

Vaporization and thermodynamic properties of samarium dicarbide and sub-stoichiometric disamarium tricarbide

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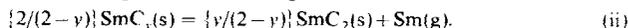
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The vaporization reactions of $\text{SmC}_2(\text{s})$ and Pu_2C_3 -type $\text{SmC}_y(\text{s})$, $1.36 < y < 1.45$) have been characterized and equilibrium pressures have been measured using a target-collection effusion technique. The carbides vaporize incongruently as follows:



The complex reaction for SmC_y occurs because the composition of the carbon-rich boundary of the phase decreases as temperature increases. For reaction (i), the equilibrium pressure is described by $\log_{10}\{(p/p^\circ)(\text{Sm}, \text{g}, 1548 \text{ K} < T < 2049 \text{ K})\} = (3.60 \pm 0.01) - (14309 \pm 21)(T/\text{K})^{-1}$. The non-linear pressure equation for reaction (ii) is $\log_{10}\{(p/p^\circ)(\text{Sm}, \text{g}, 1.42 < y < 1.44, 1372 \text{ K} < T < 1636 \text{ K})\} = \{12.009 - 28449(T/\text{K})^{-1} + 7018500(T/\text{K})^{-2} \pm 0.038\}$. Thermodynamic values for the vaporization and formation reactions of $\text{SmC}_2(\text{s})$ and $\text{SmC}_y(\text{s})$ at 298.15 K have been calculated: $\Delta H_f^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K}) = -(96.2 \pm 7.5) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta H_f^\circ(\text{SmC}_{1.43}, \text{s}, 298.15 \text{ K}) = -(89.0 \pm 8.0) \text{ kJ} \cdot \text{mol}^{-1}$. The thermodynamic results are discussed and compared with values reported for other lanthanide carbides.

1. Introduction

As noted in our recent report on the phase equilibria in (samarium + oxygen + carbon),⁽¹⁾ an interest in the thermodynamic properties of the lanthanide carbides at high temperatures is promoted by their importance in nuclear-reactor technology. The importance of the samarium system is enhanced by the behavior of that lanthanide as a neutron poison. The thermodynamic properties of SmC_2 and of other lanthanide dicarbides have been extensively investigated and are reviewed in the compilation by Gschneidner and Kippenhan.⁽²⁾

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Initial workers reported the existence of three carbide phases (LnC_2 , Ln_2C_3 , Ln_3C) for several lanthanides,⁽³⁾ and more recent studies have supported the existence of these phases in (samarium + carbon).⁽⁴⁾ The few results compiled for miscellaneous lanthanide carbides⁽²⁾ demonstrate that the investigation of their properties is limited. Values are presented for six Ln_2C_3 phases ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{and Ho}$), but for none of the Ln_3C phases. Furthermore, an unexpectedly wide variation is observed in the enthalpies of formation for Ln_2C_3 phases: $\Delta H_f^\circ(\text{Ce}_2\text{C}_3, \text{s}, 298.15 \text{ K}) = -88.2 \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta H_f^\circ(\text{Sm}_2\text{C}_3, \text{s}, 1531 \text{ K}) = -254.4 \text{ kJ}\cdot\text{mol}^{-1}$; and $\Delta H_f^\circ(\text{Ho}_2\text{C}_3, \text{s}, 298.15 \text{ K}) = -58.2 \text{ kJ}\cdot\text{mol}^{-1}$. Since the average $\Delta H_f^\circ(\text{LnC}_2, \text{s}, 298.15 \text{ K})$ recommended for six lanthanides and yttrium is $-(97.9 \pm 10.5) \text{ kJ}\cdot\text{mol}^{-1}$,⁽²⁾ the reliability of the values for the Ln_2C_3 phases must be questioned. Our investigation of the samarium carbides was motivated by a desire fully to characterize the vaporization behavior of a ($\text{Ln} + \text{carbon}$) system, to address the apparent inconsistencies in thermodynamics of Ln_2C_3 and to provide initial thermochemical values for a representative Ln_3C phase. (Samarium + carbon) was selected because of the apparent existence of four well-defined two-phase regions ($\text{Sm} + \text{Sm}_3\text{C}$, $\text{Sm}_3\text{C} + \text{Sm}_2\text{C}_3$, $\text{Sm}_2\text{C}_3 + \text{SmC}_2$, $\text{SmC}_2 + \text{C}$) in which equilibrium vapor pressures could be measured.

