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Authors

Miller, Alan R.
Searcy, Alan W.

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Department of Mineral Technology and
Lawrence Radiation Laboratory, Inorganic Materials Research Division,
University of California, Berkeley, California

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ABSTRACT

Sublimation pressures were measured for indium sesquisulfide between 950 °K and 1130 °K by the Knudsen effusion method, and the composition of the vapor was investigated with a mass spectrometer. The solid sublimes almost exclusively by the reaction $\text{In}_2\text{S}_3(\text{s}) = \text{In}_2\text{S}(\text{g}) + \text{S}_2(\text{g})$ for which ΔH_{298} is calculated to be 147.4 ± 3 kcal. The equilibrium constant is given in the experimental range by the equation $-\log K = \frac{30,660}{T} - 17.94$. The heat of formation of $\text{In}_2\text{S}(\text{g})$ at 298 °K is calculated to be $+14.6 \pm 5$ kcal. The free-surface sublimation rate is about .01 times the equilibrium rate at 1000 °K.

THE SUBLIMATION OF INDIUM SESQUISULFIDE¹Alan R. Miller² and Alan W. Searcy

Department of Mineral Technology and
Lawrence Radiation Laboratory, Inorganic Materials Research Division,
University of California, Berkeley, California

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INTRODUCTION

To engender better understanding of mechanisms of sublimation reactions and, in particular, of the conditions under which sublimation rates are low, equilibrium and kinetic studies for a variety of solids are needed. Suitable solids for study must sublime to yield vapors which have overall compositions that are the same as those of the solid so that kinetics of the surface steps are not obscured by the presence of condensed phase reaction products. The solids should preferably have sublimation pressures in ranges convenient for measurement at only moderately high temperatures and should be obtainable in pure forms. A material that will yield vapor molecules that have structural units distinctly different from those in the solid is desirable in order to increase the probability that the sublimation will show a high activation energy.

Indium sesquisulfide was chosen for investigation because it was expected to satisfy these requirements. Indium sesquisulfide can be precipitated from aqueous solutions³ or prepared directly from the elements.⁴ Its heat of formation was measured by Hahn and Burow with a bomb calorimeter.⁵ They reported the standard heat of formation to be -101.6 kcal/mole.

Rooymans⁶ has presented evidence that the material identified by Hahn and Klingler³ as a low temperature α -phase is simply a poorly crystalline form of the material they had designated as a high temperature β -phase. Rooymans argued that an initial precipitate from acid solutions did not form crystals large enough to produce a sharp X-ray diffraction pattern until heated to 300 °C, and that " α -phase" lines of the Hahn and Klingler structure were simply the strongest lines of the poorly crystallized material.

Prior investigation of the vaporization of indium sesquisulfide has been made by Rumyantsev, Zhitenava, and Kochkin⁷ who also used the Knudsen effusion method with the sample heated in a fused silica cell. They (incorrectly) assumed $\text{In}_2\text{S}_3(\text{g})$ molecules to be the major vapor species. Rumyantsev et al. reported a distinct change in slope of their vapor pressure plot at about 800 °K which they suggest was due to a phase transition. This explanation cannot be correct because their data would require that the higher temperature condensed phase form from the lower temperature modification with a negative heat of transition. It has been shown^{8, 9} that the higher temperature crystallographic modification of any phase must always form from a lower temperature modification with a positive heat of transition. The equations reported by Rumyantsev et al., therefore, must be in error at least in one of the temperature ranges above or below the change in slope.

The objectives of the present investigation were to establish whether or not indium sesquisulfide sublimes to a vapor of overall composition which is the same as that of the solid (i.e., sublimes congruently), to identify the major vapor species by a mass spectrometer

study, to measure the equilibrium rate of sublimation of the phase by the Knudsen effusion weight loss method, and to measure the rate of sublimation from a free surface of the solid.

EXPERIMENTAL

Preparation and Purification of Indium Sesquisulfide

Indium which was stated by the supplier (Indium Corporation of America) to be 99.999% pure was dissolved in HCl. The resultant solution was heated to dryness. A one-tenth molal solution of ammonium acetate was added to the white indium chloride. HCl was also added to bring the acidity to pH 3.

