FOREWORD

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This report covers work done from July 1962 to July 1963.

The authors wish to thank Professor P. Goldfinger for his interest and encouragement, Dr. P. C. Newmann (Philips) for the InS and In$_2$S$_3$ samples and Professor M. Leroy (Institut Meurice, Bruxelles) for analyzing them.
ABSTRACT

Investigation of the saturated vapor above InS, In$_2$S$_3$ and In$_2$S$_3$+In samples and of the superheated vapor has yielded

In$_2$S(g)  2In(g)+1/2S$_2$(g)  $\Delta H_{298}^o$=98.2±5.0 kcal/mole

In$_2$S$_2$(g)  In(g)+1/2S$_2$(g)  $\Delta H_{298}^o$=26.5±6.0 " "

InS(g)  In(g)+1/2S$_2$(g)  $\Delta H_{298}^o$=17.4±4.0 " "

Combining these data with $D_e^{298}$(S$_2$)=102.0±2.0 kcal/mole one obtains:

$\Delta H_{298}^o$(at.In$_2$S)=149.2±5.5;  $D_e^{298}$(InS)=68.4±4.5;

$\Delta H_{298}^o$(at.In$_2$S$_2$)=226.7±8.0;  $D_e^{298}$(dim,InS)=89.9±11.0 kcal/moles.

This technical documentary report has been reviewed and is approved.

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Chief, Ceramics and Graphite Branch
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Air Force Materials Laboratory
Contrails
INTRODUCTION

Mass spectrometry has contributed to a large extent to the knowledge of the thermodynamic properties of solid and gaseous oxides \((1,2,3)\). On the other hand, little is yet know concerning the vaporization and thermodynamic properties of sulfides \((4-10)\), selenides and tellurides. The similarity in properties of these compounds is well known and interesting data could be put to light by an investigation of whole groups of compounds.

Indium oxide has been studied \((1,11,11a)\) by mass spectrometric techniques and it has been shown that in the gas phase above \(\text{In}_2\text{O}_3\) (s), \(\text{In}_2\text{O}_3\) and \(\text{O}_2\) molecules and \(\text{In}\) atoms are the predominant species. A value of \(119.6\pm5.0\ \text{kcal/mole}\) for the atomization energy of \(\text{In}_2\text{O}(g)\) and an upper limit (most probably very close to the real value) for the dissociation energy of the \(\text{InO}\) molecules \(D_0^0<75\ \text{kcal/mole}\) were obtained.

The indium-sulfur system has a complex phase diagram. Thermal, microscopic and roentgenographic studies \((12,13)\) have shown the existence of several stoechiometric compounds: \(\text{InS}\), \(\text{In}_2\text{S}_5\) and \(\text{In}_2\text{S}_3\). A thermal effect at \(370^\circ\text{K}\) was interpreted to indicate the decomposition of an unstable compound \(\text{In}_3\text{S}_4\) \((12)\). No evidence was found in the more recent study \((12)\) for the existence of a compound \(\text{In}_2\text{S}\) previously assumed \((14,15)\). The free energy of formation has been measured by Thompson, Stubbs and Schuffle \((16)\) for \(\text{In}_2\text{S}_3\), \(\text{In}_3\text{S}_4\), \(\text{InS}\) and for an assumed compound

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In$_5$S$_6$. Hahn and Burrow\textsuperscript{(17)} have measured the enthalpy of formation of InS and In$_2$S$_3$. More recently, Spandau and Klanberg\textsuperscript{(18)} have measured the vapor pressure above melts of InS+In and In$_2$S$_3$+4In. Assuming the vapor phase to be composed of gaseous In$_2$S molecules and using the enthalpies of formation mentioned above, the latter authors calculated for the atomization enthalpy of gaseous In$_2$S a value of $\Delta H^0_{\text{at}}(\text{at, In}_2\text{S}) = 162\pm12$ kcal/mole.