The scope and direction of our effort has been substantially altered by the results of our reinvestigation of (samarium + oxygen + carbon).⁽¹⁾ That study evolved from our inability to reproduce earlier results and yielded two major findings. (a) The existence of the cubic Sm_3C phase could not be confirmed; however, an anion-deficient f.c.c. phase with identical lattice parameters was found at the $\text{SmO}_{0.5}\text{C}_{0.4}$ composition. (b) The cubic Pu_2C_3 -type phase, designed as SmC_y in this report, was found to be sub-stoichiometric, to exist over the range $1.36 < y < 1.45$, and to have a carbon-rich phase boundary which decreased in carbon content with increasing temperature. The retrograde composition variation, which is attributed to anion intervalence involving acetylide (C_2^{2-}) and methanide (C^{4-}) ions and to shifts in the $\text{C}_2^{2-} + 6e^- = 2\text{C}^{4-}$ equilibrium with temperature, has introduced unanticipated difficulties in the interpretation and evaluation of thermodynamic properties for SmC_y . Although the scope of the investigation has been reduced by the absence of a Sm_3C phase, a reinvestigation of SmC_2 vaporization has been included to provide an internally consistent set of results for evaluating thermodynamic quantities across the system and to provide a mechanism for checking the accuracy of our pressure measurements with the results of other investigators. The phase equilibria and vaporization reactions of the carbides are described in the preceding study which provides a basis for the present investigation.⁽¹⁾

2. Experimental

PREPARATION AND CHARACTERIZATION

Samples of SmC_2 and SmC_y were prepared by the reaction of samarium metal (99.9 moles per cent of rare earth, Rare Earth Research Corporation) with degassed powdered graphite (spectrographic grade, Ultracarbon) in sealed tantalum

containers at a greatest temperature of 2200 K.⁽¹⁾ The preparative products and the condensed residues of vaporization experiments were analyzed by X-ray diffraction procedures; results were obtained with a Guinier-Haegg camera using Cu K α_1 radiation and Si (0.543062 nm) as an internal standard. Metal and carbon contents were obtained by ignition in a carbon analysis train with gravimetric determination of residual Sm₂O₃ and Ascarite-collected CO₂. All manipulations of the air-sensitive carbides were performed in a glovebox containing a recirculated Ar atmosphere which was purged of both water and oxygen.

The polycrystalline carbide samples used in the vaporization experiments were from reaction mixtures with $n(\text{C})/n(\text{Sm})$ mole ratios of 2.0, 1.6, and 1.3.⁽¹⁾ The product at the 2.0 mole ratio was a golden metallic CaC₂-type phase with tetragonal lattice parameters of $a = (0.3771 \pm 0.0002)$ nm and $c = (0.6316 \pm 0.0006)$ nm. The product at the 1.3 mole ratio was silver metallic and contained a Pu₂C₃-type phase with cubic parameters $a = (0.8399 \pm 0.0002)$ nm. This lattice parameter corresponds to that of the metal-rich boundary of the Pu₂C₃-type phase and implies that the sample was a mixture of Sm(s) and SmC_{1.35}(s).⁽¹⁾ A mixture of the cubic and tetragonal carbides was present at the 1.6 mole ratio. Effusion samples (0.2 to 0.4 g) were finely crushed prior to use in vaporization experiments.

VAPOR-PRESSURE MEASUREMENTS

Equilibrium vapor pressures of samarium were measured using a target-collection effusion technique. As in previous studies with lanthanide carbides,^(5,6) molybdenum effusion cells with knife-edged orifices were used as containers. The orifice areas (1.039×10^{-3} , 2.523×10^{-3} , and 5.473×10^{-3} cm²) were determined from planimetric measurements of photomicrographs. For the (SmC₂+C) and (SmC_y+SmC₂) two-phase regions, pressure measurements were made both at successively increasing and decreasing temperatures in the 1548 to 2049 K and the 1372 to 1636 K ranges, respectively. Cell-cavity temperatures were measured using an optical pyrometer with a calibration traceable to N.B.S. The collection apparatus and X-ray fluorescence procedures used for determining the quantity of samarium effusate condensed on the Cu target are described in a previous report.⁽⁷⁾

The experimental procedures were checked by measuring the vapor pressure of gold (N.B.S. standard reference material 745) and verifying that the results were in agreement with the recommended values. Gold samples were contained in graphite effusion cells. The target collection and fluorescence procedures were identical to those used for the samarium carbides. For the vaporization of Au, a third-law value of $\Delta H^\circ(298.15 \text{ K}) = (366.1 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ was obtained from 23 points. The recommended value is $(367.04 \pm 0.90) \text{ kJ} \cdot \text{mol}^{-1}$.

