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MASTER

Lanthanide Boride Systems and Properties

Part I: Lanthanide-Boron-Carbon Systems

Part II: Vaporization and Stabilities of Lanthanide Borides

(Ph.D. Thesis)

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The High Temperature Vaporization and
Thermodynamic Properties of Titanium Monosulfide¹

TiS

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A high temperature investigation of the vaporization of titanium monosulfide has been accomplished through the use of total collection Knudsen effusion measurements, mass spectrometric analysis of the vapor, and x-ray diffraction studies of the condensed phases. The vaporization of stoichiometric TiS has been shown to be congruent, and the products are TiS molecules and probably Ti and S atoms. Thirty-eight vapor pressure measurements over the temperature range 1804-2186°K give second-law and third-law heats of sublimation, ΔH_{298}° , as 127.8 ± 3.0 and 130.0 ± 3.0 kcal/mole, respectively, in excellent agreement with each other. Reliable values for vapor pressures and mass transport can be obtained from equation (4).

The melting point of the monosulfide is $2200 \pm 20^\circ\text{K}$. Two new crystalline phases in the Ti-S system have been found.

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(1) Abstracted in part from Ph.D. thesis of Hugo F. Franzen, University of Kansas, 1962.

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INTRODUCTION

A high temperature vaporization study of a refractory substance is an excellent method for deriving the thermodynamic properties and stability relationships of gaseous substances, and it is the only convenient method for many chemical systems. The work reported here is one of a number of such studies performed at this laboratory with the purpose of determining the stabilities of gaseous molecules. The specific purposes of this work were to establish the vaporization behavior of the sulfides of titanium, to identify the species of importance in the vapor arising from the most refractory sulfide of titanium, and to measure its vapor pressure and heat of sublimation.

Early work by Biltz, Ehrlich, and Meisel² characterized the higher sulfides of

(2) W. Biltz, P. Ehrlich, and K. Meisel, Z. anorg. u. allg. Chem., 234, 97 (1934).

titanium, namely TiS_3 , TiS_2 , and Ti_2S_3 , and showed that each of these phases loses sulfur preferentially when vaporized at temperatures below 1100°C . These workers also verified the existence of the monosulfide phase. The monosulfide was known to be approximately isostructural with NiAs. Later work indicated the existence of a second phase with the approximate stoichiometry of the monosulfide. Hahn and Harder,³

(3) H. Hahn and B. Harder, Z. anorg. u. allg. Chem., 288, 241 (1956).

who discovered this latter phase, believed that it was the stable form of TiS and that the transition from the unstable NiAs structure occurs at an observable rate at temperatures below 1000°C . On the other hand, Bartram,⁴ who performed an extensive

(4) S. Bartram, The Crystallography of Some Titanium Sulfides, Ph.D. thesis, Rutgers University, New Brunswick, New Jersey (1958).

crystallographic study of the sulfides of titanium, found that this phase was a titanium deficient phase which resulted from the TiS phase by the addition of sulfur. Accordingly, he called this phase Ti_{1-x}S .

Many workers^{2,4-7} have reported sulfides lower in sulfur content than TiS , but

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- (5) R. P. Abendroth and A. W. Schlechten, Trans. AIME, 215, 145 (1959).
(6) H. Hahn and P. Ness, Z. anorg. u. allg. Chem., 302, 17 (1959).
(7) N. E. ^FAilonenko and V. I. ^yKudr^vgavtse^vl', Doklady Akad Nauk S.S.S.R., 88, 891 (1953).
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no definitive study indicating the homogeneity ranges and the temperatures of stability of these phases has been performed.

The present work consisted of the preparation of pure titanium sulfide, the characterization of the vaporization processes, a qualitative mass spectrometric analysis of the vapor arising from TiS , the measurement of the vapor pressure of TiS by the Knudsen effusion technique, and the calculation of the heat of sublimation of TiS .

EXPERIMENTAL

Preparation.--Samples of titanium monosulfide and titanium-deficient monosulfide were prepared by heating National Formulary quality sublimed sulfur with iodide process titanium in approximately equal molar amounts in sealed, evacuated fused silica tubes for about six hours at 800°C . The sulfur was at least 99.5% sulfur, and the titanium, which was supplied by the New Jersey Zinc Company, contained about 0.05% of impurities, principally aluminum and lead. The reaction product was brown with a bluish exterior. The exterior contaminants resulting from interaction of the sample with the fused silica were scraped off the sample, and the sample was then annealed in a tungsten crucible for several hours at about 1400°C in high vacuum. The final products were gold colored and were found by x-ray diffraction to be the TiS phase, the Ti_{1-x}S phase, or a mixture of both.

