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Publication Date
2011-01-26
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(M. S. thesis)

December 1977

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

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Thermodynamic Properties of SeS

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ABSTRACT

Mass-spectrometry and Knudsen effusion experiments were used to study the equilibrium partial pressure of SeS formed by reaction of S₂ and Se₂ which were produced by thermally decomposing a mixture of In₂S₃ and In₂Se₃ in a Knudsen effusion cell. The heat of formation of SeS(g) was determined by the second law method to be \(-0.6 \pm 3.0\) kcal/mole. The entropy of formation of SeS(g) was calculated from spectrographic data in Ahmed and Barrow to be 1.5 cal/degree-mole at 298°K.
INTRODUCTION

While extensive work has been done on interchalcogen diatomic molecules over some 90 years, only estimated thermodynamic data are available for SeS gas. Since group II and group III sulfides and selenides, as well as their solid solutions, have been widely used in the semiconductor industry in the form of coatings applied by vacuum deposition, SeS gas, which is known to be stable at 700°C - 1000°C, might be present in the vapor phase in concentration high enough to influence the coating compositions. Thus, it appears of practical interest to study the thermodynamic properties of SeS in order to provide a better understanding of the vacuum deposition processes used in this industry.

In 1964, Umilin, et al. observed the SeS molecule together with many other Se-S gas molecules, in a mass-spectrometric study of the Se-S system. SeS was confirmed to be a stable specie by Chernozubov and Selivanov in 1970. Drowart and Goldfinger, in a review of the group VI-VI diatomics, estimated from trends for related molecules that the dissociation energy of SeS, $D_0$ (SeS), is about 90 kcal/mole. From this value the standard heat of formation of SeS (g) from $S_2$ (g) and Se2 (g) gases is calculated to be 2.8 kcal/mole.

Recently, Ahmed and Barrow were able to measure spectroscopically, for the first time, the ground state vibration frequency for SeS (g). They found it to be 556.03 cm$^{-1}$ and predicted a value of 85 kcal/mole for Do (SeS (g)), which is equivalent to $\Delta H_f = 2.2$ kcal/mole. However, neither the enthalpy nor the entropy of formation of SeS (g) has been experimentally determined so far.
In the present study, the Knudsen effusion method together with mass-spectrometry was used to determine partial pressures of \( S_2 \), \( Se_2 \), and \( SeS \) which were in equilibrium in the reaction

\[
\frac{1}{2} S_2(g) + \frac{1}{2} Se_2(g) = SeS(g)
\]  

(1)

The condensed elements were not suitable sources of \( S_2 \) and \( Se_2 \) gases for the reaction because of the complexity of the equilibrium vapors of both elements.\(^8,9\) Korenev,\(^10\) et al. used the CdS-CdSe and ZnS-ZnSe systems as sources of \( S_2 \) and \( Se_2 \) vapors. Because \( ^{64}Zn^+ \) and \( ^{64}Se^+ \), the most abundant ion from \( S_2 \) vapor, happen to possess the same mass number, they used mass number 65 (\(^{32}S^{33}S\)) to calculate the ion current density of \( S_2^+ \). This technique can't assure great accuracy because the abundance ratio,\(^11\) on which their calculations were based are somewhat uncertain. Furthermore, the mass 65 \( S_2^+ \) peak, because it has only about 1.6% the intensity of the mass 64 peak, is difficult to measure. For the CdS-CdSe system, Korenev, et al. were unable to distinguish \( ^{112}Cd^+ \) from \( ^{112}SeS^+ \).

Miller and Searcy\(^12\) in their study on sublimation of indium sesquisulfide showed that \( In_2S_3 \) sublimes by the reaction:

\[
In_2S_3(g) = In_2S(g) + S_2(g)
\]

\( In_2Se_3 \) has been studied by Grimberg,\(^13\) et al., who found \( In_2Se_3(s) \)

\[ In_2Se(g) + Se_2(g) \]  

to be the principal reaction for decomposition at temperatures around 900°C, though at lower temperatures the equilibrium vapor contains \( Se_n \) gases for \( n = 2, 3, 5, 6, 7, 8 \).

\( In_2S_3 \) and \( In_2Se_3 \) yield comparable \( S_2 \) and \( Se_2 \) pressures, and ions produced by electron collisions with vapor molecules in these systems do not have identical mass peaks. Accordingly, mixture of \( In_2S_3 \) and \( In_2Se_3 \) were used as vapor sources in this study. To obtain equilibrium data for
reaction (1), it is not necessary to know whether In$_2$S$_3$ and In$_2$Se$_3$ react to form ternary condensed phases, because such reactions would not change the equilibrium for reaction (1).

