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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

PART VII. THERMODYNAMIC STUDY OF TIN AND LEAD SULFIDE USING A MASS SPECTROMETER

TECHNICAL DOCUMENTARY REPORT No. WADD 60-782
PART VII

APRIL 1962

DIRECTORATE OF MATERIALS AND PROCESSES
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7350, Task No. 735001

(Prepared under Contract No. AF 61(052)-225 by the Université Libre de Bruxelles, Brussels, Belgium; Reginald Colin and John Drowart)
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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001 "Non-graphitic." The work was administered under the direction of the Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. F. W. Vahldiek was the project engineer.

This report covers work conducted from March 1961 to March 1962.

WADD Technical Report 60-782, Parts I, II, III, V, VI have already been published. Part VIII is in preparation with Part IV to follow when it becomes available.

The authors wish to thank Professor P. Goldfinger for his interest and encouragement, Professor M. Denayer for the natural galena samples, Mr. M. Lucas for preparing sulfides of high purity and Mr. J. Orszag for assistance with the PbS experiments.
ABSTRACT

Reaction enthalpies, $\Delta H^\circ_{298}$, in kcal/mole, determined were

$\text{SnS(s)} \rightarrow \text{SnS(g)}: 52.6 \pm 1.6$ kcal/mole;

$2 \text{SnS(s)} \rightarrow \text{Sn}_2\text{S}_2(g): 56.5 \pm 5.0$;

$\text{PbS(s)} \rightarrow \text{PbS(g)}: 55.7 \pm 1.6$;

$2 \text{PbS(s)} \rightarrow \text{Pb}_2\text{S}_2(g): 66.6 \pm 5.0$;

$\text{SnPbS}_2(g) \rightarrow \text{SnS(g)} + \text{PbS(g)}: 46.5 \pm 5.0$;

$\text{PbS(g)} \rightarrow \text{Pb}(g) + \frac{1}{2} \text{S}_2(g): 28.8 \pm 2.6$.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

[Signature]

W. C. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Materials Central
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INTRODUCTION

The vaporization of Tin Sulfide was studied and its vapor pressure determined as a function of temperature by the Knudsen effusion method by Hsiao and Schlechten\(^{(1)}\), Richards\(^{(2)}\), St Clair, Shibler and Solet\(^{(3)}\), and Klushin and Chernykh\(^{(4)}\).

The vaporization of Lead Sulfide was noted by Pelouse and Fremp\(^{(5)}\) and its vapor pressure measured by the effusion method by Schenck and Albers\(^{(6)}\), Vesselowskii\(^{(7)}\), Hsiao and Schlechten\(^{(1)}\), Sudo\(^{(8)}\), and Miller and Abdeev\(^{(9)}\).

The molecule SnS has been the subject of several spectroscopic investigations\(^{10-17}\) from which molecular constants for the ground and a number of excited states were derived. In particular, a dissociation energy \(D^0\text{(SnS)} = 111 \pm 6\) kcal/mole was determined spectroscopically by Barrow, Drummond and Rowlinson. The latter authors suggested that a supposed predisassociation\(^{(11,12)}\) leading to a lower value, \(D^0\text{(SnS)} \leq 68.5\) kcal/mole may well be reinterpreted as an interaction between neighbouring excited states.

The molecule PbS was studied by optical spectroscopy by Rochester and Howell\(^{(18)}\), Bell and Harvey\(^{(19)}\) and Vago and Barrow\(^{(20)}\). While the electronic ground state was determined to be a \(\Sigma\) state\(^{(18,19)}\), a convergence limit was

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obtained\(^{(20)}\) for an excited state of this molecule at about 104.9 kcal/mole. From thermochemical data, Brewer\(^{(21)}\) obtained 75 kcal/mole for the dissociation energy.

The present paper reports a mass spectrometric investigation of the vaporization of Tin Sulfide, Lead Sulfide and a mixture of Tin and Lead Sulfides.

EXPERIMENTAL.