3. Results

EQUILIBRIUM RESULTS

Both SmC₂(s) and SmC_y(s) vaporize incongruently with the formation of Sm(g) as the only significant vapor species.⁽¹⁾ The dicarbide reaction shown by equation (1) has

been thoroughly characterized in several mass-spectrometric studies reviewed by Seiver and Eick.⁽⁶⁾



Equilibrium pressures for the process defined by equation (1) have been redetermined by 20 points obtained in three independent effusion experiments. The temperature dependence of the Sm pressure measured in the present study is described by

$$\log_{10}\{p(\text{Sm, g, } 1545 \text{ K} < T < 2049 \text{ K})/101.325 \text{ kPa}\} \\ = (3.60 \pm 0.01) - (14309 \pm 21)(T/\text{K})^{-1}. \quad (2)$$

The second-law enthalpy and entropy of vaporization at the median temperature of 1799 K are $(273.9 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$ and $(68.9 \pm 0.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, respectively.

The vaporization reaction for SmC_y is described by



The complex coefficients are a consequence of the retrograde dependence of the carbon-rich phase boundary of SmC_y on temperature. Previously described results of equilibrium studies for the temperature range of the vapor-pressure measurements show that the mole ratio $n(\text{C})/n(\text{Sm})$ and the cubic lattice parameter of the Pu_2C_3 -type phase both decrease with increasing temperature.⁽¹⁾ At 1400 K, $y = 1.44$ and $a = 0.8446 \text{ nm}$; at 1600 K, $y = 1.42$ and $a = 0.8434 \text{ nm}$. The lattice parameter of SmC_y varies linearly with temperature over the range 1300 to 2200 K, and it is reasonable to assume that Vegard's law is obeyed over the comparatively limited range of the vapor-pressure measurements; *i.e.* that y decreases linearly with increasing temperature.

The equilibrium pressure of samarium for equation (3) has been measured at 22 temperatures in 7 independent effusion experiments. The values of $\log_{10}\{p/101.325 \text{ kPa}\}$ are presented in table 1 and plotted against T^{-1} in figure 1. The five points indicated by solid circles are the average plateau pressures obtained during measurements along pressure-composition isotherms of (samarium + carbon) (compare figure 2 of reference 1). As shown in table 1, each of these points is based on three or more isothermal measurements in the composition range $1.45 < n(\text{C})/n(\text{Sm}) < 1.85$. Careful examination of figure 1 shows that the graph is not linear. The temperature dependence of $\log_{10}(p/101.325 \text{ kPa})$ is described by a binomial relation:

$$\log_{10}\{p(\text{Sm, g, } 1372 \text{ K} < T < 1636 \text{ K})/101.325 \text{ kPa}\} \\ = \{12.009 - 28849(T/\text{K})^{-1} + 7018500(T/\text{K})^{-2}\} \pm 0.038. \quad (4)$$

An important aspect of the equilibrium process for SmC_y is reflected by the dependence of $\log_{10}(p/101.325 \text{ kPa})$ on $(T/\text{K})^{-1}$ being both non-linear and steeper than that for vaporization of SmC_2 . If a linear relation is used to approximate the values in figure 1 a slope of -18450 and an intercept of 8.53 are obtained. As is expected from the fact that SmC_2 is formed by vaporization of SmC_y , the Sm activity at a given temperature in the $(\text{SmC}_y + \text{SmC}_2)$ region is higher than in the $(\text{Sm} + \text{C})$ region. However, use of the approximate slope to evaluate $\Delta H^\circ(1504 \text{ K})$ for equation (3)

TABLE 1. Equilibrium vapor pressure of Sm(g) for the vaporization reaction $\{2/(2-y)\}SmC_y(s) = \{y/(2-y)\}SmC_2(s) + Sm(g)$; ^a orifice areas *a*

