LITERATURE REVIEW OF METAL SULFIDE VAPORIZATION AND EXPERIMENTAL STUDY OF LEAD SULFIDE VAPORIZATION AND COMPLEXATION

by

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ABSTRACT

A thorough literature review of metal sulfide vaporization was performed. The systems lacking sufficient data or showing unreliable experimental data were identified.

Conventional transpiration experiments were conducted for the lead-sulfur system to redetermine the vaporization data for the reaction:

\[ \text{PbS}(s) \rightarrow \text{PbS}(g) \]  

The temperature range studied was 724-951°C, and the standard Gibbs free energy obtained for the above reaction is:

\[ \Delta G^\circ_T = 49,395 - 30.975^\circ T \text{ (cal/mole)} \]  

The literature review for the lead-sulfur system proved the existing transpiration data to be unreliable. The dissociative vaporization of lead sulfide had been neglected by all but one previous investigator. The results of this study are a definite improvement on the vaporization data for reaction (1). A hydrogen/hydrogen
sulfide carrier gas was used to hinder the dissociative vaporization of lead sulfide, and reproducibility of any experiment was very good.

Mass spectrometric experiments on the system As-Pb-S enabled the identification of the complex species AsPbS₂(g). The formation of this vapor complex in the arsenic sulfide-lead sulfide system was confirmed by use of a specially designed double zone transpiration apparatus. However, it was not possible to quantify the effect of complexation on the rate of vaporization of lead sulfide due to the interaction between the arsenic sulfide vapors and the solid lead sulfide samples.

Complexation studies on the systems Sb-Pb-S, Bi-Pb-S, and Cd-Pb-S were also performed using the double zone transpiration apparatus. For different reasons these experiments were unsuccessful in identifying vapor complexation effects.
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I. INTRODUCTION

1.1 THE VAPORIZATION OF METAL SULFIDES

Several important metals occur in nature mostly as sulfides. When such an occurrence is determined to be an exploitable ore body, the sulfide ore is extracted and submitted to the necessary processing operations. Commonly the sulfide concentrate would undergo pyrometallurgical processing such as roasting or smelting. Considerable attention has been focused on the vaporization of sulfides during high temperature processing as a consequence of increasing concern with environmental issues. The formation of gaseous sulfides that might intrude the work place and the emission of fumes, such as during the direct smelting of galena, are serious problems that require attention.

The availability of reliable thermodynamic data on the vaporization of metal sulfides is important to the control and operation of pyrometallurgical processes, in order to permit the quantification of the amount of metal sulfide lost to the gas phase. Such data are also very important in the design of new processes or, in the case of sulfides that are used as solid lubricants (MoS$_2$ and WS$_2$), to
determine their stability range.

In 1951 Hsiao and Schlechten [1] foresaw the need to establish data on the vaporization of metal sulfides. They determined the apparent vapor pressure of a number of metal sulfides by measuring the rate of weight loss of a sulfide sample when heated under vacuum. Their data have been used for many years in compilations that have been prepared on the thermodynamic properties of compounds.

The advent of modern laboratory instrumentation and techniques, especially the use of mass spectrometry, has made possible a deeper understanding of the volatilization processes for many inorganic materials. Starting in the late 1950’s and throughout the 1960’s Drowart and co-workers [2-5] used mass spectrometry to study the vaporization of a number of compounds, among them some sulfides. Their work and that of other researchers [6-10] has shed some light on the complex chemistry of sulfide vaporization. It has been shown that a metal sulfide may vaporize congruently or incongruently. Congruent vaporization is the vaporization process where the elements of a certain compound are present in the gas phase in the same ratio as that observed in the compound itself. Reactions (1.1) and (1.2) are examples of congruent vaporization, while reaction (1.3) is an example of
incongruent vaporization.

$$\text{MeS}(s) = \text{MeS}(g) \quad (1.1)$$

$$\text{MeS}(s) = \text{Me}(g) + \frac{1}{2} \text{S}_2(g) \quad (1.2)$$

$$\text{MeS}(s) = \text{Me}(s) + \frac{1}{2} \text{S}_2(g) \quad (1.3)$$

Sulfides may vaporize by a very simple process such as in reaction (1.1), or they may rather dissociate as in reactions (1.2) and (1.3). In some instances, it has been found that the vaporization process is actually a combination of the three processes shown above (reactions (1.1) thru (1.3)). More complex mechanisms may occur when instead of reaction (1.3) stoichiometric compounds such as \(\text{Me}_2\text{S}_3(s)\) or non-stoichiometric solids, \(\text{Me}_x\text{S}_y\), are formed. Further, the gaseous sulfide produced by reaction (1.1) may in some cases aggregate in the form of polymeric gaseous species, such as \(\text{Pb}_2\text{S}_2(g)\) or \(\text{Sn}_2\text{S}_2(g)\), and the dissociation of the molecule \(\text{S}_2(g)\) may also have to be considered.

An interesting aspect of sulfide vaporization is still practically untouched by investigators. The formation of vapor complexes may significantly enhance the vaporization of several species. Such topic is discussed in detail in
section 2.3.2. Colin and Drowart [4] identified the species SnPbS$_2$(g) in a mass spectrometric study of a mixture of tin and lead sulfides. This is clear evidence that during the processing of a sulfide concentrate the presence of impurities could enhance volatilization through the formation of complex species. For example, such complexation could be important in the direct smelting of galena, first, because of the relatively high level of fumes, and second, because lead sulfide vapor complexes have already been identified.

The work of Hsiao and Schlechten [1] is outdated today because they lacked information on which species were formed during the volatilization process. Further, all they were able to measure was the "apparent" vapor pressure of a metal sulfide. There are in the literature more recent data on the vaporization of a limited number of metal sulfides. Thus, an updated summary on metal sulfide vaporization would not only gather together these data but would also allow for the identification of those metal sulfides which still lack reliable vaporization data.
1.2 PURPOSE AND ORGANIZATION OF THIS STUDY

The purpose of this research effort was twofold:

1. Thoroughly review the literature on metal sulfide vaporization, and
2. Use mass spectrometric and transpiration experiments to study the vaporization chemistry of one or more sulfide systems that were identified as having poor vaporization data.

During the first phase of the research, the METALS ABSTRACTS and the CHEMICAL ABSTRACTS data bases were thoroughly searched in an attempt to retrieve all the previously published data on metal sulfide vaporization. The information gathered for each metal-sulfur system was analyzed and the findings of this study are presented in the literature review section of this work (Chapter 2). The recommended vaporization data, as well as comments regarding the status of such data, accompanies the summary of findings for each of the systems that have been examined.

The second phase of this study consisted of a series of mass spectrometric and transpiration experiments focusing on the identification of vapor species and the quantification of the vaporization data for the systems
selected from the first phase of the research.
II. LITERATURE REVIEW

The literature review presented here consists of two distinct sections. The first one deals with the general topic of metal sulfide vaporization. Its purpose was to review previous work on the subject, and from an analysis of such work, identify metal-sulfur systems which have not yet been thoroughly studied. Those systems for which the data published seems reasonable were also reviewed and the best data available are presented. The second section of this literature review includes a detailed look at previous work on the systems selected for experimental study.

2.1 VAPORIZATION IN METAL-SULFUR SYSTEMS

2.1.1 Aluminum-sulfur

Ficalora et al [11] used a time-of-flight mass spectrometer with a Knudsen cell assembly to determine the various species present when Al(g) is equilibrated with S_2(g), Se_2(g), or Te_2(g). For the aluminum-sulfur system the species observed were AlS(g), Al_2S(g) and Al_2S_2(g). In order to calculate thermodynamic data it was assumed that Al(1) existed at unit activity inside the Knudsen
cell. Aluminum was, therefore, used as an internal standard to convert ion intensities to pressures. Second-law enthalpies were determined for reactions (2.1), (2.2), and (2.3).

\[
\text{Al}(g) + \frac{1}{2} \text{S}_2(g) = \text{AlS}(g) \tag{2.1}
\]

\[
2 \text{Al}(g) + \frac{1}{2} \text{S}_2(g) = \text{Al}_2\text{S}_2(g) \tag{2.2}
\]

\[
2 \text{Al}(g) + \text{S}_2(g) = \text{Al}_2\text{S}_2(g) \tag{2.3}
\]

Uy and Drowart [2] analyzed the data reported by Ficalora et al [11] using the third-law method. They observed systematic discrepancies between the reported second-law results and the calculated third-law results for the reactions studied (reactions 2.1 thru 2.3), suggesting errors in temperature measurements, reevaporation of \( \text{S}_2(g) \) from sources other than the Knudsen cell, an aluminum activity lower than unity, or a combination of these possibilities. A new mass spectrometric investigation was performed and data were generated for reactions (2.4), (2.5) and (2.6).

\[
\text{AlS}(g) + \text{S}(g) = \text{Al}(g) + \text{S}_2(g) \tag{2.4}
\]
\[
\text{Al}_2\text{S}_2(g) + 2 \text{S}(g) = 2 \text{AlS}(g) + \text{S}_2(g) \tag{2.6}
\]

The JANAF Thermochemical Tables \cite{12} provide a complete table of thermodynamic properties for the species \(\text{AlS}(g)\). However, the data provided in this table are totally derived from estimated molecular parameters and neither of the above mentioned papers were analyzed.

Mills \cite{13} reviewed all three previously mentioned sources and compiled a new table of data for the species \(\text{AlS}(g)\). He also included some data for the other gaseous species, citing Uy and Drowart \cite{2} as his primary source.

Mills \cite{13} has also tabulated thermodynamic functions for \(\text{Al}_2\text{S}_3(s)\), however, Ferrante et al \cite{14} in a recent investigation determined such data from 0 to 900K and reported results quite different from those published by Mills \cite{13}. Tables for the vaporization of aluminum (III) sulfide are therefore not provided here because of the lack of reliable high temperature (above 1000K) thermodynamic data for the condensed phase.
2.1.2 Chromium-sulfur

The species CrS\((g)\) has been identified by Drowart et al [3] in a mass spectrometric study of exchange reactions between gaseous monosulfides. The dissociation energy for this molecule was determined through the study of reaction (2.7).

\[
\text{Cr}(g) + \text{MnS}(g) = \text{CrS}(g) + \text{Mn}(g) \quad (2.7)
\]

In his review Mills [13] presents a table of thermodynamic properties for CrS\((g)\) based on estimated molecular parameters and on the work by Drowart et al [3].

There has been no direct study of the vaporization of chromium sulfide. Free energy equations for the probable vaporization reactions are presented in Table 2.1. These equations were used to calculate the vapor pressures of the major species above CrS\(_S\) as shown in Table 2.2. By analogy with other elements from group VIB in the periodic table it could be anticipated that chromium sulfide would rather dissociate than vaporize as the molecule CrS\((g)\). The results in Table 2.2 confirm this point: Cr\((g)\) and S\(_2\)(g) are indeed the major species, followed by CrS\((g)\) and S\((g)\). The pressure of gaseous chromium shown in Table 2.2
### TABLE 2.1

**Recommended Thermodynamic Data for the Vaporization of Chromium Sulfide**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy (cal/mol)</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrS&lt;sub&gt;(s)&lt;/sub&gt; = CrS&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>109256 - 37.46*T</td>
<td>1500-1800K</td>
</tr>
<tr>
<td>CrS&lt;sub&gt;(s)&lt;/sub&gt; = Cr&lt;sub&gt;(g)&lt;/sub&gt; + 1/2 S&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>140170 - 45.94*T</td>
<td>1375-1500K</td>
</tr>
<tr>
<td>1/2 S&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;(g)&lt;/sub&gt; = S&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>51908 - 14.515*T</td>
<td>1400-1800K</td>
</tr>
</tbody>
</table>

* Free energy data calculated from heats of formation and fef data from Mills [13].

** Calculated from data by Hager and Elliott [15] and the JANAF Thermochemical Tables [16].

*** Data from the JANAF Thermochemical Tables [17].

### TABLE 2.2

**Vapor Pressure of the Major Species Above CrS<sub>(s)</sub>**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>P&lt;sub&gt;S&lt;/sub&gt;</th>
<th>P&lt;sub&gt;S&lt;sub&gt;2&lt;/sub&gt;&lt;/sub&gt;</th>
<th>P&lt;sub&gt;Cr&lt;/sub&gt;</th>
<th>P&lt;sub&gt;CrS&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>1.03 E-9</td>
<td>7.68 E-9</td>
<td>1.64 E-8</td>
<td>1.35 E-9</td>
</tr>
<tr>
<td>1500</td>
<td>1.11 E-8</td>
<td>7.18 E-8</td>
<td>1.54 E-7</td>
<td>1.85 E-8</td>
</tr>
<tr>
<td>1600</td>
<td>8.58 E-8</td>
<td>5.06 E-7</td>
<td>1.10 E-6</td>
<td>1.83 E-7</td>
</tr>
<tr>
<td>1700</td>
<td>5.31 E-7</td>
<td>2.84 E-6</td>
<td>6.21 E-6</td>
<td>1.38 E-6</td>
</tr>
</tbody>
</table>
are below the saturation pressure for chromium metal.

2.1.3 Cobalt-sulfur

The species CoS(g) was identified by Drowart et al [3] in a mass spectrometric investigation of exchange reactions between gaseous monosulfides. The dissociation energy was determined from a study of reaction (2.9).

\[ \text{Co}(g) + \text{MnS}(g) = \text{CoS}(g) + \text{Mn}(g) \]  (2.9)

In a thermodynamic study of cobalt sulfides, Rosenqvist [18] has reported several condensed compounds. The phases Co₄S₃ and CoS have rather large homogeneity ranges and are stable only at high temperatures. Chen and Chang [19] have determined the activity of sulfur as a function of composition at high temperatures using a gas equilibration technique. They used their data and data reported in the literature in developing thermodynamic equations for the condensed phases as a function of temperature and composition.

The present literature survey has not identified any research dealing specifically with the vaporization of cobalt sulfides. The lack of thermodynamic data for
CoS\(_{(g)}\) does not allow the vapor pressure for the species CoS\(_{(g)}\) to be calculated. The equations given by Chen and Chang [19] are presented on Table 2.3. The equilibrium pressures of Co\(_{(g)}\), S\(_2\)(g) and S\(_{(g)}\) were calculated using Chen and Chang’s [19] equations and data from Hultgren et al [20] (Co\(_{(g)}\)) and the JANAF Thermochemical Tables [17] (S\(_2\)(g), S\(_{(g)}\)) and are presented in Table 2.4. The relatively high sulfur vapor pressures given in Table 2.4 should be noted. It is suggested that the data presented here be used with reservations until further experimental work is performed for this system.

2.1.4 Copper-sulfur

Drowart et al [3] identified the species CuS\(_{(g)}\) in a mass spectrometric investigation of exchange reactions between gaseous monosulfides. Manganese sulfide was used as a reference species and the dissociation energy of CuS\(_{(g)}\) was determined by studying reaction (2.10).

\[
\text{Cu}_{(g)} + \text{MnS}_{(g)} = \text{CuS}_{(g)} + \text{Mn}_{(g)} \quad (2.10)
\]

Kellogg [21] critically reviewed studies of the Cu-S system at high temperature (800-1600 K). His work did not
**TABLE 2.3**

Free Energy of Formation of $\text{Co}_{(1-y)} \text{S}_s(s)$

$(773 < T < 1373 \text{ K})$

**Reaction:** $\text{Co}_{1-y} \text{S}_s(s) = \text{Co}_s(s) + \frac{1}{2} \text{S}_2(g)$

<table>
<thead>
<tr>
<th>$X_S$ (Sulfur Atomic Fraction)</th>
<th>Free Energy, $\Delta G^0_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>$17184 - 3.19T - 0.63T \ln(T)$</td>
</tr>
<tr>
<td>0.52</td>
<td>$17356 - 2.48T - 0.75T \ln(T)$</td>
</tr>
<tr>
<td>0.53</td>
<td>$17395 - 1.11T - 0.96T \ln(T)$</td>
</tr>
<tr>
<td>0.54</td>
<td>$17306 + 0.88T - 1.25T \ln(T)$</td>
</tr>
</tbody>
</table>

**TABLE 2.4**

Partial Pressure of Co, $\text{S}_2$ and S Above $\text{Co}_{0.965}$

(sulfur atomic fraction = 0.51)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{S_2}$ (atm)</th>
<th>$P_S$ (atm)</th>
<th>$P_{Co}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>7.81 E-3</td>
<td>6.09 E-10</td>
<td>2.20 E-15</td>
</tr>
<tr>
<td>1100</td>
<td>1.77 E-2</td>
<td>9.76 E-9</td>
<td>2.20 E-13</td>
</tr>
<tr>
<td>1200</td>
<td>3.50 E-2</td>
<td>9.86 E-8</td>
<td>1.10 E-11</td>
</tr>
<tr>
<td>1300</td>
<td>6.24 E-2</td>
<td>6.98 E-7</td>
<td>2.67 E-10</td>
</tr>
</tbody>
</table>
include the solid phase CuS (covellite) since this phase decomposes on heating to Cu$_2$S(s) at temperatures near 500°C. His comments concerning the gas phase are as follows:

"The vapor in equilibrium with the system Cu-S contains Cu(g), S$_2$(g) and S(g). Binary species such as CuS(g) and Cu$_2$S(g), if present at all, are negligible. The partial pressure of Cu(g) is at a maximum above pure copper (in the copper-sulfur phase diagram), and is very small even there ($P_{Cu} = 1.2 \times 10^{-6}$ atm at 1127°C). The partial pressures of S$_2$(g) and S(g) are also small except for compositions richer in sulfur than Cu$_2$S."