The main features of the mass spectrometer and Knudsen effusion cell design have been described previously\(^{(22,24)}\). In the present work, small quartz cells containing the samples were placed inside molybdenum crucibles heated by radiation from a tungsten filament surrounding it. Temperatures were measured with a Pt-PtRh (10\%) thermocouple. The thermocouple junction was placed beneath the quartz cell within the molybdenum crucible. To avoid temperature errors due to thermal conduction through the thermocouple wires these were wound in several coils inside the crucible and insulated by tiny quartz tubes.

Effusion holes of 4 to 8 x 10\(^{-3}\) cm\(^2\) were used in different experiments. Their area was small compared to the area of the sample. The finite thickness of the effusion hole was taken into account and an appropriate Clausing correction factor\(^{(25)}\) applied. The weight of the samples was usually about 100mg.
In the initial experiments with Tin Sulfide, commercial samples of SnS were used. As a result of oxydation these samples contain SnO, the vaporization of which was found to interfere with that of SnS. In subsequent experiments, commercial samples of SnS$_2$ or samples of pure SnS, prepared by reduction of SnO by $H_2$S were used. The reason for using SnS$_2$ is that this substance decomposes at low temperatures to SnS and a complex mixture of polyatomic sulfur molecules. If the SnS$_2$ sample contains oxides, these are simultaneously reduced to SnS, as shown by the effusion of SO$_2$ molecules. These processes were observed in the mass spectrometer around 500°K.

The PbS samples were either prepared from PbO$^{(26)}$ or taken from natural galena crystals.

EXPERIMENTAL RESULTS.

A. Composition of the vapor.

1. SnS

The atomic and molecular ions, characteristic of this system were $S^+$, $Sn^+$, $SnS^+$, $Sn_2^+$, $Sn_2S^+$ and $Sn_2S_2^+$, approximate relative intensities for nominal 70 ev electrons being $8 \times 10^{-2}$ / $8.2 \times 10^{-2}$/1/$3.6 \times 10^{-3}$/6/$7 \times 10^{-3}$/4.2 / $10^{-2}$ respectively.

All of these ions were identified from their mass, isotopic distribution and through interception of the molecular beam$^{(27)}$. 
Approximate ionization efficiency curves were measured for each of these ions. The linear extrapolation method was used, the energy scale being calibrated with the appearance potential of water (28) used as a standard. The corrected appearance potential were 16.5 ± 2.0, 12.5 ± 0.5, 9.7 ± 0.5, 16.5 ± 1, 12.4 ± 1, and 9.4 ± 0.5 ev respectively for S⁺, Sn⁺, SnS⁺, Sn₂⁺, Sn₂S⁺ and Sn₂S₂⁺. These appearance potentials as well as the relative intensities of the ions indicate that SnS⁺ and Sn₂S⁺ are parent ions, while Sn⁺, Sn₂⁺ and Sn₂S⁺ are fragment ions. Possible trimer Sn₃S₃ and tetramer Sn₄S₄ molecules, whose intensity relative to SnS was equal or smaller than 5 x 10⁻⁴ could not be identified with certainty. All measurements given below for this system were taken with nominal 70 ev electrons.

2. PbS

The ions observed in this system and identified as above were S⁺, S₂⁺, Pb⁺, PbS⁺ and Pb₂S₂⁺. The corrected appearance potentials measured were respectively 16.0 ± 2, 9.6 ± 0.5, 7.5 and 11.6 ± 0.5, 8.6 ± 0.5 and 9.2 ± 0.5 ev. The first appearance potential of Pb⁺ agrees within experimental error with the spectroscopic ionization potential of lead (29). This appearance potential was therefore attributed to the direct ionization of atomic lead present in the vapor. This interpretation is
supported by the simultaneous presence in the vapor of molecular sulfur as indicated by the appearance potential of S_2^+. The appearance potentials of PbS^+ and Pb_2S_2^+ and their relative intensity (I(Pb_2S_2^+)/I(PbS^+) ≈ 6 x 10^{-3}) indicated direct ionization of the corresponding molecules. The second appearance potential of the ion Pb^+, 11.6 ± 0.5 ev. was ascribed to fragmentation of the PbS molecule. The difference between the measured ionization and fragmentation potentials thus gave 4.1 ± 0.7 ev. as upper limit for the dissociation energy of the PbS molecule, a value which is much less reliable than but compatible with the thermodynamic value to be discussed below.