The compositions of the solid samples were determined by combustion in a platinum crucible in air and weighing as TiO_2 . The phase analyses were accomplished by Debye-Scherrer x-ray diffraction techniques. Standard Norelco 114.6 millimeter diameter cameras were used with a Norelco generator producing copper ($K_{\alpha_1} = 1.54050 \text{ \AA}$) radiation.

Effusion Experiments.--Total collection effusion studies were performed in the vacuum line shown in Figure 1. The vacuum, which was generally better than 5×10^{-6} Torr, was obtained by two mercury diffusion pumps in series backed by a mechanical forepump. The tungsten crucible was approximately 16 mm long and 16 mm in diameter. A 1.5 mm black-body hole was drilled to a depth of 5 mm in the bottom of the crucible. Two different lids had knife-edged orifices with areas of about 3.1 and 0.6 mm². The orifice areas were calculated from the diameter as measured with a traveling microscope. The orifice areas appeared to vary a few percent during the experiments; it was assumed that the orifice areas varied linearly with time. The areas used are probably in error by less than one percent.

The crucible was heated inductively by a General Electric 20 kw 500 kc oscillator with an eleven-turn, water-cooled copper work coil 9 cm in diameter fabricated from one-fourth inch tubing. At the beginning of an experimental run, the temperature was raised to the desired value from about 1000°C in as short a time as possible. The temperature, which was measured by sighting through a calibrated window and prism into the black-body hole in the bottom of the crucible with a Leeds and Northrup disappearing filament optical pyrometer calibrated at the U.S.N.B.S., was generally uniform to within a few degrees after about three minutes. The elapsed time during a total collection run was measured to the nearest minute. The same equipment was used for the characterization of the vaporization behavior of the titanium sulfides.

The amount of titanium transported to the water cooled Vycor cap was determined by colorimetric analysis. The transported material was dissolved in hot 2N sulfuric

acid and the resulting solution was diluted to a known volume with an excess of 3% hydrogen peroxide-2N sulfuric acid solution. The concentration of titanium in the effusate was determined colorimetrically at 425 mμ. The procedure was standardized with National Bureau of Standards TiO₂ sample No. 154-a. The titanium transport together with the fact that TiS_{1.00} vaporizes congruently yields the total weight loss from the crucible.

Mass Spectrometric Experiments.--Mass spectrometer experiments were performed in a Nuclide Analysis Associates high temperature mass spectrometer. The Dempster-type instrument is a 60° sector magnetic field, first order direction focusing spectrometer with 12 inch radius. The sample was heated by electron bombardment in a tungsten Knudsen crucible, about 19 mm in diameter and 38 mm tall. The molecules effused through an orifice about 1 mm in diameter and were ionized by seventy-volt electrons. The signal was detected by an electron multiplier at a given mass when a shutter above the Knudsen crucible was closed. The masses were established by counting background peaks between known peaks and the peak of interest. The temperature was measured as previously described.

RESULTS

Characterization of the Vaporization Behavior.--A Ti₂S sample, described later, formed a thin gold coat thought to be TiS when it was partially vaporized at about 1710°K, about 50° below its melting point. Vaporization of a sufficient quantity of this sample to allow identification of the gold material was not practicable owing to the low melting point and the low volatility (3×10^{-3} mg/min at 1710°K) of the sample. This observation indicates that the Ti₂S phase loses titanium preferentially to form a surface layer of TiS.

The work of Biltz et al.² showed that the higher sulfides lose sulfur preferentially at high temperatures. A sample of synthetic composition S/Ti = 1.05 was found to

consist solely of the TiS and the $Ti_{1-x}S$ phases. After this sample had been heated at about 1918°K in a tungsten Knudsen crucible in high vacuum for a time sufficient to vaporize twelve percent of the original sample, the residue was found to consist of the TiS phase only. This observation indicates that the conclusion of Hahn and Harder³ concerning this phase is incorrect and that the $Ti_{1-x}S$ phase loses sulfur preferentially.

