lack of correlation may be a reflection of the uncertainties in the data used in the calculations, the idea previously advanced that the actinide electron-transfer reaction may be nonadiabatic[19] could well be a factor in the discrepancy between calculated and observed values of the entropies of activation.

In summary, the linear relationship observed between the $\Delta G°$ and ΔG^* for the series of related reactions between Np(VI) and selected phenothiazines is qualitatively accommodated by the Marcus theory of outer-sphere electron-transfer reactions. Quantitative comparisons between values calculated by the use of this theory and the experimental results do not provide compelling evidence that these systems conform to the criteria necessary for such calculations. Additional studies with isostructural Pu(VI) and/or Am(VI) as oxidants for selected phenothiazines should provide additional insight into the delineation of nonadiabaticity as a source of some of the discrepancies since they will provide a wider range of $\Delta G°$ values.

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Phase Equilibria in the Samarium–Oxygen–Carbon System. The Existence of Trisamarium Monocarbide

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Composition and vaporization studies in the temperature range 1400–2200 K show that four condensed phases exist in the binary and ternary regions of the Sm–O–C system. A CaC_2-type dicarbide, a nonstoichiometric Pu_2C_3-type phase between $SmC_{1.36}$ and $SmC_{1.45}$, and a stoichiometric NaCl-type oxide carbide near the $SmO_{0.5}C_{0.4}$ and Sm_2O_3 are observed. The Pu_2C_3-type carbide, SmC_y, vaporizes to form Sm(g) and SmC_2(s), which in turn vaporizes to Sm(g) + C(s). The vaporization products of the oxide carbide are Sm(g) + SmC_y(s) + Sm_2O_3(s). The cubic lattice parameter and the carbon content of SmC_y decrease with increasing equilibration temperature. Hydrolysis data for SmC_y indicate that its carbide species are a mixture of diatomic (acetylide) and monoatomic (methanide) ions; its nonstoichiometric behavior is consistent with a mechanism of anion altervalence based on an acetylide–methanide equilibrium process. $SmO_{0.5}C_{0.4}$ is best described as an oxide methanide containing randomly distributed anion vacancies. The present results fail to confirm the existence of a metal-rich carbide near the Sm_3C composition and suggest that the phase observed in an earlier study was actually the oxide carbide.

Introduction

An interest in the high-temperature properties of the lanthanide carbide systems has been promoted by their importance to nuclear reactor technology. The formation of carbides by the reaction of lanthanide fission products with carbide fuels or graphite moderator materials is expected. Additional interest in the carbides has developed because of increased metallurgical applications of the lanthanides in steels and other alloys. The early work of Spedding et al.[1] remains as the most comprehensive investigation of the phase equilibria and structural properties of the carbides, which include the CaC_2-type dicarbides, the Pu_2C_3-type dimetal tricarbides, and Fe_4N-type trimetal monocarbides. Much of the subsequent work has concentrated on the vaporization behavior and thermodynamic properties of the dicarbides.

The samarium system is an attractive candidate for an in-depth study of the equilibrium and thermodynamic properties of the carbides. This system is of particular interest because Sm is an effective neutron poison. The development of suitable fuel reprocessing procedures is based on an adequate understanding of the Sm–C system. The equilibria and structural properties of the samarium carbides have been reinvestigated by Lallement et al.[2] and by Venet and co-workers.[3,4] Since only small variations are reported for the lattice parameter of SmC_2, Sm_2C_3, and Sm_3C, the existence of well-defined two-phase regions is implied, and the measurement of equilibrium vapor pressures in those regions should be possible.

The initial objective of this study was the determination of the thermodynamic properties of the samarium carbides. However, the results of our preliminary preparative and vaporization experiments were substantially inconsistent with the anticipated behavior. A reinvestigation of the phase equilibria and properties of the Sm–C system was initiated. After subsequent results demonstrated that low levels of oxygen contamination were important, the study was expanded to the oxygen-containing ternary system. In evaluation of our results, an attempt has been made to consider both the equilibrium behavior and the crystal chemistry of the phases in the Sm–O–C system.

Experimental Section

Materials. Samarium chips were freshly cut from ingot metal (99.9%, Rare Earth Research Corp.). Powdered graphite was prepared by dry machining of spectrographic grade rods (Ultra Carbon) and vacuum degassing at 2000 °C. Sm_2O_3 (99.99%, American Potash and Chemical Co.) was calcined and stored in sealed containers over Ascarite.