EXPERIMENTAL

An EAI Quadrupole Residual Gas Analyzer, series QUAD 250, equipped with a 14 stage, Be-Cu electron multiplier with a gain greater than $10^6$ was used in this study.

The samples of In$_2$S$_3$ and In$_2$Se$_3$, which were stated by the suppliers (Alfa Inorganics Ventron and Apache Chemicals, Inc., respectively) to be 99.99% pure were preheated separately in Knudsen cells to give the composition which vaporizes congruently. Then, the two solids were mixed and heated in a Knudsen cell to produce S$_2$(g) and Se$_2$(g). The cell, which was made of 99.5% alumina, was heated in the mass-spectrometer by conduction through an alumina heat shield from a 0.0635 cm diameter tungsten wire surrounded by a tantalum heat shield.

Experiments were performed with cell lids of two different orifice diameters to test whether equilibrium was achieved inside the cell, and to correct for non-equilibrium if necessary. Orifice diameters were 0.52 and 1.03 mm, as determined by a traveling microscope, and the channel lengths of the lids were 1.38 and 1.40 mm, respectively.

Background pressures ranged from $2.0 \times 10^{-7}$ to $3.5 \times 10^{-7}$ torr, as measured by an ion gauge, before each run following an overnight bakeout. A movable shutter was provided to separate the ions formed directly from molecules of the beam which originated in the cell from ions formed from molecules that had undergone one or more collisions outside the cell before reaching the collector.
The ions produced by collisions with 36 volt electrons, \( S_2^+ \), \( Se_2^+ \), \( SeS^+ \), \( In^+ \), \( Se^+ \), \( S^+ \), etc, were observed with the cell heated to the temperature range between 830°C and 930°C. The ion species were identified from their isotopic abundance ratios.

Temperatures were measured with a chromel-alumel thermocouple inserted in the thermocouple cavity at the center of the bottom of the Knudsen cell. The temperature, which was recorded by a Doric temperature indicator, was calibrated by comparing the vapor pressure of NaCl determined by isothermal weight loss Knudsen effusion measurements with the pressure calculated from the JANAF Tables. 15

Attempts to obtain values of the proportionality constants between ion intensities and partial pressures of \( S_2 \) and \( Se_2 \) from measurements of weight losses of materials of known vapor pressures were not successful because small changes in alignment caused marked changes in ion signals from run to run. Attempts were made to obtain a calibration by measuring weight losses of NaCl when heated in cells with \( In_2S_3 \) and \( In_2Se_3 \). Unfortunately, the data could not be used because x-ray diffraction examination showed that reaction occurred.

Another way to calculate the relative partial pressures is to accept the ionization cross-section data of others 16,17,18 and to assume that the sensitivity of the electron multiplier is inversely proportional to the square root of the mass of the vapor species.

This approach was adopted. The proportionality constant \( k_1 \) in the relation \( P_1 = k_1 I_1 T \), where \( P_1 \) is the partial pressure of species 1 and \( I_1 \) is its ion intensity, was assumed to be \( \frac{K(E_{max} - AP) \sqrt{M}}{(E-AP) \sigma} \), where \( K \) is a constant, \( AP \) the appearance potential, \( E_{max} \) the ionization potential for maximum cross-section, \( \sigma \) the cross-section at maximum, \( E \) the ionization
potential applied, and $M_i$ the mass number of species $i$. Assuming stable mass-spectrometer performance, this procedure should yield reliable data for the temperature dependence of the equilibrium constant for reaction (1). The heat of reaction could, therefore, be obtained from the temperature variation. Entropies for $S_2(g)$ and $Se_2(g)$ are known. The entropy of $SeS$, and therefore, the entropy of reaction was obtained by evaluating the entropies for the various modes of excitation of $SeS$.