In this paper, a mass spectrometric investigation of the saturated vapor above InS, In$_2$S$_3$ and above a mixture of In$_2$S$_3$ and In and of superheated vapor is reported. The In-Se and In-Te systems have also been studied and will be the object of a forthcoming publication.
EXPERIMENTAL

The main features of the mass spectrometer and Knudsen effusion cell have been described previously (19-21).

In the present work, the saturated vapor was studied using small quartz cells, placed inside molybdenum crucibles heated by radiation from a concentric tungsten loop. Temperatures were measured with a Pt-PtRh (10%) thermocouple, whose junction was placed beneath the quartz cell within the molybdenum crucible. To avoid temperature errors due to thermal conduction through the thermocouple wires (0.1 mm diameter), these were wound in several coils inside the crucible and insulated by tiny quartz tubes. Effusion holes of 1 to $4 \times 10^{-3}$ cm$^2$ were used in different experiments. Their area was small compared to the area of the sample. The weight of the sample was usually about 100 mg.

The superheated vapor was studied using 5cm long double quartz cells placed inside a carbon oven surrounded by a thin tantalum sheet (Fig.1). Each section of the double cell was heated individually by radiation from a tungsten loop. When necessary electron bombardment was applied. The upper section was always maintained at a higher temperature than the lower one containing the sample. A small quartz plug was placed in the bottle neck connecting both sections as shown in Fig.1. Its main function was to avoid vapor coming from the lower compartment to effuse.
directly without impinging several times on the walls of the hotter section; it also aids in reading the temperature of the upper section by means of an optical pyrometer aiming the effusion hole.

In neither type of experiment did the quartz cells show signs of reaction with the sample.

The analysis of the In and S content gave for the InS sample 79.16% In and 19.53% S (calculated 78.16 and 21.84%) and for the In$_2$S$_3$ sample 74.34% In and 24.41% S (calculated 70.47 and 29.53%).
Fig.1: Double cell: 1 quartz cell; 2 quartz plug; 3 sample; 4 carbon crucible; 5 tantalum sheet; 6 tungsten loop; 7 effusion orifice; 8 radiation shields.
EXPERIMENTAL RESULTS

The vaporization of samples of initial composition InS and \( \text{In}_2\text{S}_3 \) and of mixtures \( \text{In}_2\text{S}_3 + 12\text{In} \) was studied in single cells in the temperature ranges 880-1260\(^\circ\)K, 960-1220\(^\circ\)K and 940-1100\(^\circ\)K respectively. Vapors superheated up to 1540\(^\circ\)K were studied in double cells, whose lower section heated at temperatures similar to those in the single cell experiments, contained \( \text{In}_2\text{S}_3 \) samples.

A. Composition of the vapor.

1. Single cell experiments.

The characteristic atomic and molecular ions observed were \( \text{S}^+, \text{S}_2^+, \text{In}^+, \text{InS}^+, \text{In}_2^+, \text{In}_2\text{S}^+, \) and \( \text{In}_2\text{S}_2^+ \). All of these ions were identified from their mass and isotopic distribution. The interception of the molecular beam\(^{(1)}\) further showed these ions to be formed from neutral species originating from the Knudsen cell. Ionization efficiency curves were measured for each of these ions, except \( \text{S}^+ \), to define which molecules gave rise to their formation. For all the ions, except \( \text{In}^+ \) and \( \text{InS}^+ \), the ionization efficiency varied essentially linearly for several volts above the appearance potential. For \( \text{In}^+ \) and \( \text{InS}^+ \), it was the resultant of two essentially linear components. Approximate appearance potentials, assembled in Table I, were derived from these curves using the linear extrapolation method. The energy scale was first calibrated with the known appearance potentials of water\(^{(22)}\) or mercury\(^{(23)}\) to establish that \( \text{In}^+ \) was,
in the low energy part of its ionization efficiency curve, a parent ion. The known ionization potential of In$^{(23)}$ was subsequently used as a reference for the other ions. The onsets of the second process in the ionization curves of In$^+$ and InS$^+$ at 8.7±1.0 and 11.7±1.0 eV, respectively were attributed to the fragmentation of In$_2$S molecules. The appearance potential of S$_2^+$ measured here, 9.6 0.5 eV, is in agreement with a value obtained previously$^{(9)}$ and confirmed in a recent study$^{(24)}$. It shows the presence of S$_2$ molecules in the vapor above the InS and In$_2$S$_3$ samples. The low appearance potentials of InS$^+$, In$_2$S$^+$ and In$_2$S$_2^+$ (7.0±0.5; 7.6±0.5 and 6.4±0.5 eV) indicate their formation from the corresponding molecules by direct ionization. The high value of the appearance potential of In$_2^+$, 10.8±1.0 eV, compared to 5.8±0.3 eV measured$^{(25)}$ for the approximate ionization potential, shows this ion to be formed by fragmentation of the In$_2$S molecules. It was finally concluded from thermodynamic considerations that S$^+$ had to be a fragment ion.

