})$, surprisingly large at ±8 $\mathrm{kJ\cdot mol^{-1}}$,[3] will help define $D^\circ_m(\mathrm{SiTe})$ even more precisely.

In an earlier publication,[15] we observed that $D^\circ_m(\mathrm{Ge}X)$, with X = S, Se, or Te, decreased almost linearly from GeS to GeTe. A comparable trend should occur for $D^\circ_m(\mathrm{Si}X)$ because of the similarity in bonding. Gurvich *et al.*[16] selected $D^\circ_m(\mathrm{SiS}) = (613.7\pm2.4)$ $\mathrm{kJ\cdot mol^{-1}}$ on the basis of a very short extrapolation of vibrational levels of the $E\,^1\Sigma^+$ electronic state, reported[17] up to 50670 $\mathrm{cm^{-1}}$, and this value is believed to be reliable. In the case of the selenium analog, the situation is somewhat different. Mills[12] recommended $D^\circ_m(\mathrm{SiSe}) = (484\pm21)$ $\mathrm{kJ\cdot mol^{-1}}$ on the basis of thermochemical measurements and in preference to the spectroscopic value of $\approx$525 $\mathrm{kJ\cdot mol^{-1}}$ from the studies of Vago and Barrow[18] as assessed by Gaydon.[19] Subsequently, Huber and Herzberg[14] extrapolated the same vibrational levels of the $E\,^1\Sigma^+$ state and obtained $D^\circ_m(\mathrm{SiSe})$ = 544 $\mathrm{kJ\cdot mol^{-1}}$. In light of the values of $D^\circ_m(\mathrm{Ge}X)$, the spectroscopic $D^\circ_m(\mathrm{SiSe})$ appears to be more reasonable than the thermochemical result, even though it incorporates a 90 $\mathrm{kJ\cdot mol^{-1}}$ extrapolation. Knudsen-effusion studies of the high-temperature vaporization of silicon selenide to SiSe(g) could help resolve the discrepancy. It has been shown[20] that SiSe(cr) cannot be prepared, but an investigation of the high-temperature dissociation of the diselenide [$SiSe_2(cr) + Si(cr) = 2SiSe(g)$] has been reported.[21] Results from that study can be used to derive a value of $\Delta_f H^\circ_m$(SiSe, g) and, thus, D°_m(SiSe), but a reliable value of $\Delta_f H^\circ_m$($SiSe_2$, cr, 298.15 K), hitherto unavailable, is required. Preliminary measurements[22] of that quantity in progress at this laboratory are in harmony with $D^\circ_m(\mathrm{SiSe}) \approx (534 \pm 10)$ kJ·mol^{-1}, and thus tend to support the spectroscopic value. If that D°_m is corroborated, then the progression of $D^\circ_m(\mathrm{Si}X)$ for X = S, Se, Te will indeed be approximately linear, in parallel with $D^\circ_m(\mathrm{Ge}X)$.

From Table 2, we take $\Delta_r H^\circ_m(298.15\ \mathrm{K}) = (124.9 \pm 1.6)$ kJ·mol^{-1} for reaction (3) and combine it with $\frac{1}{2}\Delta_f H^\circ_m$($Te_2$, g) = (81.6 ± 0.3) kJ·mol^{-1} [4] to yield $\Delta_f H^\circ_m$(SiTe, g, 298.15 K) = (206.5 ± 1.6) kJ·mol^{-1} for:

$$\mathrm{Si(cr)} + \mathrm{Te(cr)} = \mathrm{SiTe(g)}. \qquad (6)$$

This value for the standard molar enthalpy of formation of SiTe(g) agrees within the combined uncertainties with Mills's[12] selection, (220 ± 13) kJ·mol^{-1}, but is more precise because we have taken a weighted mean for $\Delta_r H^\circ_m$ of reaction (3).

We wish to call attention to $\Delta_f H^\circ_m$ and $\Delta_f G^\circ_m$ in Table 1. Both quantities refer to reaction (3); thus, *the thermochemical reference state of tellurium is arbitrarily taken to be* Te_2*(g)* throughout the entire temperature range of the table.