Mills [13] also reviewed previous studies on copper sulfides. Based on the work of Drowart et al [3] and on estimated molecular parameters Mills compiled a table of thermodynamic data for the species CuS(g). These data together with data on Cu$_2$S(s,l) from Ferrante et al [22] and data on Cu(g), S(g) and S$_2$(g) from the JANAF Thermochemical Tables [12] enabled the compilation of Tables 2.5 and 2.6.

In his review Mills [13] cites several studies on the dissociation pressure of Cu$_2$S(s,l) [23-26]. The experimental results of these investigations are not in
**TABLE 2.5**

Recommended Thermodynamic Data for the Vaporization of Cu$_2$S
(Temperature range: 1000-1300K)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Free Energy, $\Delta G^o_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$S(s) = 2 Cu(s) + 1/2 S$_2$(g)</td>
<td>30340 - 7.284*T</td>
</tr>
<tr>
<td>Cu$_2$S(s) = Cu(s) + CuS(g)</td>
<td>89883 - 29.942*T</td>
</tr>
</tbody>
</table>

**TABLE 2.6**

Vapor Pressure of the Major Species Above Cu$_2$S(s)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{CuS}$</td>
</tr>
<tr>
<td>1000</td>
<td>7.92 E-14</td>
</tr>
<tr>
<td>1100</td>
<td>4.84 E-12</td>
</tr>
<tr>
<td>1200</td>
<td>1.49 E-10</td>
</tr>
<tr>
<td>1300</td>
<td>2.71 E-9</td>
</tr>
</tbody>
</table>
good agreement with each other.

2.1.5 Iron-sulfur

Marquart and Berkowitz [7] used mass spectrometry to study the dissociation energies of several metal sulfides. By analyzing the mass spectrum above solid FeS they were able to determine an upper limit for the dissociation energy of FeS(g).

Drowart et al [3] also determined the dissociation energy for FeS(g) in a mass spectrometric study of exchange reactions between gaseous monosulfides.

The JANAF Thermochemical Tables [17] provide a table of thermodynamic functions for the species FeS(g) compiled from the above cited experimental works, from spectroscopic data available in the literature and from estimated molecular parameters. This table as well as others available from the JANAF Thermochemical Tables [17] (FeS(s), Fe(g), S₂(g) and S(g)) were used to compile Tables 2.7 and 2.8.
TABLE 2.7
Recommended Thermodynamic Data for the Vaporization of Iron Monosulfide

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{FeS}<em>\text{(s)} = \text{FeS}</em>\text{(g)}$</td>
<td>$107350 - 36.95^\circ T$</td>
</tr>
<tr>
<td>$\text{FeS}<em>\text{(s)} = \text{Fe}</em>\text{(s)} + \frac{1}{2} \text{S}_2\text{(g)}$</td>
<td>$37555 - 14.19^\circ T$</td>
</tr>
</tbody>
</table>

TABLE 2.8
Vapor Pressure of the Major Species Above FeS$_\text{(s)}$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{\text{FeS}}$</td>
</tr>
<tr>
<td>1000</td>
<td>$4.10 \times 10^{-16}$</td>
</tr>
<tr>
<td>1100</td>
<td>$5.57 \times 10^{-14}$</td>
</tr>
<tr>
<td>1200</td>
<td>$3.34 \times 10^{-12}$</td>
</tr>
<tr>
<td>1300</td>
<td>$1.07 \times 10^{-10}$</td>
</tr>
<tr>
<td>1400</td>
<td>$2.07 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
2.1.6 Lead-sulfur

Colin and Drowart [4] have shown from mass spectrometric studies that sublimation occurs essentially by reaction (2.11). However, small amounts of Pb$_2$S$_2$(g) were also detected in the vapor phase.

\[
PbS(s) = PbS(g) \quad (2.11)
\]

The appreciable vapor pressure of PbS$_{(s)}$ even at moderate temperatures has raised some interest in the sublimation process. The feasibility of the vapor phase reduction of lead sulfide to metallic lead using hydrogen as reductant was investigated by Cole et al [27]. The kinetics of vaporization of lead sulfide was subject of a recent study by El-Rahaiby and Rao [28].

Mills [13] has reviewed the sublimation studies on the lead-sulfur system, however, a more recent review is provided by the JANAF Thermochemical Tables [16]. In this review, an uncertainty on the heat of formation for PbS$_{(g)}$ is attributed to "possible decomposition and/or action during sublimation". The adopted $\Delta H_f^{\circ}$,298 value is said to be a compromise between conflicting spectroscopic, mass spectrometric and sublimation studies. It is further
pointed out in the review that there is a 4 kcal difference between the dissociation energy of PbS(g) calculated from statistical mechanics and the value obtained from the adopted heat of formation. Most of the studies reviewed by the JANAF Thermochemical Tables [16] consist of Knudsen or torsion effusion studies. It should be stressed that such experimental techniques are particularly vulnerable to error if there is a significant degree of dissociation accompanying vaporization.

The above mentioned inconsistencies suggest that experimental work be performed on the lead-sulfur system. The experimental technique should, however, provide for the control of the sulfur potential in order to avoid dissociation. The data provided by the JANAF Thermochemical Tables [12,16] (PbS(g), Pb(l) and Pb(g)) and data on Pb2S2(g) from Kellogg [29] were used to compile Tables 2.9 and 2.10.

On the basis of the review given above, this system has been selected for experimental study. Furthermore, reliable vaporization data are needed for the optimization of current processes as well as for the development of new lead smelting technologies.
### TABLE 2.9

**Recommended Thermodynamic Data for the Vaporization of Lead Sulfide**
*(Temperature range: 1000-1300K)*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PbS}(s) = \text{PbS}(g)$</td>
<td>$51650 - 33.08^\circ T$</td>
</tr>
<tr>
<td>$2\text{PbS}(g) = \text{Pb}_2\text{S}_2(g)$</td>
<td>$-42817 + 33.70^\circ T$</td>
</tr>
<tr>
<td>$\text{PbS}(s) = \text{Pb}(g) + \frac{1}{2}\text{S}_2(g)$</td>
<td>$82681 - 42.74^\circ T$</td>
</tr>
</tbody>
</table>

### TABLE 2.10

**Vapor Pressure of the Major Species Above PbS\(_{(s)}\)**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{\text{PbS}}$ (atm)</th>
<th>$P_{\text{Pb}_2\text{S}_2}$ (atm)</th>
<th>$P_{\text{Pb}}$ (atm)</th>
<th>$P_{\text{S}_2}$ (atm)</th>
<th>$P_{\text{S}}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>$8.75 \times 10^{-5}$</td>
<td>$7.52 \times 10^{-7}$</td>
<td>$1.91 \times 10^{-6}$</td>
<td>$9.55 \times 10^{-7}$</td>
<td>$6.77 \times 10^{-12}$</td>
</tr>
<tr>
<td>1100</td>
<td>$9.29 \times 10^{-4}$</td>
<td>$1.20 \times 10^{-5}$</td>
<td>$2.38 \times 10^{-5}$</td>
<td>$1.19 \times 10^{-5}$</td>
<td>$2.54 \times 10^{-10}$</td>
</tr>
<tr>
<td>1200</td>
<td>$6.66 \times 10^{-3}$</td>
<td>$1.20 \times 10^{-4}$</td>
<td>$1.95 \times 10^{-4}$</td>
<td>$9.73 \times 10^{-5}$</td>
<td>$5.20 \times 10^{-9}$</td>
</tr>
<tr>
<td>1300</td>
<td>$3.52 \times 10^{-2}$</td>
<td>$8.45 \times 10^{-4}$</td>
<td>$1.15 \times 10^{-3}$</td>
<td>$5.76 \times 10^{-4}$</td>
<td>$6.72 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
2.1.7 Manganese-sulfur

Colin et al [6] studied the existence of gaseous sulfides of transition elements using mass spectrometry. They proposed that reaction (2.12) is the predominant vaporization reaction for MnS\(_{(s)}\). They also studied the dissociation energy of the molecule MnS\(_{(g)}\).

\[
\text{MnS}_{(s)} = \text{Mn}_{(g)} + \frac{1}{2} \text{S}_2\(_{(g)}\) \quad (2.12)
\]

Wiedemeier and Schafer [30] demonstrated that MnS\(_{(s)}\) vaporizes congruently. They performed Knudsen effusion measurements on the vaporization of MnS\(_{(s)}\) and used reaction (2.12) as the vaporization reaction.

Wiedemeier and Giles [31] undertook a Knudsen cell mass spectrometric investigation of the vaporization of MnS\(_{(s)}\). It was shown that reaction (2.12) is indeed the predominant reaction. Small amounts of S\(_{(g)}\) and MnS\(_{(g)}\) and minute amounts of the species MnS\(_2\(_{(g)}\) and MnS\(_3\(_{(g)}\) were also detected.

Drowart et al [3] used mass spectrometry to study exchange reactions between gaseous monosulfides. They used MnS\(_{(g)}\) as a reference species in the determination of the dissociation energy of CrS\(_{(g)}\), FeS\(_{(g)}\), CoS\(_{(g)}\), NiS\(_{(g)}\)
and CuS\(_2\) g). Mills [13] reviewed all of the above mentioned studies and his compilation includes quite complete thermodynamic data tables for the species MnS\(_2\) g). Table 2.11 presents free energy equations for reaction (2.13) calculated from heats of formation and fef data published by Mills [13]. The free energy equations for reactions (2.12) and (2.14) are also presented in Table 2.11. These equations were calculated using data from Mills [13] (MnS\(_2\) g)), from Hultgren et al [20] (Mn\(_2\) g)) and from the JANAF Thermochemical Tables [17] (S\(_2\) g) and S\(_2\) g).

\[
\text{MnS}(s) = \text{MnS}_2(g) \quad (2.13)
\]

\[
\frac{1}{2} \text{S}_2(g) = \text{S}(g) \quad (2.14)
\]

The partial pressures of the major species above manganese monosulfide were calculated from the data in Table 2.11 and are presented in Table 2.12. In their mass spectrometric investigation Wiedemeier and Giles [31] determined that at 1664 K diatomic MnS\(_2\) g) constitutes 0.3% or less of the vapor. Our calculations yield a value slightly over 0.1% at 1700 K, showing that the calculated values are in good agreement with the experimental data.
TABLE 2.11
Recommended Thermodynamic Data for the
Vaporization of Manganese Monosulfide
(Temperature range: 1400-1800K)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{MnS}_s = \text{Mn}_g + \frac{1}{2} \text{S}_2(g)$</td>
<td>$129201 - 43.615^\circ T$</td>
</tr>
<tr>
<td>$\text{MnS}_s = \text{MnS}_g$</td>
<td>$110395 - 31.280^\circ T$</td>
</tr>
<tr>
<td>$\frac{1}{2} \text{S}_2(g) = \text{S}_g$</td>
<td>$51908 - 14.515^\circ T$</td>
</tr>
</tbody>
</table>

TABLE 2.12
Vapor Pressure of the Major Species Above $\text{MnS}_s$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_S$ atm</th>
<th>$P_{S_2}$ atm</th>
<th>$P_{\text{Mn}}$ atm</th>
<th>$P_{\text{MnS}}$ atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>2.61 E-9</td>
<td>4.97 E-8</td>
<td>1.03 E-7</td>
<td>4.00 E-11</td>
</tr>
<tr>
<td>1500</td>
<td>2.53 E-8</td>
<td>3.93 E-7</td>
<td>8.12 E-7</td>
<td>5.64 E-10</td>
</tr>
<tr>
<td>1600</td>
<td>1.86 E-7</td>
<td>2.38 E-6</td>
<td>4.95 E-6</td>
<td>5.71 E-9</td>
</tr>
<tr>
<td>1700</td>
<td>1.08 E-6</td>
<td>1.17 E-5</td>
<td>2.44 E-5</td>
<td>4.40 E-8</td>
</tr>
<tr>
<td>1800</td>
<td>5.13 E-6</td>
<td>4.80 E-5</td>
<td>1.01 E-4</td>
<td>2.70 E-7</td>
</tr>
</tbody>
</table>
the results also confirm that Mn(g) and S_2(g) are the major species followed by S(g) and MnS(g). The pressure of gaseous manganese is well below the saturation pressure for manganese metal.

2.1.8 Molybdenum-sulfur

The literature survey for this system shows that no gaseous sulfide species have been detected. McCabe [32] measured the equilibrium sulfur pressure for reaction (2.15) using the Knudsen effusion method. The dissociation pressure for molybdenite (reaction (2.16)) was studied by Isakova [33].

\[ \text{Mo}_2\text{S}_3(s) = 2 \text{Mo}(s) + \frac{3}{2} \text{S}_2(g) \]  
\[ \text{MoS}_2(s) = \text{Mo}_2\text{S}_3(s) + \frac{1}{2} \text{S}_2(g) \]

These data, as well as data from other studies, have been used in the development of the tabular values given in the 1982 supplement to the JANAF Thermochemical Tables [17]. The data available from the JANAF Thermochemical Tables [17] (Mo(s), Mo(g), S(g), S_2(g), and \text{Mo}_2\text{S}_3(s)) were used to compile Tables 2.13 and 2.14.
### TABLE 2.13

**Recommended Thermodynamic Data for the Vaporization of Molybdenum Sesquisulfide**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mo}_2\text{S}_3(s) = 2 \text{Mo}(s) + \frac{3}{2} \text{S}_2(g)$</td>
<td>$133398 - 57.40^\circ T$</td>
</tr>
</tbody>
</table>

### TABLE 2.14

**Vapor Pressure of the Major Species Above Mo$_2$S$_3$**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{S_2}$ (atm)</th>
<th>$P_S$ (atm)</th>
<th>$P_{Mo}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>1.64 E-4</td>
<td>1.55 E-6</td>
<td>1.74 E-14</td>
</tr>
<tr>
<td>1700</td>
<td>8.52 E-4</td>
<td>9.21 E-6</td>
<td>3.05 E-13</td>
</tr>
<tr>
<td>1800</td>
<td>3.68 E-3</td>
<td>4.50 E-5</td>
<td>3.88 E-12</td>
</tr>
<tr>
<td>1900</td>
<td>1.36 E-2</td>
<td>1.86 E-4</td>
<td>3.79 E-11</td>
</tr>
<tr>
<td>2000</td>
<td>4.42 E-2</td>
<td>6.66 E-4</td>
<td>2.94 E-10</td>
</tr>
</tbody>
</table>
2.1.9 **Nickel-sulfur**

The species \( \text{NiS}(g) \) was identified by Drowart et al [3] in a mass spectrometric study of exchange reactions between gaseous monosulfides. The dissociation energy for this molecule was determined through a study of reaction (2.17).

\[
\text{Ni}(g) + \text{MnS}(g) = \text{NiS}(g) + \text{Mn}(g)
\]  

(2.17)

The JANAF Thermochemical Tables [17] present a table of thermodynamic functions for the species \( \text{NiS}(g) \) compiled from the experimental work of Drowart et al [3], from spectroscopic data available in the literature and from estimated molecular parameters.

In the only identified piece of work dealing specifically with vaporization, Fukanaka and Toguri [34] discuss the rate of vaporization of \( \text{Ni}_3\text{S}_2(g) \). The major gas phase components were identified as \( \text{Ni}(g) \) and \( \text{S}_2(g) \).