The saturated vapor above InS and In$_2$S$_3$ is thus mainly composed of In$_2$S and S$_2$ molecules with small amounts of In atoms, InS and In$_2$S$_2$ molecules.

During the experiments with InS and In$_2$S$_3$ samples, the S$^+$/In$_2$S$^+$ ratio did however not remain constant with temperature nor time, thus indicating a variation in composition of the condensed phase. Values of this ratio varying from $10^{-3}$ to 2 were
observed. Temperatures where a variation of this ratio was observed could be correlated with the known decomposition temperatures of the *various* indium-sulfur compounds. Other ion intensity ratios for nominal 35 eV electrons are given in Table I.

The vapor in equilibrium with the mixture In$_2$S$_3$+12In contained only In$_2$S molecules with small concentrations of atomic indium; no S$_2$ molecules could be detected.

2. **Double cell experiments.**

When the double cell was used, the composition of the vapor could be varied gradually by increasing the temperature of the upper section, thus provoking dissociation of the molecules. The composition could be varied from one similar to that observed in the single cell experiments to one where mainly S$_2$ molecules and In atoms with small concentrations of InS and In$_2$S molecules were present. Maximum relative intensities obtained in the double cell experiments are also given in Table I. On superheating the vapor, the InS molecule became slightly more abundant relative to the In$_2$S molecule, whereas the concentration of the In$_2$S$_2$ molecule fell below the detection limit of the instrument. The In$_2^+/In_2S^+$ ratio had a constant value in both type of experiments, which is what one would expect for a fragment ion.
**TABLE I. Appearance Potentials and Relative Intensities**

<table>
<thead>
<tr>
<th>Appearance potential (in eV.)</th>
<th>S(^+)</th>
<th>In(^+)</th>
<th>InS(^+)</th>
<th>In(_2)</th>
<th>In(_2)S(^+)</th>
<th>In(_2)S(_2)(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent ion</td>
<td>9.6±0.5</td>
<td>5.8±0.5</td>
<td>7.0±0.5</td>
<td>-</td>
<td>7.6±0.5</td>
<td>6.4±0.5</td>
</tr>
<tr>
<td>Fragment ion</td>
<td></td>
<td>8.7±1.0</td>
<td>11.7±0.5</td>
<td>10.8±0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative intensity (for 35 eV)</td>
<td>Single cell</td>
<td>see</td>
<td>2.10(^{-1})</td>
<td>2.10(^{-2})</td>
<td>9.10(^{-2})</td>
<td>1</td>
</tr>
<tr>
<td>Double cell</td>
<td>texte</td>
<td>11</td>
<td>9.10(^{-2})</td>
<td>9.10(^{-2})</td>
<td>1</td>
<td>&lt;10(^{-4})</td>
</tr>
</tbody>
</table>
B. Pressure Determination

