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THE VAPOR PRESSURE OF INDIUM SULFIDES AS FUNCTIONS OF COMPOSITION AND TEMPERATURE

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THE VAPOR PRESSURE OF INDIUM SULFIDES
AS FUNCTIONS OF COMPOSITION AND TEMPERATURE

Alan R. Miller
(Ph. D. Thesis)

October 21, 1963
THE VAPOR PRESSURE OF INDIUM SULFIDES
AS FUNCTIONS OF COMPOSITION AND TEMPERATURE

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THE VAPOR PRESSURE OF INDIUM SULFIDES
AS FUNCTIONS OF COMPOSITION AND TEMPERATURE

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October 21, 1963

ABSTRACT

A dynamic method for obtaining pressure-vs-composition data
in two-component systems is demonstrated for part of the indium-
sulfur system. The composition range of the phase designated as
indium sesquisulfide was investigated by means of x-ray diffraction
and mass spectrometry in the temperature interval 600° to 900° C.
The results show that the phase has a significantly wide solubility range
and that the reported In₃S₄ phase does not exist. The major vapor spe-
cies above indium sesquisulfide in this temperature interval are In₂S
and S₂.

The activity of sulfur in the condensed phase was deliberately
changed in a series of experiments. Indium or sulfur was fused with
the indium sesquisulfide to form various compositions, which when
heated in the mass spectrometer returned to the sesquisulfide com-
position. The major vapor species, observed in a mass spectrometer
as the condensed-phase composition was changing, were used to calcu-
late the free energy of formation as a function of composition and
temperature for indium sesquisulfide and a phase of approximate
composition In₅S₆.

The heat of formation of In₂S(g) at 298° K was calculated to be
14.6 ± 5 kcal/mole. The free-surface sublimation rate was about 0.01
times the equilibrium rate at 1000° K.
I. INTRODUCTION

For determination of the partial pressures of vapor species in multicomponent phase systems by a dynamic method (such as the Knudsen effusion method), a choice of conditions that yield pressures that do not change with time at constant temperature is usually considered essential. Time-independent pressures for a two-component system can be obtained by bringing two condensed phases to equilibrium with the vapor. Some, but not all, two-component systems have particular compositions for which vaporization is congruent. These compositions of congruent vaporization can also be studied by dynamic-pressure-measurement techniques. The pressures that characterize other single-phase compositions are not readily studied.

If a method is available, however, that makes possible continuous determination of the change in composition and pressure with time at constant temperature, a dynamic method for pressure measurement can be used to obtain pressure-vs-composition data in single-phase regions of arbitrary compositions. The mass spectrometer would seem to be especially suitable for use in obtaining pressure-vs-composition data, because with a mass spectrometer, continuous records of the partial pressures of all species in a complex vapor can be obtained. But apparently no experimental evaluation of this use of the mass spectrometer has been made. The principal purpose of this thesis is to make such an evaluation.

The indium sesquisulfide phase was chosen for study (a) because I had previously obtained reliable measurements of the total vapor pressure at the composition of congruent sublimation as a function of temperature, (b) because the vapor-pressure range is a convenient one for study with a high-temperature mass spectrometer, and (c) because our preliminary investigations revealed the indium sesquisulfide phase to have a relatively wide solid-solution range at high temperatures (this was unrecognized in previous investigations).

A portion of the indium-sulfur phase diagram, published in Reference 1, is reproduced in Fig. 1. The shaded area represents the indium sesquisulfide single-phase region found in this study.
Fig. 1. Phase diagram of the system In$_2$S$_3$-In (after Stubbs et al., Ref. 1). The shaded area represents the indium sesquisulfide region found in this study.
A previous thesis reported a study of the total vapor pressure of indium sesquisulfide by means of a Knudsen cell technique. Since the vapor species of indium sesquisulfide were not then known, the heat of vaporization was calculated by both the second- and third-law methods for five possible vapor species. The choice of species that provided best agreement between the two methods was assumed to be correct. Although our initial results indicated that InS and S₂ were the most probable vapor species, corrected calculations showed that In₂S and S₂ were the species actually present.

Prior investigation of the vaporization of indium sesquisulfide has been made by Rumyantsev, Zhitenava, and Kochkin, who also used the Knudsen effusion method with the sample heated over the same temperature interval in a fused-silica cell. They (incorrectly) assumed In₂S₃(g) molecules to be the major vapor species. Rumyantsev et al. reported a distinct change at about 800°K in the slope of their vapor-pressure plot. They suggested that this change 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 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.

Actually, their individual experimental points agree rather well with those reported by me in a previous thesis. The range of values for the heat of formation of In₂S₃ at 298°K, calculated by the third-law method, is within the limits of experimental error (except for the three lowest-temperature points of Rumyantsev et al.). The lowest-temperature point deviates the most: 142.3 vs the mean of 147.4 kcal/mole given in Reference 2. (The values derived from the two lowest temperatures in Reference 2 were calculated to be 148.4 and 148.9 kcal/mole.)
Isakova, Nesterov, and Shendiapin\textsuperscript{5} have studied the vaporization of indium sesquisulfide between 920° and 1360° C by means of a transpiration method and a static (presumably Knudsen cell) method. They also incorrectly assumed that the major vapor species were In\textsubscript{2}S\textsubscript{3}(g) molecules. Their results, when corrected for vapor species In\textsubscript{2}S(g) and S\textsubscript{2}(g), are

\[ -\log K = \frac{25,925}{T} - 14.08, \]

where \( K \) is the equilibrium constant for the reaction In\textsubscript{2}S\textsubscript{3}(s) \( \rightarrow \) In\textsubscript{2}S(g) + S\textsubscript{2}(g) and \( T \) is the absolute temperature. Their data at the lowest temperature, when combined with the free-energy functions given here, yield a heat of formation for In\textsubscript{2}S\textsubscript{3} at 298° K of 146.8 kcal/mole.