TABLE 1. Thermodynamic properties of SiTe(g); R = 8.31451 J·K^{-1}·mol^{-1}, p° = 0.1 MPa, T' = 298.15 K[a]

$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{p,m}}{R}$	$\frac{\Delta^T_{T'} H^\circ_m}{10^3 \cdot R \cdot \mathrm{K}}$	$\frac{(\Delta^T_0 S^\circ_m - \Delta^T_{T'} H^\circ_m/T)}{R}$	$\frac{\Delta^T_0 S^\circ_m}{R}$	$\frac{\Delta_f H^\circ_m}{10^3 \cdot R \cdot \mathrm{K}}$	$\frac{\Delta_f G^\circ_m}{10^3 \cdot R \cdot \mathrm{K}}$
0	0	−1.119	∞	0	14.89	14.89
100	3.548	−0.769	32.822	25.135	15.03	13.89
200	3.904	−0.397	29.683	27.699	15.06	12.74
298.15	4.153	0.000	29.310	29.310	15.02	11.59
300	4.156	0.008	29.310	29.336	15.02	11.58
400	4.286	0.430	29.475	30.551	14.96	10.44
600	4.397	1.301	30.146	32.314	14.81	8.20
800	4.440	2.185	30.854	33.585	14.59	6.04
1000	4.461	3.075	31.503	34.579	14.34	3.93
1200	4.472	3.969	32.086	35.393	14.05	2.87
1400	4.480	4.864	32.609	36.083	13.75	−0.14
1600 [b]	4.485	5.761	33.081	36.682	13.43	−2.09
1800	4.488	6.658	33.511	37.210	7.08	−3.62
2000	4.490	7.556	33.905	37.683	6.81	−4.77

[a] Note that $\Delta_f H^\circ_m$ and $\Delta_f G^\circ_m$ both refer to the formation reaction: Si(cr or l) + $\frac{1}{2}Te_2(g)$ = SiTe(g), as explained in the text.

[b] There is a transition at T = 1685 K, the melting temperature of Si.

TABLE 2. Enthalpy of the reaction: $Si(cr) + \frac{1}{2}Te_2(g) = SiTe(g)$ at $T' = 298.15$ K and $p^\circ = 0.1$ MPa, and derivation of $D^\circ_m(SiTe)$

Reference	Second law $\Delta_r H^\circ_m/(kJ\cdot mol^{-1})$	Third law $\Delta_r H^\circ_m/(kJ\cdot mol^{-1})$
Exsteen *et al.*[2]	120.1 ± 3.0	127.4 ± 4.5
Brebrick[10]	124.6 ± 2.5	132.4 ± 4.0

$<\Delta_r H^\circ_m> = (124.9 \pm 1.6)\ kJ\cdot mol^{-1\,a}$

$$\begin{aligned}
SiTe(g, T') &= Si(cr, T') + \tfrac{1}{2}Te_2(g, T'), & \Delta_r H^\circ_m &= -(124.9 \pm 1.6)\ kJ\cdot mol^{-1\ a}\\
\tfrac{1}{2}Te_2(g, T') &= Te(g, T'), & \Delta_r H^\circ_m &= (127.9 \pm 0.5)\ kJ\cdot mol^{-1\ b}\\
Si(cr, T') &= Si(g, T'), & \Delta_r H^\circ_m &= (450 \pm 8)\ kJ\cdot mol^{-1\ c}\\
Te(g, T') &= Te(g, T \rightarrow 0), & \Delta_r H^\circ_m &= -(6.2 \pm 0.2)\ kJ\cdot mol^{-1\ b}\\
Si(g, T') &= Si(g, T \rightarrow 0), & \Delta_r H^\circ_m &= -(7.6 \pm 0.3)\ kJ\cdot mol^{-1\ c}\\
SiTe(g, T \rightarrow 0) &= SiTe(g, T'), & \Delta_r H^\circ_m &= (9.3 \pm 0.3)\ kJ\cdot mol^{-1\ d}\\
\hline
SiTe(g, T \rightarrow 0) &= Si(g, T \rightarrow 0) + Te(g, T \rightarrow 0), & \Delta_r H^\circ_m &= D^\circ_m(SiTe) = (448 \pm 8)\ kJ\cdot mol^{-1\ e}
\end{aligned}$$

[a] Weighted mean of the four values at the top of the table, as discussed in text.
[b] Reference 4.
[c] Reference 3.
[d] Table 1.
[e] For the dissociation of $SiTe(^1\Sigma)$ to $Si(^3P)$ and $Te(^3P)$.

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