The partial pressure $P_A$ of a neutral species $A$ present in the evaporation cell is given by the relation (20)

$$k(\gamma)_A P_A = I_A T$$

$(I = \text{ion intensity}; \ T = \text{absolute temperature}; \ \sigma = \text{ionization cross section}; \ \gamma = \text{secondary electron multiplier efficiency}; \ k = \text{geometric constant of the instrument})$. To derive absolute values of the pressures in both types of cells, the samples (either InS and In$_2$S$_3$) were weighted and vaporized completely (1), the ion intensities of the major species being integrated with time. The $k(\gamma)_A$ values for the major species were then readily obtained from the Hertz-Knudsen equation

$$G_A = P_A s \left\{ \frac{M_A}{2\pi R T} \right\}^{1/2} \Delta t$$

$(G_A = \text{weight of material of molecular mass } M_A \text{ evaporated through the cell orifice of area } s \text{ during the time interval } \Delta t)$. On combining equations (1) and (2) and introducing correction for the weight loss due to the minor species ($B, C, \ldots$) one obtains:

$$k(\gamma)_A = \frac{s}{G} \left\{ \frac{M_A}{2\pi R} \right\}^{1/2} \Sigma I_A T^{1/2} \Delta t \left\{ 1 + \frac{(\gamma)_A}{(\gamma)_B} \left( \frac{M_B}{M_A} \right)^{1/2} \frac{\Sigma I_B T^{1/2} \Delta t}{\Sigma I_A T^{1/2} \Delta t} \ldots \right\}$$
These integrations also yield a value of the ratio of the product of ionization cross section and multiplier efficiency for the major species; a constant value of $(\sigma \gamma)_{S_2}/(\sigma \gamma)_{In_2S} = 2.5 \pm 0.3$ both for 35 and 70 eV electrons was obtained in the single cell experiments.

In order to obtain absolute pressures for the double cell experiments, where depending on the temperature of the upper section of the cell the major species were either In$_2$S and S$_2$ or In and S$_2$, as well as to obtain the relative partial pressure of the minor species in both types of experiments, the ionization cross sections and multiplier efficiencies in Table II were necessary. Ionization cross sections were estimated from Otvos and Stevenson's data$^{(26)}$, assuming by analogy with a number of dimeric molecules$^{(27-30)}$ that the ratio $\sigma_X/\sigma_X = 1.6$. Multiplier efficiencies were taken from a calibration curve$^{(31)}$ of a multiplier analogous to the one used here and which is similar to a curve given by Inghram, Hayden and Hess$^{(32)}$. Molecular effects were taken into account as suggested by Stanton, Chupka and Inghram$^{(33)}$. Whenever, in order to avoid fragmentation, the ion intensities of the minor species were measured at a low electron energy, the following relation was applied:

$$\frac{P_A}{P_B} = \frac{I_A \times (\sigma \gamma)_B \times (E-A_B) \times A_A \times T_1}{I_B \times (\sigma \gamma)_A \times (E-A_A) \times A_B \times T_2}$$

($A =$ appearance potential, in eV; $E =$ energy of the ionizing electrons, in eV.)
C. Gaseous Equilibria.

Due to the fact that the composition of the condensed phase varied with temperature and time and that the initial samples were not quite stoechiometric nor pure, it was preferred to study the following gaseous equilibria

\[
\begin{align*}
\text{In}_2\text{S}(g) & \rightarrow 2\text{In}(g) + 1/2 \text{S}_2(g) & (I) \\
\text{In}_2\text{S}_2(g) & \rightarrow \text{In}_2\text{S}(g) + 1/2 \text{S}_2(g) & (II) \\
\text{InS}(g) & \rightarrow \text{In}(g) + 1/2 \text{S}_2(g) & (III)
\end{align*}
\]

for which reproducible results could be obtained at different temperatures and pressures. The enthalpy changes for these reactions calculated from the relation

\[
\Delta G^0_T = -RT \ln K = -RT \ln \prod_i P_i^{v_i} = \Delta H^0_{298} - T \Delta \left\{ -\left( \frac{G^0_T - H^0_{298}}{T} \right) \right\}
\]

(\(\Delta G^0_T\) = free energy change; \(R\) = gas constant; \(K\) = equilibrium constant; \(P_i\) = partial pressure; \(v_i\) = stoechiometric coefficient; \(\Delta H^0_{298}\) = enthalpy change at 298°K; \(-\left( \frac{G^0_T - H^0_{298}}{T} \right)\) = free energy function) were used, together with the known dissociation energy of the \(\text{S}_2\) molecule \(D^0_{298} = 102\pm20 \text{kcal/mole}^{(5,34,35)}\) to obtain the following thermochemical data.