In this study the vapor species were identified with a mass spectrometer, and the partial pressures of these species were then measured as a function of temperature in the two-phase region on the indium-rich side of the indium sesquisulfide phase, and as a function of composition and temperature in the indium sesquisulfide-phase solid-solution region.
II. COMPOSITION RANGE OF THE In$_2$S$_3$ PHASE AND SURVEY BY X-RAY DIFFRACTION OF COMPOSITION OF OTHER PHASES

Although indium sesquisulfide as initially prepared is red-orange, after heating at 800°C it turns black. The x-ray diffraction powder pattern, however, remains the same, identical to that reported by Hahn and Klingler for β-In$_2$S$_3$.

The diffraction patterns of indium sesquisulfide samples prepared by heating at about 600°C with excess sulfur, then cooled to room temperature and x-rayed, were also identical to the diffraction patterns of β-In$_2$S$_3$. Samples of composition between 41.5 and 42 at.%, prepared by heating elemental indium with In$_2$S$_3$, showed a single phase with the 40% (β-In$_2$S$_3$) pattern but with a contraction in the unit-cell volume.

The patterns of samples containing 43 to 45% In indicated that two phases were present, one of which had the contracted In$_2$S$_3$ pattern. The other pattern matched that obtained from the sample quenched in the mass spectrometer at a time when the ion intensities were rapidly changing (46.5% In). From the diffraction-vs-composition studies, the maximum solubility of indium in the phase of ideal-composition In$_2$S$_3$ appears to occur at 42 at.% indium at the temperature of our experiments.

The diffraction pattern of the sample of 46.5 at.% In agreed in position and approximate intensities with the pattern of a phase previously reported to have the approximate formula In$_5$S$_6$. For convenience in subsequent discussions, this phase will be designated InS$_{1+}$.

The x-ray diffraction pattern of the 50 at.% In sample (nominally InS) appeared to be that of a third single phase, and patterns of samples ranging from 46.5 to 50 at.% In contained lines of both InS and InS$_{1+}$. The InS pattern (Table I), however, did not agree with the one reported by Schuffle. Perhaps there are two crystallographic modifications of this phase.

A sample of over-all composition In$_2$S yielded the diffraction patterns of indium and of InS as found in this study.
Table I. Values of x-ray diffraction pattern of InS from this study with copper Ka radiation.

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<thead>
<tr>
<th>$2\theta$</th>
<th>dÅ</th>
<th>Relative intensity of lines</th>
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</thead>
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<td>43.21</td>
<td>2.09</td>
<td>S</td>
</tr>
<tr>
<td>48.15</td>
<td>1.89</td>
<td>S</td>
</tr>
<tr>
<td>50.34</td>
<td>1.81</td>
<td>W</td>
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<tr>
<td>52.09</td>
<td>1.75</td>
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<tr>
<td>56.03</td>
<td>1.64</td>
<td>W</td>
</tr>
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<td>1.53</td>
<td>S+</td>
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<td>M</td>
</tr>
<tr>
<td>65.01</td>
<td>1.43</td>
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<td>1.21</td>
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<td>W+</td>
</tr>
<tr>
<td>116.30</td>
<td>0.907</td>
<td>M+</td>
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</table>

S is strong. + means greater strength.
W is weak. - means less strength.
M is medium.
III. MASS-SPECTROMETER IDENTIFICATION OF THE VAPOR SPECIES

An Inghran-type mass spectrometer, made by Nuclide Analysis Associates, was used to identify the major species of indium sesquisulfide when it was 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.

Indium sesquisulfide (prepared as described earlier\(^2\)) was analyzed by K. C. Conway of the Pacific Experiment Station of the U. S. Bureau of Mines. The material was 70.49% In, 28.84% S, and 0.10% SiO\(_2\) by weight. A weight loss of 1.28% was produced by heating this material at 500°C for 1 hour in a stream of nitrogen. In subsequent mass-spectrometric experiments, InCl\(^+\) was the principal ion detected during initial vacuum sublimation in this general temperature range.

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

The ions S\(_2^+\), In\(^+\), InS\(^+\), In\(_2^+S^+\) were observed when the vapor that effused from the cell was bombarded with 60-V electrons. When a graphite crucible 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 atom of carbon) in weight, whereas a total of 500 mg (1.5×10\(^{-3}\) mole) 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 In\(^+\)/In\(_2^+S^+\), InS\(^+\)/In\(_2^+S^+\), and In\(_2^+\)/In\(_2^+S^+\) remained constant over the temperature range 970° to 1250° K, indicating that the major fraction of each of these ions was produced by interaction of the
electron beam with the same parent molecule. The simplest molecule that could be the common parent of these ions is In$_2$S; therefore In$^+$, In$_2^+$, and InS$^+$ must all be produced mainly by fragmentation rather than by simple ionization of gaseous In, In$_2$, and InS.

Purely thermodynamic arguments also suggests that the In$^+$ and In$_2^+$ ions must be produced by fragmentation of something other than the corresponding neutral species. The partial pressure of In gas that would be produced by the reaction In$_2$S$_3$(s) = 2 In(g) + $3/2$ S$_2$(g) can be calculated from the heat of formation of indium sesquisulfide and from standard thermodynamic tables for the elements. The calculated pressure is several orders of magnitude lower than those found in the Knudsen experiments. As In$_2$ gas is a minor species in the saturated vapor of elemental indium, it would be even less important above indium sesquisulfide because the reduced indium activity in the sesquisulfide necessarily favors dissociation of the dimer.

The intensity of the InS$^+$ peak was less than 1% of the intensity of the In$_2$S$^+$ peak, so that even if part of the InS$^+$ were produced from ionization of an InS gas species, the partial pressure of that species is fixed at less than 1%.