Several condensed phase compounds have been reported for the nickel-sulfur system. The nickel-sulfur phase diagram has been the subject of various recent investigations [36-38]. Data from the JANAF Thermochemical Tables [17] on \( \text{Ni}(s), \text{Ni}(g), \text{NiS}(s,l), \text{NiS}(g), \text{S}_2(g) \) and \( \text{S}(g) \) where used in the compilation of Tables 2.15 and 2.16.
TABLE 2.15

Recommended Thermodynamic Data for the Vaporization of Nickel Monosulfide
(For NiS(s), temperature range: 900-1249K)
(For NiS(l), temperature range: 1249-1500K)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS(s) $\rightarrow$ NiS(g)</td>
<td>102008 - 40.60*T</td>
</tr>
<tr>
<td>NiS(s) $\rightarrow$ Ni(s) + 1/2 S$_2$(g)</td>
<td>33623 - 17.55*T</td>
</tr>
<tr>
<td>NiS(l) $\rightarrow$ NiS(g)</td>
<td>91916 - 32.53*T</td>
</tr>
<tr>
<td>NiS(l) $\rightarrow$ Ni(s) + 1/2 S$_2$(g)</td>
<td>24656 - 10.34*T</td>
</tr>
</tbody>
</table>

TABLE 2.16

Vapor Pressure of the Major Species Above NiS$_{(s,l)}$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{NiS}$ (atm)</th>
<th>$P_{Ni}$ (atm)</th>
<th>$P_{S_2}$ (atm)</th>
<th>$P_S$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>4.03 E-12</td>
<td>2.26 E-13</td>
<td>2.04 E-6</td>
<td>1.05 E-10</td>
</tr>
<tr>
<td>1200</td>
<td>1.97 E-10</td>
<td>1.08 E-11</td>
<td>2.65 E-5</td>
<td>2.71 E-9</td>
</tr>
<tr>
<td>1300</td>
<td>4.53 E-9</td>
<td>2.83 E-10</td>
<td>1.70 E-4</td>
<td>3.65 E-8</td>
</tr>
<tr>
<td>1400</td>
<td>5.76 E-8</td>
<td>4.62 E-9</td>
<td>6.63 E-4</td>
<td>1.89 E-6</td>
</tr>
</tbody>
</table>
It should be noticed, however, that NiS\(_{(s)}\) shows a relatively wide homogeneity range and that the composition range for the melt is even wider.

2.1.10 Silicon-sulfur

Colin and Drowart [5] used mass spectrometry to study the vaporization of SiS\(_{2}(s)\). They observed that the vaporization occurs mainly through reaction (2.18), but the molecule SiS\(_{2}(g)\) was also identified.

\[
\text{SiS}_2(s) = \text{SiS}(g) + \frac{1}{2} \text{S}_2(g) \tag{2.18}
\]

Rosenqvist and Tungevisk [39] used a transpiration method and obtained the free energy equation for reaction (2.19).

\[
2 \text{Si}(s) + \text{S}_2(g) = 2 \text{SiS}(g) \tag{2.19}
\]

The above mentioned investigations and the available spectroscopic data were used in the compilation of a table of thermodynamic functions for SiS\(_{(g)}\) presented by the JANAF Thermochemical Tables [40]. However, this tabulation as well as the one for SiS\(_{2}(s)\) show a relatively wide error.
range.

Mills [13] reviewed basically the same information analyzed by the JANAF Thermochemical Tables [40] but reported slightly different values for the thermodynamic functions of both \( \text{SiS}_2(g) \) and \( \text{SiS}_2(s) \).

Byerley and Teo [41,42] studied reactions (2.20) and (2.21) using a Knudsen-effusion gravimetric technique. Their experimental results were analyzed using the second-law and the third-law methods and the results are reported in Table 2.17.

\[
\text{SiS}_2(s) + \text{Si}(s) = 2 \text{SiS}(g) \quad (2.20)
\]

\[
\text{SiS}_2(s) = \text{SiS}(g) + \frac{1}{2} \text{S}_2(g) \quad (2.21)
\]

Due to the large discrepancy between the second-law and the third-law results for Byerley and Teo’s experimental data for reaction (2.21), and to the observation that a third-law analysis of their data for reactions (2.20) and (2.21) exhibits some degree of temperature dependence, the data of Byerley and Teo [41,42] were not adopted. Data from Mills [13] were used to compile Tables 2.18 and 2.19, on the basis that these data give results that are intermediate between the values of Byerley and Teo [41,42]
### Table 2.17
Analysis of the Results of Byerley and Teo [41,42]

<table>
<thead>
<tr>
<th>Reaction (2.20)</th>
<th>$\Delta H^\circ_{r,298K}$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Second-law analysis</strong></td>
<td>57015</td>
</tr>
<tr>
<td><strong>Third-law analysis</strong></td>
<td>55640</td>
</tr>
<tr>
<td>Calculated from JANAF Tables [40]</td>
<td>50825</td>
</tr>
<tr>
<td>Calculated from Mills [13]</td>
<td>53400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction (2.21)</th>
<th>$\Delta H^\circ_{r,298K}$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Second-law analysis</strong></td>
<td>102110</td>
</tr>
<tr>
<td><strong>Third-law analysis</strong></td>
<td>95800</td>
</tr>
<tr>
<td>Calculated from JANAF Tables [40]</td>
<td>91100</td>
</tr>
<tr>
<td>Calculated from Mills [13]</td>
<td>94255</td>
</tr>
</tbody>
</table>
TABLE 2.18
Recommended Thermodynamic Data for the Vaporization of SiS_2(s)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, ΔG^0_T (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiS_2(s)  = SiS(g) + 1/2 S_2(g)</td>
<td>88752 - 52.64*T</td>
</tr>
<tr>
<td>SiS_2(s)  = Si(g) + S_2(g)</td>
<td>184335 - 67.52*T</td>
</tr>
</tbody>
</table>

TABLE 2.19
Vapor Pressure of the Major Species Above SiS_2(s)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>P_{SiS}</th>
<th>P_{Si}</th>
<th>P_{S_2}</th>
<th>P_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>6.89 E-6</td>
<td>8.51 E-21</td>
<td>3.45 E-6</td>
<td>1.29 E-11</td>
</tr>
<tr>
<td>1100</td>
<td>1.03 E-4</td>
<td>2.62 E-18</td>
<td>5.16 E-5</td>
<td>5.29 E-10</td>
</tr>
<tr>
<td>1200</td>
<td>9.86 E-4</td>
<td>3.09 E-16</td>
<td>4.93 E-4</td>
<td>1.17 E-8</td>
</tr>
<tr>
<td>1300</td>
<td>6.65 E-3</td>
<td>1.76 E-14</td>
<td>3.32 E-3</td>
<td>1.61 E-7</td>
</tr>
</tbody>
</table>
and those of the JANAF Thermochemical Tables [40].

2.1.11 Tantalum-sulfur

Blitz and Kocher [43] were the first to study the evaporation of tantalum sulfides \( \text{TaS}_3(s) \) and \( \text{TaS}_2(s) \). For \( \text{TaS}_3(s) \) they evaluated their vapor pressure data assuming sublimation occurs by reaction (2.22). They reported that at 1070K the sublimation pressure of \( \text{TaS}_2(s) \) was too low to measure.

\[
\text{TaS}_3(s) = \text{TaS}_2(s) + \frac{1}{2} \text{S}_2(g) \tag{2.22}
\]

Bukhanevich et al [44] used mass spectrometry to study the vaporization of \( \text{TaS}_2(s) \). At 1700K they reported peaks for the following ions: \( S^+ \), \( \text{S}_2^+ \), \( \text{S}_3^+ \), \( \text{S}_4^+ \), \( \text{S}_5^+ \), and \( \text{S}_6^+ \). No peaks for tantalum or any tantalum bearing species were observed. They further measured evaporation rates using an automated balance at high vacuum and high temperature. The heat of dissociation for \( \text{TaS}_2(s) \) was calculated assuming that diatomic sulfur was the only species in the gas phase.

Mills [13] reports that the molecules \( \text{TaS}(g) \) and \( \text{TaS}_3(g) \) have been observed. He presents a table of thermodynamic properties for the species \( \text{TaS}(g) \) based
exclusively on estimated data and parameters.

The works of Bukhanevich et al [44], Mills [13] and Larson and Elliott [45] suggest reactions (2.23) and (2.24) as the probable vaporization reactions for TaS$_2$(s).

$$TaS_2(s) = Ta(s) + S_2(g) \quad (2.23)$$

$$TaS_2(s) = TaS(g) + \frac{1}{2} S_2(g) \quad (2.24)$$

The data available in the literature were used to obtain Tables 2.20 and 2.21. Free energy equations for reactions (2.23) and (2.24) are presented in Table 2.20. These equations were used to calculate the vapor pressure of the major species above TaS$_2$(s). The data for reaction (2.23), from Larson and Elliott [45], were extrapolated to higher temperatures to obtain the values shown in Table 2.21. The vapor pressure of metallic tantalum was found to be negligible ($PTa = 2.1 E-17$ atm at 1700K). It was observed during the calculations of partial pressures that for temperatures above 1434K a sufficiently high pressure of $S_2(g)$ will be established by reaction (2.24) that it will hinder reaction (2.23) from occurring. Gaseous tantalum monosulfide is thus the major species. This finding contradicts the work by Bukhanevich et al [44].
TABLE 2.20

Recommended Thermodynamic Data for the Vaporization of Tantalum Disulfide

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^0_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{TaS}_2(s) = \text{Ta}(s) + \frac{1}{2} \text{S}_2(g)$</td>
<td>$98810 - 31.15^*T$</td>
</tr>
<tr>
<td>$\text{TaS}_2(s) = \text{TaS}(g) + \frac{1}{2} \text{S}_2(g)$</td>
<td>$232696 - 107.03^*T$</td>
</tr>
</tbody>
</table>

* From Larson and Elliott [45]. (Temperature range: 850-1100K)

** Data from: Larson and Elliott [45] ($\text{TaS}_2(s)$), JANAF Tables [17] ($\text{S}_2(g)$), and Mills [13] ($\text{TaS}(g)$).

TABLE 2.21

Vapor Pressure of the Major Species Above $\text{TaS}_2(s)$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_S$ (atm)</th>
<th>$P_{\text{S}_2}$ (atm)</th>
<th>$P_{\text{TaS}}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400</td>
<td>5.76 E-10</td>
<td>2.41 E-9</td>
<td>2.36 E-9</td>
</tr>
<tr>
<td>1500</td>
<td>9.81 E-9</td>
<td>5.84 E-8</td>
<td>1.27 E-7</td>
</tr>
<tr>
<td>1600</td>
<td>1.50 E-7</td>
<td>1.54 E-6</td>
<td>3.24 E-6</td>
</tr>
<tr>
<td>1700</td>
<td>1.66 E-6</td>
<td>2.76 E-5</td>
<td>5.68 E-5</td>
</tr>
</tbody>
</table>
The recommended data presented in Table 2.20 should be used with reservations. The little information available for the tantalum-sulfur system is contradictory.

2.1.12 Tin-sulfur

Mass spectrometric studies reported by Colin and Drowart [4] have shown that sublimation occurs predominantly by reaction (2.25), although the molecule Sn$_2$S$_2$(g) was also detected in the gas phase.

\[ \text{SnS}(g) = \text{SnS}_2(g) \quad (2.25) \]

In a review of Vaporization Chemistry in Extractive Metallurgy, Kellogg [29] selected the data of Colin and Drowart [4], among others, as the most reliable. Mills [13] lists several investigators and their respective vapor pressure measurements in his compilation. He also compiled a table of thermodynamic functions for the species SnS$_2$(g) based on the results of Colin and Drowart [4] and Cp data given by Kelley [46].

Subsequent to the above mentioned reviews Davey and Joffre [47] used the transpiration method to determine the vapor pressures of pure solid and liquid SnS. The results
obtained are in excellent agreement with Kellogg's [29] values from the mass spectrometric data of Colin and Drowart [4].

The data given by Kellogg [29] were used in the compilation of Tables 2.22 and 2.23. The results presented in Table 2.23 are in reasonable agreement with values listed by Mills [13].

2.1.13 Titanium-sulfur

Frazen and Gilles [48] were the first to study the high temperature vaporization of titanium monosulfide. They determined that TiS\(_{(s)}\) vaporizes congruently and through preliminary mass spectrometric measurements it was observed that "TiS\(_{(g)}\) constituted nearly 25% and possibly near 100% of the vapor". A series of Knudsen-effusion experiments were performed and the results were analyzed assuming that TiS\(_{(g)}\) was the only species being generated.

Edwards et al [49] used Knudsen cell mass spectrometry to study the vaporization of TiS\(_{(s)}\). It was found that a significant portion of the gas phase constituted of the elements Ti\(_{(g)}\) and S\(_{(g)}\). Small quantities of the species TiS\(_{2}\)(g) were also reported. Persistence of TiO\(^+\) of unknown origin in the mass spectrum from titanium monosulfide was
**TABLE 2.22**

Recommended Thermodynamic Data for the Vaporization of Tin Monosulfide  
(Temperature Range: 1200-1400K)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SnS}_1 = \text{SnS}_g$</td>
<td>$39204 - 25.39^*T$</td>
</tr>
<tr>
<td>$2 \text{SnS}_g = \text{Sn}_2\text{S}_2(g)$</td>
<td>$-46888 + 37.96^*T$</td>
</tr>
<tr>
<td>$\text{SnS}_1 = \text{Sn}_1 + 1/2 \text{S}_2(g)$</td>
<td>$33260 - 15.48^*T$</td>
</tr>
</tbody>
</table>

**TABLE 2.23**

Vapor Pressure of the Major Species Above $\text{SnS}_1$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{\text{SnS}}$</th>
<th>$P_{\text{Sn}_2\text{S}_2}$</th>
<th>$P_{\text{Sn}}$</th>
<th>$P_{\text{S}_2}$</th>
<th>$P_{\text{S}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>2.56 E-2</td>
<td>3.68 E-4</td>
<td>2.75 E-8</td>
<td>4.48 E-6</td>
<td>1.12 E-9</td>
</tr>
<tr>
<td>1300</td>
<td>9.08 E-2</td>
<td>3.18 E-3</td>
<td>2.64 E-7</td>
<td>3.83 E-7</td>
<td>1.73 E-8</td>
</tr>
<tr>
<td>1400</td>
<td>2.68 E-1</td>
<td>7.61 E-3</td>
<td>1.83 E-6</td>
<td>2.41 E-4</td>
<td>1.82 E-7</td>
</tr>
</tbody>
</table>
also reported.

Mills [13] analyzed studies as late as the one by Edwards et al [49] in his compilation of thermodynamic data for inorganic sulfides, selenides, and tellurides. He reported values for thermodynamic properties of TiS(g) with approximately 10% uncertainty.

Pelino et al [50] used a computer automated simultaneous torsion-effusion method to establish the vaporization thermodynamics of titanium monosulfide, TiS(s), from 2039 to 2168K. Their data were combined with mass spectrometric data from Edwards et al [49] to yield thermodynamic data for the following reactions:

\[
\text{TiS}(s) = \text{TiS}(g) \quad (2.26)
\]

\[
\text{TiS}(s) = \text{Ti}(g) + S(g) \quad (2.27)
\]

\[
\text{TiS}(s) = \text{Ti}(g) + \frac{1}{2} S_2(g) \quad (2.28)
\]

\[
\text{TiS}(g) = \text{Ti}(g) + S(g) \quad (2.29)
\]

The species TiS\(_2\)(g) was not important at the temperature range of their study. Combination of data for reactions (2.27) and (2.28) yielded a dissociation enthalpy
at 298K of $S_2(g)$ in good agreement with the value reported by Mills [13]. When submitted to a third-law analysis the results did not show any sign of temperature dependence, which strengthens their reliability.

Table 2.24 contains the recommended free energy equations for reactions (2.26) thru (2.29) based on the study of Pelino et al [50]. These data were used to calculate the vapor pressure of the major species above TiS$_2(s)$, presented in Table 2.25. This pressure data indicates that reaction (2.27) is the most important vaporization reaction, followed by reactions (2.28) and (2.26) respectively. The saturation vapor pressure for liquid titanium is approximately one order of magnitude larger than the vapor pressures calculated for Ti$_1(g)$.

2.1.14 Tungsten-sulfur

The literature survey found no evidence of the existence of gaseous tungsten sulfides (same as in the molybdenum-sulfur system). The solids reported are WS$_2$ and WS$_3$. Bolgar et al [51] measured the $S_2(g)$ dissociation pressure for the disulfide. Mills [13] lists several investigators who studied the free energy of formation of WS$_2(s)$. The results of Hager
TABLE 2.24
Recommended Thermodynamic Data for the Vaporization of Titanium Monosulfide (Temperature range: 2000-2200K)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiS$<em>{(s)}$ = TiS$</em>{(g)}$</td>
<td>138742 - 37.76*T</td>
</tr>
<tr>
<td>TiS$<em>{(s)}$ = Ti$</em>{(g)}$ + S$_{(g)}$</td>
<td>241865 - 65.90*T</td>
</tr>
<tr>
<td>TiS$<em>{(s)}$ = Ti$</em>{(g)}$ + 1/2 S$_2(g)$</td>
<td>189583 - 51.24*T</td>
</tr>
<tr>
<td>TiS$<em>{(g)}$ = Ti$</em>{(g)}$ + S$_{(g)}$</td>
<td>103123 - 28.15*T</td>
</tr>
</tbody>
</table>

TABLE 2.25
Vapor Pressure of the Major Species Above TiS$_{(s)}$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{TiS}$</td>
</tr>
<tr>
<td>2000</td>
<td>8.89 E-7</td>
</tr>
<tr>
<td>2100</td>
<td>3.73 E-6</td>
</tr>
<tr>
<td>2200</td>
<td>1.37 E-5</td>
</tr>
</tbody>
</table>
and Elliott [15] and data from the JANAF Thermochemical Tables [17] \((\text{S}_2(\text{g}), \text{S}(\text{g}))\) were used in the compilation of Tables 2.26 and 2.27.