To establish more firmly the congruent vaporization of TiS, sulfur-rich and sulfur-deficient samples were partially vaporized. Four consecutive heatings of a sulfur-rich sample at $1980 \pm 10^\circ K$ resulted in residues with the consecutive S/Ti ratios: 1.04, 1.03, 1.02, and 1.00. From the other side of stoichiometry a sample with the S/Ti ratio of 0.96, when heated at a temperature of $1990 \pm 10^\circ K$, resulted in a residue with the composition $S/Ti = 0.99$. The uncertainty in the S/Ti ratios is in all cases mentioned less than 0.02. Thus there exists at about 1975°K a congruently vaporizing composition at $TiS_{1.00 \pm 0.02}$.

Other experiments suggested that congruent vaporization may occur at slightly different compositions at different temperatures. For example, the residue from the effusion experiment at the highest temperature, 2186°K, was found to have $S/Ti = 1.04 \pm 0.01$ after extensive heating of a monosulfide sample at consecutively higher temperatures. The residue from effusion experiments at 1895°K was found to have $S/Ti = 0.97 \pm 0.01$ after 25% had vaporized, even though the sample was originally sulfur-rich. In the high temperature case a new phase constituted the residue; in the low temperature case the residue was composed solely of the NiAs-like monosulfide. The existence of a high temperature modification of the monosulfide will be discussed below.

The TiS phase thus probably exhibits a slight dependence of congruent composition on temperature, but the vaporization data were obtained in the temperature range at

which this composition is $\text{TiS}_{1.00 \pm 0.04}$. It was assumed in the treatment of the data that the congruently vaporizing sample was pure monosulfide.

An experiment was performed to establish the absence of interaction of TiS with the tungsten crucible. A 9.45 mg weight loss by the crucible and sample was observed to result from a 15.5 hour heating at 1923°K . After this vaporization the sample was easily removed from the crucible, and the latter itself was observed to have lost only 0.05 milligrams. This loss that was probably not significant and was, in any case, a negligible portion of the total weight loss. Thus no significant interaction between the titanium monosulfide and the tungsten crucible occurred. At the temperatures and sulfur pressures of the experiments no stable tungsten sulfide is known either in the vapor or in the solid phase.

Effusion Measurements. --The effusion results are given in Table I and shown in Figure 2. **The measurements were made in both increasing and decreasing temperature order in a non-systematic way.**

In Table I the first three columns contain the corrected temperature $\underline{I}$, time $\underline{t}$ in minutes, and mass of titanium (not TiS) collected $\underline{m}$ in mg as established by the colorimetric assay. The errors in these quantities are approximately $\pm 3^\circ\text{C}$, $\pm 1/4$ min and ± 0.01 mg, respectively. In the fourth column are given the orifice areas in mm^2 . The fifth column contains values of the pressure calculated from the Knudsen equation,

$$P_E = \underline{m} \underline{I}^{1/2} / 1.594 \times 10^4 \underline{a} \sqrt{79.96} \text{ atm}, \quad (1)$$

in which the constant in the denominator is $44.33 \times 60 \times 10^3 \times 47.90/10^2 \times 79.96$, and the argument of the radical is the molecular weight of TiS and P_E is the pressure calculated as if TiS(g) is the only vaporization product. A plot of $\log P_E$ vs. $\underline{I}/\underline{T}$ is given in Figure 2. The calculated errors in the P_E values obtained from the errors in the experimentally measured quantities are less than five percent. As is usually the case in high temperature work, the scatter of the individual points is considerably greater.