The last important possibility to be considered is that the In$_2$S$^+$ ion is produced by fragmentation of a more complex molecule such as In$_2$S$_2$ or In$_2$S$_3$.

That the parent molecule was In$_2$S was clearly demonstrated by the intensity-vs-composition study described in Sec. IV. So long as the In$_2$S$_3$ solid phase was present, the product of the intensities of In$_2$S$^+$ and S$_2^+$ at a fixed temperature remained constant to within 50%, while the ratio S$_2^+$/In$_2$S$^+$ varied from 0.0012 to 0.5. This is the expected result for the reaction In$_2$S$_3$(s) = In$_2$S(g) + S$_2$(g), but would not be expected for the other possible vaporization reactions. At the highest temperatures, In$_2$S$_2^+$ was observed; the maximum intensity of In$_2$S$_2^+$ was 0.1% of the In$_2$S$^+$ intensity. No other ions were detected by scanning as high as mass 1500. This identification allows calculation of thermodynamic quantities for the reaction

$$\text{In}_2\text{S}_3(s) \rightarrow \text{In}_2\text{S}(g) + \text{S}_2(g)$$  (1)
from total-pressure measurements reported in a previous thesis. Table II summarizes the equilibrium-constant calculations from the Knudsen effusion studies for this reaction. The measurements were reported in the earlier thesis. The 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, I assume the molecule In₂S 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) and by comparison of ionic radii of Sn, Si, and In. Stretching and bending constants were chosen as $3.7 \times 10^5$ and $1.75 \times 10^4$ dyn/cm, respectively. The standard entropy at 298°K was then calculated as 76 entropy units (eu); and $-\frac{(F^\circ - H^\circ 298)}{T}$ 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 In₂S₃ solid at 298°K has recently been determined by E. G. King and W. W. Weller. The high-temperature heat content of In₂S₃ was estimated by assuming that \(C_p\) varies linearly with temperature and reaches 35 cal deg⁻¹ mole⁻¹ at the melting point. These data were then used to calculate free-energy functions for solid In₂S₃. 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 reaction (1) 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 Burow (-101.6 ± 3 kcal) and the heat of formation of S₂ gas (30.8 kcal) tabulated by Stull and Sinke, the heat of formation of In₂S(g) is calculated to be +14.6 ± 6 kcal.

Klanberg and Spandau have measured by the transpiration method the vapor pressure of In₂S(g) above melts with an over-all
Table II. Data for the reaction $\text{In}_2\text{S}_3(\text{s}) = \text{In}_2\text{S}(\text{g}) + \text{S}_2(\text{g})$.

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<th>Temp (°K)</th>
<th>Time (min)</th>
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<th>$-\log_{10} K_{eq}$</th>
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<td>366</td>
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</table>
composition of In$_2$S between 986° and 1198° C. They found the pressure
of In$_2$S(g) to be expressed by

$$-\log P_{\text{In}_2\text{S(atm)}} = \frac{9320.3}{T} - 5.0404$$

and, using $\Delta H^\circ_f(298\text{°K}) = -33.6$ kcal/mole for InS(s), calculated

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

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

From a mass-spectrometer study of vapor-phase equilibria, Colin and Drowart\textsuperscript{17} report $\Delta H^\circ_{298\text{°}} = 98.2 \pm 5.0$ kcal/mole for the
reaction

$$\text{In}_2\text{S(g)} = \frac{1}{2} \text{S}_2\text{(g)} + 2 \text{In(g)}.$$}

This leads to a heat of formation of 18.5 kcal/mole for In$_2$S(g). If the
free-energy functions calculated in this study are substituted for those
estimated by Colin and Drowart, a value of 13.8 kcal/mole is obtained.

The ion In$_2$O$^+$ was observable during heating of indium sesqui-
sulfide whenever an air leak developed in the vacuum system, even
though the residual pressure was less than $10^{-6}$ mm Hg. The ion
InGaS$^+$ was seen when indium sesquisulfide was heated subsequent to
several runs during which large amounts of GaN had been vaporized
in the mass spectrometer. These ions were at negligible intensities
during the studies reported in the remainder of this thesis.
IV. MASS-SPECTROMETER EXPERIMENTAL MEASUREMENTS

In this part of the study, indium sesquisulfide samples were prepared by adding enough indium to give over-all compositions of 42 to 50 at.% indium, and sealing them into evacuated fused-silica tubes. Indium sesquisulfide samples rich in sulfur were prepared by adding sulfur and heating in a fused-silica tube during evacuation. Sealed reaction tubes were not used because of the possibility of explosions. x-Ray diffraction pictures were taken of each sample after heating.

The mass spectrometer was used to measure the ion intensities of In$_2$S and S$_2$ molecules effusing from the cell. For the intensity studies, samples were placed in a cylindrical, fused-silica Knudsen cell 1.5 cm high and 1.2 cm in diameter. The fused-silica lids had cylindrical orifices that were 1.6 cm long and had three different diameters: 0.86, 1.22, and 1.80 mm. The cell was placed inside a tantalum crucible fitted with a tantalum lid. The bottom of the glass cell was ground flat and a 2-mil strip of tantalum was placed between the cylindrical walls of the two crucibles in order to effect better heat transfer. The entire assembly was supported by three tungsten rods and heated by radiation from two concentric tungsten filaments.