### 2.1.15 Vanadium-sulfur

The species \(\text{VS}(\text{g})\) was first identified by Drowart et al [3]. Owzarski and Frazen [52] studied the vaporization and thermodynamics of vanadium monosulfide at high temperatures using an uncalibrated Knudsen cell mass spectrometer. They reported that at high temperatures vanadium monosulfide vaporizes congruently through two major reactions, (2.30) and (2.31), with a minor contribution from reaction (2.32).

\[
\text{VS}(\text{s}) = \text{VS}(\text{g}) \quad (2.30)
\]

\[
\text{VS}(\text{s}) = \text{V}(\text{g}) + \text{S}(\text{g}) \quad (2.31)
\]

\[
\text{VS}(\text{s}) = \frac{1}{2} \text{VS}_2(\text{g}) + \frac{1}{2} \text{V}(\text{g}) \quad (2.32)
\]

Edwards et al [53] measured the vapor pressure over \(\text{VS}(\text{s})\) by the simultaneous Knudsen-torsion effusion method. Using the distribution of vapor species reported by
TABLE 2.26

Recommended Thermodynamic Data for the Vaporization of Tungsten Disulfide

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^\circ_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{WS}_2(s) = \text{W}(s) + \text{S}_2(g)$</td>
<td>80400 - 18.70*T</td>
</tr>
</tbody>
</table>

TABLE 2.27

Vapor Pressure of the Major Species Above $\text{WS}_2(s)$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{S_2}$ (atm)</th>
<th>$P_S$ (atm)</th>
<th>$P_W$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>1.27 E-7</td>
<td>4.30 E-8</td>
<td>5.80 E-21</td>
</tr>
<tr>
<td>1700</td>
<td>5.63 E-7</td>
<td>2.37 E-7</td>
<td>2.63 E-19</td>
</tr>
<tr>
<td>1800</td>
<td>2.11 E-6</td>
<td>1.08 E-6</td>
<td>7.78 E-18</td>
</tr>
<tr>
<td>1900</td>
<td>6.89 E-6</td>
<td>4.18 E-6</td>
<td>1.61 E-16</td>
</tr>
<tr>
<td>2000</td>
<td>2.00 E-5</td>
<td>1.42 E-5</td>
<td>2.47 E-15</td>
</tr>
</tbody>
</table>
Owzarski and Frazen [52] they were able to calculate limiting values for the equilibrium constants and thermodynamics of the reactions studied.

In a recent work, Botor and Edwards [54] used Knudsen cell mass spectrometry to determine the equilibrium constants for reactions (2.30), (2.31), (2.33), and (2.34).

\[
VS(g) = V(g) + S(g) \quad (2.33)
\]

\[
1/2 S_2(g) = S(g) \quad (2.34)
\]

The enthalpy of dissociation of \( S_2(g) \) at 298K obtained by Botor and Edwards [54] is in good agreement with values from the JANAF Thermochemical Tables [17] and from Mills [13], a fact that tends to confirm their other results.

The work of Botor and Edwards [54] was the last one in a series of gradual improvements in the knowledge of vaporization in the vanadium-sulfur system. Their work was the basis for the recommended data. They did not report their experimental results, instead, they presented equations for each of their two sets of experiments. The data given in Table 2.28 are those for the set which showed the greatest internal consistency.
### TABLE 2.28

Recommended Thermodynamic Data for the Vaporization of Vanadium Monosulfide (Temperature range: 1700-2000K)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Free Energy, $\Delta G^\circ$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$VS_{(s)} = VS_{(g)}$</td>
<td>$105303 - 27.63*T$</td>
</tr>
<tr>
<td>$VS_{(s)} = V_{(g)} + S_{(g)}$</td>
<td>$223224 - 56.76*T$</td>
</tr>
<tr>
<td>$VS_{(g)} = V_{(g)} + S_{(g)}$</td>
<td>$120044 - 30.24*T$</td>
</tr>
</tbody>
</table>

### TABLE 2.29

Vapor Pressure of the Major Species Above $VS_{(s)}$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_S$</th>
<th>$P_{S_2}$</th>
<th>$P_V$</th>
<th>$P_{VS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1700</td>
<td>$6.69 \times 10^{-9}$</td>
<td>$4.51 \times 10^{-10}$</td>
<td>$7.60 \times 10^{-9}$</td>
<td>$3.16 \times 10^{-8}$</td>
</tr>
<tr>
<td>1800</td>
<td>$4.16 \times 10^{-8}$</td>
<td>$3.16 \times 10^{-9}$</td>
<td>$4.80 \times 10^{-8}$</td>
<td>$1.79 \times 10^{-7}$</td>
</tr>
<tr>
<td>1900</td>
<td>$2.14 \times 10^{-7}$</td>
<td>$1.80 \times 10^{-8}$</td>
<td>$2.50 \times 10^{-7}$</td>
<td>$8.42 \times 10^{-7}$</td>
</tr>
<tr>
<td>2000</td>
<td>$9.30 \times 10^{-7}$</td>
<td>$8.61 \times 10^{-8}$</td>
<td>$1.10 \times 10^{-6}$</td>
<td>$3.40 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
For temperatures lower than approximately 1480K, vanadium monosulfide will not vaporize congruently, it will rather lose sulfur to the gaseous phase, as reported by Edwards et al [53] and confirmed by Botor and Edwards [54].

The vapor pressure for the major species above VS(s) were calculated from the data in Table 2.28. These pressures are shown in Table 2.29. Gaseous vanadium monosulfide is the most abundant species in the gas phase, followed by V(g), S(g), and finally S2(g). It should be mentioned that for the temperature range given in Table 2.29 the vapor pressure of vanadium is less than, but of the same order of magnitude, as the saturation pressure for solid vanadium.

2.1.16 Zinc-sulfur

McCabe [55] used the Knudsen effusion method to determine the pressure of gas in equilibrium with sphalerite for the temperature range 680-825°C. By comparing the dissociation pressure calculated from thermodynamic data with his experimental results he concluded that the vaporization of ZnS(s) occurs predominantly through reaction (2.35).
\[ \text{ZnS}_\text{s} = \text{Zn}_\text{g} + \frac{1}{2} \text{S}_2\text{g} \quad (2.35) \]

Marquart and Berkowitz [7] confirmed the dissociative vaporization in a mass spectrometric study in which they were unable to detect a measurable ion intensity that could be attributed to a ZnS\(_\text{g}\) parent molecule. Using estimated molecular parameters they were able to calculate an upper limit for the dissociation energy of ZnS\(_\text{g}\). Subsequent mass spectrometric studies by Goldfinger and Jeunehomme [8] and by De Maria et al [9] provided the basis for Pashinkin and Salamantin [10] and Mills [13] to compile tables of thermodynamic functions for the species ZnS\(_\text{g}\). Mills [13] has also listed several sublimation studies which he analyzed in his review work.

The thermodynamic data provided by Mills [13] were used to compile Tables 2.30 and 2.31. The data given in Table 2.31 show that ZnS\(_\text{g}\) is indeed a minor species.
TABLE 2.30

Recommended Thermodynamic Data for the Vaporization of Zinc Monosulfide

For Sphalerite (Temperature range: 900-1293K):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^0_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ZnS}(s) = \text{ZnS}(g)$</td>
<td>94697 - 38.78*T</td>
</tr>
<tr>
<td>$\text{ZnS}(s) = \text{Zn}(g) + \frac{1}{2} \text{S}_2(g)$</td>
<td>93296 - 48.31*T</td>
</tr>
</tbody>
</table>

For Wurzite (Temperature range: 1293-1400K):

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Free Energy, $\Delta G^0_T$ (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ZnS}(s) = \text{ZnS}(g)$</td>
<td>91033 - 35.86*T</td>
</tr>
<tr>
<td>$\text{ZnS}(g) = \text{Zn}(g) + \frac{1}{2} \text{S}_2(g)$</td>
<td>89491 - 45.28*T</td>
</tr>
</tbody>
</table>

TABLE 2.31

Vapor Pressure of the Major Species Above ZnS$\,(s)$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$P_{\text{Zn}}$</th>
<th>$P_{\text{ZnS}}$</th>
<th>$P_{\text{S}_2}$</th>
<th>$P_{\text{S}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>3.51 E-7</td>
<td>6.00 E-13</td>
<td>1.76 E-7</td>
<td>2.89 E-12</td>
</tr>
<tr>
<td>1100</td>
<td>6.04 E-5</td>
<td>4.57 E-11</td>
<td>3.02 E-6</td>
<td>1.28 E-10</td>
</tr>
<tr>
<td>1200</td>
<td>6.47 E-5</td>
<td>1.69 E-9</td>
<td>3.24 E-5</td>
<td>3.00 E-9</td>
</tr>
<tr>
<td>1300</td>
<td>4.65 E-4</td>
<td>3.41 E-8</td>
<td>2.33 E-4</td>
<td>4.27 E-8</td>
</tr>
<tr>
<td>1400</td>
<td>2.42 E-3</td>
<td>4.22 E-7</td>
<td>1.21 E-3</td>
<td>4.07 E-7</td>
</tr>
</tbody>
</table>
2.2 SELECTION OF SYSTEM FOR EXPERIMENTAL STUDY

Among the systems that lack reliable vaporization data, the lead-sulfur system stands out from the others. Fuming is a serious problem during the direct smelting of galena, and the vapor pressure of lead sulfide is appreciable even at moderate temperatures. While other systems, like copper-sulfur and nickel-sulfur, do require further research, it was felt that a study of vaporization in the lead-sulfur system would find more applications to current industrial processes, as well as in possible upcoming innovative technologies. It was also decided to investigate the possible enhancement of lead sulfide vaporization due to the formation of vapor complexes.

2.3 LEAD SULFIDE VAPORIZATION

2.3.1 The Vapor Pressure of Lead Sulfide

The literature data for the vaporization of lead sulfide are shown in Figure 2.1. Colin and Drowart [4] have shown from mass spectrometric studies that reactions (2.11), (2.36), and (2.37) are the vaporization reactions for lead sulfide:
FIGURE 2.1 - Vapor Pressure as a Function of Temperature for the Reaction PbS(s) = PbS(g), as Reported in the Literature.
\[ \text{PbS}(s) = \text{PbS}(g) \]  \hspace{1cm} (2.11)

\[ 2 \text{PbS}(s) = \text{Pb}_2\text{S}_2(g) \]  \hspace{1cm} (2.36)

\[ \text{PbS}(s) = \text{Pb}(g) + \frac{1}{2} \text{S}_2(g) \]  \hspace{1cm} (2.37)

Their study established that reaction (2.11) accounts for nearly all the vaporization. Partial pressures were derived from ion intensities in the spectra obtained. The relative ionization cross sections needed for these derivations were either estimated or obtained from analogy with similar molecules. Colin and Drowart [4] were able to study the three vaporization reactions independently, whereas other investigators analyzed their data in terms of \( \text{PbS}(g) \) formation only. The data shown in Figure 2.1 is therefore the experimental data for reaction (2.11).

Sudo [56] used a Knudsen effusion/thermo-balance apparatus for his vapor pressure measurements. The kinetic theory of gases was used to calculate the vapor pressure from the measured rate of vaporization. Due to the fact that reactions (2.36) and (2.37) were neglected, one should expect the results of this investigation to give vapor pressures that are too high. On the other hand, the deposition of vaporized materials on the hanging rod
would give results that are too low. The investigator assumed this amount of deposition to be negligible and did not take it into consideration.

Transpiration experiments using argon as the carrier gas were performed by Boev et al [57]. The weight loss of the lead sulfide samples was measured, and vapor pressures were calculated using the procedure described in section 3.2.1. The experimental results show as much as 66% variation for measurements at a single temperature. The reproducibility of his results is questionable.

The transpiration technique has been a widely used method for measuring vapor pressures. However, prior to the work of Alcock and Hooper [58] some investigators assumed that the carrier gas was unsaturated at all flow rates and would only be perfectly saturated when the gas was stationary. For this reason, graphs of apparent vapor pressure against flow rate were extrapolated to zero flow rate and this value was taken as the true vapor pressure. Isakova et al [59] have used the above method for treating their transpiration data. Argon was used as the carrier gas at flow rates not exceeding 80 ml/hr (1.33 cc/min). The scatter of the results is quite large, and the data are probably too high, in view of what is nowadays the accepted method for interpretation of transpiration data (refer to
section 3.2.1). It is interesting to observe that Isakova and co-workers noticed the presence of a yellow (elemental sulfur) condensate. However, it was assumed in the calculations that the vapor consisted of PbS molecules. The presence of a sulfur deposit confirms that some dissociative vaporization (reaction (2.37)) did take place.

Hansen and Munir [60] used the torsion-effusion technique to measure the vapor pressure of lead sulfide in the temperature range 604°-747°C (range not fully shown in Figure 2.1). The congruency of sublimation was attested by using X-ray observations on samples which had lost at least 30% of their initial weight. It was assumed that the pressure obtained by measuring the momentum of the effusing molecules was the equilibrium pressure established by reaction (2.11). Again the vapor pressure data obtained for reaction (2.11) should be high due to neglecting reactions (2.36) and (2.37).

In summary, the literature review shows that no investigators, other than Colin and Drowart [4], have obtained experimental results that account for the contributions of reactions (2.36) and (2.37). The data from Table 2.9 indicate that the dissociation and the dimerization reactions may each contribute to as much as 3% of the total lead lost to the gas phase in the temperature
range 1000-1300K. Furthermore, both transpiration investigations exhibit some scatter, and in one of them the data were incorrectly interpreted and equilibrium conditions might not have existed.

2.3.2 Lead Sulfide Vapor Phase Complexation

Complexation has been found to significantly enhance the vaporization of some compounds. A review of the literature indicates that complexation in chloride, oxide, and sulfide systems has been the subject of a number of studies [61-65].

Chloride systems have been the subject of most of the research regarding complexation. As an example, the vapor pressures of both gold chloride and silver chloride have been found to be enhanced in the presence of iron chloride [61,62]. The vapor pressures of these noble metal chlorides have been found to be increased by as much as 2000% [62]. The role of iron chloride as a complexing agent has also been identified for the chlorides of zinc, lead, and cadmium [63].

As an example of complexation in oxide systems, the vaporization of antimony oxide has been found to increase in the presence of arsenic oxide vapor [64,65]. In this
system three vapor species have been identified:
$\text{As}_3\text{SbO}_6(g)$, $\text{As}_2\text{Sb}_2\text{O}_6(g)$, and $\text{AsSb}_3\text{O}_6(g)$. In his review, "Vaporization Chemistry in Extractive Metallurgy", Kellogg [29] reports the vapor complexes $\text{CaMoO}_4(g)$, $\text{CaMoO}_3(g)$, $\text{MgWO}_4(g)$, and $\text{MgWO}_3(g)$.

Complexation in sulfide systems has not been studied in much detail. The only research identified in the literature review was a mass-spectrometric investigation by Colin and Drowart [4]. They studied the vaporization of lead sulfide, tin sulfide, and a mixture of lead and tin sulfide. During their studies on PbS-SnS mixtures, the species $\text{SnPbS}_2(g)$ was identified.

Although not much is known regarding complexation in sulfide systems, it is anticipated that other species would complex with lead sulfide. It has been found that, in the solid state, arsenic sulfide, antimony sulfide, and bismuth sulfide show a quite remarkable level of interaction with lead sulfide. The systems Me-Pb-S (where Me = As, Sb or Bi) were reviewed, and a very large number of compounds of the type $\text{Me}_x\text{Pb}_y\text{S}_z$ were found to exist. Furthermore, arsenic, antimony, and bismuth are commonly found, as impurities, in galena ores as well as in concentrates. The above facts led to the decision to investigate arsenic sulfide, antimony sulfide, and bismuth sulfide as possible
complexing agents for lead sulfide. A fourth choice, cadmium sulfide, was made based on two facts. First, cadmium is also commonly present in lead ores, and second, cadmium sulfide vaporizes congruently, but through a dissociative reaction. It was decided it would be of interest to check the possible interaction between a metallic vapor species and lead sulfide.

In the next section the vaporization of the metal sulfides that have been selected as complexing agents will be reviewed.

2.3.2.1 Vaporization Characteristics of the Complexing Agents

The vaporization of arsenic, antimony, and bismuth sulfides has been reviewed by Kaiser [66]. Further, a literature survey was undertaken in order to update the work by Kaiser, and to include the cadmium-sulfur system.