Preparative Procedures. The carbides were prepared by weighing Sm and C in the proper ratios to give compositions in the range 0.3

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$<$ C:Sm $<$ 2.0. The reactant mixtures were sealed in outgassed containers fashioned from 0.67-cm o.d. Ta tubing by arc welding in an Ar atmosphere. All reaction containers were weighed before and after heating to verify the integrity of the welds and determine if samarium vapor had been lost during heating. In all cases, reaction between Ta and C was retarded by forming a passive TaC layer in the container prior to use; the graphite-packed tubes were heated at 1900–2000 °C for several hours. Samples were heated in a high-vacuum (1×10^{-6} torr) tungsten-mesh resistance furnace. Several reaction and annealing procedures were attempted; however, products with the highest crystallinity were obtained when samples were first heated at 1550 °C for 3 h. The reaction container was then inverted and the reaction sequence completed by heating for an additional 3 h at 1550 °C, raising the temperature to 2000 °C for 0.5 h, and cooling to ambient temperature in vacuo. Oxide carbide samples were prepared by a similar procedure in which Sm_2O_3 and C were initially mixed in the desired O:C ratio. Such mixtures were combined with the requisite quantities of metal to give reaction mixtures in the ranges $0.50 \leq$ O:Sm ≤ 0.75 and $0.25 \leq$ C:Sm ≤ 0.50. These samples were heated for 3-h periods in both vertical orientations at 1550 °C and cooled in vacuo. All manipulations of the products were performed in a glovebox with a recirculating Ar atmosphere that was purged of H_2O and O_2.

Analytical Procedure. Reaction products were analyzed by using X-ray and chemical methods. Powder X-ray diffraction data were obtained with a forward-focusing 114.6-mm diameter Haegg-type Guinier camera with Cu $K\alpha_1$ radiation and Si (a = 5.430 62 Å) as an internal standard. Metal and carbon contents of the carbide and oxide carbide were determined by ignition of samples (0.2–0.3 g) in a carbon analysis train with gravimetric measurement of residual Sm_2O_3 and Ascarite-collected CO_2. Oxygen contents of the oxide carbide were determined indirectly by difference and directly by a procedure employing vacuum vaporization of gaseous Sm from $SmO_{0.5}C_{0.4}$ samples (0.4–0.6 g) in an open Mo cup at 1200 °C. In each test, half of the vaporization residue, a mixture of carbides and Sm_2O_3, was treated with a weak (pH 3) HCl solution to dissolve the carbide phases. The insoluble oxide was filtered, dried, and weighed to determine the oxygen content of the initial oxide carbide sample. The other half of the residue was subjected to total C analysis, and the carbon content calculated for the initial sample was compared with those of unvaporized $SmO_{0.5}C_{0.4}$ samples. The hydrocarbon products formed by vapor-phase hydrolysis of carbide and oxide carbide samples were identified by mass spectrometry. Density measurements were made by the buoyancy method using bromoform.

Vaporization Procedures. Equilibrium vapor pressures of Sm were measured in accessible regions of the Sm–O–C system by a target collection effusion technique. These measurements were made by Mo effusion cells by using procedures which have been outlined previously.[5] Pressures were measured with finely ground samples along the Sm–C section of the composition range 1.4 $<$ C:Sm $<$ 2.0 as well as along the constant O:C ratio of the oxide carbide phase. In an initial set of experiments, the condensed equilibrium phases in both the carbide and oxide carbide systems were identified by X-ray diffraction as the mole fraction of Sm was decreased by vaporization. In a similar set of tests, equilibrium pressures of Sm were measured at constant temperatures in the 1137–1302 °C range.

The temperature dependence of the phase-boundary composition of the equilibrium Pu_2C_3-type SmC_y phase was determined by analyses of carbide samples prepared in a dual-chamber effusion cell. The observed equilibrium between the solid oxide carbide, solid SmC_y, solid Sm_2O_3, and gaseous Sm was employed to prepare samples of pure SmC_y in the 1225–1625 °C range. Carbide samples from a C:Sm = 1.3 reaction product were placed in a Mo effusion cell, and a carbide-passivated Ta cup containing a small quantity of oxide carbide was placed above the carbide. The cell was heated at the desired temperature for a short time period and cooled rapidly by quenching in 400-torr Ar before an X-ray sample was taken from the residue in the Ta cup. Periods of isothermal heating were continued until diffraction data showed that the oxide carbide, SmC_y, and Sm_2O_3 were in coexistence. This condition indicated that the equilibrium carbide composition had been attained in the cell and that additional samarium had not been lost from the carbide sample. The compositions of the equilibrium SmC_y phase at 1127 and 1327 °C were determined by chemical methods. Cubic lattice parameters of these and other phase-boundary SmC_y samples equilibrated at various temperatures with oxide carbide–oxide mixtures and with the dicarbide were accurately determined by repeated measurement of the spacing of the 631 reflection of the Pu_2C_3-type phase relative to the 331 reflection of Si.

Table I. Equilibrium Phases at Selected Reaction Compositions of the Sm–O–C System

molar ratios		
O:Sm	C:Sm[a]	phases detected by X-ray diffraction
0	2.0	CaC_2-type carbide
0	1.5, 1.6	Pu_2C_3-type + CaC_2-type carbides
0	1.3, 1.4	Pu_2C_3-type carbide
0	0.3, 0.6, 1.0	α-Sm + Pu_2C_3-type carbide
0.50	0.50	NaCl-type oxide carbide + Pu_2C_3-type carbide
0.50	0.40	NaCl-type oxide carbide[b]
0.75	0.25	NaCl-type oxide carbide + B-type Sm_2O_3

[a] C:Sm ratios producing the same results are grouped as single entries. [b] The presence of unreacted Sm could not be detected.