Temperatures were measured with a Pt-(Pt 10% Rh) thermocouple embedded in a cavity in the underside of the tantalum crucible. The thermocouple was calibrated against another Pt-(Pt 10% Rh) thermocouple inserted through the orifice into the Knudsen cell and immersed in an indium sesquisulfide sample. Although the two thermocouples readings differed linearly, two different calibrations were obtained with two different runs (Fig. 2). This behavior suggests that for different runs at a given temperature, the difference between (a) the temperature of the interior of the glass crucible and (b) the temperature at the base of the tantalum crucible, did not remain constant. The mean temperature of the exterior couple was 5° higher at 600° C and 10° lower at 800° C than the temperature of the interior. But the average deviations in these differences were 8° C at 600° C and 3° at 800° C.
Fig. 2. First calibration, temperature at base of cell vs temperature inside cell. ● one run, □ another run.
The inner fused-silica crucible was removed after each experimental run without disturbing the tantalum crucible. This arrangement was so stable that a plot of thermocouple temperature vs furnace power made from the initial runs could be used for subsequent runs to select the desired operating temperature to within 2°. However, the difference between the sample temperature and the temperature in the base of the cell is clearly sensitive to small variations in sample size or cell arrangement.

Plots of $-R \ln \frac{I_{\text{In}_2S_2}}{T^2}$ vs $1/T$ for any particular vaporization run of indium sesquisulfide were straight lines in the temperature range 600° to 960° C. The slope of these lines should provide a second-law heat vaporization. However, although the lines for each run were straight, the slopes differed from run to run, giving 130, 136, 141, 142, 143, and 145 kcal/mole, with an average of 139.5 ± 4.4 kcal/mole. The value previously determined from Knudsen cell weight-loss experiments—141 kcal/mole—is expected to be more reliable. The variations in the temperature scale noted during the calibration runs are enough to cause 6 kcal variation in the measured slopes.

The indium-rich samples were heated at 600°, 650°, 700°, 750°, and 800° C; the sulfur-rich samples were heated at 600°, 650°, 700° and 750° C. Several 40-at.% samples were heated to between 880° and 950° C. During each run the intensities of the ions $\text{In}_2\text{S}^+$ and $\text{S}_2^+$, the major vapor species, were alternately recorded on a strip chart until the ion intensities became constant with time (Fig. 3). The sample was then quickly cooled to room temperature. The samples were weighed before and after heating, and x-ray diffraction powder patterns were made at the conclusion of each run.

Several samples, initially 50-at.% indium, were heated in the temperature range 600° to 750° C; all showed constant ion intensities at first, then a rapid change in intensities in a very short time period (Fig. 4). The rapid change indicated that a narrow, single-phase region was being traversed. The experiment was repeated, therefore, at 700° C and the sample was quickly cooled when the middle of the composition of sharp intensity change was reached. An x-ray diffraction
Fig. 3. Ion ($\text{In}_2\text{S}^+$ and $\text{S}_2^+$) intensities vs time in the indium sesquisulfide region.
Fig. 4. Ion (In$_2$S$^+$ and S$_2^+$) intensities as functions of time in the InS region.
pattern was obtained for the product, which was calculated to have an over-all composition of 46.7 at.% indium, with an uncertainty of about 0.5% in this composition.

A. Pressure-vs-Composition Data from Ion-Intensity vs Time

Provided that the intensity of an ion that is produced from each major vapor species can be followed as a function of time at constant temperature, a pressure-vs-composition plot can be derived.

The pressure $P_1$ at any given time is related to the intensity $I_1$ by the equation

$$P_1 = UI_1T,$$

where $T$ is the absolute temperature and $U$ is a constant. The constant in this equation is dependent on the ionization cross section of the vapor species and on the response of the electron multiplier to each particular kind of ion.

The constant can be evaluated for $\text{In}_2\text{S}$ and $S_2$ by taking advantage of the circumstance that the partial pressure of each of these species is known at known compositions of congruent sublimation. The compositions for congruent sublimation are fixed at $\text{InS}_{1.48 \pm 0.03}$ at 600°C to 800°C by the fact that degassing of the material (in the mass spectrometer) showed that this analysis proceeded with no significant change in relative intensities $\text{In}_2\text{S}^+$ and $S_2^+$. Changes in the temperature of a sample that was known from its unchanging ratio $\text{In}_2\text{S}^+/S_2^+$ to sublime congruently produced only small temporary variations in the ion ratio.

For congruent sublimation, we have the equation

$$P_{\text{In}_2\text{S}}/P_{S_2} = (n_{\text{In}_2\text{S}}/n_{S_2}) (M_{\text{In}_2\text{S}}/M_{S_2})^{1/2},$$

where $n_{\text{In}_2\text{S}}/n_{S_2}$ is the ratio of (a) the number of moles of $\text{In}_2\text{S}$ to (b) the number of moles of $S_2$ in the condensed phase, and $M_{\text{In}_2\text{S}}$ and $M_{S_2}$ are the molecular weights of the vapor species. Since $P_{\text{In}_2\text{S}^+}P_{S_2^+}$ is known by the Knudsen effusion experiments previously carried out, the partial pressures of both species at the composition for congruent
sublimation are known. The total weight loss of the sample during the run is determined, and K can be calculated with a probable error of less than 20%, rather than with the probable error of a factor of 2 that is usually estimated when K is evaluated from comparison of the intensities of the observed ions with the intensity of an ion from a foreign substance, such as silver, of known vapor pressure.

Provided that the initial sample composition and weight are known, the composition at subsequent times can be calculated from pressure data by means of the Knudsen-effusion equation. The number of moles of each species that leave a Knudsen cell per unit time is given by $Z_i = P_i (2\pi M_i R T)^{-1/2} A k$, where $M$ is the molecular weight of the ion of interest, $R$ is the gas constant, $A$ is the area of the orifice, and $k$ is the Clausing correction. The fused-silica crucibles described earlier were used.