A) Arsenic (III) sulfide

Kaiser [66] reported conflicting data in the literature review regarding the primary vapor species above $\text{As}_2\text{S}_3$. After analyzing all the data available, $\text{As}_4\text{S}_6(g)$ was chosen
as the primary vapor species. The volatilization reactions and free energy equations reported by Kaiser are as follows:

\[
2 \text{As}_2\text{S}_3(s) = \text{As}_4\text{S}_6(g) \tag{2.38}
\]

\[
\Delta G^0_R = 37720 - 51.75*T \quad \text{cal/mol} \quad (476-536K) \tag{2.39}
\]

\[
2 \text{As}_2\text{S}_3(l) = \text{As}_4\text{S}_6(g) \tag{2.40}
\]

\[
\Delta G^0_R = 18570 - 18.90*T \quad \text{cal/mol} \quad (623-980K) \tag{2.41}
\]

Subsequent mass spectrometric investigations by Lau et al [67] and Brittain et al [68] suggest that the saturated vapor pressure over As$_2$S$_3$ contains mainly As$_2$S$_3$(g), As$_4$S$_4$(g), and S$_2$(g). Data for the species AsS(g) and As$_4$S$_4$(g) have been recently published by Mah [69] in a compilation of thermodynamic data for arsenic sulfide reactions. Chakraborti and Lynch [70] have reported data for As$_4$S$_4$(g) in excellent agreement with data by Mah. However, their data for AsS(g) differs from Mah’s data. They also provide information on the species As$_2$S$_3$(g).

The literature review for the As-Pb-S system showed that several solid mixed sulfides have been identified.
Among the most common ones are sartorite (As$_2$PbS$_4$), baumhauerite (As$_4$Pb$_3$S$_9$), rathite (As$_9$Pb$_7$S$_{20}$), dufrenoysite (As$_2$Pb$_2$S$_5$), gratonite (As$_4$Pb$_9$S$_{15}$), and jordanite (As$_7$Pb$_{13}$S$_{23}$). No gas phase complexes have been reported.

B) Antimony (III) sulfide

The literature reviewed by Kaiser [66] indicates that antimony trisulfide may volatilize by several simultaneous reactions. However, the only vapor species that was positively identified as a major species in all vapor composition studies was SbS(g). A number of other species of higher molecular weight have been reported by some workers [71-73]. The reactions and free energy equations reported by Kaiser [66] are as follows:

\[
\begin{align*}
\text{Sb}_2\text{S}_3(s) & = 2 \text{SbS}(g) + \frac{1}{2} \text{S}_2(g) \\
\Delta G^o & = 128560 - 117.03^\circ T \text{ (cal/mol)} \quad (670-822K) \\
\text{Sb}_2\text{S}_3(l) & = 2 \text{SbS}(g) + \frac{1}{2} \text{S}_2(g) \\
\Delta G^o & = 81160 - 59.48^\circ T \text{ (cal/mol)} \quad (917-1413K)
\end{align*}
\]
Only one recent study, subsequent to Kaiser’s [66] review, on the vaporization of antimony trisulfide has been identified. Madsen et al [74] used a modified transpiration apparatus, and showed that the average molecular weight of gaseous species in equilibrium with Sb$_2$S$_3$ is a function of temperature. All previous researchers acknowledged that several species were present in the gas phase, but all of them assumed a simple reaction in order to calculate vapor pressure values from their Knudsen cell and transpiration data.

Madsen et al [74] have calculated that the average molecular weight for the gaseous species decreases from 286 g/mol at 870K to 112 g/mol at 1045K. It is interesting to notice that an average molecular weight of 136 g/mol would have been measured if reactions (2.42) or (2.44) were indeed the volatilization reactions. Madsen et al do stress the need for additional mass spectrometry work to determine quantitatively the various gaseous species that exist as a function of temperature.

The literature review for the Sb-Pb-S system did not reveal any complex vapor species, but several condensed phase mixed sulfides were identified. The most important ones are zinckenite (PbSb$_2$S$_4$), boulangerite (Pb$_5$Sb$_4$S$_{11}$), and robinsonite (PbSb$_{10}$S$_{16}$).
C) Bismuth (III) sulfide

The vaporization of bismuth trisulfide has been the subject of very few investigations. Kaiser [66] selected the species BiS(g) as the vapor species above bismuth trisulfide. However, she was only interested in vapor species containing bismuth. A recent work by Piacente et al [75] does confirm previous investigations [76,77] in that the primary vaporization reaction is reaction (2.46) with small amounts of BiS(g) also present.

\[
\text{Bi}_2\text{S}_3(s) = 2\text{Bi}(s, l) + \frac{3}{2}\text{S}_2(g) \quad (2.46)
\]

The literature review for the Bi-Pb-S system identified the compounds galenobismutite (Bi$_2$PbS$_4$), cosalite (Bi$_2$Pb$_2$S$_5$), lillianite (Bi$_2$Pb$_3$S$_6$), beegerite (Bi$_2$Pb$_6$S$_9$), and several others of higher molecular weight. Once again, no gaseous complex species have been reported.

D) Cadmium sulfide

Goldfinger and Jeunehomme [8] have shown by mass spectrometric studies that cadmium sulfide vaporizes through the dissociation reaction (2.47). The free energy
data listed by Kellogg [29] is presented in equation (2.48). No mixed species, gaseous nor condensed, has been reported for the Cd-Pb-S system.

\[ \text{CdS}(s) = \text{Cd}(g) + \frac{1}{2} \text{S}_2(g) \]  

\[ \Delta G^0_R = 74251 - 44.15^\circ \text{T} \text{ (cal/mol)} \]  

(1100-1500K)
III. EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental portion of this study included three distinct sets of experiments. A Knudsen cell-mass spectrometer was used for the identification of possible lead sulfide vapor complexes. A double zone transpiration apparatus was used for quantifying the vaporization of lead sulfide. The transpiration apparatus was also used to examine the possible enhancement of lead sulfide vaporization due to complexation. A thorough description of the equipment and experimental procedures is now given.

3.1 THE MASS SPECTROMETER

A CVC Model 12 Time-of-Flight Mass Spectrometer (TOFMS) fitted with a Knudsen Cell Inlet System was used. Through the years the equipment has been submitted to three upgrading modifications. Its electronics were updated to solid state components by the installation of a modified CVC-MARK-4 Retrofit unit. A CVC MA-030 mass marker unit was later added to the portable mass spectrometer electronics console. Finally, a CVC MA-031 sensitivity enhancer was also installed in the electronics console. The TOFMS can be seen in Figure 3.1. It operates in a
FIGURE 3.1 - Overall View of the Knudsen Cell - Mass Spectrometer and Supporting Electronics.
pulsed mode (10,000 cycles per second) and provides mass spectra for any gaseous sample introduced to its ion source. A very detailed theory of operation for the TOFMS has been given by Patsos [78], therefore only a brief description of a single cycle of operation is given below.

The gas sample, which is a molecular beam effusing from the Knudsen cell, enters the mass spectrometer after passing through a series of collimating slits. Upon reaching the ionization chamber the molecular beam is ionized by an electron bombardment pulse, thus producing positively charged ions (cations). Reaction (3.1) is an example of such an ionization process:

\[ \text{PbS}(g) + e^- = \text{PbS}^+(g) + 2e^- \quad (3.1) \]

Immediately after the electron pulse, a series of potentials applied to the ion drawout grids removes the cations from the ionization region and accelerates them down the flight tube. The same amount of potential energy is provided to all cations. This potential energy is transformed to kinetic energy according to the relation:

\[ e_i E = \frac{1}{2} m_i v_i^2 \quad (3.2) \]

where: \( e_i \) = charge of ion i
\[ E = \text{potential drop through ion grids} \]
\[ m_i = \text{mass of ion } i \]
\[ v_i = \text{velocity of ion } i \]

From relation (3.2) it is obvious that ions will travel down the flight tube at different velocities, depending on their mass to charge ratio. Therefore, a packet of ions of a certain m/e ratio reaches the detector at a unique time.

The impact of ion packets on the detector produces secondary electrons which are amplified to a measurable current by the magnetic electron multiplier. Thus, an ion current, \( I_i^+ \), is produced by each packet of ions arriving at the detector. A mass spectrum of the initial molecular beam is obtained by plotting all these currents against their corresponding mass to charge ratio. A schematic of the mass spectrometer is presented in Figure 3.2.

A necessary condition for the operation of the mass spectrometer is the use of a high vacuum system which will maintain a residual pressure of less than \( 1 \times 10^{-5} \) torr in the ionization, flight tube, and detector regions. It is a necessary condition in order to avoid collisions between the ions being analyzed and the residual gases.
FIGURE 3.2 - Schematic of the Ion Source, Flight Tube, Detector and Supporting Electronics.
3.1.1 The Knudsen Cell Inlet System

The Knudsen cell inlet assembly can be seen in Figure 3.3. The Knudsen cell is supported by three tungsten rods, which fit in three wells at the bottom of the cell. A fourth and larger well, drilled at the center of the cell, houses the thermocouple. The cell is surrounded by a series of tantalum heat shields. The lids of the heat shields are slitted to allow direct passage of the molecular beam through the shutter isolation valve and into the mass spectrometer ion source. The shutter isolation valve assemblage is located right above the lids and it is a three position valve. The first position isolates the Knudsen cell inlet system from the mass spectrometer ion source by a vacuum seal. The second position allows the molecular beam to enter the ion source uninterrupted. The third position places a cold stainless steel plate between the Knudsen cell and the ion source. The stainless plate condensates the high temperature molecular beam issuing from the Knudsen cell, thus allowing background determinations. Such background determinations are necessary in order to determine whether an observed peak is due to the beam effusing from the Knudsen cell, or if it originates from residual gases inside the ionization
FIGURE 3.3 - Cut-Away View of the Knudsen-Cell Inlet System
The Knudsen cell is heated by means of two U-shaped tungsten filaments. The furnace has two distinct modes of heating: radiation and bombardment. In the radiation mode, the cell temperature is controlled between room temperature and 1100K by varying the current passing through the filaments. The bombardment mode is used for temperatures from 1100K up to 2500K. In this mode the filaments are at -1200 volts, while the cell is held at ground potential. Thus, high energy electrons bombard the cell and increases its temperature. Again, the temperature is controlled by varying the filament current.

The Knudsen cell tower assembly sits on three rods, two of which are stationary. The third rod is adjustable from the exterior, thus allowing for appropriate positioning of the cell under vacuum. The thermocouple used for temperature measurement extends through the tower assembly base via an O-ring seal, as can be seen in Figure 3.3.

A thorough description of the experimental procedure for the Knudsen cell Time-of-Flight Mass Spectrometer is given by Patsos [78].
3.2 THE TRANSPARATION APPARATUS

The transpiration technique, also referred to as the entrainment, gas-saturation, or transportation technique, is a very widely used method for measuring vapor pressures. It is applicable over a range of pressures from $10^{-3}$ torr to $10^2$ torr. In this study the technique has been used to measure the vapor pressure of lead sulfide. A specially designed transpiration apparatus was used in an attempt to establish the influence of other sulfide vapors in the vaporization of lead sulfide.

3.2.1 The Transpiration Technique

In the transpiration method, a gas stream, which may be either inert or reactive, is passed over a condensed sample at a rate such that equilibrium is established between condensed and vapor phases. The condensed sample is held at constant temperature within a reaction furnace. The saturated gas stream transports the volatile species from the reaction zone to a condenser system capable of recovering the volatile component. Either the weight loss of the condensed phase, or the amount of material recovered by condensation can be then used to calculate the apparent
vapor pressure. Vapor pressures are calculated from a mass balance of both the material transported as well as the carrier gas. Such calculations are based upon the assumption of "plug" or bulk flow transport of the volatile component from the saturation chamber to the condenser system.

The calculated vapor pressure is referred to as "apparent" vapor pressure because in some instances the amount of material transported may not correspond to an equilibrium saturation of the carrier gas. It has been shown by Norman and Winchell [79] and by Alcock and Hooper [58] that an equilibrium plateau region exists when the calculated vapor pressure is plotted as a function of the carrier gas flow rate. The typical shape of the apparent vapor pressure against flow rate curve is shown in Figure 3.4. At low flow rates the rate of diffusion of volatiles throughout the carrier gas causes a total mass flow rate larger than that established by the chemical reaction. The observed result is an "apparent" vapor pressure higher than the equilibrium vapor pressure due to the additional mass transport by the diffusion mechanism. At flow rates higher than those in the plateau region the observed effect is a decrease in the measured vapor pressure. At these high flow rates the rate of
FIGURE 3.4 - Typical Shape of the Curve of Apparent Vapor Pressure versus Carrier Gas Flow Rate.
volatilization is not fast enough to saturate the carrier gas. Therefore, equilibrium conditions are not attained.

In order to get reliable data one must make sure that all vapor pressure measurements are taken at flow rates within the plateau region. If such is the case, the vapor pressure of a species (in this study PbS) may be calculated using the relation:

\[
P_{\text{PbS}} = \frac{M_{\text{PbS}}}{(M_{\text{PbS}} + M_{\text{cg}})} \times P_T \tag{3.3}
\]

where:
- \(P_{\text{PbS}}\) = equilibrium vapor pressure of PbS
- \(M_{\text{PbS}}\) = moles of PbS transported
- \(M_{\text{cg}}\) = moles of carrier gas
- \(P_T\) = total reactor pressure

The above calculation is made under the assumption of ideal gas behavior, and requires measurement of the following parameters:

(a) amount of material transported,
(b) carrier gas flow rate,
(c) temperature and pressure of the carrier gas at the point where flow rate is measured,
(d) carrier gas composition,
(e) reaction temperature and pressure, and
In spite of its wide use, the transpiration technique is limited to systems for which the vapor species have been previously identified. In a case where the molecularity of a vapor species, $A_xB_y$, is unknown, one must use another experimental technique, such as mass spectrometry, in order to positively identify the vapor species prior to using the transpiration method.

### 3.2.2 Description of the Transpiration Apparatus

An overall view of the transpiration apparatus used in this study is shown in Figure 3.5. The apparatus is a specially designed double-zone transpiration reactor which may be used for conventional transpiration experiments as well as for experiments in which the carrier gas is doped with a complexing agent. It consists of:

(a) a gas train designed to deliver the carrier gas at prescribed flow rates,

(b) a saturation furnace which may contain no samples, in case a conventional transpiration experiment is being carried out, or it may contain the desired complexing agent, in the case of complexation runs,

(c) a reaction furnace which for this study contained
the lead sulfide sample,
(d) a sample inlet system for positioning of the lead sulfide and complexing agent samples in the furnace,
(e) a condenser system capable of recovering the volatile species from the off gas, and
(f) a temperature measuring system.

3.2.2.1 The Gas Train The carrier gas must be delivered to the transpiration furnaces at a constant, measurable rate. This was accomplished by means of the gas train. A photograph and a schematic of the gas train are given in Figures 3.6 and 3.7, respectively.

The carrier gas, in this study, consisted of a mixture of high purity hydrogen and hydrogen sulfide which, upon equilibration inside the transpiration furnace, established a sulfur potential in the reaction tube that hindered the dissociative vaporization of PbS. High purity pre-purified hydrogen (99.995%) was drawn from a commercial compressed gas cylinder, and C.P. grade (99.7%) hydrogen sulfide was drawn from a commercial liquefied gas cylinder.

The gases were dispensed from their respective tanks by using commercial regulators and shut-off valves. Constant head tanks were used to eliminate any fluctuation in the
FIGURE 3.6 - Gas Purification Train
FIGURE 3.7 - Schematic Diagram of the Gas Purification Train.
delivery pressure. Each tank is 5-ft tall, constructed of heavy wall glass, and filled with mineral oil. A rubber stopper with a glass T and an exhaust line inserted through it was used to cap the tanks. Two legs of the glass T were connected to the delivery line and the third leg was submerged in the oil tank. The delivery pressure, and thus the gas flow rate, was controlled by adjusting the depth of the glass T inserted into the constant head tank. Tygon tubing was used in the hydrogen delivery line and Teflon tubing for the hydrogen sulfide delivery line.

Residual moisture was removed from both gases by passing them through drying columns. Two columns of anhydrous magnesium perchlorate were used for the hydrogen sulfide line, and a column of silica gel and another of magnesium perchlorate were used for the hydrogen line. Hydrogen was further purified by passing through copper turnings at 500°C to remove oxygen.

Capillary flow meters were used to measure the flow rate of the gases. The flow of gas through the capillary causes a displacement in the meter fluid. Each flow meter was calibrated using the technique described by Annamalai [80]. In order to make displacement readings easier, a small quantity of p-nitrobenzeneazoresorcinol was dissolved in the dibutylphthlate flow meter fluid, giving it
a yellow color.

After being metered, the hydrogen and hydrogen sulfide streams were fed into a packed bed mixing column, and from there into the reaction tube.

Industrial grade nitrogen was used for the auxiliary gas line. Flow control was also achieved by using a constant head tank and a capillary flow meter. The purpose of this auxiliary gas line was twofold:

1) During a run, nitrogen was flushed through the annular space between the reaction tube and the outer protection tube. Failure in either tube could be detected by monitoring the nitrogen bubbler at the exit end of the system;

2) In order to insert/remove samples, or to measure changes in the temperature profile, the system had to be unsealed. Due to the hazards of exposure of the H₂/H₂S carrier gas mixture, the system had to be evacuated and then back filled with nitrogen prior to breaking the seal. A series of valves allowed the nitrogen stream to be switched for this purpose.