1) the atomization energy of gaseous \(\text{In}_2\text{S}: \Delta H^0_{298}(\text{at}, \text{In}_2\text{S})\)
2) the dissociation energy of gaseous \(\text{InS}: D^0_{298}(\text{InS})\)
3) the atomization energy of gaseous \(\text{In}_2\text{S}_2: \Delta H^0_{298}(\text{at}, \text{In}_2\text{S}_2)\)
4) the dimerization energy of gaseous \(\text{InS}: \Delta H^0_{298}(\text{dim}, \text{InS})\)
<table>
<thead>
<tr>
<th>Species</th>
<th>Cross section</th>
<th>Multiplier Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>24.8</td>
<td>0.58</td>
</tr>
<tr>
<td>S₂</td>
<td>20.5</td>
<td>0.91</td>
</tr>
<tr>
<td>InS</td>
<td>30.0</td>
<td>0.42</td>
</tr>
<tr>
<td>In₂S</td>
<td>20.0</td>
<td>0.38</td>
</tr>
<tr>
<td>In₂S₂</td>
<td>48.0</td>
<td>0.38</td>
</tr>
</tbody>
</table>
The free energy functions for gaseous In and $S_2$ were taken from Stull and Sinke's compilations$^{(36)}$. Those for InS, In$_2S$ and In$_2S_2$ were estimated. For InS, the free energy function was calculated assuming an internuclear distance of 2.5 Å. The vibration frequency $\omega$ was estimated at $420 \text{ cm}^{-1}$ from the empirical relation $\omega(\text{M}-\text{O})/\omega(\text{M}-\text{S}) = 1.68 \pm 0.10$ which holds for $\text{M}=\text{C}, \text{Si}, \text{Ge}, \text{Pb}$ and $\text{Al}^{(37,39)}$. The value of $\omega(\text{In}-\text{O}) = 703.08 \text{ cm}^{-1}$ was taken from the spectroscopic data of Watson and Shamon$^{(38)}$. By analogy with gaseous Al$_2O$ and AlS$^{(39)}$ the ground state of InS was assumed to be $^2\Sigma$. The In$_2S$ molecule (as previously Al$_2O^{(42)}$ and In$_2O^{(11)}$) was assumed to have a In-S-In bent structure with a bond angle of 100° by analogy with $H_2S$, $SO_2$, $(CH_2)_2S$ and $SeI_2^{(40)}$. The translational and rotational entropy and free energy function were readily obtained from statistical mechanical formulae$^{(40)}$. The frequencies of the three normal vibrations were calculated to be $\omega_1 = 535 \text{ cm}^{-1}$, $\omega_2 = 500 \text{ cm}^{-1}$ and $\omega_3 = 133 \text{ cm}^{-1}$ by assuming the stretching force constant $k_1$ of the In-S bond to be identical to the one in the InS molecule; the bending force constant $k_6$ was estimated on the basis that $k_6/k_1 = 0.094$ which holds for $SO_2$ and $H_2S^{(40)}$ ($l$ = internuclear distance). It is difficult to estimate the electronic contribution to the free energy function for this molecule. There are no spectroscopic data available for any triatomic molecule of this type in the $\text{III}_B-\text{VI}$ group. Moreover In$_2S$ being a heavy molecule little can be predicted for the configuration and relative positions of the
ground and excited electronic states. Due to the lack of data it was assumed that the ground state was a singlet. Although there is some spectroscopic evidence\(^{41,45}\) for a linear structure of the \( \text{B}_2\text{O}_2 \) molecule it is difficult to say whether this structure is maintained when both B and O are replaced by heavier atoms of the same groups. In any case, the free energy function is not very sensitive to a change of structure as was shown for \( \text{Al}_2\text{O}_2 \)^\(^{(42)}\). The free energy function of \( \text{In}_2\text{S}_2 \) was taken identical to that of \( \text{As}_4 \)^\(^{(36)}\), a tetratomic molecule of approximately the same mass, the uncertainty being estimated at \( \pm 5 \) cal/mole/°. The different free energy functions used are summarized in Table III.