No.	$\frac{10^4 a}{\text{cm}^2}$	$\frac{T}{\text{K}}$	$-\log_{10} \left\{ \frac{p(\text{Sm})}{p} \right\}^b$	No.	$\frac{10^4 a}{\text{cm}^2}$	$\frac{T}{\text{K}}$	$-\log_{10} \left\{ \frac{p(\text{Sm})}{p} \right\}^b$
1	2.523	1458	4.517	6	1.039	1473	4.386
		1458	4.537			1386	4.217
		1458	4.524			1575	3.454
2	1.039	1511	3.933	7	1.039	1575	3.485
		1511	3.991			1575	3.465
		1511	3.035			1495	4.117
3	5.437	1426	4.762	7	1.039	1531	3.833
		1426	4.769			1551	3.613
		1426	4.851			1608	3.213
4	5.437	1410	4.936	7	1.039	1623	3.107
		1410	4.922			1636	2.976
		1410	4.909			1613	3.212
		1410	4.928			1588	3.365
5	5.437	1373	5.207	7	1.039	1557	3.610
		1411	4.862			1513	4.029
		1451	4.555			1509	4.098

^a The results are listed in chronological order of measurement. The average results of experiments 1 to 4 and 6 are shown by solid circles in figure 1.

^b $p = 101.325 \text{ kPa}$.

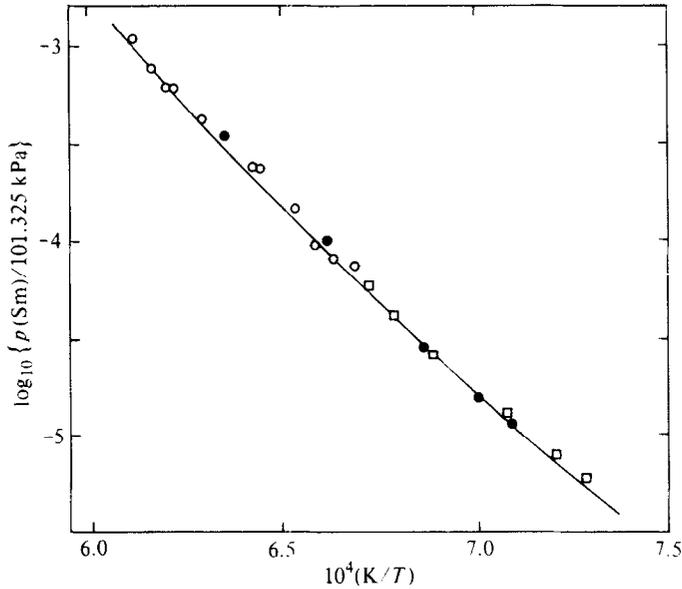


FIGURE 1. Dependence of $\log_{10} \{ p(\text{Sm, g}) / 101.325 \text{ kPa} \}$ on $(T/\text{K})^{-1}$ for the $(SmC_v + SmC_2)$ region in the range 1372 to 1636 K.

yields an apparent enthalpy of vaporization that is $79 \text{ kJ} \cdot \text{mol}^{-1}$ more positive than $\Delta H^\circ(1799 \text{ K})$ for equation (1). These observations are inconsistent and demonstrate that thermodynamic quantities for equation (3) cannot be correctly evaluated using the second-law method. This conclusion is consistent with the temperature dependence of γ in equation (3). Since a different vaporization reaction occurs at each temperature, ΔH° and ΔS° for the process must be different at each temperature and can be obtained for a given T and γ only by the third-law method.

THERMODYNAMIC RESULTS

The results of the equilibrium measurements have been reduced to 298.15 K using estimated thermal functions for $\text{SmC}_2(\text{s})$ and $\text{SmC}_y(\text{s})$. High-temperature heat-capacity equations for the carbides have been estimated from that of $\text{Sm}_2\text{O}_3(\text{s})$,⁽⁸⁾ using the modified Kopp's-rule method.⁽⁹⁾ The resulting equations are of the form $C_p^\circ/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = A + B(T/\text{K}) + C(T/\text{K})^{-2}$; the values for A , B , and C are 77.0, 9.71×10^{-3} , and -9.00×10^{-5} for SmC_2 and 62.8, 9.7×10^{-3} , and -9.00×10^{-5} for SmC_y . The calculated enthalpy and entropy increments are given in table 2. As noted, the functions for SmC_2 have been corrected for the tetragonal-to-cubic transition of the dicarbide at 1440 K.⁽¹⁰⁾ A value of $\Delta H_{\text{tr}}^\circ(\text{SmC}_2, \text{s}, 1440 \text{ K}) = 5.57 \text{ kJ} \cdot \text{mol}^{-1}$ has been obtained by adopting the enthalpy change reported for the tetragonal-to-cubic transition of $\text{CaC}_2(\text{s})$.⁽¹¹⁾