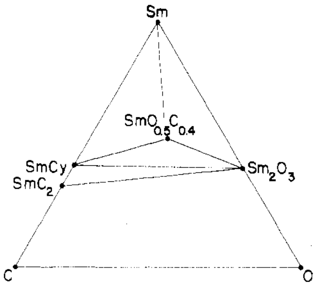

Figure 1. Sm–O–C phase diagram at 1500 K. (The composition of nonstoichiometric SmC_y in equilibrium both with $SmO_{0.5}C_{0.4}(s)$–$Sm_2O_3(s)$ and with $SmC_2(s)$ is approximately $SmC_{1.43}$ at 1500 K; the gaseous oxides of carbon are not shown.)

Results

Phase Equilibria in the Sm–O–C System. Preparative Results. The equilibrium phases formed at selected compositions in the Sm–O–C system are summarized in Table I. The 1500 K section of the ternary-phase diagram in Figure 1 shows that only four binary and ternary phases are observed. In the X-ray diffraction spectrum of metal-rich (C:Sm $<$ 1.0) products, a set of diffuse lines assignable to rhombohedral (α-type) samarium and the sharp pattern of Pu_2C_3-type carbide were the only observed reflections. The existence of Sm_3C could not be confirmed by numerous preparative attempts with diffferent reaction times (2–10 h) and temperatures (1000–2000 °C) and different annealing procedures.

Analytical Results. The compositions of the carbide and oxide carbide phases were obtained with crystallographically pure samples. Pure oxide carbide was first obtained as the apparent result of a zone-melting process in the inverted reaction container. After a reactant mixture with O:Sm = 0.50 and C:Sm = 0.50 had been heated in the inverted position, the larger fraction was a mixture of SmC_y and oxide carbide. The analytical results for crystallographically pure oxide carbide samples are given in Table II. Metal and carbon analyses (cf. tests 1–4) gave 92.2 ± 0.2 mass % Sm and 2.7 ± 0.3 mass % C. The oxygen content determined by partial vaporization and acidic dissolution (tests 5 and 6) was 5.0 ± 0.3 mass % which was in excellent agreement with 5.1% value obtained by difference. The average carbon content of the partially vaporized samples (tests 5 and 6) is in excellent agreement with that of initial oxide carbide (tests 1–4) and shows that carbon-containing vapor species such as CO are not products of the vaporization reaction. Evidence for the presence of unbound carbon was not observed. On the basis of these results, the oxide carbide composition is

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(5) Haschke, J. M. *High Temp Sci.* **1977**, *9*, 77.

Table II. Analytical Results for the Oxide Carbide Phase

	mmol/g of sample				
test[a]	Sm	C	O[b]	C:Sm	O:Sm[b]
1	6.137	2.253	(3.13)	0.37	(0.51)
2	6.146	2.147	(3.14)	0.35	(0.51)
3	6.123	2.468	(3.11)	0.40	(0.50)
4	6.119	2.483	(3.14)	0.41	(0.50)
av 1–4	6.13 ± 0.02	2.34 ± 0.16	(3.13)	0.38 ± 0.03	(0.51)
5[c]		2.081	3.318	0.34	0.54
6[c]		2.399	2.919	0.39	0.48
av 5, 6		2.29 ± 0.11	3.12 ± 0.20	0.37 ± 0.03	0.51 ± 0.03

[a] Tests 1 and 2–4 were made with samples from different preparations. Analyses 1–4 were gravimetric measurements for Sm and C contents as Sm_2O_3 and CO_2. In analyses 5 and 6 the oxide carbide was vaporized to form a carbide–Sm_2O_3 mixture; O and C were then determined as insoluble Sm_2O_3 and as CO_2, respectively, in separate analyses of the divided residue. [b] Values in parentheses are obtained by difference. [c] The C and O contents are normalized to the mass of the initial (unvaporized) sample; the C:Sm and O:Sm ratios were calculated by using the average value of 6.13 mmol of Sm/g of sample.

$SmO_{0.51\pm0.03}C_{0.38\pm0.03}$ or nominally $SmC_{0.5}C_{0.4}$. As shown in Table I, the products obtained at this reaction stoichiometry were monophasic oxide carbides.

The preparation of pure samples of the Pu_2C_3-type carbide was limited to the middle of the temperature range normally accessible to effusion measurements. The compositions of SmC_y samples prepared by the dual-chamber procedure at 1127 and 1327 °C were $SmC_{1.44\pm0.02}$ and $SmC_{1.42\pm0.02}$, respectively.