Table IV gives the enthalpy change for reaction (I). The average value \( \Delta H^0_{298}(I) = 98.2 \pm 4.0 \) kcal/mole combined with \( D^0_{298}(\text{S}_2) = 102.0 \pm 2.0 \) kcal/mole yields a value for the atomization energy of \( \text{In}_2\text{S} \) of:

\[
\Delta H^0_{298}(\text{at.}\text{In}_2\text{S}) = 149.2 \pm 5.5 \text{ kcal/mole}
\]

Table V gives the enthalpy change for reaction (II). The average value \( \Delta H^0_{298}(\text{II}) = 26.5 \pm 6.0 \) kcal/mole combined with \( D^0_{298}(\text{S}_2) \) leads to \( \Delta H^0_{298}(\text{at.}\text{In}_2\text{S}_2) = 226.7 \pm 8.0 \) kcal/mole.

Table VI gives the enthalpy change for reaction (III). The average value \( \Delta H^0_{298}(\text{III}) = 17.4 \pm 4.0 \) kcal/mole combined with \( D^0_{298}(\text{S}_2) \) leads to \( D^0_{298}(\text{InS}) = 68.4 \pm 4.5 \) kcal/mole.

Finally, using the above data one may calculate the dimerization energy of \( \text{InS} \): \( \Delta H^0_{298}(\text{dim.}\text{InS}) = 89.9 \pm 11.0 \) kcal/mole.
TABLE III. Free Energy Function $-(G_T - H_{298})/T$
(in cal/mole/°)

<table>
<thead>
<tr>
<th>Species</th>
<th>800</th>
<th>1000</th>
<th>1200</th>
<th>1400</th>
<th>1600</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$^{(37)}$</td>
<td>43.4</td>
<td>44.2</td>
<td>45.0</td>
<td>45.7</td>
<td>46.3</td>
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<tr>
<td>S$_2^{(37)}$</td>
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<td>59.9</td>
<td>60.9</td>
<td>61.8</td>
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<td>81.9</td>
<td>84.8</td>
<td>87.4</td>
<td>89.6</td>
<td>91.8</td>
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</table>
TABLE IV. Enthalpy Change $\Delta H_{298}^\circ$ for the reaction

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

<table>
<thead>
<tr>
<th>Experiment n°</th>
<th>Sample</th>
<th>Cell</th>
<th>$T^\circ$K</th>
<th>$\log p(\text{In})$ (atm)</th>
<th>$-\log p(S_2)$ (atm)</th>
<th>$-\log p(\text{In}_2S)$ (atm)</th>
<th>$\Delta H_{298}^\circ$ kcal/mole</th>
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<tr>
<td>6503A</td>
<td>$\text{In}_2\text{S}_3$</td>
<td>Double cell</td>
<td>1390</td>
<td>5.01</td>
<td>5.19</td>
<td>5.00</td>
<td>99.9</td>
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<td>6503B</td>
<td>$\text{In}_2\text{S}_3$</td>
<td>Double cell</td>
<td>1297</td>
<td>5.74</td>
<td>6.20</td>
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<td>5.37</td>
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</tbody>
</table>
TABLE V. Enthalpy Change $\Delta H_{298}^0$ for the Reaction
\[ \text{In}_2\text{S}_2(g) + \text{In}_2\text{S}(g) + 1/2\text{S}_2(g) \]