Values of $S^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K}) = 87.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $S^\circ(\text{SmC}_{1.43}, \text{s}, 298.15 \text{ K}) = 84.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ have been estimated using the adaptation of Latimer's method⁽¹²⁾ proposed for lanthanide solids by Westrum.⁽¹³⁾ In

TABLE 2. Estimated thermal functions for $\text{SmC}_2(\text{s})$ and $\text{SmC}_{1.43}(\text{s})$

T K	$H(T) - H(298.15 \text{ K})$ $\text{kJ} \cdot \text{mol}^{-1}$	$S(T) - S(298.15 \text{ K})$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$-\{G(T) - H(298.15 \text{ K})\}/T$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
SmC_2			
1400	91.34	124.8	147.5

1500	105.99	134.9	152.2
1600	115.20	140.8	156.7
1700	124.24	146.4	161.2
1800	134.04	151.8	165.2
1900	143.16	156.9	169.1
2000	152.75	161.8	173.3
$\text{SmC}_{1.43}$			
1400	75.93	103.1	133.0

1500	83.47	108.3	136.8
1600	91.34	113.3	140.4

^a The $\Delta H_{\text{tr}}^\circ$ of $5.57 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S_{\text{tr}}^\circ$ of $3.87 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for the tetragonal-to-cubic transition at 1440 K are included.

adaptation of Latimer's method^(1,2) proposed for lanthanide solids by Westrum.^(1,3) In the CaC_2 -type lanthanide dicarbides, the cations are trivalent and the anions are acetylinic.^(1,4) In the stoichiometric Pu_2C_3 -type phase, the same ionic species are present,⁽¹⁾ and the metallic SmC_2 and $\text{SmC}_{1.43}$ phases are formulated as $(\text{Sm}^{\text{III}})(\text{C}_2^{2-})(\text{e}^-)$ and as $(\text{Sm}^{\text{III}})(\text{C}_2^{2-})_{0.68}(\text{C}^{4-})_{0.07}(\text{e}^-)_{1.36}$, respectively. The entropies were obtained by combining Westrum's values for the lattice ($54.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and magnetic ($15.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) contributions of Sm^{III} ,^(1,3) with the average lattice contribution ($13.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) calculated for the C_2^{2-} ion. This value was derived from values of $S^\circ(298.15 \text{ K})$ for nine acetylinic metal carbides^(11,15) by subtracting their cationic contributions. The values of $-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T$ listed for the carbides in table 2 are based on these entropy estimates.

Thermodynamic values for vaporization of SmC_2 according to equation (1) at 298.15 K have been calculated using thermal functions from table 2 and those of $\text{Sm}(\text{g})$,⁽¹⁶⁾ and $\text{C}(\text{s})$.⁽¹⁷⁾ Results obtained by the second- and third-law methods are presented in table 3. Values for $\Delta H_f^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K})$ in table 3 have been obtained from the vaporization results and $\Delta H_f^\circ(\text{Sm}, \text{g}, 298.15 \text{ K})$.⁽¹⁶⁾ The value of $S^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K})$, which was estimated for third-law calculations and obtained from the second-law $\Delta S^\circ(298.15 \text{ K})$, and the values of $S^\circ(\text{Sm}, \text{g}, 298.15 \text{ K})$,⁽¹⁶⁾ and $S^\circ(\text{C}, \text{s}, 298.15 \text{ K})$,⁽¹⁷⁾ for second-law calculations have been used to derive values of $\Delta G_f^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K})$.