The total entropy for $SeS$ is

$$S_{SeS} = S_t + S_r + S_v + S_e$$

where $S_t$ is the translational entropy, $S_r$ the rotational entropy, $S_v$ the vibrational entropy, and $S_e$ the electronic entropy. The values of $S_t$, $S_r$, $S_v$, and $S_e$ are determined by the following relations derived from statistical thermodynamics:

$$S_t = R \ln \left( \frac{2\pi (M_s + M_{Se})}{h^2} \right)^{3/2} \left( \frac{kT}{p} \right)^{5/2} + 5/2$$

$$S_r = R \ln \left( \frac{8 \pi^2 kT}{h^2} + 1 \right)$$

$$S_v = R \ln \left( 1 + e^{-\theta_v/T} \right) + \frac{\theta_v/T}{e^{\theta_v/T} - 1}$$

$$S_e = R \ln \left( 1 + 2 e^{-\theta_e/T} \right) + \frac{2 \theta_e/T}{e^{\theta_e/T} - 1}$$

where $h$ is the Plank constant, $k$ Boltzmann constant, $M_s$ mass of a sulfur atom, $M_{Se}$ mass of a selenium atom, $R$ the gas constant, $I = \frac{M_s M_{Se}}{M_s + M_{Se}} r_{SeS}^2$ is the moment of inertia of the $SeS$ molecule, where $r_{SeS}$ is the inter-atomic distance; $\theta_v = \frac{hc}{k} \omega_e$ where $\omega_e$ is the characteristic vibration wave number, and $\theta_e = \frac{hc}{k} \omega'$ where $\omega'$ is the ground state splitting. Ahmed and Barrow have reported $\omega_e = 556.03$ cm$^{-1}$, $\omega' = 205.0$ cm$^{-1}$, and $r_{SeS} = 2.029$Å for the ground state ($^3\Sigma^-$) of $SeS$. 
RESULTS AND DISCUSSION

Calculated values of the entropy and heat capacity of SeS and values of $\Delta S$, $\Delta C_p$, and $(\Delta H^o_T - \Delta H^o_{298})$ for reaction (1), which are derived from these data and JANAF data for $S_2$ and $Se_2$ are reported in Table I. As would be expected from the regularities usually shown for entropies and heat capacities of reaction, $\Delta S$ for reaction (1) is close to $R \ln 2 = 1.38$ cal per degree per mole of SeS, $\Delta C_p$ is essentially zero at all temperatures, and the heat of reaction changes by only a few calories between $0^\circ K$ and $1250^\circ K$.

At temperature around $750^\circ C$, the ion peaks of $S_2^+$, $Se_2^+$, $SeS^+$, $S^+$, and $Se^+$ were observable in the mass-spectrometer. However, they were quite small compared with the background intensities until the temperature reached $830^\circ C$. At temperatures above $930^\circ C$, the samples were exhausted within 30 minutes. Thus, the temperature range suitable for this study was between $830^\circ C$ and $930^\circ C$.

It was reported$^{10}$ that during the isothermal evaporation of the ZnS-ZnSe system, the solid composition changed. The $In_2S_3-In_2Se_3$ system showed similar behavior. When the system was heated isothermally, the $S_2^+$ peak increased by a factor of 70% over a three hour period.

This change could not be due to a change in sensitivity or to poisoning of the electron multiplier, for this should decrease the $S_2^+$ peak instead of increasing it. Fortunately, the changes in the ion peaks were slow so that one can assume no change in vapor composition during each set of ion intensity measurements made at a fixed temperature. The ion peak of $S^+$ was about 10% that of $S_2^+$ at $830^\circ C$ and about 18% at $930^\circ C$ while the ion peak of $Se^+$ was about 160% that of $Se_2^+$ at $830^\circ C$ and about
Table 1. Calculated Thermodynamic Data.

