Thermodynamic Properties of Gaseous Silicon Monotelluride and the Bond Dissociation Enthalpy $D_m^\alpha$(SiTe) at $T \rightarrow 0$

P. A. G. O'Hare

Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-0001

Received February 9, 1993; revised manuscript received August 17, 1993

Statistical-thermodynamic calculations have been combined with the results of high-temperature Knudsen-effusion studies of the vaporization of Si$_2$Te$_3$ to calculate the thermodynamic properties of SiTe(g) from $T \rightarrow 0$ to $T = 2000$ K. The dissociation enthalpy $D_m^\alpha$(SiTe, $T \rightarrow 0$) is $(448 \pm 8)$ kJ mol$^{-1}$; its value is discussed vis-à-vis the other silicon monocahnelcogenides.

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

Contents

1. Introduction .......................... 1455
2. Calculations .......................... 1455
3. Results ............................ 1456
4. Discussion ........................... 1456
5. Acknowledgments ....................... 1458
6. References .......................... 1458

List of Tables

1. Thermodynamic properties of SiTe(g) ........... 1457
2. Enthalpy of the reaction: Si(cr) + Te$_2$(g) = SiTe(g) at $T = 298.15$ K and $p^* = 0.1$ MPa, and derivation of $D_m^\alpha$(SiTe) ................... 1458

1. Introduction

For efficient technological applications of Si$_2$Te$_3$ (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 $\Delta H^\alpha_{m} \cdot T = 298.15$ K were mostly concerned, but also at high temperatures. According to Exstein et al.$^2$, vaporization of Si$_2$Te$_3$ occurs as follows (no value of $x$ was given):

\[ \text{Si}_2\text{Te}_3 \text{(cr)} = (2-x)\text{Si} \text{(cr)} + \frac{1}{2}(3-x)\text{Te}_2 \text{(g)} + x\text{SiTe(g)} \]

(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 $A^2\Sigma^+ - X^2\Sigma^+$ band system of the emission spectrum of Si$_2$Te$_3$, 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$_2$Te$_3$ 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$_2$Te$^3$) = 0.99839, where $\mu$ 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,$^8$ and 129.9062 g mol$^{-1}$ for $^{130}$Te.$^8$ The following relations from Herzberg$^6$ were adopted in the present study: $\omega_d$(SiTe) = $\omega_d$(Si$_2$Te$^3$)/$\rho$; $\omega_{xt}$(SiTe) = $\omega_{xt}$(Si$_2$Te$^3$)/$\rho$; $B_d$(SiTe) = $B_d$(Si$_2$Te$^3$)/$\rho^2$; $\alpha_d$(SiTe) = $\alpha_d$(Si$_2$Te$^3$)/$\rho$; and $D_d$(SiTe) = $D_d$(Si$_2$Te$^3$)/$\rho^2$. The resulting adjusted spectroscopic constants (the Gopal et al. values for Si$_2$Te$_3$ are in parentheses) were: $\omega_d = 481.44$ cm$^{-1}$ (480.66 cm$^{-1}$); $\omega_{xt} = 1.3471$ cm$^{-1}$ (1.3428 cm$^{-1}$); $B_d = 0.14212$ cm$^{-1}$ (0.141661 cm$^{-1}$); $\alpha_d = 0.5353$ (0.5327$^{10^{-3}}$); and $D_d = 0.49\cdot10^{-7}$ (0.49$^{10^{-7}}$). 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$^{-1}$.
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 (≈ 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 < 2000 K the effect on the results was negligible when the lowest excited state (\(^2\Pi\)) was included. Therefore, the quantities in Table 1 were determined solely on the basis of the ground (\(^2\Sigma^+\)) electronic state. Also included in the table are values of the standard molar enthalpy of formation, \(\Delta H^\circ_T\), and the standard Gibbs free energy of formation, \(\Delta G^\circ_T\). Those quantities have as their bases \(\Delta H^\circ_T\)(298.15 K), the derivations 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 ±0.002 X, and both \(\Delta H^\circ_T\) and \(\Delta G^\circ_T\) 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\(^{10}\) values, which he listed at five temperatures only, are quite close to ours and tend to deviate from them by approximately one percent. 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, \(p(Te_2)\), reported by Exesteen et al.\(^2\) and Brebrick\(^{10}\) for the dissociation of SiTe(g), according to:

\[
\text{SiTe}(cr) = 2\text{Si}(cr) + (3/2)\text{Te}_2(g),
\]

(2)

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

\[
\text{Si}(cr) + 3/2\text{Te}_2(g) = \text{SiTe}(g)
\]

(3)

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

\[
\lg[p(\text{SiTe})/0.1\text{ MPa} = -(12.1 ± 0.3)10^4(K/T) + (8.3 ± 0.4),
\]

(4)

and Brebrick, for 873 ≤ \(T/K\) ≤ 1213, reported:

\[
\lg[p(\text{SiTe})/0.1\text{ MPa} = -12.3110^4(K/T) + 8.176.
\]