Measurements of partial pressures of Pb were made with electrons of maximum 11.5 ev to avoid the presence of Pb^+ fragment ions in the spectra. For the measurements of PbS and Pb_2S_2 pressures, electrons of energies varying from 10 to 70 ev were used.

3. SnS → PbS.

In addition to the atomic and molecular ions observed in the two separate systems given above, the molecular ion SnPbS_2^+ was identified, its appearance potential being 9 ± 1 ev.
B. Pressure Data.

Relative partial pressures were derived from the ion intensities by the relation

\[
\frac{P_1}{P_2} = \frac{I_1 \sigma_2 \left( \frac{E - A_2}{A_2} \right) \gamma_2 T_1}{I_2 \sigma_1 \left( \frac{E - A_1}{A_1} \right) \gamma_1 T_2}
\]

where \( P \) = partial pressure, in atm; \( I \) = ion intensity in arbitrary units; \( \sigma \) = relative cross section at the maximum of the ionization efficiency curve; \( A \) = appearance potential in ev; \( E \) = energy of the ionizing electrons, in ev; \( \gamma \) = secondary electron multiplier efficiency, corrected for molecular effects if necessary and \( T \) = absolute temperature.

By analogy with a number of dimeric molecules\(^{(30,33)}\) the ratio 1.6 was used for the cross sections of \( S_2 \), \( Sn_2S_2 \) and \( Pb_2S_2 \) relative to \( S \), \( SnS \) and \( PbS \) respectively. The relative ionization cross section of PbS was taken as eight tenths of the sum of the cross sections of atomic lead and sulfur given by Otvos and Stevenson\(^{(34)}\). The secondary multiplier efficiency was estimated from the calibration\(^{(35)}\) curve of a multiplier analogous to the one used here, which was in agreement with the curve given by Inghram, Hayden and Hess\(^{(36)}\). Molecular
The various relative cross sections and multiplier efficiencies including molecular effects are summarized in Table I.

In order to derive the absolute values of the pressure, a number of quantitative vaporization self-calibrations were carried out. Weighed quantities of either SnS or PbS (about 50 mg) were therefore vaporized completely and the SnS⁺ or PbS⁺ intensities integrated with time.

The average pressures obtained are summarized and compared with available literature data. For both sulfides the pressures determined here are in good agreement.
with the literature data, except for the measurements of Hsiao and Schlechten, which also for other sulfides are systematically low by a factor of 5 to 10 and more.

C. Enthalpies of Sublimation and Dissociation.

Enthalpies of sublimation were derived in the present study both from second and third laws of thermodynamics and are summarized in Table II.

The necessary entropies and heat contents for solid and gaseous SnS and PbS, were taken from Kelley\(^{(38)}\) while those of gaseous Pb and S\(_2\) were taken from Stull and Sinke\(^{(39)}\). The entropies of gaseous Sn\(_2\)S\(_2\) and Pb\(_2\)S\(_2\) were taken identical to those of the molecules As\(_4\) and Sn\(_4\)\(^{(39)}\) respectively. It was assumed that the moments of inertia are roughly the same and that the decrease in symmetry number for Sn\(_2\)S\(_2\) and Pb\(_2\)S\(_2\) compensates for an increase in the vibration frequencies. The entropy of SnS-PbS was taken as the average of the preceding ones, corrected for the change in symmetry number.

The best average values chosen were based on the third law results for SnS and PbS, since the entropies of these molecules are known from spectroscopic data\(^{(10,20)}\). In the case of Sn\(_2\)S\(_2\) and Pb\(_2\)S\(_2\) the arithmetic average of all results was taken; while the agreement between second and third law results indicates the entropies used to be fairly accurate.
TABLE II. Enthalpies of Sublimation. $\Delta H^{\circ}_{298}$