<table>
<thead>
<tr>
<th>Temp. (°K)</th>
<th>SeS S cal/°K</th>
<th>SeS Cp cal/°K</th>
<th>1/2 S₂(g) + 1/2 Se₂(g) ΔS cal/°K</th>
<th>1/2 S₂(g) + 1/2 Se₂(g) ΔCp cal/°K</th>
<th>ΔH°₂₉₈ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>58.50</td>
<td>8.557</td>
<td>1.50</td>
<td>-0.127</td>
<td>0.000</td>
</tr>
<tr>
<td>300</td>
<td>58.56</td>
<td>8.560</td>
<td>1.50</td>
<td>-0.126</td>
<td>0.000</td>
</tr>
<tr>
<td>400</td>
<td>61.03</td>
<td>8.664</td>
<td>1.47</td>
<td>-0.111</td>
<td>-0.013</td>
</tr>
<tr>
<td>500</td>
<td>62.97</td>
<td>8.741</td>
<td>1.45</td>
<td>-0.078</td>
<td>-0.022</td>
</tr>
<tr>
<td>600</td>
<td>64.57</td>
<td>8.792</td>
<td>1.43</td>
<td>-0.055</td>
<td>-0.029</td>
</tr>
<tr>
<td>700</td>
<td>65.93</td>
<td>8.827</td>
<td>1.43</td>
<td>-0.040</td>
<td>-0.033</td>
</tr>
<tr>
<td>800</td>
<td>67.11</td>
<td>8.850</td>
<td>1.42</td>
<td>-0.031</td>
<td>-0.037</td>
</tr>
<tr>
<td>900</td>
<td>68.16</td>
<td>8.868</td>
<td>1.42</td>
<td>-0.024</td>
<td>-0.040</td>
</tr>
<tr>
<td>1000</td>
<td>69.09</td>
<td>8.881</td>
<td>1.42</td>
<td>-0.020</td>
<td>-0.042</td>
</tr>
<tr>
<td>1050</td>
<td>69.52</td>
<td>8.887</td>
<td>1.42</td>
<td>-0.017</td>
<td>-0.043</td>
</tr>
<tr>
<td>1100</td>
<td>69.94</td>
<td>8.891</td>
<td>1.42</td>
<td>-0.016</td>
<td>-0.043</td>
</tr>
<tr>
<td>1150</td>
<td>70.33</td>
<td>8.896</td>
<td>1.41</td>
<td>-0.014</td>
<td>-0.044</td>
</tr>
<tr>
<td>1200</td>
<td>70.71</td>
<td>8.899</td>
<td>1.41</td>
<td>-0.012</td>
<td>-0.045</td>
</tr>
<tr>
<td>1250</td>
<td>71.07</td>
<td>8.903</td>
<td>1.41</td>
<td>-0.011</td>
<td>-0.045</td>
</tr>
</tbody>
</table>
The fact that the ratios $\frac{\text{Se}^+}{\text{Se}_2^+}$ and $\frac{\text{Se}^+}{\text{SeS}^+}$ decreased continuously and fell below 15% and 9.2% respectively at higher temperatures indicates that most of the Se$^+$ ions were not formed by fragmentation of Se$_2$ or SeS.

The ionization efficiency curves for S$_2^+$, Se$_2^+$, SeS$^+$, S$^+$, and Se$^+$, which were determined at 845°C (Fig. 1), showed no changes of the slopes of a kind to indicate that fragmentation processes contributed to the S$_2^+$, Se$_2^+$, or SeS$^+$ measured intensities.

The sensitivity dropped to 40% of the initial value after 6 hours through poisoning of the electron multiplier as In$_2$S$_3$ was heated alone at 840°C. In addition, the ion intensities were sensitive to electronics. This problem caused scatter, since the electronic controls were too coarse for exact duplicate settings, and the instability of the electronic components caused changes in the ion intensities.

Equilibrium constants measured for different temperatures at different runs are listed in Table 2, and are plotted in Fig. 2. The heat of formation of SeS was calculated from the slope of the $\ln K_{eq}$ vs. 1/T plot according to the relation: $\Delta H^\circ = (-R)(\text{slope})$, where R is the gas constant.

Combined data for four runs with the 1.03 mm orifice yield $-2.1 \pm 2.6$ kcal/mole, and those with the 0.52 mm orifice yield $2.5 \pm 3.6$ kcal/mole.

The discrepancy between the two sets of data appears to be caused by the low Se$_2$ intensities gotten with the 0.52 mm orifice. The S$_2$ and SeS intensities are reduced by a factor of ~12-15 in going from 1.03 mm to the 0.52 mm orifice, whereas the Se$_2$ intensities are reduced by a factor of ~50-60. This increases the value of $K_{eq}$ by a factor of ~2, as the plot shows.
Table 2. Ion Intensities and Calculated Equilibrium Constants for the Reaction (1).