The observed intensities of the ions $\text{In}_2\text{S}^+$ and $\text{S}_2^+$ were tabulated at small, equal time intervals; typical curves are shown in Figs. 3 and 4. The total weight lost (in mg) for each ion ($Y_j$) was calculated by means of the relationship

$$Y_j = \frac{I_j P_j A k \Delta t}{I_f} \left( \frac{M_j}{T} \right)^{1/2} 2.66 \times 10^6,$$

where $I_j$ is the sum of the differential intensities column for ion $j$, $I_f$ is the final intensity of ion $j$ (at the compositions for congruent sublimation), $P_j$ is the partial pressure at the congruent sublimation point (i.e., the pressure that produced the measured intensity $I_f$), and $\Delta t$ is the width of the differential time intervals in minutes.

As a first approximation, the final composition was assumed to be stoichiometric and the partial pressures were then calculated accordingly. The sums of the two losses ($Y_{\text{In}_2\text{S}}$ and $Y_{\text{S}_2}$) are compared with directly measured losses in Table III. Most of the calculated total weight losses agree with the directly measured total weight loss to within a factor of 2. However, at $750^\circ C$ the vaporization of the 41.7 at.% indium sample produced a measured weight loss 6 times the calculated value, and at $600^\circ C$ vaporization of the sulfur-rich sample
Table III. Comparison of observed and calculated weight losses.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>In-rich</th>
<th>S-rich</th>
<th>Calc</th>
<th>Obs</th>
<th>Calc</th>
<th>Obs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs</td>
<td>Calc</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.2</td>
<td>0.500</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>0.8</td>
<td>0.602</td>
<td>0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>7.2</td>
<td>2.98</td>
<td>0.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>15.1</td>
<td>12.8</td>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>4.8</td>
<td>0.78</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Obs = observed
Calc = calculated

produced a weight loss of 5 times the calculated value. These high losses are believed to be due in part to escape of vapor between the crucible and lid rather than through the orifice, and in part to incorrect temperature measurements.

A single correction factor, c, was included in Eq. (3) for correcting both $Y_{In_2S}$ and $Y_{S_2}$ so that the calculated weight loss would agree with the directly measured loss. The final composition was then calculated from the known initial weight and composition of the condensed phase, the weight of $In_2S$ and $S_2$ molecules vaporized, and the final weight of sample (Table IV). The weight of indium lost due to $In_2S$ molecules was subtracted from the weight of indium initially present to obtain the weight of indium remaining in the sample.
Table IV. Calculation for congruent sublimation composition.

<table>
<thead>
<tr>
<th>Initial weight (grams)</th>
<th>Final weight (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In(<em>{0.44})S(</em>{0.56})</td>
<td>(\rightarrow) In(_2)S(g) + S(<em>2)(g) + In(</em>{1-x})S(_x)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight</th>
<th>3.70</th>
<th>0.768</th>
<th>0.032</th>
<th>2.90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of In</td>
<td>2.73</td>
<td>0.674</td>
<td>--</td>
<td>2.06</td>
</tr>
<tr>
<td>Weight of S</td>
<td>0.97</td>
<td>0.094</td>
<td>0.032</td>
<td>0.84</td>
</tr>
</tbody>
</table>

If this calculated composition for congruent sublimation differed from the stoichiometric composition, a second approximation was made in which the partial pressures that characterize the calculated composition for congruent sublimation were assumed to be the final pressures. These pressures were calculated assuming that the \(\Delta F^\circ\) for reaction (4) is the same at the congruent subliming composition as at the stoichiometric composition. Since the free energy of formation per gram atom changes very little with small changes in composition, this approximation introduces a negligible error. With \(x\), the mole fraction of sulfur,

\[
\text{In}_{(1-x)}S_x(s) = \left( \frac{1-x}{2} \right) \text{In}_2\text{S(g)} + \left( \frac{3x-1}{4} \right) \text{S}_2(g) \quad (4)
\]

This gives the relationship

\[
[P^\circ_{\text{In}_2\text{S}}]^{0.2} [P^\circ_{\text{S}_2}]^{0.2} = [P_{\text{In}_2\text{S}}]^{(1-x)/2} [P_{\text{S}_2}]^{(3x-1)/2}, \quad (5)
\]

where \(P^\circ\) is the partial pressure at stoichiometry. And since
The simultaneous solution of (5) and (6) provides partial pressures closer to those at the congruent subliming composition.

Although the result of the second approximation usually agreed (to within 0.1 at.%) with the results of the first approximation, the correction is necessary in order to prevent the pressure-vs-composition curves from anomalously reversing.

In order to obtain pressure-vs-composition plots from the differential intensity vs time data, differential weight losses were obtained next. These differential weight losses, \( Z_i \), in mg, are given by the relation (7)

\[
Z_i = \frac{I_i}{I_f} P A k \Delta t \left( \frac{M}{T} \right)^{1/2} c 2.66 \times 10^6 ,
\]

where \( I_i \) and \( I_f \) are the differential intensity and final intensity, respectively, and \( c \) is the previously determined correction factor. The other terms are the same as for (3). Differential indium weight losses were obtained by multiplying the differential In\(_2\)S(g) weight losses by 0.87747. The weight of indium remaining and the weight of sample remaining after each differential weight loss can be calculated by subtraction. The wt\% indium in the sample at any time is, of course, the weight of indium in the sample divided by the weight of sample. These values were then converted to at.% indium 100(1-x) and sulfur (100x).
The partial pressures of In$_2$S and S$_2$ are plotted in Figs. 5 and 6 for the regions including the In$_2$S$_3$ and InS$_{1+}$ phases. The compositions for congruent sublimation were calculated in this manner to be 40.0, 40.5, 40.7, 40.3, and 40.3 at. % indium at 600°, 650°, 700°, 750°, and 800°C. This compares with 40.3 at. % indium found by correcting the analytical data for loss of indium chloride. The compositions for congruent sublimation reported above were used to calculate the compositions of the sulfur-rich samples at the time the mass spectrometer runs were initiated. These compositions are found to have been 39.5, 40.4, 40.5, and 40.0 at. % indium at 600°, 650°, 700°, and 750°C.