As discussed in the preceding section, thermodynamic results for the vaporization of $\text{SmC}_y(\text{s})$ have been evaluated only by the third-law method. The values of y in equation (3) for three temperatures in the experimental range⁽¹⁾ are presented with other pertinent data in table 4. Since $-\{G^\circ(T) - H^\circ(298.15 \text{ K})\}/T$ values for $\text{SmC}_{1.42}$ and $\text{SmC}_{1.44}$ are virtually identical to those of $\text{SmC}_{1.43}$, the values

TABLE 3. Thermodynamic values for vaporization and formation of $\text{SmC}_2(\text{s})$ and $\text{SmC}_{1.43}(\text{s})$ at 298.15 K^a

	$\text{SmC}_2(\text{s})$		$\text{SmC}_{1.43}(\text{s})$
	Second law	Third law	Third law
$\Delta H^\circ(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1})^b$	303.1 ± 7.5	311.0 ± 1.7	282.1
$\Delta S^\circ(298.15 \text{ K})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})^b$	101.7 ± 6.3	(106.3)	(108.4)
$\Delta H_f^\circ(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1})$	-96.2 ± 7.5	$-(104.3 \pm 3.3)$	$-(89.9 \pm 8.0)$
$\Delta S_f^\circ(298.15 \text{ K})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	11.7 ± 6.3	(7.1)	(6.7)
$\Delta G_f^\circ(298.15 \text{ K})/(\text{kJ} \cdot \text{mol}^{-1})$	-99.5 ± 8.0	$-(106.3)$	$-(92.4)$
$S^\circ(298.15 \text{ K})/(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$	92.5 ± 6.3	(87.9)	(84.1)

^a Values in parentheses are based on the estimated values of $S^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K}) = 87.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and $S^\circ(\text{SmC}_{1.43}, \text{s}, 298.15 \text{ K}) = 84.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The uncertainties in second-law ΔH° and ΔS° and third-law ΔH° for $\text{SmC}_2(\text{s})$ include statistical variations from the analysis of results and a ± 20 per cent uncertainty in estimated $\{H^\circ(T) - H^\circ(298.15 \text{ K})\}$ and $\{S^\circ(T) - S^\circ(298.15 \text{ K})\}$. For $\Delta H_f^\circ(298.15 \text{ K})$, $\Delta S_f^\circ(298.15 \text{ K})$, and $\Delta G_f^\circ(298.15 \text{ K})$ of $\text{SmC}_2(\text{s})$, the uncertainties are accumulated values for the formation reaction. Statistical variations are not available for $\text{SmC}_{1.43}(\text{s})$, and an estimated uncertainty of $3.0 \text{ kJ} \cdot \text{mol}^{-1}$ is included in its $\Delta H_f^\circ(298.15 \text{ K})$.

^b The vaporization reactions for $\text{SmC}_2(\text{s})$ and $\text{SmC}_{1.43}(\text{s})$ are given by equations (1) and (3), respectively.

TABLE 4. Thermodynamic results for $\text{SmC}_y(\text{s})$ in equilibrium with $\text{SmC}_2(\text{s})$ and $\text{Sm}(\text{g})$ at compositions across the experimental temperature range

$\frac{T}{\text{K}}$	y	$\log_{10} \left\{ \frac{p(\text{Sm}, \text{g})}{p} \right\}$	$\Delta \left[\frac{G(T) - H(298.15 \text{ K})}{T} \right]$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	ΔH (298.15 K, eqn 3) $\text{kJ} \cdot \text{mol}^{-1}$	ΔH_f (298.15 K) $\text{kJ} \cdot \text{mol}^{-1}$
1400	1.44	-5.016	-110.7	289.3	-92.1
1500	1.43	-4.104	-109.6	282.1	-90.4
1600	1.42	-3.280	-109.2	275.4	-87.9

^a $p = 101.325 \text{ kPa}$.

reported for the intermediate composition in table 2 have been used in all calculations. The resulting values of $\Delta H^\circ(298.15 \text{ K})$ for equation (3) show a definite temperature trend which is reflected in the corresponding $\Delta H_f^\circ(\text{SmC}_{1.43}, \text{s}, 298.15 \text{ K})$ derived using $\Delta H_f^\circ(\text{Sm}, \text{g}, 298.15 \text{ K})^{(16)}$ and the average $\Delta H_f^\circ(\text{SmC}_2, \text{s}, 298.15 \text{ K})$ from table 3. The other thermodynamic quantities for $\text{SmC}_{1.43}$ in table 3 have been obtained using the results for SmC_2 , the estimated $S^\circ(\text{SmC}_{1.43}, \text{s}, 298.15 \text{ K})$, and data for the elements.^(16,17)