Hydrogen sulfide, bubbled through the solution, precipitated yellow indium sulfide by the reaction

provided that the pH was maintained between 3.4 and 1.5. In solutions of pH greater than 3.4, indium hydroxide precipitates and at pH lower than 1.5 the indium sulfide is soluble.

One molal ammonium acetate solution was added continuously during precipitation because the precipitation reaction produces hydrogen ion and the buffering action of acetate ion is inefficient at pH 3.

The yellow precipitate was decanted and washed four times to remove most of the adsorbed ions and free sulfur. Dilute hydrochloric acid was added after each wash to keep the acidity at pH 3.

Three and one-half grams of the impure sulfide were precipitated from two liters of solution. The precipitate was dried at 110°C in air. The product was an orange powder which yielded a weak and diffuse diffraction pattern.

When heated at 350 °C in vacuum for 2 hrs. the sample decreased in weight by about 7% and a dark red powder remained. This powder yielded a sharp X-ray diffraction pattern of many lines. The line spacings and intensities corresponded to the pattern of the phase identified as β - In_2S_3 by Hahn and Klingler and subsequently re-indexed by Rooymans. The yield of the sulfide was 98% based on the original indium.

The product, as analyzed by K. C. Conway of the Pacific Experiment Station of the U. S. Bureau of Mines, was 70.49% In, 28.84% S, and 0.10% SiO_2 . A weight loss of 1.28% was produced by heating for 1 hr. at 500 °C in a stream of nitrogen. In our subsequent mass spectrometric experiments, InCl^+ was the principal ion detected during initial vacuum sublimation under conditions of our vapor pressure measurements.

The InCl^+ could have been produced by ionization of InCl or by fragmentation and ionization of InCl_3 . If the 1.28% weight loss is ascribed to escape of InCl , the formula of the indium sulfide phase is calculated to be $\text{InS}_{1.485}$. If the weight loss is ascribed to escape of InCl_3 , the formula of the indium sulfide phase is calculated to be $\text{InS}_{1.475}$. Probably the analysis is accurate in suggesting that the composition for congruent sublimation is slightly poorer in sulfur than is the stoichiometric compound.

The InCl^+ intensity in the mass spectrometer became immeasurable after a few weight percent of solid was vaporized. Halide vapor species could not have significantly contributed to the weight losses measured in the Knudsen effusion studies since several weight percent of each sample was vaporized prior to the start of each series of runs.

Congruent sublimation of the indium sesquisulfide on heating was confirmed experimentally. One-half gram samples of In_2S_3 were used for weight-loss runs in experiments with lids of three different orifice diameters. Between heatings small amounts of sample were removed for X-ray diffraction examinations. From 60% to 97% of each sample was evaporated. Although the samples changed in appearance from dark red to black as evaporation progressed, the X-ray diffraction pattern remained unchanged.

The few weak diffraction lines obtained for the pattern of the initial precipitate after it was dried at 110°C corresponded in position to the strongest lines of the sharp $\beta\text{-In}_2\text{S}_3$ pattern. The material did not undergo a structural change when heated for 2 hrs. at 800°C and cooled at 50°C/min . The conclusion of Rooymans that " $\alpha\text{-In}_2\text{S}_3$ " is simply an impure and poorly crystalline form of $\beta\text{-In}_2\text{S}_3$ is apparently correct.

Sublimation Pressure Studies

A Knudsen effusion cell was machined from National Carbon Company grade AUC graphite. Cylindrical effusion holes of approximately 1.5, 1.0, and 0.5 mm diameter, d , as determined by a traveling microscope, were used; the length of each orifice was about twice its diameter so that the Clausing factors were each about 0.4.¹⁰ The cell was cylindrical in shape, 1.6 cm high and 1.4 cm in diameter. A larger graphite crucible surrounded the cell and was in turn supported by a graphite stand.

The entire assembly was supported by the closed end of a vertical fused silica tube. The system was evacuated to a pressure of 10^{-5} mm Hg.