The compositions of congruent sublimation must be considered uncertain to between 0.5 and 1 at.%. An average value of 40.3 at. % indium, which corresponds to a formula InS$_{1.48}$, can be used in the temperature range 600° to 800°C. That the composition for congruent sublimation varied by no more than about 0.1 at. % in the temperature range between 700° and 800°C is demonstrated by experiments in which the temperature of congruently subliming samples was suddenly changed and the resultant variation in S$_2^+$/In$_2$S$^+$ ion ratios was studied.

The results of a first experiment conducted in a silica crucible are summarized in Table V, which shows the temperatures, in the sequence followed, at which the sample was held, and the initial and final (i.e., steady-state) intensity ratios of S$_2^+$ to In$_2$S$^+$ that resulted.

The value 0.7 for the S$_2^+$/In$_2$S$^+$ ratio is characteristic of the composition for congruent sublimation. The high initial S$_2^+$/In$_2$S$^+$ ratio obtained when the temperature was first dropped to 768°C presumably resulted because the composition for congruent sublimation at 838°C was richer in sulfur than the composition for congruent sublimation at 768°C. By similar analysis the composition for congruent sublimation at 726°C is concluded to contain less sulfur than does the composition for congruent sublimation at either 768 or 838°C.

That composition for congruent sublimation did not shift continuously in a single direction with temperature was surprising. The experiment was repeated, therefore, in a graphite crucible.
Fig. 5. Vapor pressures of In$_2$S(g) and S$_2$(g) vs composition in the indium sesquisulfide region.
Fig. 6. Vapor pressures of In$_2$S(g) and S$_2$(g) vs composition in the InS region.
Table V. The $S_2^+/In_2S^+$ ratio above indium sesquisulfide immediately after a temperature change (initial) and after the composition has attained that for congruent sublimation at the same temperature (final).

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Initial $S_2^+/In_2S^+$</th>
<th>Final $S_2^+/In_2S^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>838</td>
<td>--</td>
<td>0.72</td>
</tr>
<tr>
<td>768</td>
<td>1.2</td>
<td>0.67</td>
</tr>
<tr>
<td>726</td>
<td>0.5</td>
<td>0.7</td>
</tr>
<tr>
<td>838</td>
<td>0.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>

For these measurements the thermocouple was securely wedged into place and was then calibrated against a second thermocouple introduced into the crucible through an orifice in the lid and forced against the bottom. Ohmmeter readings were taken (a) before and (b) after loading the crucible assembly into the mass spectrometer, and (c) after the sample was heated, to assure that both thermocouples were touching the crucible. These readings were taken (a) between the two thermocouples and (b) between the thermocouples and an external pin electrically connected to the cell. A plot of the difference between the thermocouples as a function of the calibrating thermocouple (Fig. 7) produced a straight line between 600° and 900° C with no points deviating by more than 1°.

The calibrating thermocouple was then removed and the crucible lid changed to one with a smaller orifice (0.075 cm diam). A 26-mg sample of indium sesquisulfide, which had previously been heated to 800° C in vacuum, was loaded into the crucible. After the cell assembly was positioned in the mass spectrometer, an ohmmeter reading was taken between the cell and the thermocouple to assure that the thermocouple was still positioned as before.

The temperature sequence followed and the measured initial and final $S_2^+/In_2S^+$ intensity ratios are summarized in Table VI. From the
Fig. 7. Second calibration, temperature difference between inside and outside cell as a function of temperature inside cell.
Table VI. The S$_2^+$/In$_2$S$_2^+$ ratio above indium sesquisulfide immediately after a temperature change (initial) and after the composition has attained that for congruent sublimation at the same temperature (final).

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Initial S$_2^+$/In$_2$S$_2^+$</th>
<th>Final S$_2^+$/In$_2$S$_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>4.1</td>
<td>0.46</td>
</tr>
<tr>
<td>750</td>
<td>0.36</td>
<td>0.59</td>
</tr>
<tr>
<td>700</td>
<td>0.61</td>
<td>0.55</td>
</tr>
</tbody>
</table>

time-vs-temperature plots obtained during the second of these composition-variation experiments, the maximum variation of the composition for congruent sublimation is calculated to be less than 0.1 at.%

When the temperature is raised above 850°C, however, the composition for congruent vaporization is dramatically shifted. When samples that had been equilibrated in the mass spectrometer at a composition for congruent sublimation at temperatures below 850°C were raised to a temperature of 880° to 950°C, the S$_2^+$/In$_2$S$_2^+$ intensity ratio rose to 2.2. When a sample was held at these higher temperatures, the S$_2^+$/In$_2$S$_2^+$ ratio decreased to a constant value of 0.5. Samples quenched after this treatment have the same x-ray diffraction pattern as samples of overall composition 43 to 45 at.% indium.

Presumably, at about 850°C the composition for congruent sublimation under the steady-state conditions of our experiments coincides with the indium-rich phase boundary of the indium sesquisulfide solid solution. At higher temperatures the composition for congruent vaporization moves to about InS$_{1.3}$ or InS$_{1.2}$ in the liquid-solution range.

Samples whose initial compositions corresponded to InS were heated to 600°, 650°, 700°, and 750°C in the mass spectrometer. All showed similar behavior. An example of the intensity-vs-time plots is presented in Fig. 4 for the time periods necessary to allow the
composition to vary across the $\text{InS}_{4+}$ single-phase region. The pressure-vs-composition plots derived from these data are presented in Fig. 6. At 750°C only the pressures in the two-phase region are known because the weight of the sample was not measured.