4. Discussion

The effusion results for SmC_2 vaporization provide an alternate method for evaluating the accuracy of our pressure measurements. This capability is especially critical for establishing the fact that the concave upward curvature of $\log_{10}\{p(\text{Sm}, \text{g})/101.325 \text{ kPa}\}$ against T^{-1} for the $(\text{SmC}_y + \text{SmC}_2)$ region does not result from an experimental effect such as secondary evaporation of samarium in the effusion apparatus. This is particularly important because the results of an earlier vaporization study in the range $1.7 < n(\text{C})/n(\text{Sm}) < 2.0$ by Avery *et al.* did not indicate anomalous behavior.⁽¹⁸⁾ Vapor-pressure equation (2) is in good agreement with that measured by Seiver and Eick and with the result of several earlier studies reviewed in their report.⁽⁶⁾ The slope and intercept values for $\log_{10}\{p(\text{Sm}, \text{g})/101.325 \text{ kPa}\}$ against $(T/\text{K})^{-1}$ obtained by Seiver and Eick are $-(14218 \pm 200)$ and (3.84 ± 0.11) , respectively; the combined pressure equation obtained by Seiver and Eick from their results and the results of selected earlier reports has values of $-(13700 \pm 130)$ and (3.54 ± 0.09) , respectively. Since secondary evaporation would be less in the lower-temperature range of the SmC_y measurements than in that of SmC_2 , the observed curvature in figure 1 can only be attributed to thermochemical properties of (samarium + carbon).

The pressure behavior in $(\text{SmC}_y + \text{SmC}_2)$ is unusual, but not unique. A similar upward curvature is observed in the plot of $\log_{10}\{p(\text{Yb}, \text{g})/101.325 \text{ kPa}\}$ against $(T/\text{K})^{-1}$ for the sub-stoichiometric diytterbium tricarbide in equilibrium with ytterbium dicarbide.⁽¹⁹⁾ In that system, the phase-boundary composition of the sub-stoichiometric phase is found to decrease in carbon content with decreasing temperature. An anomalous slope-relation of $\log_{10}\{p(\text{Ho}, \text{g})/101.325 \text{ kPa}\}$ against $(T/\text{K})^{-1}$ is also found in (holmium + carbon).⁽²⁰⁾ Although the second-law method was not used in evaluation, the obvious inconsistency was not discussed. These

results suggest that a general feature of the ($\text{LnC}_{1.5} + \text{LnC}_2$) equilibrium systems of the lanthanides, with the possible exception of Eu, is an increasing sub-stoichiometry of the $\text{LnC}_{1.5}$ phase with increasing temperature.

Our equilibrium pressures are not in good agreement with the results reported previously for ($\text{SmC}_{1.5} + \text{SmC}_2$).⁽¹⁸⁾ The earlier work shows a linear plot of $\log_{10}\{p(\text{Sm, g})/101.325 \text{ kPa}\}$ against $(T/\text{K})^{-1}$ for the composition range $1.7 < n(\text{C})/n(\text{Sm}) < 2.0$. In addition, the absolute pressures differ substantially. Our pressures are consistently higher. The ratios $\{p(\text{Sm, g, this study})/p(\text{Sm, g, Avery et al.})\}$ at 1400, 1500, and 1600 K are 4.2, 7.3, and 13.7, respectively.

A possible explanation for the difference in the effusion results is suggested by the time dependence of $p(\text{Sm, g})$ for ($\text{SmC}_y + \text{SmC}_2$). The isotherms of $\log_{10}\{p(\text{Sm, g})/101.325 \text{ kPa}\}$ against time presented for SmC_y vaporization⁽¹¹⁾ show that the pressure was initially constant for approximately 2 h at a value in agreement with pressure equation (4) and then began to decrease slowly. The results at 1440 and 1575 K are particularly instructive. The test at 1440 K was fortuitously terminated shortly after the pressure began to drop. Total mass-losses show that the terminal mole ratio $n(\text{C})/n(\text{Sm})$ was (1.87 ± 0.03) . The test at 1575 K continued for 2 to 3 h after the pressure began to drop below the plateau value of 33 Pa. At termination, the measured pressure of 2.2 Pa was still a factor of 10 greater than the equilibrium value of 0.33 Pa calculated for SmC_2 at 1557 K using equation (2). These results demonstrate that the measured effusion pressures in our tests decreased steadily when the $n(\text{C})/n(\text{Sm})$ exceeded 1.85 or 1.90.