3.2.2.2 Saturation and Reaction Furnaces A double furnace arrangement consisting of two Marshall resistance furnaces positioned horizontally and place end-to-end was
used in this study. The first furnace, referred to as the saturation furnace, was used for doping the carrier gas with the desired complexing agent. The second, or reaction furnace, was the one where the lead sulfide samples were held for both the baseline as well as the complexation runs. A photograph of the furnaces and a schematic diagram of the reactor system are given in Figures 3.8 and 3.9.

The reactor consisted of two concentric mullite tubes placed in the bore of the furnaces. The outer tube (2.375 in. O.D. x 2.125 in. I.D. x 55 in. L.) served to protect the furnace windings and the lab environment from the hot flammable and poisonous gases in case the inner reaction tube broke during a run. The annular space between the two tubes was flushed with nitrogen and vented to an exit bubbler system, as previously described. The reaction tube (0.750 in. O.D. x 0.563 in. I.D. x 59 in. L.) was held in place by two rubber stoppers sealed with silicone cement. The rubber stoppers and the silicone cement were protected from the high temperatures of the furnaces by copper cooling coils wrapped around each end of the outer protection tube. Cold water circulated through the copper tubing.

Tapered ground Pyrex joints were fused to both ends of the mullite reaction tube. This allowed a gas-tight
FIGURE 3.8 - Saturation and Reaction Furnaces.
FIGURE 3.9 - Schematic Diagram of the Transpiration Apparatus.
connection of both the sample inlet system and the condenser system to the reaction tube.

3.2.2.3 Sample Inlet System  The sample inlet system was designed to permit moving the samples in and out of the reaction zone under sealed conditions. It consisted of a sample carrier tube and a guide tube. The quartz sample carrier tube (0.433 in. O.D. x 55 in. L.) was closed at one end and had a magnet glued to the other end. This magnet allowed the movement of the carrier tube by means of a magnetic coupling arrangement. Two 4.5 in. long slots were cut in the carrier tube, and four alumina boats could be placed in each of these slotted sections. These sections were positioned such that when the sample carrier tube was slid into the reaction tube one of them would lie in the constant temperature zone of the saturation furnace, and the other would lie on the constant temperature zone of the reaction furnace. Quartz wool was placed in the bore of the carrier tube to minimize the cross-sectional area available for gas flow. The Pyrex guide tube (0.875 in. diameter x 54.5 in. L.) was closed on one end and fitted with an outer joint on the other end, so that it could be connected to the inner joint of the reaction tube. The guide tube was used to hold the sample carrier tube when it
was outside the reaction zone.

3.2.2.4 Condenser System The condenser system consisted of a quartz sheath and a pyrex cold finger condenser cooled with a mixture of water/ethylene glycol. The cold finger was inserted into the condenser sleeve and sealed to it with a tapered ground Pyrex joint. The condenser sleeve was then slid into the reaction tube and sealed with the inner joint of the reaction tube. The purpose of the sheath was to protect the condenser from the high temperatures of the reaction tube and to force the saturated vapors to flow over the cold finger.

3.2.2.5 Temperature Measuring System The temperature in the reaction zone was measured with a chromel-alumel (type-K) thermocouple which had been previously calibrated against the melting points of pure tin, zinc and aluminum. This thermocouple was inserted in a quartz protection tube which was then fitted concentrically within a quartz tube (to simulate the sample carrier tube). The assembly was slid inside the reaction tube and it was thus possible to measure the temperature at various points inside the reactor under sealed conditions, simulating those existing during an actual run. A second thermocouple, external to
the reaction tube, was placed in a thin-walled mullite tube located between the reaction and the protection tubes. A temperature profile was obtained by taking measurements with both thermocouples at various positions along the furnaces. In this way, the temperature inside the reaction tube could be determined during a run from readings made with the external thermocouple.

3.2.3 Experimental Procedure

Samples of pure PbS(s) were loaded into four alumina boats and each boat was carefully weighed on a 5-decimal place analytical balance. For complexation runs, the complexing agents were also placed on boats and weighed. The boats were stored in a dessicator until an acceptable temperature profile had been obtained. At that time, the temperature measuring assembly was slid out of the reaction tube. The guide tube, with the sample carrier tube half way inside it, was held in a position such that the sample boats could be safely positioned into their designated positions, in the sample carrier tube. The carrier tube was slid into the guide tube which was then sealed against the reaction tube. The system was evacuated with a mechanical vacuum pump and backfilled with nitrogen. The
system was then evacuated a second time and backfilled with the carrier gas to be used for that run. Final adjustments to the flow rates were made at this time, now that the carrier gas was flowing through the whole system. The sample carrier tube was then slid into the reactor system at a rate of 1 inch every 30 seconds. The start of a run was initialized as soon as the carrier tube was placed in position. During the run, the ambient temperature and pressure, the furnace temperature and pressure, and the gas flow rates were monitored. Run times varied from 2 to 24 hours, with the majority of the runs lasting 6 hours.

At the completion of a run the samples were removed from the reactor, once again at a rate of 1 inch every 30 seconds. The carrier gas was switched to provide a pure nitrogen flush for approximately 20 minutes, to remove all volatiles from the reaction zone. The system was then evacuated and backfilled with nitrogen to assure that there was no residual H₂ or H₂S. The sample boats were re-weighed and the samples were saved. The condenser system was also removed and placed in a column leach vessel. Concentrated HBr and HCl were used to dissolve the condensate. The leach liquor and the wash water were poured into a 1000 ml Pyrex flask, and diluted to 1000 ml. Samples of the solution were taken, saved in plastic
bottles, and labelled for identification prior to future analysis.

All the information from a run was inputted into a computer program which calculated the vapor pressure of PbS. An example of these calculations is given in Appendix A, and the program and a sample run are shown in Appendix B.

Selected strip solutions were analyzed by atomic absorption spectroscopy to check the mass balance closure. Solid samples from selected runs were analyzed by x-ray powder diffraction. A Rigaku vertical diffractometer using Cu-Kα radiation was used for this purpose. The purpose of the X-ray analysis was to determine the phases existing in the boats before and after the runs.

3.2.4 Experimental Errors Analysis

The variables measured during a transpiration run were: reactor temperature and pressure, room temperature and pressure, carrier gas flow rate, weight of material transported and run time. An estimate of the error in measuring each of these variables will now be presented.

The chromel-alumel thermocouple used for temperature measurements was found to be in error by less than ±1K when
it was calibrated. In addition to this, it was observed that the temperature at a given point inside the reaction zone fluctuated as much as ±3K during a run. Therefore, the total error in measuring the reactor temperature is assumed to be ±4K.

The ambient temperature was measured by a thermometer which was calibrated at 1°C intervals. On the basis that the accuracy of the thermometer is the same as its readability, the temperatures could be measured to within ±0.5°C. The reactor pressure was calculated as the sum of the barometric pressure and the reactor manometer pressure. An error of ±0.5 mm Hg is assigned for the sum of the readings. It should be mentioned that both ambient temperature and pressure were observed to vary by as much as 5°C and 4 mm Hg, respectively, over the span of some long runs. In these situations the measurements taken during the run were averaged in order to obtain the values used for the calculations.

Annamalai [80] states that an error of ±1 cc/min can be expected in the measurements of the carrier gas flow rates when using a capillary type flow meter. The same error is used in this study.

The weight of material transported was obtained from a 5-decimal place analytical balance. The total weight loss
was obtained from eight individual boat measurements, and for an error of ±0.05 mg for each measurement, then the error in the weight of material transported is less that 0.4 mg.

The measurement of total run time was determined from the elapsed time, starting when the samples were in position, until the time when their withdrawal was initiated. The fact that the samples were not yet at temperature when the run started was considered to be offset by the time they were still at temperature when the carrier tube was being withdrawn. Since most of the runs were for 6 hours these effects were insignificant, in any case.
IV. RESULTS AND DISCUSSION

4.1 Mass Spectrometric Experiments

4.1.1 Temperature Measurement and Sensitivity of the Equipment

A chromel-alumel (type-K) thermocouple was used for temperature measurement inside the tower assembly. This thermocouple was calibrated by plotting the cooling curves of metal samples placed inside the Knudsen cell. The metals used were tin, lead, and aluminum.

Subsequent to calibrating the thermocouple it was attempted to establish the sensitivity of the mass spectrometer. A zinc sample was placed in the Knudsen cell and the temperature inside the Knudsen cell controlled in such a way as to determine at which temperature (and therefore at which vapor pressure) the spectrometer was able to detect the zinc vapor. This attempt was unsuccessful due to the presence of a background noise of unknown origin from 35 to 103 amu. Because of its higher mass, cadmium was used in a second attempt, and it was possible to identify its peaks (from 110 to 116 amu) at 237°C. That corresponds to a vapor pressure of
3.42x10^{-6} \text{ atm or } 2.5x10^{-3} \text{ torr. It should be stated that the equipment should be able to detect vapor species with partial pressures of } 10^{-4} \text{ torr which indicated that the spectrometer was not operating at its maximum sensitivity.}

The CVC MA-030 mass marker unit was calibrated using the peak of the cation $N_2^+$ (28 amu) as the low mass set point and the peak of the most abundant Hg$^+$ isotope (202 amu) as the high temperature set point. The nitrogen was present in the spectra because of an air leak that could not be located. However, this air leak was very small, and the total pressure in the flight tube could be maintained below $10^{-6}$ torr when liquid nitrogen was used. The mercury originates from the mercury diffusion pump installed in the system.

4.1.2 Mass Spectrometric Results

Only a limited number of mass spectrometric experiments were performed because of the background noise observed in the equipment.

Figure 4.1 shows the spectra obtained for a pure lead sulfide sample at 750°C. The peaks for the cation PbS$^+$, seen in this figure, correspond to a vapor pressure of approximately 0.12 torr. Three separate peaks are observed
FIGURE 4.1 - Spectrum for PbS at 750°C and 19.8 eV.
for PbS\(^+\) because of the three isotopes of lead (sulfur has only one major isotope). Comparatively large peaks for the species Pb\(^+\) were also observed. These peaks originate from any lead present in the vapor phase as well as from the dissociative ionization of PbS\(_g\) molecules.

In order to obtain a sample of lead sulfide doped with arsenic sulfide a special preparation procedure was followed. A mixture containing 90 wt.% PbS and 10 wt.% As\(_2\)S\(_3\) was placed in a glass tube container. This container was then connected to a vacuum system and evacuated. After allowing the mixture to stay under vacuum a few minutes, a torch was used to heat up the wall of the tube right above the level of the sulfide mixture. The heat, coupled with the vacuum, caused the tube to collapse thus making an evacuated, sealed capsule containing the sulfide mixture. This capsule was placed in a furnace at 570\(^\circ\)C and kept there for three days. The lead sulfide was thus saturated with arsenic sulfide. Chemical analysis showed the doped lead sulfide to contain slightly over 3 wt.% arsenic.

Mass spectrometric experiments were run on samples of this doped lead sulfide. The species observed in the spectra obtained are listed in Table 4.1. A tiny peak was observed at 347 amu during the highest temperature


<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>As³⁺</td>
<td>Pb⁺</td>
</tr>
<tr>
<td>AsS⁺</td>
<td>S₈⁺</td>
</tr>
<tr>
<td>As₂S₂⁺</td>
<td>AsPbS₂⁺</td>
</tr>
<tr>
<td>As₂S₃⁺</td>
<td></td>
</tr>
<tr>
<td>As₂S₄⁺</td>
<td></td>
</tr>
<tr>
<td>As⁺</td>
<td></td>
</tr>
<tr>
<td>As₃⁺</td>
<td></td>
</tr>
<tr>
<td>As₃S₂⁺</td>
<td></td>
</tr>
<tr>
<td>As₃S₃⁺</td>
<td></td>
</tr>
<tr>
<td>As₄⁺</td>
<td></td>
</tr>
<tr>
<td>As₄S₃⁺</td>
<td></td>
</tr>
</tbody>
</table>
experiment (683°C). This appears to correspond to the cation AsPb$S^+_2$, thus confirming the existence of a complex vapor species in the arsenic sulfide-lead sulfide system. It should be mentioned that the experiments with the doped lead sulfide samples required very rapid heating of the sample. The high vapor pressure of arsenic sulfide and its low concentration required this procedure in order to avoid the depletion of the arsenic sulfide and consequent disappearance of the vapor complex.

4.2 TRANSPIRATION EXPERIMENTS

A series of transpiration experiments were conducted to determine the vapor pressure of lead sulfide over the temperature range 724°-951°C. The results of these experiments were then used as a basis for determining the influence of the selected complexing agents in the vaporization of lead sulfide.

4.2.1 Measurement of the Vapor Pressure of Lead Sulfide

Both transpiration studies referenced in the literature review used an inert gas (argon) as the carrier gas. In this study, a hydrogen/hydrogen sulfide gas mixture was
used as the carrier gas in order to control the sulfur potential. The vapor pressure/stability diagram for the Pb-S system (constructed from data given in Table 2.9), shown in Figure 4.2, shows that the use of this gas mixture enables the establishment of a sulfur potential inside the reactor which will hinder the dissociative vaporization of lead sulfide. For a \( \frac{P_{H_2S}}{P_{H_2}} \) ratio of 1.0, the partial pressure of lead gas was calculated to be less than 0.4% of the pressure of \( PbS(g) \) at 810°C. The dimerization reaction contributes less than 1.7% of the total vapor pressure over the temperature range studied, and thus has not been considered in the analysis of the data. It was therefore assumed that the total weight loss is due to the reaction:

\[
PbS(s) = PbS(g)
\]  

(2.11)

The data from this investigation should, therefore, be more reliable than the experimental data available in the literature, where there was no attempt to minimize the dissociative vaporization reaction.

The equilibrium constants obtained for reaction (2.11) are shown as a function of flow rate in Figure 4.3. These results confirm that equilibrium saturation had been achieved and that the results are independent of total run
FIGURE 4.2 - Vapor Pressure/Stability Diagram for the Pb-S System at 810°C.
FIGURE 4.3 - Equilibrium Constants for the Reaction \( \text{PbS(s)} = \text{PbS(g)} \) as a Function of Carrier Gas Flow Rate, Run Time, and Sample Origin.
time and of the sample that was used. Four different samples were used in this investigation and a brief summary of experimental observations regarding each one of them follows.

1) Alfa Products Lead (II) Sulfide (99.9%) - Preliminary transpiration experiments using this material yielded vapor pressure values well below the literature data. The material was analyzed using X-ray diffraction and peaks other than those for PbS were observed in the pattern. When a sample was reused, the measured vapor pressure came closer to the other experimental values, and the extraneous peaks were less pronounced in the X-ray diffraction pattern. This sample was abandoned early in the investigation.

2) Johnson Matthey Puratronic Lead (II) Sulfide (99.995%) - This material was used throughout this investigation. During preliminary tests a single sample was used in consecutive experiments, and the results obtained showed good agreement with the results obtained from fresh samples. A fresh sample, as well as samples from the two highest temperatures, the two lowest temperatures, and the reruns experiments were analyzed by X-ray
diffraction. In all cases there was a perfect match with the standard diffraction pattern for PbS.

3) Natural Galena (sample 1) - This sample was obtained from the Colorado School of Mines Geology Department. Its X-ray diffraction spectra was found to match very well the standard pattern for PbS. Results of transpiration experiments using both fresh and reused samples were very reproducible. However, the measured vapor pressure was slightly lower than that obtained with the sample from Johnson Matthey.

4) Natural Galena (sample 2) - This sample was purchased from Ward’s Natural Science Establishment. The vapor pressure of this sample agreed very well with the results obtained using the sample from Johnson Matthey. This sample was also analyzed using X-ray diffraction and once again there was good agreement with the standard PbS pattern.

The H$_2$S/H$_2$ ratios used in the transpiration experiments were calculated from the data for the dissociation reaction in Table 2.9. It was observed that in the lower end of the temperature range of this investigation a carrier gas
containing 30% H₂S and 70% H₂ would assure the vapor
pressure of lead to be less than 1% of the vapor pressure
of lead sulfide (P_{Pb} < 0.01 P_{PbS}). At higher temperatures
a higher H₂S/H₂ ratio would be needed to maintain the same
constraint. Figure 4.4 shows the equilibrium constants
obtained for reaction (2.11) as a function of carrier gas
flow rate and composition. Carrier gas mixtures containing
30% H₂S and 60% H₂S yielded practically the same value for
the equilibrium constant for reaction (2.11) at the three
temperatures shown in Figure 4.4. Based on this finding,
carrier gas mixtures containing 30% H₂S and 70% H₂ were
used from 724° to 846°C and a carrier containing 60% H₂S
and 40% H₂ was used for experiments between 846° and 951°C.