B. The Free Energy of Formation of $\text{In}_2\text{S}_3$ and $\text{InS}_{4+}$

The pressure-vs-composition curves (Fig. 5) were used to calculate the free energy of reaction (8) as a function of composition for the indium sesquisulfide phase. Calculations were performed for one gram atom of solid. On this basis, the stoichiometric composition, for example, is written $\text{In}_{0.4}\text{S}_{0.6}$.

$$\frac{1-x}{2} \text{In}_2\text{S}(g) + \frac{3x-1}{4} \text{S}_2(g) = \text{In}_{1-x}\text{S}_x(s). \quad (8)$$

The free energy of reaction (9) was calculated from the published values for the elements $^{45}$ and the values determined for $\text{In}_2\text{S}(g)$ in this study (Table VII). Equation (8) was added to $(1-x)/2$ times Eq. (9),

$$2 \text{In}(l) + \left( \frac{1}{2} \right) \text{S}_2(g) = \text{In}_2\text{S}(g), \quad (9)$$

to give the free energy of formation for $\text{In}_{1-x}\text{S}_x(s)$:

$$(1-x) \text{In}(l) + \left( \frac{x}{2} \right) \text{S}_2(g) = \text{In}_{1-x}\text{S}_x(s). \quad (10)$$

The results are shown in Fig. 8 as solid lines.

In reaction (8) the slope of $\Delta F^\circ$ vs composition for $\text{In}_2\text{S}_3$ between 40 and 44 at.% should change smoothly with temperature and must always have a positive curvature, $^{19}$ instead of the negative curvature indicated by the experimental data at 600° and 650°C. In order to determine more definitely the change in slope with temperature, $\Delta F^\circ$ was calculated at 600°, 650°, 700°, and 750°C and at various compositions between 40 and 44 at.% indium, from the experimental value at 800°C and with the assumption of a simple model for the entropy of
Fig. 8. Free energy of formation of indium sesquisulfide as a function of composition and temperature. Solid line calculated from experimental data. Dashed line calculated from solid curve at 800°C and the assumption of a single model described in text.
Table VII. The free energy of formation of In$_2$S(g) (kcal/mole) as a function of temperature.

$$2 \text{In(l)} + \left(\frac{1}{2}\right) \text{S}_2(g) = \text{In}_2\text{S}(g)$$

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>$-\Delta F_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>17.7</td>
</tr>
<tr>
<td>650</td>
<td>18.5</td>
</tr>
<tr>
<td>700</td>
<td>19.2</td>
</tr>
<tr>
<td>750</td>
<td>19.9</td>
</tr>
<tr>
<td>800</td>
<td>20.6</td>
</tr>
<tr>
<td>850</td>
<td>21.4</td>
</tr>
</tbody>
</table>

formation. For example, the entropy of formation at 44 at.% indium was calculated from

$$\Delta S^\circ_T = S^\circ_{\text{In}_{44}S_{56}} - (0.44) S^\circ_{\text{In}(l)} - (0.285) S^\circ_{\text{S}_2(g)} + \Delta S^\circ_m,$$  \hspace{1cm} (11)

where $\Delta S^\circ_m$ is the difference between the entropy of mixing of the elements and vacant lattice sites at 44 at.% indium and at 40 at.% indium.

The $\Delta H^\circ$ of sublimation at each composition, which is known to be essentially constant over the temperature region studied, was calculated from the expression

$$\Delta F^\circ_T = \Delta H^\circ - T \Delta S^\circ_T$$  \hspace{1cm} (12)

by use of the values of $\Delta F^\circ$ at 800° C and $\Delta S^\circ_{800}$. These values of $\Delta H^\circ$ (Table VIII) were then used with expression (11) to calculate the values of $\Delta F^\circ$ at various compositions between 40 and 44 at.% indium (shown as dashed lines in Fig. 8). The resultant calculated curves are within the experimental error in agreement with the curves of negative curvature that were calculated directly from the experimental data. These new calculated curves probably represent the true composition dependence of $\Delta F^\circ$ for formation more correctly than the curves of negative curvature.
Table VIII. The heat of formation of indium sesquisulfide (kcal/g atom) as a function of composition for the temperature range 600° to 800°C

\[(1-x) \ln(t) + \left(\frac{x}{2}\right) S_2(g) = \ln_{1-x} S_x\]

<table>
<thead>
<tr>
<th>At.% In (100 x)</th>
<th>$-\Delta H^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>28.9</td>
</tr>
<tr>
<td>42</td>
<td>28.6</td>
</tr>
<tr>
<td>43</td>
<td>28.2</td>
</tr>
<tr>
<td>44</td>
<td>27.9</td>
</tr>
</tbody>
</table>

The heat and free energy of formation of $\text{InS}_{1+}$ (chosen as $\text{In}_{0.467}\text{S}_{0.533}$) were determined at 600°, 650°, 700°, and 750°C at the sulfur-rich boundary (Fig. 6). Since the phase is only a few tenths of an atomic percent wide, $\Delta F$ and $\Delta H$ per gram atom must be essentially constant with composition across the phase.

The free energy was determined, as for the indium sesquisulfide phase, by adding Eq. (8) to $(1-x)/2$ times Eq. (9). The entropy of solid $\text{InS}_{1+}$ was determined by use of (13), which averages the entropy of $\text{In}_2\text{S}_3$ and In.

$$0.111 \ln(t) + 0.178 \ln_2 S_3(s) = \ln_{0.467} S_{0.533}(s).$$

The equation for the entropy of formation

$$\Delta S^\circ_T = S^\circ_{\ln_{0.467} S_{0.533}} - 0.46 S^\circ_\ln(t) - 0.267 S^\circ_{S_2(g)},$$

was used to calculate the heat of formation

$$\Delta H^\circ_T = \Delta F^\circ_T + T\Delta S^\circ_T.$$ 

The results are shown in Table IX.
Table IX. The heat and free energy of formation of $\text{InS}_{1+}$ (kcal/gm atom).