(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 for Te\(_2\)(g). Exesteen et al. and Brebrick did not list experimental pressures at individual tempera-
tures. Accordingly, we have calculated the molar enthalpy change \(\Delta H^\circ_T\) and the molar Gibbs free energy change \(\Delta G^\circ_T\) of reaction (3) from Eqs. (4) and (5) at the mean temperature \(<T\>\) 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 \(\Delta H^\circ_T\), weighted as the inverse of the squares of the uncertainties, is \(<\Delta H^\circ_T> = (124.9 ± 1.6)\) kJ mol\(^{-1}\). At the bottom of Table 2 is a Hess cycle that leads to \(D^\circ_T(\text{SiTe})\), the standard molar dissociation enthalpy of SiTe(\(^2\Sigma^+\)) at \(T \to 0\), where the Si(g) and Te(g) products are each taken to be in their \(^3\)P\(_2\) ground-state configurations. In his assessment of the thermochemistry of SiTe, Mills\(^{12}\) listed \(D^\circ_T\) that ranged from 540 kJ mol\(^{-1}\) to 430 kJ 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 \(D^\circ_T(\text{SiTe})\). In summary, they gave 550 kJ mol\(^{-1}\) (the linear Birge-Sponer extrapolation of \(\omega_0\) as the upper limit; estimated 479 kJ mol\(^{-1}\) by comparing \(D^\circ_T(\text{Si}-X)\) for \(X = O, S, Se,\) and \(Te\); and regarded Huber and Herzberg's\(^{14}\) selection of the thermochemical value of 443 kJ 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 SiTe(g) yield four values of \(\Delta H^\circ_T(\text{SiTe}, g, 298.15\text{ K})\) that are in excellent agreement. Those, in turn, lead to \(D^\circ_T(\text{SiTe})\) that is close to Huber and Herzberg's\(^{14}\) choice. It is clear that \(D^\circ_T(\text{SiTe})\) from thermochemistry is now known with an accuracy of at least ±10 kJ mol\(^{-1}\). Any diminution of the uncertainty attached to \(\Delta H^\circ_T(\text{Si}, g)\), surprisingly large at ±8 kJ mol\(^{-1}\), will help define \(D^\circ_T(\text{SiTe})\) even more precisely.

In an earlier publication,\(^{15}\) we observed that \(D^\circ_T(\text{GeX})\), with \(X = S, Se,\) or \(Te\), decreased almost linearly from GeS to GeTe. A comparable trend should occur for \(D^\circ_T(\text{SiX})\) because of the similarity in bonding. Gurvich et al.\(^{16}\) selected \(D^\circ_T(\text{SiS}) = (613.7 ± 2.4)\) kJ 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 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 \(D^\circ_T(\text{SiSe}) = (484 ± 21)\) kJ mol\(^{-1}\) on the basis of the thermochemical measurements and in preference to the spectroscopic value of ≈ 525 kJ 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 \(D^\circ_T(\text{SiSe}) = 544\) kJ mol\(^{-1}\). In light of the values of \(D^\circ_T(\text{GeX})\), the spectroscopic \(D^\circ_T(\text{SiSe})\) appears to be more reasonable than the thermochemical result, even though it incorporates a 90 kJ 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\(^{26}\) that SiSe(cr) cannot be prepared, but an investigation of the high-temperature dissociation of the diselenide \([\text{SiSe}_2(\text{cr}) + \text{Si(cr)} = 2\text{SiSe(g)}]\) has been reported.\(^{27}\) Results from that study can be used to derive a value of \(\Delta H^\circ_\text{m}(\text{SiSe, g})\) and, thus, \(D^\circ_\text{m}(\text{SiSe})\), but a reliable value of \(\Delta H^\circ_\text{m}(\text{SiSe}_2, \text{cr}, 298.15 \text{ K})\), hitherto unavailable, is required. Preliminary measurements\(^{22}\) of that quantity in progress at this laboratory are in harmony with \(D^\circ_\text{m}(\text{SiSe}) = (534 \pm 10)\) kJ mol\(^{-1}\), and thus tend to support the spectroscopic value. If that \(D^\circ_\text{m}\) is corroborated, then the progression of \(D^\circ_\text{m}(\text{SiX})\) for \(X = \text{S, Se, Te}\) will indeed be approximately linear, in parallel with \(D^\circ_\text{m}(\text{GeX})\).

From Table 2, we take \(\Delta H^\circ_\text{m}(298.15 \text{ K}) = (124.9 \pm 1.6)\) kJ mol\(^{-1}\) for reaction (3) and combine it with \(\frac{1}{2}\Delta H^\circ_\text{m}\)

\[
\text{(Te}_2, \text{g}) = (81.6 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}\] 4 to yield \(\Delta H^\circ_\text{m}(\text{SiTe, g, 298.15 K}) = (206.5 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}\) for:

\[
\text{Si(cr)} + \text{Te(cr)} = \text{SiTe(g)}. \tag{6}
\]

This value for the standard molar enthalpy of formation of SiTe(g) agrees within the combined uncertainties with Mills'\(^{17}\) selection, \((220 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}\), but is more precise because we have taken a weighted mean for \(\Delta H^\circ_\text{m}\) of reaction (3).