A vertical tube furnace, mounted on a counterweighted dolly, could be raised rapidly over the fused silica tube and sample. The time required to reach the desired temperature was always less than 1% of the heating time employed. Heating time and temperature for each run were chosen to obtain a weight loss of about 10 mg.

The temperature of the sample was measured with a millivolt potentiometer connected to a Pt-Pt 10% Rh thermocouple. The thermocouple was insulated with fused silica and inserted into a hole in the larger crucible. The temperature of this thermocouple was calibrated in experiments in which a second Pt-Pt 10% Rh thermocouple was inserted through the crucible orifice into indium sulfide powder. The thermocouple used for effusion studies recorded a temperature 2° higher than the temperature of the sulfide powder over the entire experimental range. The two thermocouples were both calibrated against a standardized couple and were both found to read 2° low. An on-off controller, operated by a thermocouple located near the furnace windings, maintained the sample temperature within 2° of the desired value.

A lid with no hole was used to establish the weight loss through the walls or through cracks at the lid edges of the cell. This loss can be expressed as

$$-\log_{10} Y = \frac{16,300}{T} - 10.6, \quad (1)$$

where Y is the number of moles of In_2S_3 lost per second and T the absolute temperature. The loss amounts to 37% of the loss through the smallest orifice, 10% of the loss through the middle-sized orifice, and 6% of that through the largest orifice. These results demonstrate the

danger of the assumption that a dependence of apparent pressure on orifice area in Knudsen effusion studies necessarily reflects a low evaporation coefficient.

Free-Surface Sublimation Studies

The approximate rate of free-surface sublimation of indium sesquisulfide at 970° and 1003°K was calculated from the weight losses of indium sesquisulfide disks which were forced into graphite cups so that only one end surface of a disk was exposed. Disks 0.65 cm in diameter and 0.2 cm high were prepared by pressing to 2000 psi in National Carbon Company's AUC grade graphite. The disks were heated 5°C per min and held at 800°C for 20 min. This technique yielded samples of about 94% theoretical density. Microscopic examination suggests that the porosity consisted mainly of very small pores or of closed pores. Graphite from the die was removed from one end of the disk by grinding on wet 400- and 600-mesh silicon carbide paper. The X-ray diffraction pattern obtained from a crushed cylinder then showed only the β - In_2S_3 pattern.

The disks were pushed into a graphite cup so that one end and the cylindrical surface of the disk were forced to within a maximum distance of 0.002 cm from the graphite surface. At vaporizing temperature the gap was slightly smaller because the coefficient of thermal expansion of graphite is lower than that of indium sesquisulfide.

Temperatures were measured with a Pt-Pt 10% Rh thermocouple inserted in a hole in the graphite near the exposed surface of the disk. An optical pyrometer was used to calibrate the thermocouple at 830°

and 865 °C. These were the lowest temperatures for which reproducible optical measurements could be made but were too high for free-surface sublimation experiments using the 0.65 cm diameter disks. Black body cavities 0.158 cm in diameter and 0.317, 0.476, and 0.793 cm deep were drilled into the graphite cup. The apparent temperature of the holes, the graphite surface, and the adjacent indium sesquisulfide surface were read with an optical pyrometer. The black body holes gave identical temperatures of 830° and 868 °C when the apparent surface temperatures of the graphite were 826° and 860 °C, respectively. Apparent surface temperatures of the indium sesquisulfide were then 819° and 850 °C. Since the apparent temperature of the graphite surface is lower than that read in the black body cavities, light reflected from the graphite and indium sulfide surfaces cannot have made the brightness temperatures of either surface greater than the true temperature. The unknown emissivity of the indium sesquisulfide surface is expected to be lower than that of graphite which has an exceptionally high emissivity.¹¹ The true surface temperature must be above the apparent temperature and is probably no higher than the black body temperature. The surface temperature is known, therefore, to within $\pm 15^\circ$ at worst. For our calculations the surface temperatures were assumed to be equal to 832° and 863 °C. Sublimation rates were measured at 697° and 730 °C.