$$0.467 \text{In}(l) + 0.266 \text{S}_2(g) = \text{In}_{0.467} \text{S}_{0.533}(s)$$

<table>
<thead>
<tr>
<th>$T(°C)$</th>
<th>$-\Delta H_f^\circ$</th>
<th>$-\Delta F_f^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>27.3</td>
<td>16.6</td>
</tr>
<tr>
<td>650</td>
<td>27.3</td>
<td>16.1</td>
</tr>
<tr>
<td>700</td>
<td>27.5</td>
<td>15.7</td>
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<td>750</td>
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V. 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 that 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 graphite (National Carbon Company's AUC grade). The disks were heated in vacuum at a temperature increased 5° C per min and held at 800° C for 20 min. These samples had a density about 94% of theoretical. Examination at 20X magnification suggests that the porosity was due to very small interstices, some of which were not connected. Graphite from the die was removed from one end of the disk by grinding it on wet 400- and 600-mesh silicon carbide paper. The x-ray diffraction pattern of a crushed cylinder then showed only the $\beta$-In$_2$S$_3$ 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 surfaces. 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 they were too high for free surface sublimation experiments with the 0.65-cm diameter disks. Blackbody 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 measured with an optical pyrometer. The blackbody holes had 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 was lower than that read in the blackbody 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. The true surface temperature must be above the apparent temperature and is probably no higher than the blackbody temperature. The surface temperature is known, therefore, to within ±10°. For our calculations the surface temperatures were assumed to be 832° and 863°C.

Sublimation rates were measured at 697° and 730°C. After a few milligrams had vaporized, the surface of the sample 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, defined here as the ratio of the observed to the equilibrium vaporization rate, was calculated from the gross dimensions of the sample surface, neglecting surface roughness, and therefore represents an upper limit to the true value of α. The assumption that the fraction of surface occupied by grooves can be assigned an effective α of unity suggests a lower limit for α. From these considerations, the limits of α were calculated to be 0.005 < α < 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.
VI. DISCUSSION

The most recent investigation\(^1\) of the condensed phases of the indium-indium sesquisulfide system led to the identification of the phases \(\text{In}_2\text{S}_3\), \(\text{In}_5\text{S}_6\), and \(\text{InS}\) by x-ray diffraction examination of room-temperature samples. In addition, a phase of approximate composition \(\text{In}_3\text{S}_4\) was inferred [from cooling curves and D. T. A. (differential thermal analysis)] to be present at temperatures above \(370^\circ\text{C}\). The present study appears to disprove the existence of a separate \(\text{In}_3\text{S}_4\) phase and to prove that \(\text{In}_2\text{S}_3\) has a significantly wide solubility range at high temperatures. In fact this phase is wide enough to include the composition \(\text{In}_3\text{S}_4\).

My diffraction pattern vs composition study indicates that a single-phase region extends from about \(\text{InS}_{1.5}\) on the sulfur-rich side (the limit depends on the sulfur pressure and the temperature) to about \(\text{InS}_{1.35}\) at the indium-rich phase boundary. The pressure-vs-composition studies, however, indicate lower sulfur contents at higher temperatures for the indium-rich phase boundary. The pressure data indicate that the phase boundary lies at \(\text{InS}_{1.29}\) at \(600^\circ\text{C}\) and \(\text{InS}_{1.20}\) at \(700^\circ\text{C}\). Quenching is often ineffective in preserving the compositions stable at annealing temperatures, and the wider solution range indicated by the partial pressure vs composition studies should be accepted as better measures of the high-temperature solid-solution limits. These limits, coupled with the x-ray data, indicate that the sesquisulfide solution range widens rapidly with increased temperature.

On the other hand, the pressure-vs-composition curves show distinctly that no discrete phase of composition near \(\text{In}_3\text{S}_4\) is stable in the temperature range between \(600^\circ\text{C}\) and about \(650^\circ\text{C}\), at which temperature the sesquisulfide phase boundary reaches this composition. Probably the thermal effect noted by Stubbs et al. at \(370^\circ\text{C}\) was the precipitation of \(\text{InS}_{4+}\) from the supersaturated solution of indium in the indium sesquisulfide phase. Such precipitation reactions are necessarily exothermic.\(^4\)

This study demonstrated that a mass spectrometer can be used for the dynamic study of a two-component system. The ion intensities
of the vapor species can be recorded as the composition of the condensed sample changes at constant temperature. By this means, the existence of single phases, stable at the temperature of the experiment and in the composition region traversed, are determined. It is necessary only that the composition of the sample change from noncongruent to congruent subliming during heating, and that the partial pressures of all species be measurable. (If the partial pressure of one species can be determined at only one, known composition, in principle the Gibbs-Duhem equation can be used to calculate the pressure at other compositions.)

The absolute composition of the single-phase boundaries traversed at the experimental temperatures can also be determined. The initial and final composition of the sample and the weight loss during the experiment can be used to convert the intensity-vs-time data to pressure-vs-composition data. The results of this study indicate that such calculations can be accurate to within a few tenths an at. %.

If the slow step in the evaporation of indium sesquisulfide from a free surface is due entirely to an energy barrier, an $\alpha$ of 0.01 leads to an activation energy of 167 kcal/mole of $\text{In}_2\text{S}_3$ for congruent sublimation at 298° K. This value is about 20 kcal more than the equilibrium heat of sublimation.
ACKNOWLEDGMENTS

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FOOTNOTES AND REFERENCES

10. Uncertainties in the calculation of the entropy and free-energy functions consider that In$_2$S may be linear.


21. The assumption that the cavities, the polished graphite surface, and the indium sesquisulfide surface were at the same temperature and that the emissivity of polished graphite is 0.77 suggests an emissivity value of 0.52 for indium sesquisulfide.
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