We wish to call attention to \(\Delta G^\circ_\text{m}\) and \(\Delta G^\circ_\text{p}\) in Table 1. Both quantities refer to reaction (3); thus, the thermochronical reference state of tellurium is arbitrarily taken to be Te(g) throughout the entire temperature range of the table.

### Table 1. Thermodynamic properties of SiTe(g); \(R = 8.31451 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\), \(p^* = 0.1 \text{ MPa}, T^* = 298.15 \text{ K}\)

<table>
<thead>
<tr>
<th>(T) K</th>
<th>(C^\circ_\text{m}) (R)</th>
<th>(\Delta H^\circ_\text{m})</th>
<th>(\Delta S^\circ_\text{m}(\text{SiTe}) - \Delta S^\circ_\text{m}(\text{SiTe}(T)))</th>
<th>(\Delta S^\circ_\text{m})</th>
<th>(\Delta H^\circ_\text{m})</th>
<th>(\Delta G^\circ_\text{m})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>–1.119</td>
<td>(\infty)</td>
<td>0</td>
<td>14.89</td>
<td>14.89</td>
</tr>
<tr>
<td>100</td>
<td>3.548</td>
<td>–0.769</td>
<td>32.822</td>
<td>25.135</td>
<td>15.03</td>
<td>13.89</td>
</tr>
<tr>
<td>200</td>
<td>3.904</td>
<td>–0.397</td>
<td>29.683</td>
<td>27.699</td>
<td>15.06</td>
<td>12.74</td>
</tr>
<tr>
<td>298.15</td>
<td>4.153</td>
<td>0.000</td>
<td>29.310</td>
<td>29.310</td>
<td>15.02</td>
<td>11.59</td>
</tr>
<tr>
<td>300</td>
<td>4.156</td>
<td>0.008</td>
<td>29.310</td>
<td>29.336</td>
<td>15.02</td>
<td>11.58</td>
</tr>
<tr>
<td>400</td>
<td>4.286</td>
<td>0.430</td>
<td>29.475</td>
<td>30.551</td>
<td>14.96</td>
<td>10.44</td>
</tr>
<tr>
<td>600</td>
<td>4.397</td>
<td>1.301</td>
<td>30.146</td>
<td>32.314</td>
<td>14.81</td>
<td>8.20</td>
</tr>
<tr>
<td>800</td>
<td>4.440</td>
<td>2.185</td>
<td>30.854</td>
<td>33.585</td>
<td>14.59</td>
<td>6.04</td>
</tr>
<tr>
<td>1000</td>
<td>4.461</td>
<td>3.075</td>
<td>31.503</td>
<td>34.579</td>
<td>14.34</td>
<td>3.93</td>
</tr>
<tr>
<td>1200</td>
<td>4.472</td>
<td>3.969</td>
<td>32.086</td>
<td>35.393</td>
<td>14.05</td>
<td>2.87</td>
</tr>
<tr>
<td>1400</td>
<td>4.480</td>
<td>4.864</td>
<td>32.609</td>
<td>36.083</td>
<td>13.75</td>
<td>–0.14</td>
</tr>
<tr>
<td>1600</td>
<td>4.485</td>
<td>5.761</td>
<td>33.081</td>
<td>36.682</td>
<td>13.43</td>
<td>–2.09</td>
</tr>
</tbody>
</table>

*Note that \(\Delta H^\circ_\text{m}\) and \(\Delta G^\circ_\text{m}\) both refer to the formation reaction: Si(cr or l) + \(\frac{1}{2}\)Te(g) = SiTe(g), as explained in the text.

*There is a transition at \(T = 1685 \text{ K}\), the melting temperature of Si.
TABLE 2. Enthalpy of the reaction: Si(cr) + \[Te_2(g)\] = SiTe(g) at \[T' = 298.15 \text{ K and } p^* = 0.1 \text{ MPa, and derivation of } D_{298}^\circ(\text{SiTe})

<table>
<thead>
<tr>
<th>Reference</th>
<th>Second law (\Delta H^\circ_{298}(\text{kJ-mol}^{-1}))</th>
<th>Third law (\Delta H^\circ_{298}(\text{kJ-mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exsteen et al.(^2)</td>
<td>120.1 ± 3.0</td>
<td>127.4 ± 4.5</td>
</tr>
<tr>
<td>Brebrick (^3)</td>
<td>124.0 ± 2.0</td>
<td>132.4 ± 4.0</td>
</tr>
</tbody>
</table>

\(<\Delta H^\circ_{298}> = (124.9 ± 1.6) \text{ kJ-mol}^{-1}\)

\[^a\]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('\Sigma') to Si(cr) and Te('\Gamma').

5. Acknowledgment

We are grateful to Dr. G. Lakshminarayana (BARC, Bombay) for helpful correspondence, and to Drs. M. W. Chase, Jr. and David B. Neumann (NIST) for access to the JANAF programs and for assistance with the calculations.

6. References

20S. Susman, Argonne National Laboratory, personal communication.
22I. Tomaszewicz, P. A. G. O'Hare, unpublished results.