Vaporization Behavior. Incongruent vaporization reactions observed for the SmC_y and $SmO_{0.5}C_{0.4}$ phases are consistent with the phase diagram in Figure 1. As Sm(g) is lost by the oxide carbide, Pu_2C_3-type SmC_y(s) and B-type Sm_2O_3(s) products are formed. As Sm(g) is lost by SmC_y(s), the condensed product is $SmC_{2.0}$(s). In each case, the isothermal system is thermodynamically invariant. The time dependence of the samarium pressure in the $SmO_{0.5}C_{0.4}$ equilibrium system at 1426, 1458, and 1511 K is shown in Figure 2. The initial pressure is characteristic of the oxide carbide. However, as each of these experiments proceeds, the pressure remains constant until the oxide carbide is depleted; the pressure then drops to a second plateau characteristic of the SmC_y–SmC_2 equilibrium system and finally drops again after the SmC_y phase is depleted. In the tests at 1410 and 1575 K, SmC_y was the initial phase, and the first plateaus are characteristic of the SmC_y–SmC_2 system and consistent with the second plateaus obtained with the oxide carbide. The pressure drops occurring after depletion of SmC_y are larger and more gradual than observed after depletion of $SmO_{0.5}C_{0.4}$. This behavior is a consequence of the relatively low Sm pressure in the SmC_2–C equilibrium system. Attainment of that pressure plateau in the present temperature range is very slow.

A combination of analytical and gravimetric measurements has been used to verify that samarium is the only significant vapor species in the metal-rich regions of the Sm–O–C system. Since earlier mass spectrometric studies have demonstrated that Sm(g) is the only observable component of the equilibrium vapor in the SmC_2–C region,[6] the same vapor phase must exist in the more metal-rich regions of the binary section. As noted above, carbon analyses have shown that the gaseous vaporization products of the oxide carbide do not contain carbon. Mass-balance effusion experiments with $SmO_{0.5}C_{0.4}$ samples were conducted at 1300 K until X-ray analysis showed that the residue contained only Sm_2O_3 and SmC_y. The average mass loss (40.4 ± 0.9%) is in good agreement with the theoretical change of 36.7% for eq 1. The difference in these

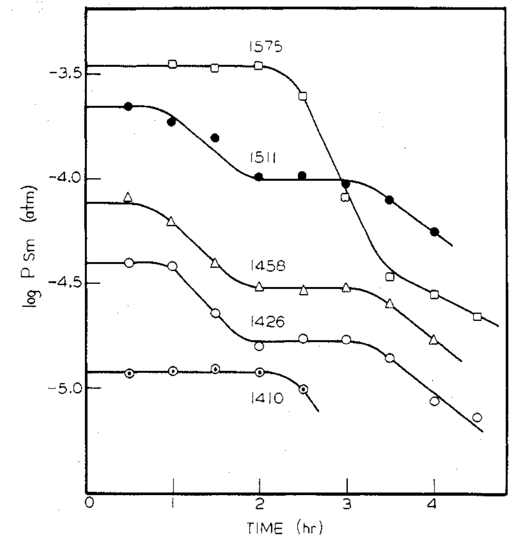

Figure 2. Time dependence of the pressure of Sm(g) in equilibrium with the oxide carbide and the Pu_2C_3-type carbide while Sm is lost by effusion. (At 1426, 1458, and 1511 K, the initial plateau is characteristic of the $SmO_{0.5}C_{0.4}$(s)–Sm_2O_3(s)–SmC_y(s)–Sm(g) system; the second plateaus at these temperatures and the initial plateaus at 1410 and 1575 K are characteristic of the SmC_y(s)–SmC_2(s)–Sm(g) system.)

Table III. Selected Properties of Carbon-Containing Phases Observed in the Sm–O–C System

			lattice parameters[a]		
phase[e]	structure type (space group)	color	a, Å	c, Å	d_x, g/cm^3
$SmC_{2.0}$[b]	CaC_2 (*I*4/*mmm*)	gold	3.763 (1)	6.321 (4)	6.47
$SmC_{1.45}$[c]	Pu_2C_3 (*I*43*d*)	nickel	8.451 (1)		7.38[d]
$SmC_{1.36}$[c]	Pu_2C_3 (*I*43*d*)	silver	8.399 (1)		7.47[d]
$SmO_{0.51}C_{0.38}$	NaCl (*Fm*3*m*)	steel	5.066 (2)		8.33[d]

[a] Uncertainties in the last digits are given in parentheses. [b] SmC_2 is in equilibrium with Pu_2C_3-type carbide. [c] Compositions were determined by Vegard's law extrapolation. [d] The density of SmC_y is calculated by assuming no vacancies; that of oxide carbide is calculated for the anion vacancy model. [e] Electrical conductivity is high for all phases.

$$SmO_{0.51}C_{0.38}(s) \rightarrow 0.170Sm_2O_3(s) + 0.262SmC_{1.45}(s) + 0.398Sm(g) \quad (1)$$

values is attributed to partial vaporization of the SmC_y product.

A systematic variation of the lattice parameter of SmC_y with equilibrium temperature was observed during the vaporization experiments. Values of a_0 range from 8.445 ± 0.002 Å at 1400 K to 8.435 ± 0.002 Å at 1600 K for the Pu_2C_3-type phase in equilibrium with oxide carbide and with the dicarbide.