The surface of the sample, after a few milligrams had vaporized, appeared deeply etched as if along grain boundaries. The deep grooves occupied between 1% and 4% of the gross surface area. The value of the sublimation coefficient α calculated from the gross dimensions of the sample surface with surface roughness neglected would, therefore,

be an upper limit to the true value of α . The value of α calculated from the assumption that the fraction of surface that is occupied by grooves can be assigned an effective α of unity should yield a lower limit to α . From these considerations, the limits of α were calculated to be $0.005 < \alpha < 0.04$.

Until better definition of the surface area for sublimation can be achieved, perhaps by utilization of surfaces of single crystals, attempts to refine measurements of α do not appear warranted.

Identification of Vapor Species

An Inghram-type mass spectrometer, made by Nuclide Analysis Associates, was used to identify the major species from the sesquisulfide when heated in tantalum, graphite, and fused silica crucibles by radiation from tungsten filaments. Temperatures were determined with a Pt-Pt 10% Rh thermocouple embedded in the base of the crucible. A shutter 0.05 cm wide by 1 cm long was moved across the molecular beam in order to distinguish between molecules that effused from the cell and molecules produced by secondary reactions outside the cell.

The ions S_2^+ , In^+ , InS^+ , In_2^+ , and In_2S^+ were observed when the vapor that effused from the cell was bombarded with 60-V electrons. When a graphite cell was used, CS_2^+ was also observed; however, moving the shutter across the beam did not affect the CS_2^+ intensity. Furthermore, the crucible lost less than 0.05 mg (4.2×10^{-6} g atoms of carbon) in weight, while a total of 500 mg (1.5×10^{-3} moles) of indium sulfide was sublimed. The CS_2^+ peak is not produced, therefore, by reaction of indium sulfide with graphite inside the cell. The ion intensity ratios

$\text{In}^+/\text{In}_2\text{S}^+$, $\text{InS}^+/\text{In}_2\text{S}^+$, and $\text{In}_2^+/\text{In}_2\text{S}^+$ remained constant over the temperature range 970° to 1250°K, indicating that these ions were all produced by interaction of the electron beam with the same parent molecule. That this parent molecule was In_2S was clearly demonstrated by a series of experiments to be described in a separate paper. In these experiments In_2S^+ and S_2^+ intensities were measured as functions of composition and temperature. As long as solid In_2S_3 was present, the product of the intensities of these ions at constant temperature remained constant to within 50%, while their relative intensities were varied from $\text{S}_2^+/\text{In}_2\text{S}^+ = .0012$ to $\text{S}_2^+/\text{In}_2\text{S}^+ = 0.5$. This is the expected result for the reaction $\text{In}_2\text{S}_3(\text{s}) = \text{In}_2\text{S}(\text{g}) + \text{S}_2(\text{g})$, but would not be expected for the other possible vaporization reactions. At the highest temperatures, In_2S_2^+ was observed; the maximum intensity of In_2S_2^+ was 0.1% of the In_2S^+ intensity. No other ions were detected in a scan to mass 1500.

RESULTS AND DISCUSSION

Table I summarizes the equilibrium constant calculations from the Knudsen effusion studies. The first 8 runs were made with lids for which $d = 1.50$ mm, the next 9 with lids for which $d = 1.04$ mm, the next 3 with lids for which $d = 0.475$ mm, and the last 5 with lids for which $d = 0.480$ mm. The data and least squares line are plotted in Fig. 1. No evidence of a change in slope such as reported by Rumyantsev et al. was found. Their measurements actually agree to within the experimental scatter with ours except at the lowest temperatures. Our data can be reproduced by the equation

$$-\log K = \frac{30,660}{T} - 17.94.$$

In estimating the free energy functions from which the heat of sublimation at 298°K could be calculated, the molecule In_2S was assumed to be bent with an In-S-In angle of 110 deg. The In-S distance was estimated to be 2.1 Å from the known interatomic distances in SnS(g) and SiS(g) ¹² and from comparison of ionic radii of Sn, Si, and In.¹³ Stretching and bending constants were chosen as 3.7×10^5 and 1.75×10^4 dyn/cm, respectively. The standard entropy at 298°K was then calculated as 76 eu, and $-(F_T - H_{298})/T$ was calculated to be 83.92 at 900°K, 84.96 at 1000°K, 85.91 at 1100°K, and 86.78 at 1200°K.