TABLE I

Effusion Data for Titanium Monosulfide

T (°K)	t (min)	mass Ti collected (mg)	Orifice area (mm ²)	P _E (10 ⁻⁶ atm)	$-\left(\frac{F^{\circ}-H_{298}^{\circ}}{T}\right)$		ΔH_{298}°
					TiS(s)	TiS(g)	
1804	231	0.26	3.22	0.104	27.3	66.9	129.2
1828	280	0.36	3.18	0.121	27.5	67.0	130.2
1840	197	0.37	3.22	0.176	27.5	67.0	129.5
1852	240	0.59	3.22	0.230	27.6	67.1	129.5
1853	354	0.83	3.22	0.220	27.6	67.1	129.5
1873	300	0.765	3.18	0.244	27.7	67.2	130.7
1876	395	1.07	3.18	0.259	27.8	67.2	130.4
1880	195	0.69	3.22	0.334	27.8	67.2	129.7
1883	233	0.88	3.22	0.357	27.8	67.2	129.7
1899	255	1.11	3.18	0.419	27.9	67.3	130.3
1905	240	1.28	3.22	0.507	27.9	67.3	129.9
1917	193	1.24	3.22	0.613	28.0	67.3	129.8
1925	148	1.10	3.22	0.710	28.0	67.4	129.9
1928	180	1.14	3.18	0.614	28.1	67.4	130.5
1939	197	2.01	3.22	0.979	28.1	67.4	129.5
1954	43	0.43	3.18	0.976	28.2	67.5	130.5
1962	260	0.66	0.598	1.32	28.3	67.5	129.9
1976	180	2.69	3.18	1.47	28.4	67.5	130.0
1976	240	2.63	3.18	1.03	28.4	67.6	131.6
1978	120	2.22	3.22	1.79	28.4	67.6	129.6
1993	95	1.92	3.22	1.97	28.5	67.6	129.9
1998	155	3.81	3.22	2.40	28.5	67.6	129.5
2008	65	1.84	3.22	2.76	28.6	67.7	129.5
2013	92	2.745	3.22	2.92	28.6	67.7	129.6
2022	144	0.93	0.598	3.41	28.6	67.7	129.6
2035	80	2.98	3.22	3.66	28.7	67.8	130.2
2055	40	2.11	3.22	5.21	28.8	67.8	129.9
2072	91	1.02	0.598	5.99	28.9	67.9	130.3
2079	127	2.80	0.598	11.80	29.0	67.9	127.9

TABLE I (continued)

2083	79	1.21	0.598	8.20	29.0	67.9	129.6
2092	60	0.93	0.598	8.32	29.1	68.0	129.9
2110	80	1.75	0.598	11.8	29.2	68.0	129.6
2125	42	1.04	0.598	13.4	29.3	68.1	129.8
2136	60	1.79	0.598	16.2	29.3	68.1	129.7
2136	60	1.135	0.598	10.3	29.3	68.1	131.6
2158	60	1.895	0.598	17.2	29.4	68.2	130.8
2168	60	2.01	0.598	18.3	29.5	68.3	131.2
2186	60	2.61	0.598	23.9	29.6	68.3	130.9

average 130.0 $\pm$ ^{0.1}~~0.7~~

The sixth and seventh columns contain values of the free energy functions for TiS(s) and TiS(g) . Values for the solid were obtained by assuming that the entropy of TiS(s) at 298°K is 14.8 e.u. in accordance with the tables given by Latimer,⁸ and

(8) W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, Prentice-Hall, Inc., New York (1953).

that the high temperature heat capacity of TiS(s) is given by:

$$C_p(\text{TiS}) = C_p(\text{TiO}) + 1/2 [C_p(\text{ZnS}) + C_p(\text{MnS}) - C_p(\text{ZnO}) - C_p(\text{MnO})]. \quad (2)$$

The heat capacities are given by Kelley.⁹

(9) K. K. Kelley, Contribution to the Data on Theoretical Metallurgy, Bureau of Mines Bulletin No. 584, U.S. Government Printing Office, Washington, D.C., (1960).

Values for the gas were obtained by assuming that TiS(g) has a ${}^3\Pi$ or ${}^3\Delta$ ground state, that the ratio of the monoxide vibrational frequency to the monosulfide vibrational frequency is 1.65, which is the average of this ratio for Sn, Si, Pb, Mg, and Ge, and that the internuclear distance in the monosulfide is given by:

$$r_{\text{TiS}} = r_{\text{TiO}} - 1/2 r_{\text{O}_2} + 1/2 r_{\text{S}_2}. \quad (3)$$

The values of the internuclear distances are given by Sutton.¹⁰ The final column in

(10) L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions, Special Publication No. 11, The Chemical Society, London (1958).