Properties of the Carbides and Oxide Carbide Phases. Physical Properties. Selected properties of the carbides and oxide carbide are presented in Table III. The phases are hard, have a metallic luster consistent with their high electrical conductivities, and hydrolyze rapidly in air.

Nonstoichiometry and Defects. The temperature trend observed in the phase-boundary lattice parameter of the Pu_2C_3-type carbide has been quantified by using SmC_y samples equilibrated by the dual-chamber effusion method. As shown in Figure 3, a_0 decreases linearly with the equilibration temperature over the accessible effusion range (1300–1700 K) and is in good agreement with the value observed for preparative products obtained at 2200 ± 50 K. This regular change in the lattice parameter of SmC_y suggests that the equilibrium

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[6] Seiver, R. L.; Eick, H. A. *High Temp. Sci.* **1971**, *3*, 292.

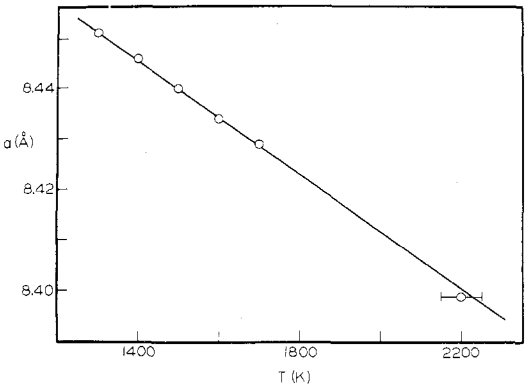

Figure 3. Temperature dependence of the cubic lattice parameter of the Pu_2C_3-type carbide, SmC_y, in equilibrium with $SmO_{0.5}C_{0.4}$(s)-Sm_2O_3(s)-Sm(g) and with SmC_2(s)-Sm(g).

(phase-boundary) composition of the Pu_2C_3-type carbide changes with temperature.

The results in Figure 3 show that SmC_y exists over a finite composition range; however, determination of its lattice parameter–stoichiometry relationship has been more difficult. The observed a_0 values vary from 8.399 to 8.451 Å, but corresponding compositions have only been determined at two points ($a_0 = 8.434$ Å at $y = 1.42$; $a_0 = 8.446$ Å at $y = 1.44$) which span a limited portion of the nonstoichiometric range. If the trend established by these data is extrapolated to the parameter limits by assuming Vegard's law dependence, the composition range of the Pu_2C_3-type phase observed in this study extends from $SmC_{1.45}$ ($a_0 = 8.451$ Å) to $SmC_{1.36}$ ($a_0 = 8.399$ Å). These results are consistent with the qualitative observations of Spedding et al.,[1] who found that a_0 varies from 8.399 to 8.426 Å at the metal-rich and carbon-rich phase boundaries, respectively, and with the measurements of Venet and co-workers[3,4] who reported that $a_0 = 8.385$ at the metal-rich boundary of $SmC_{1.37}$.

Analytical and structural data for the oxide carbide phase indicate that it has a defect structure and is stable over a narrow stoichiometry range. The lattice parameters observed for equilibrated products of preparative reactions and vaporization experiments were in the range 5.066 ± 0.002 Å. The measured density of $SmO_{0.5}C_{0.4}$ (7.7 ± 0.1 g/cm^3) is 92% of the theoretical value calculated for the NaCl-type phase with 10% anion vacancies. Although the formation of a structure with the interstitial samarium cannot be excluded, its calculated density (9.36 g/cm^3) is in poor agreement with the observed value.

When a preparative experiment was effected by heating a reaction mixture with O:Sm = 0.5 and C:Sm = 0.5 at 1000 ± 50 °C for 2 h, X-ray diffraction data for the charcoal gray product showed a fcc pattern composed of broad diffraction bands. Lattice parameters obtained for the high- and low-angle limits of the bands were 5.035 ± 0.001 and 5.067 ± 0.002 Å, respectively. The product is believed to be a metastable oxide carbide similar to the oxide carbide hydride observed in the ytterbium system.[7] The occurrence of broad-band reflections is attributed to severe concentration gradients in the nonequilibrium product. Superstructure reflections are not observed in diffraction patterns for any of the products; the defects appear to be randomly distributed.

Hydrolysis Products. Mass spectrometric analyses of the hydrocarbon products show that SmC_y and $SmO_{0.5}C_{0.4}$ contain different carbon anions. As expected for a Pu_2C_3-type carbide,[8] the major constituents of the hydrolysis products of SmC_y were C_2 hydrocarbons; however, the parent peak of CH_4 was clearly present. These results suggest that the carbide species are primarily diatomic but that a small fraction of monoatomic carbide ions are present. The major hydrolysis product of the oxide carbide is methane; trace quantities of C_2H_6 observed in the product are apparently formed by association of monoatomic ions during hydrolysis.