The entropy of In_2S_3 solid at 298°K has recently been determined by E. G. King and W. W. Weller.¹⁴ The high temperature heat content of In_2S_3 was estimated by assuming that C_p varies linearly with temperature and reaches 35 cal deg⁻¹ mole⁻¹ at the melting point.¹⁵ These data were then used to calculate free energy functions for solid In_2S_3 . The values are 52.27 at 900°K, 54.50 at 1000°K, 56.62 at 1100°K, and 58.63 at 1200°K.

A second-law treatment of the data yields 146.8 kcal for the heat of the reaction $\text{In}_2\text{S}_3(\text{s}) = \text{In}_2\text{S(g)} + \text{S}_2(\text{g})$ at 298°K compared to 147.4 ± 0.6 kcal calculated by the third-law method. The absolute uncertainty of the heat is estimated to be ± 3 kcal. When the third-law heat of reaction is combined with the heat of formation of solid indium sesquisulfide reported by Hahn and the heat of formation of S_2 gas (30.8 kcal) tabulated by Stull and Sinke,¹⁶ the heat of formation of $\text{In}_2\text{S(g)}$ is calculated to be $+14.6 \pm 5$ kcal.

Klandberg and Spandau¹⁷ have measured the vapor pressure of $\text{In}_2\text{S(g)}$ above melts which had the overall composition In_2S between 986°

and 1198 °C by the transpiration method. They found the pressure of $\text{In}_2\text{S(g)}$ to be expressed by

$$-\log P_{\text{In}_2\text{S}}(\text{atm}) = + \frac{9320.3}{T} - 5.0404 \quad (986^\circ - 1198^\circ\text{C})$$

and calculated

$$\Delta H_{298}^\circ(\text{form})[\text{In}_2\text{S(g)}] = 6.5 \pm 8 \text{ kcal/mole},$$

apparently on the assumption that the activity of the condensed phases was unchanged by solution formation. Solution would reduce the partial pressure of $\text{In}_2\text{S(g)}$ by an unknown amount.

If the slow step in the evaporation of indium sesquisulfide from a free surface is due entirely to an energy barrier, an α of 0.01 leads to an activation energy of 167 kcal/mole for the congruent sublimation at 298 °K. This value is about 20 kcal more than the equilibrium heat of sublimation.

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FOOTNOTES AND REFERENCES

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Table I. Data for the reaction $\text{In}_2\text{S}_3(\text{s}) = \text{In}_2\text{S}(\text{g}) + \text{S}_2(\text{g})$.

Temp. ° K	Time min.	Corrected wt. loss (mg)	$-\log_{10} K_{\text{eq}}$	ΔH_{298}°
1076	117	9.1	10.530	147.2
1028	301	4.2	12.040	148.0
993	1140	5.3	13.010	147.8
962	5460	9.4	13.886	147.1
982	2547	7.8	13.377	149.1
1135	66	25.1	9.130	147.7
951	6708	4.7	14.674	148.9
1098	87	11.4	10.067	147.8
1037	1054	18.4	11.362	146.0
1011	1346	7.9	12.321	147.1
1031	994	9.0	11.936	148.1
1111	91	13.1	9.498	146.5
988	3815	8.2	13.202	147.9
997	2602	7.1	12.991	148.2
947	9946	3.9	14.697	148.4
1102	82	9.6	9.682	146.4
1037	1005	13.3	11.602	147.3
1083	1023	10.5	10.386	147.5
1070	1045	7.1	10.752	147.6
1026	3837	7.0	11.910	147.2
1127	147	6.5	9.101	146.5
1042	1031	4.8	11.131	145.8
1105	113	2.8	9.614	147.5
1003	5509	4.9	12.544	147.1
1078	366	3.4	10.517	147.4

FIGURE LEGEND

Fig. 1. The equilibrium constant for the vaporization of indium sesquisulfide as a function of temperature for the reaction:

- ⊙ 1.50 mm orifice diameter
- 1.04 mm orifice diameter
- △ 0.475 mm orifice diameter
- 0.480 mm orifice diameter

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