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Molecule</th>
<th>Temperature range</th>
<th>2d Law</th>
<th>3d Law</th>
<th>Best average</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.02</td>
<td>SnS</td>
<td>835-1005</td>
<td>50.1±3.0</td>
<td>52.4±1.6</td>
<td></td>
</tr>
<tr>
<td>63.03</td>
<td>SnS</td>
<td>840-965</td>
<td>52.5</td>
<td>53.3</td>
<td>52.6±1.6</td>
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<tr>
<td>63.04</td>
<td>SnS</td>
<td>815-970</td>
<td>52.1</td>
<td>52.0</td>
<td></td>
</tr>
<tr>
<td>63.02</td>
<td>Sn$_2$S$_2$</td>
<td>835-1005</td>
<td>56.4±5.0</td>
<td>57.3±5.0</td>
<td></td>
</tr>
<tr>
<td>63.03</td>
<td>Sn$_2$S$_2$</td>
<td>885-965</td>
<td>57.0</td>
<td>58.2</td>
<td>56.5±5.0</td>
</tr>
<tr>
<td>63.04</td>
<td>Sn$_2$S$_2$</td>
<td>815-970</td>
<td>53.0</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td>63.13</td>
<td>PbS</td>
<td>985-1080</td>
<td>52.5±4.0</td>
<td>56.9±1.6</td>
<td></td>
</tr>
<tr>
<td>63.14</td>
<td>PbS</td>
<td>915-1080</td>
<td>49.7</td>
<td>55.1</td>
<td>55.7±1.6</td>
</tr>
<tr>
<td>63.15</td>
<td>PbS</td>
<td>865-1090</td>
<td>-</td>
<td>55.0</td>
<td></td>
</tr>
<tr>
<td>63.18</td>
<td>PbS</td>
<td>995-1100</td>
<td>55.5</td>
<td>55.7</td>
<td></td>
</tr>
<tr>
<td>63.18</td>
<td>Pb$_2$S$_2$</td>
<td>995-1100</td>
<td>64.5±5.0</td>
<td>67.8±5.0</td>
<td></td>
</tr>
<tr>
<td>63.22</td>
<td>Pb$_2$S$_2$</td>
<td>1129</td>
<td>-</td>
<td>66.7</td>
<td>66.6±5.0</td>
</tr>
<tr>
<td>63.27</td>
<td>Pb$_2$S$_2$</td>
<td>1140</td>
<td>-</td>
<td>67.5</td>
<td></td>
</tr>
</tbody>
</table>
Dissociation energies of both SnS and PbS molecules were derived from the thermodynamic cycle:

\[ \Delta H_{298}^{\circ} \text{(kcal/mole)} \]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Sn</th>
<th>Pb</th>
<th>Ref.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeS(g) ( \rightarrow ) MeS(a)</td>
<td>-52.6±1.6</td>
<td>-55.7±1.6</td>
<td>this work</td>
<td>this work</td>
</tr>
<tr>
<td>MeS(a) ( \rightarrow ) Me(a)+S(a)</td>
<td>+25.1±1.2</td>
<td>+22.5±0.5</td>
<td>40</td>
<td>41</td>
</tr>
<tr>
<td>Me(a) ( \rightarrow ) Me(g)</td>
<td>+72.0±0.6</td>
<td>+46.8±0.6</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>S(a) ( \rightarrow ) 1/2 S(_2)(g)</td>
<td>+15.4±1.5</td>
<td>+15.4±1.5</td>
<td>39</td>
<td>39</td>
</tr>
<tr>
<td>1/2 S(_2)(g) ( \rightarrow ) S(g)</td>
<td>+51.0±1.5</td>
<td>+51.0±1.5</td>
<td>39,42</td>
<td>39,42</td>
</tr>
<tr>
<td>MeS(g) ( \rightarrow ) Me(g)+S(g)</td>
<td>+110.9±3.0</td>
<td>+80.0±2.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In experiments with PbS, carried out with low energy electrons, either Pb, S\(_2\) or both Pb and S\(_2\) partial pressures were measured in addition to the PbS pressure. The measurements, summarized in Table III, made it possible to calculate directly the enthalpy change for the reaction

\[ \text{PbS} \rightarrow \text{Pb(g)} + 1/2 \text{S}_2(g) \]

from the corresponding equilibrium constant. In those experiments where only Pb pressures were measured, the S\(_2\) pressure (and vice versa) was deduced from the known fact that the sublimation is
stoichiometric and hence that