Discussion

The Sm–O–C Phase Diagram. The results of composition and vaporization studies are consistent with the ternary-phase diagram presented in Figure 1. Both techniques confirm the existence of a NaCl-type oxide carbide like that first described by Butherus and Eick.[9] The absence of a dimetal dioxide dicarbide in the samarium system is also consistent with their observations that the monoclinic oxide acetylide, a structural derivative of the B-type oxide,[10] exists only for La–Nd. Our observations also confirm the results of Felmlee and Eyring,[11] who concluded that samarium monoxide does not exist. It should be noted that the phase diagram in Figure 1 is generally applicable for $T \leq 1600$ K. The observations of Seiver and Eick[6] indicate that appreciable quantities of CO are generated at higher temperatures by the reaction of Sm_2O_3 with carbon, but this region of the phase diagram has not been examined in the present study.

The NaCl-Type Oxide Carbide. Samarium oxide carbide is clearly an oxide methanide similar to those which have been characterized for Nd and Yb.[9,12] Similar NaCl-type phases are also reported for La, Gd, Ho, and Er,[9] but their properties have not been characterized. It is also apparent that several of the so-called carboxides prepared by reaction of lanthanide metals with CO are members of this group.[13]

The present results suggest that the defect structure and the electrical conductivity of $SmO_{0.5}C_{0.4}$ are related properties. The hydrolysis data demonstrate that the carbide species are monoatomic and behave as methanide ions. Since the trivalent ion is known to be present in samarium metal[14] and since magnetic measurements have shown that the cations in $YbO_{0.50}C_{0.47}$ are trivalent,[7] a reasonable formulation for the samarium phase is $Sm^{III}(O^{2-})_{0.5}(C^{4-})_{0.4}\square_{0.1}(e^-)_{0.4}$, which indicates the presence of 10% anion vacancies and an inherent conduction band population of 0.4 electron/mol for maintenance of charge balance. It must be recognized that the actual existence of methanide ions in the lattice is not proposed by use of this formulation. The carbide species are probably anionic but not tetravalent. If the localized charge is less than 4–, the resulting charge imbalance is readily accommodated by increasing the electron population of the conduction band. Knowledge of the molar conduction electron population should be very instructive.

The primary inconsistencies in the reports for the cubic oxide carbides are in their compositions. The major difference between the present results and the $NdO_{0.75}C_{0.25}$ composition reported by Butherus and Eick[9] is the absence of defects in the Nd phase. The C:Ln ratios of both phases are below those of the ideal Ln_2OC compositions reported by Darnell, who based his stoichiometries solely on the observed consumption of CO during its reaction with the metal.[13] From Figure 1, it is clear that the products of the CO–Sm reaction could easily have been mixtures of $SmO_{0.5}C_{0.4}$ and amorphous carbon. The lattice parameter ($a_0 = 5.06$ Å) and the resistivity reported for Sm_2OC are in excellent agreement with those of $SmO_{0.5}C_{0.4}$. The analytically determined composition of ytterbium

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[14] Haschke, J. M.; Eick, H. A. *J. Am. Chem. Soc.* **1970**, *92*, 1526.

phase, $YbO_{0.5}C_{0.47}$, closely approaches the ideal ratio.[12] Its behavior as a semiconductor is consistent with a low defect-induced conduction band population. One is intrigued by the apparent increase in the C:Ln ratio and accompanying decrease in defect concentration and conductivity across the lanthanide series. Additional work with other lanthanides is clearly needed.

As suggested by Butherus and Eick[9] and by Darnell,[13] the NaCl-type oxide carbide probably exists across the entire lanthanide series. A known exception is the Eu phase, which is unstable relative to the monoxide and the carbides.[12] The lattice parameter (5.14 Å) reported for Eu_2OC[13] does not correlate with the parameters of adjacent oxide carbides and is identical with that of EuO.

The Pu_2C_3-Type Carbide. The observed composition range of nonstoichiometric SmC_y is $1.36 < y < 1.45$. The retrograde change in the composition of the phase in equilibrium with $SmO_{0.5}C_{0.4}$ and with SmC_2 is similar to that reported for the orthorhombic ytterbium carbide near the $YbC_{1.5}$ composition.[14] The phase-boundary shift and nonstoichiometry of SmC_y are attributed to altervalency of the carbon anions in the Pu_2C_3-type phase. This conclusion is based on the present observations and on the quantitative identification of the hydrolysis products by Svec et al.[8] and Hackstein et al.[4] Their results agree with our qualitative mass spectrometric data and suggest that the substoichiometric compositions of the Pu_2C_3-type phase result from fractional replacement of the diatomic carbide ions, C_2^{2-}, by monoatomic ions, C^{4-}.