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>$I_{S_2}^+$</th>
<th>$I_{SeS}^+$</th>
<th>$I_{Se_2}^+$</th>
<th>$K_{eq} = \alpha \frac{I_{SeS}^+}{\sqrt{I_{Se_2}^+ + I_{S_2}^+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>d = 1.03mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1117</td>
<td>4.91</td>
<td>1.38</td>
<td>0.283</td>
<td>1.22</td>
</tr>
<tr>
<td>1137</td>
<td>9.30</td>
<td>2.47</td>
<td>0.435</td>
<td>1.28</td>
</tr>
<tr>
<td>1166</td>
<td>12.00</td>
<td>3.87</td>
<td>0.977</td>
<td>1.17</td>
</tr>
<tr>
<td>1138</td>
<td>24.3</td>
<td>12.27</td>
<td>5.55</td>
<td>1.10</td>
</tr>
<tr>
<td>1154</td>
<td>28.2</td>
<td>14.52</td>
<td>8.48</td>
<td>0.979</td>
</tr>
<tr>
<td>1165</td>
<td>27.6</td>
<td>18.15</td>
<td>10.08</td>
<td>1.13</td>
</tr>
<tr>
<td>1188</td>
<td>37.2</td>
<td>23.40</td>
<td>12.51</td>
<td>1.13</td>
</tr>
<tr>
<td>1130</td>
<td>9.68</td>
<td>4.80</td>
<td>2.25</td>
<td>1.07</td>
</tr>
<tr>
<td>1156</td>
<td>11.4</td>
<td>6.87</td>
<td>3.36</td>
<td>1.16</td>
</tr>
<tr>
<td>1195</td>
<td>21.6</td>
<td>9.09</td>
<td>3.56</td>
<td>1.08</td>
</tr>
<tr>
<td>1182</td>
<td>15.7</td>
<td>7.01</td>
<td>3.66</td>
<td>0.96</td>
</tr>
<tr>
<td>1119</td>
<td>4.48</td>
<td>2.34</td>
<td>1.23</td>
<td>1.04</td>
</tr>
<tr>
<td>d = 0.52mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1125</td>
<td>1.05</td>
<td>0.71</td>
<td>0.087</td>
<td>2.45</td>
</tr>
<tr>
<td>1125</td>
<td>1.25</td>
<td>0.63</td>
<td>0.090</td>
<td>1.96</td>
</tr>
<tr>
<td>1125</td>
<td>1.25</td>
<td>0.82</td>
<td>0.093</td>
<td>2.50</td>
</tr>
<tr>
<td>1146</td>
<td>1.39</td>
<td>0.81</td>
<td>0.108</td>
<td>2.18</td>
</tr>
<tr>
<td>1146</td>
<td>1.41</td>
<td>0.87</td>
<td>0.114</td>
<td>2.26</td>
</tr>
<tr>
<td>1164</td>
<td>1.8</td>
<td>1.41</td>
<td>0.186</td>
<td>2.54</td>
</tr>
<tr>
<td>1188</td>
<td>2.75</td>
<td>1.56</td>
<td>0.192</td>
<td>2.24</td>
</tr>
<tr>
<td>1188</td>
<td>2.50</td>
<td>1.70</td>
<td>0.195</td>
<td>2.54</td>
</tr>
</tbody>
</table>

$\alpha = \frac{K_{SeS}}{(K_{Se_2} K_{S_2})^{1/2}} = 1.0428.$

d is the orifice diameter.
The species $\text{Se}_2$ is the most condensable of the three species of interest. Hence, the $\text{Se}_2$ signal probably would have the least contribution from background, and so would be the most sensitive to the alignment of the crucible orifice. Also, the 0.52mm orifice would have a tendency to channel or focus the beam, because of the small ratio of radius to length (0.26/1.38). Hence, a slight misalignment of the crucible could have a large effect on the $\text{Se}_2$ intensity, considering the 70 cm distance between the crucible and the mass filter. When the measurements with the larger orifice are assigned twice the weight of those with the small orifice, the value $\Delta H^\circ = -0.6 \pm 3.0$ kcal is found for reaction 1, which lead to $D_0^\circ(\text{SeS}) = 87.8$ kcal/mole. Experiments thus confirm the prediction\textsuperscript{2,7} that the bond energy in $\text{SeS}$ would be near the average of the bond energies of $\text{S}_2$ and $\text{Se}_2$.

To test the possible importance of $\text{SeS}$ in sulfides, which contain selenium as an impurity, partial pressures of $\text{S}_2$, $\text{Se}_2$, and $\text{SeS}$ gases at 900°C were calculated for an $\text{In}_2\text{S}_3$ sample with 1% $\text{In}_2\text{Se}_3$ impurity. Ideal solution of $\text{In}_2\text{Se}_3$ in $\text{In}_2\text{S}_3$ was assumed. Equilibrium data given by Miller and Searcy,\textsuperscript{12} and Grinberg,\textsuperscript{13} et al., on $\text{In}_2\text{S}_3$ and $\text{In}_2\text{Se}_3$ respectively, were used.