\[
\frac{Z(\text{Pb})}{Z(S_2)} = 2 = \frac{P(\text{Pb})}{P(S_2)} \left[ \frac{64.14}{207.21} \right]^{1/2}
\]

where \( Z \) = number of atoms or molecules effusing per unit time.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>( T^\circ \text{K} )</th>
<th>( \log P(\text{PbS}) \text{atm} )</th>
<th>( \log P(\text{Pb}) \text{atm} )</th>
<th>( \log P(S_2) \text{atm} )</th>
<th>( D^0_{298}(\text{PbS}) \text{kcal/mole} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.14</td>
<td>1002</td>
<td>-4.15</td>
<td>-</td>
<td>-5.98</td>
<td>79.6</td>
</tr>
<tr>
<td>63.14</td>
<td>1050</td>
<td>-3.60</td>
<td>-</td>
<td>-5.35</td>
<td>79.4</td>
</tr>
<tr>
<td>63.15</td>
<td>990</td>
<td>-4.30</td>
<td>-</td>
<td>-6.18</td>
<td>80.1</td>
</tr>
<tr>
<td>63.15</td>
<td>1040</td>
<td>-3.75</td>
<td>-</td>
<td>-5.54</td>
<td>79.6</td>
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<tr>
<td>63.18</td>
<td>1043</td>
<td>-3.70</td>
<td>-</td>
<td>-5.69</td>
<td>81.0</td>
</tr>
<tr>
<td>63.22</td>
<td>1007</td>
<td>-4.10</td>
<td>-5.20</td>
<td>-</td>
<td>78.6</td>
</tr>
<tr>
<td>63.22</td>
<td>1050</td>
<td>-3.62</td>
<td>-4.71</td>
<td>-</td>
<td>78.6</td>
</tr>
<tr>
<td>63.27</td>
<td>979</td>
<td>-4.45</td>
<td>-5.85</td>
<td>-</td>
<td>80.7</td>
</tr>
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<td>1118</td>
<td>-3.00</td>
<td>-4.12</td>
<td>-</td>
<td>79.2</td>
</tr>
<tr>
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<td>-5.00</td>
<td>-5.74</td>
<td>79.8</td>
</tr>
<tr>
<td>63.27</td>
<td>1062</td>
<td>-3.50</td>
<td>-4.69</td>
<td>-5.36</td>
<td>79.0</td>
</tr>
<tr>
<td>63.27</td>
<td>1012</td>
<td>-4.02</td>
<td>-5.32</td>
<td>-6.05</td>
<td>80.4</td>
</tr>
<tr>
<td>63.27</td>
<td>1182</td>
<td>-2.60</td>
<td>-3.79</td>
<td>-4.72</td>
<td>81.4</td>
</tr>
</tbody>
</table>

Average \( D^0_{298} = 79.8 \pm 2.6 \)

Average \( D^0 = 78.9 \pm 2.6 \)
The agreement between the dissociation energy $D_{298}^0$ of the PbS molecule obtained from the above thermodynamic cycle and from the partial pressure given in Table III is a verification of the sum of the heat of formation of PbS(s) and the heats of sublimation of gaseous Pb and $S_2$.

The dimerization energies of SnS and PbS calculated from the selected average of the sublimation enthalpies of SnS and $Sn_2S_2$ and PbS and $Pb_2S_2$ given in Table II are

$$Sn_2S_2(g) \rightarrow 2SnS(g) \quad \Delta H_{298}^0 = 48.7 \pm 5 \text{ kcal/mole}$$

$$Pb_2S_2(g) \rightarrow 2PbS(g) \quad \Delta H_{298}^0 = 44.8 \pm 5$$

Finally, the dissociation enthalpy of the SnPbS$_2$ molecule given in Table IV, was obtained from the reaction

$$2SnPbS_2(g) \rightarrow Sn_2S_2(g) + Pb_2S_2(g)$$

for which no pressure calibration is required and for which it was assumed that relative ionization cross sections and multiplier efficiencies compensate one another.
TABLE IV. Dissociation Enthalpy of the SnPbS$_2$ Molecule.