Potential origins of such pressure-composition behavior include (a) the formation of a sub-stoichiometric dicarbide phase, SmC_{2-x} , at high temperature, and (b) the formation of a product layer of SmC_2 on the particles of SmC_y . A graph of effusion pressures as the square root of time at 1575 K is linear, but the values are insufficient to establish unequivocally that the vaporization process is diffusion controlled.⁽²¹⁾ However, the formation of a product barrier is consistent with the results of our preliminary effusion experiments in which pressures were measured at successively increasing and decreasing temperatures. Unless the sample was crushed very finely, the pressures observed on the descending sequence with a partially depleted SmC_y content were consistently lower than those in the ascending sequence with a fresh sample. If a product diffusion barrier forms, the composition at which the attainment of equilibrium is hindered will vary with temperature, effusion rate, and sample surface area. Since the pressures observed by Avery and co-workers are consistently lower than those of the present study and since they assumed only that the vapor in their cell was saturated, their measurements may well have been conducted at non-equilibrium conditions.

The validity of the results of the present study is evidenced by their excellent agreement with thermochemical values for neighboring lanthanide carbides. The values of $\Delta H_f^\circ(\text{CeC}_2, \text{s}, 298.15 \text{ K})$ and $\Delta H_f^\circ(\text{CeC}_{1.5}, \text{s}, 298.15 \text{ K})$ measured by oxygen bomb calorimetry are $-(97.0 \pm 5.4)$ and $-(88.2 \pm 2.9) \text{ kJ} \cdot \text{mol}^{-1}$, respectively.⁽²²⁾ Our corresponding results for SmC_2 and $\text{SmC}_{1.5}$ are $-(96.3 \pm 7.5)$ and $-(89.9 \pm 8.0) \text{ kJ} \cdot \text{mol}^{-1}$. Although the thermodynamic quantities for the dilanthanide tricarbonides are quite limited, the solid-state e.m.f. measurements of

Anderson and Bagshaw are the most extensive.⁽²³⁾ In order to compare our results with their $\Delta G_f^\circ(\text{LnC}_{1.5}, \text{s}, 1100 \text{ K})$ results for several lanthanides, $\Delta H_f^\circ(\text{SmC}_{1.43}, \text{s}, 1100 \text{ K})$ and $\Delta S_f^\circ(\text{SmC}_{1.43}, \text{s}, 1100 \text{ K})$ have been calculated from the results in table 3, thermal functions derived from the estimated $C_p^\circ(\text{SmC}_{1.43}, \text{s})$, and thermal functions for the elements.^(17,18) The results show $\Delta G_f^\circ(\text{SmC}_{1.43}, \text{s}, 1100 \text{ K}) = -(110.5 \pm 8.5) \text{ kJ} \cdot \text{mol}^{-1}$. The average of the $\Delta G_f^\circ(\text{LnC}_{1.50}, \text{s}, 1100 \text{ K})$ values for La, Ce, Pr, and Nd is $-(110.3 \pm 4.6) \text{ kJ} \cdot \text{mol}^{-1}$.⁽²³⁾

The existence of sizeable discrepancies in the enthalpies of formation of the dilanthanide tricarbides is noted in the introduction. Examination of the original reports show that the differences are primarily a consequence of compilation error.⁽²⁾ The enthalpy of formation listed for Ce_2C_3 is actually the value for $\text{CeC}_{1.50}$ and should be doubled.⁽²³⁾ The compiled value for $\Delta H_f^\circ(\text{Sm}_2\text{C}_3, \text{s}, 1531 \text{ K})$ is the enthalpy change for the vaporization of $\text{Sm}_2\text{C}_3(\text{s})$ to form $\text{SmC}_2(\text{s})$ and $\text{Sm}(\text{g})$.⁽¹⁸⁾

The equilibrium measurements and thermodynamic results of this study support the conclusions of our earlier report on (samarium + oxygen + carbon). The anomalous increase in the equilibrium pressure of gaseous samarium with temperature and the observed shift of $\Delta H_f^\circ(\text{SmC}_y, \text{s})$ to less negative values with increasing temperature (compare table 4) are consistent with the fact that the carbon-rich phase boundary of the Pu_2C_3 -type samarium carbide has a significant retrograde temperature dependence.

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