Our results show that the metal-rich regions of the nonstoichiometric range may be approached either by increasing the metal content of the phase in a closed system or by increasing the temperature of the phase in equilibrium with oxide carbide or dicarbide. This behavior is consistent with an anion equilibrium process, $C_2^{2-} + 6e^- \rightleftarrows 2C^{4-}$, which is shifted to the right by increasing either the temperature or the electron (metal) activity of the system. As the anion equilibrium shifts to the right, the fraction of diatomic ions replaced by monoatomic ions increases and the C:Sm ratio of the phase decreases. The observed linear decrease in a_0 of SmC_y with decreasing carbon content is consistent with the replacement of C_2^{2-} ions by the relatively smaller C^{4-} ions. The trivalent cation is present in both the metal[15] and the lanthanide dicarbides,[16] and it is reasonable to assume that Sm^{III} is present in the hypothetical sesquicarbide which may be formulated as $(Sm^{III})_4(C_2^{2-})_3(e^-)_6$. The metallic luster and electrical conductivity of the phase are consistent with this description; anion altervalency of the nonstoichiometric phase is incorporated by the formulation $Sm_4(C_2)_{3-z}(C)_z$.

Examination of plausible mechanisms for accommodation of the monoatomic carbide ions is instructive. Two processes which compensate for the charge imbalance created by replacement of dinegative ions with tetranegative ions are (a) replacement accompanied by a change in the number of conductive electrons and (b) replacement accompanied by formation of anion vacancies. Since the density change across the nonstoichiometric range cannot be measured with sufficient accuracy to discriminate between these processes, the decision must be based on the analysis of hydrolysis products. In fact, the altervalence hypothesis must be questioned unless the analytically determined C_2:C ratio lies within the limits established by the band-compensated and vacancy-compensated models. Although the precise compositions of the carbide samples used in the quantitative hydrolysis studies[4,8] are now known, the diffraction data and preparative conditions suggest that they were near $SmC_{1.40}$. For the band-compensated process, this stoichiometry is formulated as $(Sm^{III})_4(C_2^{2-})_{2.600}(C^{4-})_{0.400}(e^-)_{5.200}$; for the vacancy-compensated mechanism, $SmC_{1.40}$ is described by $(Sm^{III})_4(C_2^{2-})_{2.730}(C^{4-})_{0.135}\square_{0.135}(e^-)_6$. The C_2:C ratios for these formulations are 6.5:1 and 20.2:1, respectively. The experimental ratios obtained from the data of Svec et al.[8] and Hackstein et al.[4] by assuming that the observed traces of C_3 products and C_4 products were formed by association of ions during hydrolysis are 7.6:1 and 12.0:1, respectively. These ratios are clearly within the limits of the altervalence model and are in good agreement with the predictions of the band-compensation process. The observed color change of the Pu_2C_3-type phase with composition (cf. Table II) is also consistent with a concurrent change in the conduction band population. Similar mechanisms of carbide altervalence have been proposed for nonstoichiometric phases in the Ce–C–N[17] and Yb–C[14] systems, but additional work is obviously needed to confirm their existence.

The preparation of stoichiometric Sm_2C_3 has not been achieved in this study. The apparent temperature dependence of the carbon-rich phase boundary requires that a preparative temperature of 500–600 °C be used. However, since the equilibration rate in this temperature range is expected to be very slow, the preparation of $SmC_{1.50}$ seems doubtful.

The Sm_3 Phase. The existence of a Fe_4N-type (defect NaCl-type) carbide phase in the composition range $0.25 <$ C:Sm < 0.40 was first reported by Spedding et al.[1] Subsequent work by Lallement[2] and by Venet and co-workers[3,4] has confirmed its existence. The cubic lattice parameter given for $SmC_{0.4}$ in the initial report is 5.17 Å; the latter reports show variations in a_0 from 5.059 to 5.105 Å[18] and from 5.035 to 5.065 Å.[4] Although their lattice parameters differ substantially, the phases are all identified by the authors as trisamarium monocarbide. As noted above, our results indicate that the metal-rich carbide is not formed.

Although the earlier reports are not sufficiently detailed to permit critical evaluation, the work of Venet and co-workers[3,4] is thoroughly described and amenable to review. The X-ray diffraction and metallographic results for products obtained at C:Sm ratios of 0.3, 0.5, 1.0, and 1.25 show that three condensed phases (α-Sm, Sm_3C and Sm_2C_3) coexist. This observation is obviously inconsistent with the phase rule, which constrains an invariant binary system to the coexistence of two condensed phases plus a vapor phase. An examination of the Sm–C section of Figure 1 demonstrates that the metal and two carbide phases cannot exist in equilibrium. However, the phase rule and the experimental observations are consistent with the behavior of a ternary system.