Table I contains third-law values of ΔH_{298}° calculated from data in the preceding columns on the assumption that TiS(g) is the only product. The values are $\Delta H_{298}^\circ = 130.0 \pm 0.1 \text{ kcal/mole}$ and $\Delta S_{298}^\circ = 43.8 \pm 2.0 \text{ e.u.}$

Estimates of the reliability of the entropy values were obtained by a comparison of experimental values for other monosulfides and those calculated by the described

procedure. On the basis of these assumptions the error in the entropy of the solid is less than 1.5 e.u., and the error in the entropy of the gas is less than 0.5 e.u., provided that the ground state was properly chosen. If these estimates are correct, the third-law enthalpy of vaporization of TiS is in error by less than four kilocalories.

The second-law heat and entropy of sublimation obtained from a linear least squares treatment of the results shown in Figure 2 are 117.8 ± 1.3 kcal/mole and 33.0 ± 0.6 e.u. at 2000°K. On being corrected to 298°K, these values become 127.8 ± 3.0 kcal/mole and 42.7 ± 1.5 e.u., respectively. No significant temperature trend exists in the third-law heats. The small probable error reveals the precision of the data and also the absence of a trend. The corresponding vapor pressure equation is,

$$\log P_E(\text{atm}) = -(2.575 \pm 0.029) \times 10^4/T + 7.21 \pm 0.14. \quad (4)$$

These second-law values are in excellent agreement with the third-law values. This agreement and the constancy of the third-law values indicate that temperature, analytical and other errors were small.

Mass Spectrometer Measurements.--Signals originating from the crucible with relatively high intensities were observed at masses 32, 48, 64, and 80 and a very weak peak at mass 112 at temperatures in the neighborhood of 1950°K. No other important mass peak was found up to about 400 mass units. The isotopic distributions permit the identification of the peaks at 48, 64, and 80 as Ti^+ , TiO^+ , and TiS^+ . The ion S_2^+ also contributed to mass 64. The shutterable peak at 32 was taken as S^+ and that at 112 as TiS_2 .

The relative intensities, ionization efficiency curves, and appearance potentials of TiS^+ , Ti^+ , and S^+ were not accurately determined, but the observed intensities clearly indicate that TiS(g) constitutes at least 25% and possibly nearly 100% of the vapor.

Condensed Phase Results.--A sample with the approximate composition Ti_2S was synthesized by arc melting an equal molar mixture of TiS and titanium metal. The resulting phase is a new one with a melting point of $1760 \pm 20^\circ K$ and structural work is in progress. Annealing of this sample at $1000^\circ C$ for one week resulted in a product whose powder pattern contained only TiS lines. Thus, Ti_2S is a high temperature phase which is unstable at $1000^\circ C$ with respect to the formation of TiS and probably another phase.

Another new phase was obtained as the residue from the highest temperature vaporization experiment. Its powder pattern was of very poor quality and contained lines in the front reflection region only.

A TiS sample melted when heated to $2220^\circ K$. Since another TiS sample was known to have remained solid at $2196^\circ K$, the melting point of TiS is $2200 \pm 20^\circ K$.

DISCUSSION

The excellent agreement between the second- and the third-law heats of vaporization, the absence of a significant trend in the third-law enthalpy, and the low probable errors in both the second- and the third-law heats indicate that the effusion results are very reliable. The transport of titanium monosulfide from a Knudsen cell, or the vapor pressure, can be calculated very accurately from the third-law heat of vaporization of 130.0 ± 0.1 at $298^\circ K$ and the free energy functions for TiS(s) and TiS(g) given in Table I. Alternatively, reliable values may be obtained from equation (4).

The mass spectrometric results are less definite, and hence the proportions of the vapor species are less well fixed, yet the measurements reveal the existence of both TiS(g) and its dissociation products in the vapor. If the vapor consists of as little as 25% TiS(g) which is the lower limit, the third-law heat of sublimation of TiS to form TiS(g) would be raised by only 5.5 kcal/mole.

The dissociation energy of TiS(g) cannot be obtained from the present information alone. Whenever the heat of formation of TiS(s) is measured, the dissociation energy of TiS(g) follows immediately from its heat of sublimation and the properties of the elements. Alternatively, when a reliable vapor species analysis is obtained, the dissociation energy of TiS(g) and the heat of formation of TiS(s) follow.

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Figure 1. Vacuum Apparatus for Total Collection Effusion Studies of Titanium Monosulfide.

Fig. 2. The Vapor Pressure of Titanium Monosulfide