SnPbS$_2$ $\rightarrow$ SnS + PbS

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T$^\circ$K</th>
<th>Relative Intensities (arbitrary units)</th>
<th>$\Delta H^0_{298}$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sn$_2$S$_2$   Pb$_2$S$_2$   SnPbS$_2$</td>
<td></td>
</tr>
<tr>
<td>63.25</td>
<td>1200</td>
<td>2380           100           1710</td>
<td>48.2</td>
</tr>
<tr>
<td>63.26</td>
<td>1062</td>
<td>3920           134           1050</td>
<td>46.2</td>
</tr>
<tr>
<td></td>
<td>1090</td>
<td>4020           182           1135</td>
<td>46.6</td>
</tr>
<tr>
<td>63.28</td>
<td>1115</td>
<td>947            254           614</td>
<td>45.8</td>
</tr>
<tr>
<td>1043</td>
<td>150</td>
<td>1910           643</td>
<td>45.7</td>
</tr>
<tr>
<td>1079</td>
<td>6060</td>
<td>1280           178           790</td>
<td>46.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>401           2630</td>
<td>46.4</td>
</tr>
</tbody>
</table>

Average 46.5$^{\pm}$5.0
DISCUSSION.

In a study of the absorption spectrum of the SnS molecule, Barrow, Drummond and Rowlinson\(^{16}\) derived the dissociation energy \(D_0^\neq\) of the ground state both from a repulsive state at about 56.000 cm\(^{-1}\) and from the extrapolated convergence limit at 40.850 cm\(^{-1}\) of the excited E state. Considering the only likely products forming the repulsive state to be Sn\(^{1D_2}\)+S\(^{1D_2}\), the same authors obtained \(D_0^\neq \approx 56.100 - 17.853 = 38.247\) cm\(^{-1}\) or 109.4 kcal/mole. By analogy with the molecule SnO the above authors assumed the limit for the E state to correspond to dissociation into Sn\(^{3P}\) and S\(^{3P}\), and obtained \(D_0^\neq = 111 \pm 6\) kcal/mole, the uncertainty being the spread of the \(^3P\) sublevels of Sn and S, since it could not be decided which sublevels were involved.

These values may now be compared with the value obtained here, \(D_0^0 = 110.1 \pm 3.0\) kcal/mole. If evaluated correctly, the experimental errors are such that the \(^3P_0\) and \(^3P_2\) sublevels of Sn can be excluded, since these lead to the value 116.8, 115.5 and 115.1 and 107.0, 105.8 and 105.3 kcal/mole for the \(^3P_0\), \(^3P_1\) and \(^3P_2\) sublevels of S respectively. The \(^3P_1\) sublevel of Sn leads to the values 111.9, 110.8 and 110.3 for the same sublevels of S. The E state of SnS would thus dissociate into Sn\(^{3P_1}\) + S\(^{3P}\). Which \(^3P\) sublevel of S is involved...
can not be decided, although the best agreement between the two spectroscopic values derived from the repulsive state, the convergence limit of the E state and the thermochemical value might favor the \( S(3P_0) \) sublevel. This agreement might be used to suggest a selected dissociation energy \( D_0^o(SnS) = 110.3 \pm 1.6 \) kcal/mole.

The dissociation energy of the gaseous PbS molecule determined here is in agreement with the value obtained by Brewer\(^{(21)}\) from the cycle given above, using a value of 60.2 kcal/mole for the heat of sublimation derived\(^{(43)}\) from the measurements of Schenck and Albers\(^{(6)}\).