<table>
<thead>
<tr>
<th>Experiment No</th>
<th>Sample</th>
<th>Cell</th>
<th>T*K</th>
<th>-logp(In$_2$S) (atm)</th>
<th>-logp(S$_2$) (atm)</th>
<th>-logp(In$_2$S$_2$) (atm)</th>
<th>$\Delta H_{298}^0$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>6305</td>
<td>InS</td>
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<td>1170</td>
<td>4.27</td>
<td>4.34</td>
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<td></td>
<td>1208</td>
<td>4.88</td>
<td>4.20</td>
<td>6.56</td>
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<td></td>
<td></td>
<td>1226</td>
<td>3.78</td>
<td>4.10</td>
<td>6.57</td>
<td>27.7</td>
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<td>Single cell</td>
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<td>6.85</td>
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<td></td>
<td>1205</td>
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<td>6.88</td>
<td>26.4</td>
</tr>
<tr>
<td>6503$_B$</td>
<td>In$_2$S$_3$</td>
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</tr>
</tbody>
</table>

\[ 26.5 \]
TABLE VI. Enthalpy Change $\Delta H^\circ_{298}$ for the Reaction

$\text{InS}(g) \rightarrow \text{In}(g) + \frac{1}{2}\text{S}_2(g)$

<table>
<thead>
<tr>
<th>Exper. N°</th>
<th>Samples</th>
<th>Cell</th>
<th>$T_\text{°K}$</th>
<th>-logp(In) (atm)</th>
<th>-logp(S$_2$) (atm)</th>
<th>-logp(InS) (atm)</th>
<th>$\Delta H^\circ_{298}$ kcal/mole</th>
</tr>
</thead>
<tbody>
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<td>InS</td>
<td>Single cell</td>
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<td>5.34</td>
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<td>Double cell</td>
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</tbody>
</table>
DISCUSSION

The heat of atomization of In₂S, $\Delta H_{298}^{\circ}(\text{at.In}_2\text{S}) = 150 \pm 5.2$ kcal/mole obtained in this work using the third law can be compared with the value obtained by Spandau and Klanberg(18) using the second law, $\Delta H^{\circ}(\text{at.In}_2\text{S}) = 162 \pm 12$ kcal/mole. The present investigation showed the total pressure to be practically entirely due to In₂S molecules as concluded by Spandau and Klanberg. The latter authors seem however to have assumed that the heat of mixing of liquid InS + In or In₂S + 4In compensated the difference between the evaporation enthalpy at 298°C and at the mean temperature of their measurements (1360°C). When estimating the heat capacity of liquid InS and In₂S by using approximation formulae(43) and then calculating the change in heat content $H_{1960}^{\circ} - H_{298}^{\circ}$ for the evaporation reaction one finds 12.6 kcal/mole. It would seem improbable that the heat of mixing has such a high value; it is probably 0±2 kcal/mole. The value $\Delta H_{298}^{\circ}(\text{at.In}_2\text{S})$ deduced from Spandau and Klanberg's measurements is then reduced to 150 kcal/mole in agreement with the result obtained here.

Little can be said concerning the molecular structure of In₂S₂. The high value of the dimerization energy (89.9±12 kcal/mole) compared to the value of the S-S bond of approximately 70 kcal/mole(44) and to the In-In bond such as in In₂ (25) (22.4±2.5 kcal/mole) would suggest, as in the case of Al₂O₂(42), a closed structure of the type.
rather than a linear $S=\text{In} - \text{In}=S$ or $\text{In-S-S-In}$ structure. The value of the dissociation energy of $\text{InS}$ can be used to confirm that the upper limit of the dissociation energy of $\text{InO(1la)}$ is probably very near the real value: the ratio $\Delta H^0(\text{at.In}_2X)/\Delta H^0(\text{InX})$ has a value of 2.18 for $X=S$ and of 2.39 for $X=O$ when the upper limit $D^0 < 75$ kcal is used.

A more complete discussion of these considerations will be given in the $\text{In-Se}$ and $\text{In-Te}$ paper where all known group II$_B$-group VI molecules will be considered.
REFERENCES


(8a) M. Jeunehomme, Thesis, Université Libre de Bruxelles (1962).


(31) M. Ackerman, Thesis, Université Libre de Bruxelles (1960).