The mass balance closure results are given in
Table 4.2. The amount of lead collected did not agree well
with that calculated from the weight change of the lead
sulfide samples. This lack of mass balance closure is
attributed to two factors. First, two condensates were
formed in the quartz cold finger, an elemental sulfur
deposit and a lead sulfide deposit. The elemental sulfur
was not soluble in the strip solution and it may have
trapped some of the lead sulfide particles. Second, it was
clear from visible observation that complete dissolution of
the lead sulfide was never achieved. A glassy, insoluble
**FIGURE 4.4** - Equilibrium Constants for the Reaction \( \text{PbS(s)} \rightleftharpoons \text{PbS(g)} \) as a Function of Carrier Gas Flow Rate, and Carrier Gas Composition.
### TABLE 4.2
Mass Balance Closure Results For Lead

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Expected Conc. (g/l)</th>
<th>Using Hazen Standards</th>
<th>Using CSM Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc. (g/l)</td>
<td>% of Expected</td>
<td>Conc. (g/l)</td>
</tr>
<tr>
<td>Pb- A</td>
<td>0.3542</td>
<td>0.364</td>
<td>102.8</td>
</tr>
<tr>
<td>Pb- B</td>
<td>1.9780</td>
<td>1.980</td>
<td>100.1</td>
</tr>
<tr>
<td>Pb- C</td>
<td>0.4244</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb- 8</td>
<td>0.1535</td>
<td>0.100</td>
<td>65.1</td>
</tr>
<tr>
<td>Pb- 9</td>
<td>0.1455</td>
<td>0.107</td>
<td>73.6</td>
</tr>
<tr>
<td>Pb-14</td>
<td>0.1472</td>
<td>0.018</td>
<td>12.0</td>
</tr>
<tr>
<td>Pb-15</td>
<td>0.1947</td>
<td>0.056</td>
<td>28.5</td>
</tr>
<tr>
<td>Pb-17</td>
<td>0.1718</td>
<td>0.180</td>
<td>104.8</td>
</tr>
<tr>
<td>Pb-20</td>
<td>1.5773</td>
<td>0.197</td>
<td>12.5</td>
</tr>
<tr>
<td>Pb-23</td>
<td>0.6758</td>
<td>0.130</td>
<td>19.2</td>
</tr>
<tr>
<td>Pb-26</td>
<td>0.1160</td>
<td>0.030</td>
<td>25.9</td>
</tr>
<tr>
<td>Pb-29</td>
<td>0.1232</td>
<td>0.044</td>
<td>35.6</td>
</tr>
<tr>
<td>Pb-31</td>
<td>0.1128</td>
<td>0.047</td>
<td>41.6</td>
</tr>
<tr>
<td>Pb-34</td>
<td>0.1354</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-35</td>
<td>0.0940</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pb-36</td>
<td>1.6359</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
lead sulfide film formed in the tip of the condenser sheaths. The weight losses of the lead sulfide samples were used to calculate the moles of PbS vaporized based on the observation that successive runs conducted on the same PbS sample gave the same results, and the indication from X-ray analysis that the samples had not undergone any transformation.

A comparison of the vapor pressure results of this study with data taken from the literature for the reaction:

$$\text{PbS}(s) = \text{PbS}(g)$$  \hspace{1cm} (2.11)

is given in Figure 4.5. It is interesting to notice that the temperature range of this study overlaps the temperature range of every one of the previous investigations.

The results from this experimental investigation show much less scatter than the transpiration studies presented in the literature review [57,59]. Also, these data are higher than those presented here, partially because they did not attempt to minimize the dissociative vaporization of the PbS. The torsion effusion data of Hansen and Munir [60] show very little scatter, but again, no attempt was made to account for the dissociative vaporization, and
FIGURE 4.5 - Vapor Pressure as a Function of Temperature for the Reaction PbS(s) = PbS(g) as Determined by this Study.
their data are also higher than those from this study. Sudo [56] is the only previous investigator who neglected the dissociative vaporization of lead sulfide and still obtained results that are lower than were measured in this research. However, Sudo mentions but disregards the possible deposition of vaporized material on the hanging rod of the thermal-balance used. The observed weight loss could therefore be lower than expected, leading to vapor pressure results that are also too low. Colin and Drowart [4] were able to single out reaction (2.11), but their results are lower than those from this investigation. Their results, however, were derived from the measured ion intensities, but based on assumptions regarding the relative ionization cross sections. The best fit line through Colin an Drowart’s data is quite parallel to one for this study, indicating good agreement in the enthalpy values for reaction (2.11).

Second and Third Law analyses of the experimental data were made using heat capacity and free energy function data available from the JANAF Thermochemical Tables [16]. This is a questionable exercise because these data are in fact based upon the literature data which have been discussed above. The results are shown in Figures 4.6 and 4.7, and in Table 4.3.
FIGURE 4.6 - Second Law Analysis of the Data Obtained for the Reaction PbS(s) = PbS(g).
FIGURE 4.7 - Third Law $\Delta H_{298}^\circ$ Values Obtained for the Reaction PbS(s) = PbS(g).
### TABLE 4.3
Comparison of Second and Third Law Heats of Reaction

<table>
<thead>
<tr>
<th>REACTION</th>
<th>$\Delta H^o_{298}$ (cal/g-mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2$^{nd}$ LAW</td>
</tr>
<tr>
<td>$PbS_{(s)} = PbS_{(g)}$</td>
<td>52,335</td>
</tr>
</tbody>
</table>
The data from this investigation fit very well on a straight line on the Second Law plot (see Figure 4.6). On the Third Law plot (Figure 4.7) a slight temperature trend can be noticed. From Table 4.3 it can be seen that there is a difference of approximately 2.7 kcal/mol between the \(\Delta H^0_{298}\) values calculated using the Second Law and the Third Law methods. Such discrepancy and the slight temperature dependence of the Third Law results could be attributed to uncertainties in the heat capacity and free energy data available for the species \(\text{PbS(g)}\). These data have been estimated based on analogies with the molecule \(\text{PbO(g)}\), and on tabulated electronic and molecular constants. It is difficult to place much significance in the difference between the Second and the Third Law \(\Delta H^0_{298}\) values in as much as the heat capacity and the free energy values used in these analysis were in fact estimated. In fact, the lack of agreement in the Second and Third Law values for \(\Delta H^0_{298}\) and the use of the previous studies on the vaporization of \(\text{PbS}\) for the construction of the JANAF Tables, suggests that the JANAF Thermochemical Tables [16] may not be particularly reliable.
4.2.2 Vapor Phase Complexation Experiments

4.2.2.1 Complexation with Arsenic (III) Sulfide

High purity arsenic trisulfide (99.999%) was purchased from Aldrich Chemical Company, Inc. X-ray powder diffraction analysis of a sample of this material yielded no peaks whatsoever, indicating it to be amorphous. During the first complexation run it was observed that the glassy arsenic sulfide underwent a large volume increase upon melting. The \( \text{As}_2\text{S}_3 \) boats overflowed, plugging the reactor. The run had to be aborted.

A bottle of ultrapure \( \text{As}_2\text{S}_3 \) from Alfa Products was then located and it was decided to use this material for the transpiration experiments. Four runs were carried out before it was discovered from X-ray powder diffraction pattern that the sample contained arsenolite (\( \text{As}_2\text{O}_3 \)).

Two more transpiration experiments were run using the sample acquired from Aldrich Chemical Company. Very little material was placed in the boats, to allow for the volume increase without overflowing.

The results of the arsenic sulfide complexation runs are shown in Table 4.4. The weight loss in the arsenic was consistently less than predicted using literature data.
# TABLE 4.4

Operating Conditions and Raw Data for the Complexation Runs Using Arsenic Sulfide

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration (min)</th>
<th>Gas Flow Rates (cc/min) (ambient conditions)</th>
<th>Total Pressure (atm)</th>
<th>Saturation Furnace Data</th>
<th>Reaction Furnace Data</th>
<th>% of weight loss expected from PbS baseline runs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>H₂S</td>
<td>Temp (°C) Material Wt loss (grams)</td>
<td>Temp (°C) Material Wt loss (grams)</td>
<td></td>
</tr>
<tr>
<td>As.1</td>
<td>51</td>
<td>32.8</td>
<td>49.8</td>
<td>0.824</td>
<td>374 As₂S₃ *</td>
<td>811 PbS</td>
</tr>
<tr>
<td>As.6</td>
<td>75</td>
<td>37.8</td>
<td>48.8</td>
<td>0.821</td>
<td>355 As₂S₃ 0.04681</td>
<td>805 PbS</td>
</tr>
<tr>
<td>As.7</td>
<td>180</td>
<td>37.8</td>
<td>48.8</td>
<td>0.818</td>
<td>355 As₂S₃ 0.06216</td>
<td>803 PbS</td>
</tr>
<tr>
<td>As.8</td>
<td>60</td>
<td>37.8</td>
<td>49.0</td>
<td>0.815</td>
<td>373 As₂S₃ 0.04073</td>
<td>807 PbS</td>
</tr>
</tbody>
</table>

*boats overflowed
This is possibly due to the sulfur potential inside the reactor which hinders some dissociative vaporization reactions. The weight losses observed in the lead sulfide samples seem incoherent. For some experiments the total weight loss was more than expected from the baseline vaporization runs, and for others it was less. The only trend observed was that short runs showed "enhanced" vaporization of lead sulfide. The longer runs always showed less weight loss than expected.

A final experiment was devised in order to check this observed trend. A four hour run was performed with the lead sulfide boats being removed and weighed every hour. For the fifth hour two paths were taken. In the first one, fresh lead sulfide was placed in the reaction region, with the arsenic sulfide from the previous four hours in the saturation region. In the second path, fresh arsenic sulfide was placed in the saturation region, with the lead sulfide from the previous four hours placed in the reaction region.

The results of this experiment are shown in Figure 4.8. It appears that the arsenic sulfide vapors do enhance the volatilization of lead sulfide. However, they also interact with solid lead sulfide, somehow decreasing its vaporization rate. During the first hour of the
FIGURE 4.8 - Percentage of Weight Loss Expected from the Baseline Experiments for each Hour of a Transpiration Run Using Arsenic Trisulfide as the Complexing Agent.
experiment the second effect is not as pronounced as the first and the enhanced vaporization is observed. In the subsequent hours, the lead sulfide has already been "contaminated" and vaporization rates are smaller than those observed for pure lead sulfide. Chemical analysis of the lead sulfide samples after the runs showed the presence of traces of arsenic. The first path taken for the fifth hour of the experiment does prove that a fresh sample of PbS will have its vaporization enhanced by the arsenic sulfide vapors. On the other hand, a sample that has already been exposed to these vapors for a long time will exhibit a rate of vaporization smaller than that obtained for pure lead sulfide. The enhancement observed in the first hour is taken as concrete evidence that vapor complexation does exist. Based on the mass spectrometric experiments it would appear that this complex species is AsPbS$_2$(g).

4.2.2.2 Complexation with Antimony (III) Sulfide

High purity antimony trisulfide (99.999%) was acquired from Johnson Matthey Chemicals Limited. A sample of this material was analyzed using x-ray diffraction, and the spectra obtained matched the pattern for the mineral
stibnite. Two complexation runs were attempted using this material as the complexing agent. Both experiments were unsuccessful due to interaction of the antimony sulfide vapors with the solid PbS sample. The net effect observed was a gain in weight in the PbS boats which conceals any enhanced vaporization that might have occurred. Chemical analysis of the lead sulfide samples showed the presence of considerable amounts of antimony (over 5% of the total metallic content).

The double zone transpiration technique is, therefore, not appropriate for studying the effect of antimony vapors on the vaporization of PbS. It could only be used if the amount of lead collected in the cold finger could be accurately determined.

One positive outcome of these complexation experiments has to do with the vaporization of Sb$_2$S$_3$. X-ray diffraction analysis of the antimony sulfide samples, after both runs, indicated the presence of elemental antimony. Therefore, the dissociation of the trisulfide accounts for some of the total weight loss. This could be a valuable piece of information for a future study on the vaporization chemistry of antimony sulfide.

A summary of operating conditions and raw data for the transpiration experiments performed with antimony sulfide,
bismuth sulfide, and cadmium sulfide as complexing agents is given in Table 4.5.

4.2.2.3 Complexation with Bismuth (III) Sulfide

The thermodynamic data available in the literature [66,75-77] were used to calculate the appropriate experimental conditions. It was determined that the dissociation reaction (reaction (2.46)) would account for nearly all the weight loss of the Bi$_2$S$_3$ samples. The amount of bismuth present in the vapor phase was predicted to be negligible, and therefore, no changes should be expected in the vaporization of PbS.

One transpiration experiment was conducted and the operating conditions and raw data are also given in Table 4.5. The outcome of the run was as expected: the weight loss of the lead sulfide boats was in excellent agreement with the baseline experiments. X-ray diffraction analysis of the Bi$_2$S$_3$ sample before and after the run showed it to be the mineral bismuthinite, but elemental bismuth was clearly present in the spectra of the material after the run.
TABLE 4.5

Operating Conditions and Raw Data for the Complexation Runs Using Antimony Sulfide, Bismuth Sulfide, and Cadmium Sulfide

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration (min)</th>
<th>Gas Flow Rates (cc/min)</th>
<th>Total Pressure (atm)</th>
<th>Saturation Furnace Data</th>
<th>Reaction Furnace Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>H₂S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb.1</td>
<td>120</td>
<td>32.5</td>
<td>49.2</td>
<td>0.826</td>
<td>643</td>
</tr>
<tr>
<td>Sb.2</td>
<td>120</td>
<td>32.3</td>
<td>48.8</td>
<td>0.826</td>
<td>643</td>
</tr>
<tr>
<td>Bi.1</td>
<td>315</td>
<td>37.8</td>
<td>49.0</td>
<td>0.822</td>
<td>627</td>
</tr>
<tr>
<td>Cd.1</td>
<td>360</td>
<td>38.0</td>
<td>49.0</td>
<td>0.826</td>
<td>626</td>
</tr>
</tbody>
</table>

Sb₂S₃ 0.43099 803  PbS  -0.01982
Sb₂S₃ 0.41027 804  PbS  -0.00572
Bi₂S₃ 0.41878 805  PbS  0.15939
CdS  0.00009 805  PbS  0.18183
4.2.2.4 Complexation with Cadmium Sulfide

Preliminary thermodynamic calculations for the dissociative vaporization of cadmium sulfide (reaction (2.47)) indicated that the presence of a minimal sulfur potential in the carrier gas would prevent this reaction from occurring. One transpiration experiment was undertaken and indeed the total weight loss of the cadmium sulfide boats was only 0.09 mg. The operating conditions and raw data for this run are also given in Table 4.5. The total amount of lead sulfide vaporizing reproduced the values obtained on the baseline experiments. X-ray diffraction analysis of the CdS sample showed it to be the mineral greenockite, and no alterations were observed in the diffraction pattern of the sample after the run.

The result of this experiment provides further proof that the species CdS$_{(g)}$ is not significant in the vaporization process of CdS$_{(s)}$. 
V. CONCLUSIONS

Equilibrium thermodynamic data obtained via conventional transpiration experiments have made possible the redetermination of the standard Gibbs free energy of reaction (2.11). The temperature range studied (724-951°C) overlaps all previous investigations of such reaction. The high temperature data from this investigation is particularly important since the other two high temperature studies are transpiration investigations which have been shown to not be very reliable. The thermodynamic results obtained for reaction (2.11) are given in equation (5.1).

\[
PbS(s) = PbS(g) \quad (2.11)
\]

\[
\Delta G^0_T = 49,365 - 30.975*T \quad \text{(cal/mole)} \quad (5.1)
\]

\[
(997K < T < 1224K)
\]

Mass spectrometric experiments on a lead sulfide sample doped with arsenic sulfide have enabled the identification of the species AsPbS₂(g). Further confirmation of the formation of a complex gaseous sulfide was obtained from transpiration experiments. Unfortunately, the quantification of the enhanced vaporization of lead sulfide
due to the formation of this gaseous complex was not achieved because of the interaction between the arsenic sulfide vapors and the solid PbS sample during the transpiration experiments.

The use of the double zone transpiration apparatus as a means of studying complexation in the systems Sb-Pb-S and Cd-Pb-S was not satisfactory for different reasons in each case. First, the antimony sulfide vapors were found to interact with the solid lead sulfide samples causing a weight gain in those samples, and thus concealing the detection of any enhanced vaporization. Secondly, the use of a hydrogen/hydrogen sulfide carrier gas prevented the dissociative vaporization of the cadmium sulfide. This precluded any cadmium to report to the vapor phase and thus avoided any possibility of complexation. The complexation experiment conducted using Bi$_2$S$_3$ as a complexing agent showed no effect whatsoever on the vaporization rate of lead sulfide. Therefore, it can be inferred that no significant degree of complexation exists between bismuth sulfide vapors and lead sulfide.
VI. SUGGESTIONS FOR FURTHER RESEARCH

Among the metal-sulfur systems reviewed, the cobalt-sulfur, the nickel-sulfur, and the copper-sulfur systems do require further experimental study. The same is true for the systems arsenic-sulfur and antimony-sulfur. It is suggested that mass spectrometric and transpiration studies be performed for these systems, specially for the latter two, where conflicting data were found in the literature.