Three simultaneous equations were set-up as follows:

$$\frac{P_{\text{S}_2}(P_{\text{S}_2} + 1/2 P_{\text{SeS}})}{0.99} = 6.34 \times 10^{-9}$$

$$\frac{P_{\text{Se}_2}(P_{\text{Se}_2} + 1/2 P_{\text{SeS}})}{0.01} = 1.00 \times 10^{-2}$$

$$\left(\frac{P_{\text{SeS}}}{P_{\text{S}_2}}\right)^2 = 6.97$$

where $P$'s are in atm.
The equations may be solved for $P_{S_2}$, $P_{SeS}$, and $P_{Se_2}$ as shown below:

$$P_{S_2} = 1.30 \times 10^{-5}$$

$$P_{Se_2} = 9.77 \times 10^{-3}$$

$$P_{SeS} = 9.40 \times 10^{-4}$$

The $S_2$ and $Se_2$ pressures, however, are not consistent with our experimental observations in which the most intense ion peak is $S_2^+$ instead of $Se_2^+$. No reasonable model for condensed phase reaction between $In_2S_3$ and $In_2Se_3$ would predict that an approximately equimolar mixture of the two solids would yield such a low $Se_2^+/S_2^+$ ratio if the reported vapor pressures for $In_2S_3$ and $In_2Se_3$ are correct. The data given by Grinberg, et al., may be in error and an isothermal Knudsen effusion weight loss experiment of $In_2Se_3$ will be carried out in the near future to check the vapor pressure of $Se_2(g)$.

Vapor pressures for $CdS^{19}$ and $CdSe^{20}$ are better established. A calculation of the effect of 1% $CdSe$ dissolved in an ideal solution in $CdS$ was also made. The equilibrium pressures at 1000 K were calculated from the following equations:

$$\frac{P_{S_2} \left(2P_{S_2} + 2P_{Se_2} + 2P_{SeS}\right)^2}{0.99^2} = 4.57 \times 10^{-14}$$

$$\frac{P_{Se_2} \left(2P_{S_2} + 2P_{Se_2} + 2P_{SeS}\right)^2}{(0.01)^2} = 1.34 \times 10^{-10}$$

$$\frac{P_{SeS}^2}{P_{S_2} P_{Se_2}} = 7.64$$

where $2P_{S_2} + 2P_{Se_2} + 2P_{SeS} = P_{Cd}$

And the pressures were calculated to be
Thus, the pressure of SeS gas is about five times as high as that of Se₂, and SeS is predicted to be a major Se impurity carrier in vacuum deposition processes.

ACKNOWLEDGMENT

I am deeply grateful to Professor Alan W. Searcy for his kind guidance, encouragement, and extremely helpful consultations during this work. I also thank everyone in Professor Searcy's group, especially Dr. David Meschi for his frequent technical assistance and numerous helpful suggestions.

I would like to thank the MMRD support staff for their kind assistance.

Finally, I warmly thank Gay Brazil for typing this material.

This work was supported by the Division of Basic Energy Sciences, U.S. Department of Energy.
FIGURES

Fig. 1. Ionization efficiency curves for \( S_2, \) SeS, Se\(_2\).

Fig. 2. Equilibrium constant of reaction (1) as a function of reciprocal temperature.
Fig. 1. Ion currents determined from vapors in equilibrium with mixture of In₂S₃(s) and In₂Se₃(s) at 844°C.

-15-

Ionization Voltage (volts)

I⁺ (arbitrary units)
Fig. 2. \[ \ln K_{eq} \text{ vs. } \frac{10^5}{T} \] for \( \frac{1}{2}S_2(g) + \frac{1}{2}Se(g) = SeS(g) \).

<table>
<thead>
<tr>
<th>Orifice mm</th>
<th>[ \Delta H ] kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>2.5 ± 3.6</td>
</tr>
<tr>
<td>1.03</td>
<td>-2.1 ± 2.6</td>
</tr>
</tbody>
</table>

\[ 10^5 / T, ^\circ K^{-1} \]
REFERENCES

15. JANAF Thermochemical Tables, ed. by D. R. Stull (Dow Chemical Co., Midland, Michigan).


This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.