Our observations indicate that the phase described in the most recent reports[3,4] is actually the oxide carbide. The colors, the C:Sm ratios, the structure types, and the lattice parameters of the Sm_3C phase and $SmO_{0.5}C_{0.4}$ are essentially identical. The phase with somewhat larger lattice parameters described by Lallement[2,9] also merits comment. In that work, samples were prepared by extended sintering of pressed mixtures of samarium hydride and graphite at 800–1400 °C. A recent phase study has demonstrated that a fcc carbide hydride is formed in the Yb–C–H system in the same temperature range.[7] The formation of a carbide hydride by samarium could account for their observations. The cubic parameter reported by Spedding et al.[1] is approximately 0.01 Å larger than the maximum value observed for the oxide carbide in the present study. This difference cannot be explained, and the existence of Sm_3C cannot be excluded. Although our inability to prepare the phase may be a consequence of a very slow reaction rate,

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our observations strongly suggest that the samarium phase described in earlier reports resulted from oxygen and/or hydrogen contamination. Spedding et al. were unable to explain why the trimetal monocarbide existed in some lanthanide systems but not in others. We believe that the presence or absence of anionic contaminants could account for such behavior.

However, the existence of ordered (rhombohedral) and disordered (cubic) dimetal monocarbides of the heavier rare earths has been confirmed[14,19] and it is obvious that the entire list of metal-rich carbides reported by Spedding et al. are not ternary phases. For ytterbium, the following carbon-containing cubic phases have been characterized: $YbO_{0.50}C_{0.47}$ (a_0 = 4.857 Å), $YbCH_{0.5}$ (a_0 = 4.974 Å), and $YbC_{0.5}$ (a_0 = 5.001 Å).[7,12,18] Studies of additional ternary systems of samarium and other lanthanides are needed to resolve the questions raised in this report. As part of our effort with the Sm–O–C system, thermodynamic values for the dicarbide, the Pu_2C_3-type carbide, and the oxide carbide have been obtained from equilibrium measurements and will be described in forthcoming reports.

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Registry No. Sm, 7440-19-9; O, 17778-80-2; C, 7440-44-0.

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Vaporization Behavior of MnP(s) and the Thermodynamics of the Manganese–Phosphorus System[1]

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The vaporization reaction $4MnP(s) = 2Mn_2P(s) + P_2(g)$ has been studied by mass-loss effusion in the temperature range 1071–1192 K. The reaction is kinetically inhibited. From equilibrium measurements the enthalpy of reaction at 298.15 K was found to be 35.1 ± 1.0 kK. The enthalpies of formation and atomization of MnP(s) were evaluated as −12.5 ± 0.6 and 86.2 ± 0.6 kK, respectively; the corresponding values for $Mn_2P(s)$ were −18.1 ± 0.7 and 125.4 ± 0.7 kK. An unexpectedly low value for the atomization enthalpy of MnP was confirmed. The trends in atomization enthalpies of MnP, FeP, CoP, and NiP were made reasonable by adding the respective valence-state preparation energies, thereby giving the atomization enthalpies to valence-state atoms.

Introduction

The atomization enthalpy of a solid compound may be used as a measure of its stability and of the strength of its chemical bonds. The atomization enthalpies of the phosphides of manganese, iron, cobalt, and nickel, as calculated from data in the literature,[2–7] are shown in Figure 1, and it is evident that the manganese phosphides appear to have significantly lower stabilities than the other phosphides. The atomization enthalpies of the manganese phosphides are all dependent on the enthalpy of formation of MnP(s) derived from combustion calorimetry.[2b] Because the manganese phosphides differ so markedly from the phosphides of iron, cobalt, and nickel, it was decided to study the thermodynamics of the Mn–P system in a way such that the enthalpy of formation of MnP could be evaluated independently of the heat of combustion. This was accomplished by a mass-loss effusion study of the reaction

$$4MnP(s) = 2Mn_2P(s) + P_2(g) \tag{1}$$

which, when combined with the results of the solid-state galvanic cell studies by Baratashvili and co-workers[3] of the reaction

$$Mn(s) + MnP(s) = Mn_2P(s) \tag{2}$$

and the enthalpy of formation[8] of $P_2(g)$

$$2P(s, red) = P_2(g) \tag{3}$$

gives the enthalpy of formation of MnP(s)

$$Mn(s) + P(s, red) = MnP(s)$$

$$(4) = -{}^1/_2(1) + (2) + {}^1/_2(3)$$

$$\Delta H_f°(MnP) = -\tfrac{1}{2}\Delta H_1° + \Delta H_2° + \tfrac{1}{2}\Delta H_3°$$

Experimental Section

Samples for the effusion study were prepared in the manner described earlier[6] by direct combination of manganese powder (99.95%) and red phosphorus (99.9%), both obtained from CERAC/Pure, Inc. Weighed quantities of manganese and phosphorus were loaded in a 7-mm o.d. Vycor tube in an inert-atmosphere glovebox. The tube had previously been outgassed by heating under high vacuum and was transferred to the glovebox without exposure of its inner walls to air. After being loaded, the tube was transferred to the vacuum system, again without air exposure, and the sample ampule was sealed off under high vacuum. The ampule typically was heated to about 700 °C for a period of 15–20 h. Precautions described earlier[6] were used to prevent a catastrophic buildup of phosphorus pressure. The presence of both MnP and Mn_2P, before and after effusion runs, was confirmed by comparison of the X-ray powder diffraction pattern with patterns calculated by computer[9] from published structural data.[10,11]

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