Data have been found in the literature confirming the existence of oxide vapor complexes of the Group Va elements. The possibility of the existence of sulfide vapor complexes should be studied. Mass spectrometric investigations should be conducted on the systems As-Sb-S, As-Bi-S, and Sb-Bi-S. Transpiration studies would complement the study of volatilization characteristics on these systems.

It should be observed that prior to studying the ternary systems suggested above, it is absolutely necessary to have the vaporization chemistry of both arsenic sulfide and antimony sulfide very well established.
REFERENCES


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64. J. DROWART, S. SMOES and A. VANDERAUWERA-MAHIEU, "The Atomization Enthalpies of AsSb(g), As4(g), Sb4(g), As3Sb(g), As2Sb2(g), AsSb3(g), As3Sb06(g), As2Sb206(g), and AsSb306(g). A Thermodynamic Study by the Mass-spectrometric Knudsen-cell Method", J. Chem Thermodynamics, Vol. 10, pp. 453-64, 1978.


Colorado School of Mines, 1980.


APPENDIX A

TRANSPERSION CALCULATIONS

In order to calculate the vapor pressure data from the transpiration experiments results, it is first necessary to calculate the total molar flow rate of the carrier gas. The following variables will be used for the molar flow rates in units of [moles/min]:

- \( N_1 \) = Molar Flow Rate of \( \text{H}_2\text{S} \) in the Carrier Gas
- \( N_2 \) = Molar Flow Rate of \( \text{H}_2 \) in the Carrier Gas
- \( N_3 \) = Molar Flow Rate of \( \text{S}_2 \) in the Carrier Gas
- \( N_4 \) = Molar Flow Rate of \( \text{PbS}(g) \) Transported
- \( N_{Cg} \) = Molar Flow Rate of Carrier Gas

\[
N_1 = \frac{(\text{Vol. Flow Rate of H}_2\text{S})*(\text{Reactor Pressure})}{(\text{Gas Constant})*(\text{Ambient Temperature})}
\]

\[
N_2 = \frac{(\text{Vol. Flow Rate of H}_2)*(\text{Reactor Pressure})}{(\text{Gas Constant})*(\text{Ambient Temperature})}
\]

Because of the nature of the carrier gas, the equilibrium:

\[
\text{H}_2\text{S}(g) = \text{H}_2(g) + \text{S}_2(g) \quad (A.1)
\]
had to be considered. Equilibrium yield calculations were performed, and the molar flow rate of the species $S_2$ was obtained. The molar flow rates of $H_2S$ and $H_2$ were appropriately recalculated. The total molar flow rate of the carrier gas is calculated by adding the individual values obtained for three species in the carrier gas $(N_{cg} = N_1 + N_2 + N_3)$.

The molar flow rate of $PbS(g)$ transported is obtained as follows:

\[
N_4 = \frac{\text{(Weight Loss on PbS Boats)}}{\text{(total run time)} \times (239.26)}
\]

And finally, the partial pressure of PbS may be calculated by:

\[
P_{PbS} = \frac{N_4 \times \text{(Reactor Pressure)}}{N_{cg} + N_4}
\]
APPENDIX B

LISTING AND SAMPLE OUTPUT OF DATA REDUCTION PROGRAM FOR THE LEAD SULFIDE VAPOR PRESSURE EXPERIMENTS

A computer program was written in MS-BASIC for the TI Professional Computer, to perform the calculations presented in Appendix A. A listing of the program is given in Table B.1 and a sample of the output is shown in Table B.2.
TABLE B.1 - Listing of the program "PBS-RED.BAS"

```
100  CLS : KEY OFF : GOTO 1000
110  LOCATE 4,16 : PRINT " COLORADO SCHOOL OF MINES "
120  LOCATE 5,16 : PRINT " DEPARTMENT OF METALLURGICAL ENGINEERING "
130  LOCATE 7,16 : PRINT " DETERMINATION OF THE VAPOR PRESSURE "
140  LOCATE 8,16 : PRINT " OF "
150  LOCATE 9,16 : PRINT " LEAD SULFIDE "
160  LOCATE 11,16 : PRINT " TRANSPIRATION DATA REDUCTION "
170  LOCATE 13,16 : PRINT " ROBERTO M. Z. CASTRO "
180  LOCATE 14,16 : PRINT " 1986 "
190  RETURN
200  ' Subroutine to calculate flowrate of H2
210  F1 = 10**(.439929 + .999759*LOG(D1)/LOG(10))
220  RETURN
230  ' Subroutine to calculate flowrate of H2S
240  F2 = 10**(.773363 + .995197*LOG(D2)/LOG(10))
250  RETURN
260  ' Subroutine to calculate amount of S2(g)
270  X1 = ((N2-2*X)/(N1+2*X))^2 * (N1+N2+X)/(PT^KEQ^2)
280  RETURN
1000 X1$=STRINGS(48,205) : X2$=STRING$(48.0)
1010 X3$=CHR$(201)+X1$+CHR$(187)
1020 X4$=CHR$(186)+X2$+CHR$(186)
1030 X5$=CHR$(200)+X1$+CHR$(188)
1040 FOR I=1 TO 25 : LOCATE I,1 : PRINT STRINGS(80.0) : NEXT I
1050 LOCATE 2,15.0 : PRINT X3$
1060  FOR I=1 TO 15 : LOCATE I,15 : PRINT X4$ : NEXT I
1070 LOCATE 16,15 : PRINT X5$ : GOSUB 110
1080 LOCATE 22,29 : PRINT "Hit 'RETURN' to continue"
1090 AS=INKEY$ : IF AS="" THEN 1100
1100 IF AS=CHR$(13) THEN 1110 ELSE 1090
1110 CLS
2000 .animations 3000 FR$="##.## \""
2040 LOCATE 2,15 : INPUT "Please input the run identification: ",RN$
2050 LOCATE 3,1 : PRINT STRINGS(80,205)
2060 LOCATE 5,3 : PRINT "Please input the following information:"
2070 LOCATE 8,3 : INPUT "Ambient Temperature (deg. Celsius): ",TA
2080 LOCATE 10,3 : INPUT " Ambient Pressure (in mm of Hg): ",PA
2090 LOCATE 12,3 : INPUT " Reading from H2 flowmeter (in cm): ",D1 : GOSUB 200
2100 LOCATE 13,13 : PRINT " H2 flowrate = ":USING FR$;F1;" cc/min"
2110 LOCATE 15,3 : INPUT "Reading from H2S flowmeter (in cm): ",D2 : GOSUB 230
2120 LOCATE 16,13 : PRINT " H2S flowrate = ":USING FR$;F2;" cc/min"
```
TABLE B.1 - (continued)

2130 LOCATE 18.3: INPUT " Manometer Pressure (in mm of Hg): ",PG
2150 LOCATE 23.15: PRINT "Is above Information correct? ('Y' or 'N')"
2160 AS=INKEYS$ : IF AS="" THEN 2160
2170 IF AS="Y" OR AS="y" THEN CLS : GOTO 2200
2180 IF AS="N" OR AS="n" THEN 2000
2190 GOTO 2160
2200 CLS : LOCATE 2,35 : PRINT "RUN ";RN$
2210 LOCATE 3.1 : PRINT STRINGS(80,205)
2220 LOCATE 5,3 : PRINT "Please input the following Information:
2230 LOCATE 7.15 : INPUT "Material: ", MAT$
2240 LOCATE 8.15 : INPUT "Source: ", SOUS
2250 LOCATE 9.15 : PRINT "Run time: "; RT
2260 LOCATE 9.25 : INPUT " ", RT
2270 LOCATE 12.15 : PRINT "Weight loss in PbS boats:"
2280 FOR I=1 TO 4
2290 LOCATE 13+2*I.22: PRINT "Boat ";I: grams
2300 NEXT I
2310 BS$="#.# # # #  \
2320 COLOR 0,7,0,0 : LOCATE 13+2*I.33: PRINT " 
2330 LOCATE 13+2*I.33 : INPUT ";BW(I)
2340 COLOR 7,0,0,0 : LOCATE 13+2*I.33: PRINT USING BS$;BW(I);"grams"
2350 NEXT I
2360 LOCATE 23.15: PRINT "Is above Information correct? ('Y' or 'N')"
2370 AS=INKEYS$: IF AS="" THEN 2370
2380 IF AS="Y" OR AS="y" THEN 3000
2390 IF AS="N" OR AS="n" THEN 2200
2400 GOTO 2370
3000 
3010 ' Start Calculations
3020 
3030 R=82.0575 ' gas constant (cc*atm/mol*K)
3040 T1=TA+273.15 : PT=(PA+PG)/760
3050 N1= PT*F1/(R*T1) ' H2 moles/min
3060 N2= PT*F2/(R*T1) ' H2S moles/min
3070 T2=TB+273.15
3080 DG=-21634.4 + 11.771*T2
3090 KEQ=EXP(-DG/(1.987*T2))
3100 X=(N2/N1)^2*(N1+N2)/(PT*KEQ^2)
3110 GOSUB 260
3120 IF ABS((X-I)/X)<.001 THEN X=I : GOTO 3110
3130 PS2=(X1/(N1+N2+X1))*PT : LPS2=LOG(PS2)/LOG(10)
3140 N1=N1+2*X1 : N2=N2-2*X1 : N3=X1
3150 ' N1, N2 and N3 in moles/min
3160 MPBS = BW(1)+BW(2)+BW(3)+BW(4) ' in grams
**TABLE B.1**  (continued)

3170 N4 = (MPBS/RT)/239.26
3180 PPBS = N4*PT/(N1+N2+N3+N4) ; PTORR=PPBS*760
3190 LPBS = LOG(PPBS)/LOG(10)
4000
4010 ' Print out input information and Results
4020 '
4030 CLS ; LOCATE 10,20,0 ; PRINT "Please prepare PRINTER for output."
4040 LOCATE 14,30 ; PRINT "Hit 'RETURN' when ready."
4050 A$=INKEYS ; IF A$="" THEN 4050
4060 IF A$=CHR$(13) THEN 4070 ELSE 4050
4070 CLS ; LOCATE 10,20,0 ; PRINT "Printing out Results"
4075 LPRINT : LPRINT : LPRINT
4080 LPRINT TAB(17) "***********************************************************************"
4090 LPRINT TAB(17) ** "
4100 LPRINT TAB(17) ** COLORADO SCHOOL OF MINES **
4110 LPRINT TAB(17) ** "
4120 LPRINT TAB(17) ** DETERMINATION OF THE VAPOR PRESSURE **
4130 LPRINT TAB(17) ** OF **
4140 LPRINT TAB(17) ** LEAD SULFIDE **
4150 LPRINT TAB(17) ** "
4160 LPRINT TAB(17) ** TRANSPARATION DATA REDUCTION **
4170 LPRINT TAB(17) ** "
4180 LPRINT TAB(17) ** ROBERTO M. Z. CASTRO **
4190 LPRINT TAB(17) ** 1986 **
4200 LPRINT TAB(17) ** "
4210 LPRINT TAB(17) "***********************************************************************"
4220 LPRINT : LPRINT : LPRINT
4230 LPRINT TAB(17) " **** INPUT DATA **** "
4240 LPRINT
4250 LPRINT TAB(12) " RUN : "$RNS$
4260 LPRINT TAB(12) " MATERIAL : "$MAT$
4270 LPRINT TAB(12) " SOURCE : "$SOU$
4280 LPRINT
4290 C$="\"
4300 D$="\"
4310 E$="\"
4320 F$="\"
4330 LPRINT TAB(20) USING C$;"- CONSTANT TEMPERATURE ZONE : "$TB;" deg. C"
4340 LPRINT TAB(20) USING C$;"- AMBIENT TEMPERATURE : "$TA;" deg. C"
4350 LPRINT TAB(20) USING C$;"- AMBIENT PRESSURE : "$PA;" mm Hg"
4360 LPRINT TAB(20) USING C$;"- MANOMETER PRESSURE : "$PG;" mm Hg"
4370 LPRINT TAB(20) USING C$;"- TOTAL PRESSURE : "$PT*760;" mm Hg"
4380 LPRINT TAB(50) USING C$:" atm"
4390 LPRINT TAB(20) USING C$;"- FLOWRATES : H2 = "$H2;" cc/min"
4400 LPRINT TAB(20) USING C$;" H2S = "$H2S;" cc/min"
TABLE B.1  -  (continued)

4410 LPRINT TAB(20) USING D$:"- RUN TIME : ";RT:;" minutes"
4420 LPRINT TAB(20) USING E$:"-TOTAL WEIGHT LOSS IN BOATS :";MPBS;" grams"
4430 LPRINT ; LPRINT : LPRINT : LPRINT
4440 LPRINT TAB(17) " **** RESULTS **** "
4450 LPRINT
4460 LPRINT TAB(20) USING E$:"- VAPOR PRESSURE OF PbS : ";PPBS;" atm"
4470 LPRINT TAB(20) USING E$:" ; PTORR;" torr"
4480 LPRINT TAB(20) "- EQUILIBRIUM CONSTANT FOR "
4490 LPRINT TAB(20) " REACTION: PbS(s) = PbS(g) "
4500 LPRINT TAB(20) USING E$:" LOG(K) = ";LPBS
4510 LPRINT TAB(20) "- FLOW RATES OF GASEOUS "
4520 LPRINT TAB(20) USING F$:" SPECIES: H2 : ";N1;F$1!
4530 LPRINT TAB(20) USING F$:" H2S : ";N2;F$1!
4540 LPRINT TAB(20) USING F$:" S2 : ";N3;F$1!
4550 LPRINT TAB(20) USING F$:" PbS : ";N4;F$1!
4560 LPRINT CHR$(12)
5000 '
5010 ' Options
5020 '
5030 CLS
5040 X1$=STRING$(36,205) : X2$=STRING$(36,0) : X3$=STRING$(36,196)
5050 X4$=CHR$(201)+X1$+CHR$(187)
5060 X5$=CHR$(186)+X2$+CHR$(186)
5070 X6$=CHR$(199)+X3$+CHR$(182)
5080 X7$=CHR$(200)+X1$+CHR$(188)
5090 LOCATE 3,21 : PRINT X4$
5100 FOR I=4 TO 6 : LOCATE 1,21 : PRINT X5$ : NEXT I
5110 LOCATE 7,21 : PRINT X6$
5120 FOR I=8 TO 14 : LOCATE 1,21 : PRINT X5$ : NEXT I
5130 LOCATE 15,21 : PRINT X7$
5140 LOCATE 5,24 : PRINT "YOUR OPTIONS ARE!"
5150 LOCATE 9,29 : PRINT "1 - Rerun this Program"
5160 LOCATE 11,29 : PRINT "2 - Exit to MS-DOS"
5170 LOCATE 13,29 : PRINT "3 - Exit to BASIC"
5180 LOCATE 19,28,0 : PRINT "Please choose 1, 2, or 3."
5190 AS=INKEYS : IF AS="" THEN 5190
5200 IF AS="1" THEN GOTO 1000
5210 IF AS="2" THEN CLS : SYSTEM
5220 IF AS="3" THEN CLS : NEW
5230 GOTO 5190
TABLE B.2 - Sample output of the program
"PBS-RED.BAS"

---

COLORADO SCHOOL OF MINES
DETERMINATION OF THE VAPOR PRESSURE
OF
LEAD SULFIDE
TRANSPIRATION DATA REDUCTION
ROBERTO M. Z. CASTRO
1986
---

**** INPUT DATA ****

RUN : Pb-20
MATERIAL : Synthetic PbS
SOURCE : AESAR

- CONSTANT TEMPERATURE ZONE : 921.000 deg. C
- AMBIENT TEMPERATURE : 21.000 deg. C
- AMBIENT PRESSURE : 625.200 mm Hg
- MANOMETER PRESSURE : 0.615 mm Hg
- TOTAL PRESSURE : 625.815 mm Hg
- FLOW RATES :
  H2 - 37.978 cc/min
  H2S - 56.470 cc/min
- RUN TIME : 360 minutes
- TOTAL WEIGHT LOSS IN BOATS : 1.82139 grams

**** RESULTS ****

- VAPOR PRESSURE OF PbS : 0.00535 atm
  4.06329 torr
- EQUILIBRIUM CONSTANT FOR
  REACTION: PbS(s) = PbS(g)
  LOG(K) = 2.27194
- FLOW RATES OF GASEOUS
  SPECIES:
  H2 : 0.132E-02 moles/min
  H2S : 0.190E-02 moles/min
  S2 : 0.136E-04 moles/min
  PbS : 0.211E-04 moles/min
BIOGRAPHICAL NOTE

The author was born to Luis and Santuza Castro in Palo Alto, California, on December 6, 1959. The family moved to Brazil in 1961, and the author attended primary and secondary schools in the town of Belo Horizonte, state of Minas Gerais.

The author received his Bachelor of Science degree in Metallurgical Engineering from the Universidade Federal de Minas Gerais, in Belo Horizonte, in December 1982. The author is a member of the Metallurgical Society of AIME and the Society of the Sigma Xi.

The author is married to the former Maria Merces Reis of Belo Horizonte, MG, Brazil.