In an analysis of the vibrational spectrum of the PbS molecule, Vago and Barrow\(^{(20)}\) obtained a convergence limit for an excited state of this molecule at about 4.55 ev or 104.9 kcal/mole. By analogy with \( PbO(44) \) the corresponding level can presumably be correlated\(^{(45)}\) with the elements in their \( 3P_1 \) state. Accordingly, if the corresponding excitation energies (i.e. 22.36 kcal/gram atom for \( Pb(3P_1) \) and 1.13 kcal/gram atom for \( S(3P_1) \)) are subtracted from the convergence limit, a dissociation energy \( D_0^o(PbS) \) of 81.4 kcal/mole is obtained. This value is in good agreement with the value \( D_0^o(PbS) = 79.1 \pm 2.8 \) kcal/mole obtained here. The agreement becomes even better if the above excited state would correlate with the \( 3P_0 \) sublevel of \( S \) in which case a spectroscopic value \( D_0^o(PbS) = 80.9 \) kcal/mole is obtained. This implies however that the excited \( E \) state of \( PbO \) and \( PbS \) do not correlate with the
same $^3P$ sublevels of Oxygen and Sulfur respectively. It may be noted that for the E states of SnO and SnS the correlation with the $^3P$ sublevels of Tin is probably also not the same. The thermochemical values for the dissociation energy of SnO, derived one by Brewer and Mastick (46) from an analysis of data of Ves- selowski (47) but slightly modified using more recent values for the heat of sublimation of Tin (39) and the other obtained by Platteeuw and Meyer (49) are in very good agreement with the spec- troscopic value $D_0^n = 130.9$ kcal/mole (48) equal to the dissociation limit of the E state. This agreement would imply the E state of SnO to correlate with the $^3P_0$ sublevel of Tin, while the E state of SnS probably correlates with the $^3P_1$ sublevel of Tin.

It may be noted that the agreement between the thermochem- ical and spectroscopic dissociation energies of both SnS and PbS constitutes another confirmation of the value $D_0^0 = 102$ kcal/mole for the dissociation energy of $S_2$ molecule, since this value has been used in deriving the thermochemical data.

For the dimeric molecules Sn$_2$S$_2$, and Pb$_2$S$_2$ it is interest- ing to notice that the enthalpy for dissociation into SnS and PbS diatomic molecules is roughly the same while that for SnPbS is the average of the two. Speculations about the structure of these dimeric molecules on this basis and the fact that there is no direct relation between the dimerization energies and the dissociation energies of the homonuclear metallic molecules (22) tend to favour a closed rather than a linear structure. Support
to this conclusion is that these molecules have the same outer electronic structure as $P_4$, $As_4$ and $Sb_4$ which molecules should have either a tetrahedral or a plane square structure. Of these molecules, $P_4$ is indeed known to be tetrahedral$^{(50)}$. 
LIST OF REFERENCES


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1. Tin sulfide
2. Lead sulfide
3. Reaction enthalpies
   I. AFSC Project 7350
      Task 735001
   II. Contract AF 61(052) -225
   III. University of Brussels, Brussels Belgium.
IV. Reginald Colin
    John Drowart
V. Avel fr OTS
VI. In ASIA collection

Unclassified report

Reaction enthalpies, $\Delta H^\circ_{298}$, in kcal/mole, determined were SnS(s) $\rightarrow$ SnS(g):
$52.6 \pm 1.6$ kcal/mole;
2 SnS(s) $\rightarrow$ SnS$_2$(g); $56.5 \pm 5.0$;
PbS(s) $\rightarrow$ PbS(g); $55.7 \pm 1.6$;

(over)

2 PbS(s) $\rightarrow$ Pb$_2$S$_2$(g); $66.6 \pm 5.0$
SnPbS$_2$(g) $\rightarrow$ SnS(g) + PbS(g); $46.5 \pm 5.0$;
PbS(g) $\rightarrow$ Pb(g) + 1/2 S$_2$(g); $28.8 \pm 2.6$

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$52.6 \pm 1.6$ kcal/mole;
2 SnS(a) $\rightarrow$ SnS(g): $56.5 \pm 5.0$;

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SnPbS$_2$(g) $\rightarrow$ SnS(g) + PbS(g): $46.5 \pm 5.0$;
PbS(g) $\rightarrow$ Pb(g) + 1/2 S$_2$(g): $26.8 \pm 2.6$
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2 PbS($s$) $\rightarrow$ PbS$_2$(g): $66.6 \pm 5.0$
SnPbS$_2$(g) $\rightarrow$ SnS($g$) + PbS($g$): $46.5 \pm 5.0$;
PbS($g$) $\rightarrow$ Pb($g$) + 1/2 S$_2$(g): $28.8 \pm 2.6$