FOREWORD

ABSTRACT

Reaction enthalpies, ΔH°_{298}, in kcal/mole, determined were

$SnS(s) \longrightarrow SnS(g)$: 52.6 ± 1.6 kcal/mole;

2 $SnS(s) \longrightarrow Sn_2S_2(g)$: 56.5 ± 5.0;

$PbS(s) \longrightarrow PbS(g)$: 55.7 ± 1.6;

2 $PbS(s) \longrightarrow Pb_2S_2(g)$: 66.6 ± 5.0;

$SnPbS_2(g) \longrightarrow SnS(g) + PbS(g)$: 46.5 ± 5.0;

$PbS(g) \longrightarrow Pb(g) + 1/2\ S_2(g)$: 28.8 ± 2.6.
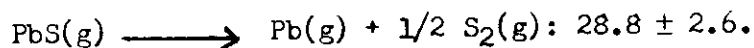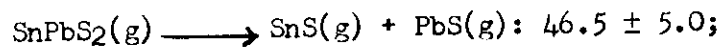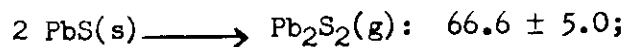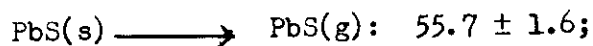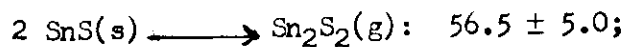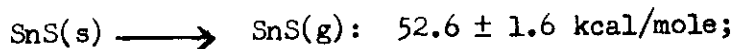
PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
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iii

TABLE OF CONTENTS

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 $D_o^o(SnS)=111 \pm 6$ kcal/mole was determined spectroscopically by Barrow, Drummond and Rowlinson. The latter authors suggested that a supposed predissociation[11,12] leading to a lower value, $D_o^o(SnS) \leqslant 68.5$ 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 $^1\Sigma$ state[18,19], a convergence limit was

1

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 $8 \times 10^{-3} cm^2$ 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.

2

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[26] of SnO by H_2S 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 8×10^{-2}/ 8.2×10^{-2}/1/3.6×10^{-3}/6.7×10^{-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].

3

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 po-
tential 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^+, Sn_2^+, Sn_2S^+ and
$Sn_2S_2^+$. These appearance potentials as well as the relative inten-
sities of the ions indicate that SnS^+ and $Sn_2S_2^+$ are parent ions,
while Sn^+, Sn_2^+ and Sn_2S^+ are fragment ions. Possible trimer Sn_3S_3
and tetramer Sn_4S_4 molecules, whose intensity relative to SnS was
equal or smaller than 5×10^{-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^+, S_2^+, Pb^+, PbS^+ and $Pb_2S_2^+$. 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 ap-
pearance 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

4

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 $(I(Pb_2S_2^+)/I(PbS^+) \approx 6 \times 10^{-3})$ 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 $4;1 \pm 0.7$ 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

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

where P = partial pressure, in atm; I = ion intensity in arbitrary units; σ = relative cross section at the maximum of the ionization efficency curve; A = appearance potential in ev; E = energy of the ionizing electrons, in ev; γ = 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

6

TABLE I. <u>Relative Ionization Cross Sections and Multiplier</u>
<u>Efficiencies.</u>

Molecule	Cross section	Multiplier Efficiency
S_2	21	1.14
SnS	44	0.65
Sn_2S_2	70	0.50
Pb	31	0.45
PbS	35	0.45
Pb_2S_2	56	0.41

effects were taken into account as suggested by Stanton, Chupka and Inghram[37].

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

7

with the literature data, except for the measurements of Hsiao
and Schlechten, which also for other sulfides are systemati-
cally 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_2S_2 and Pb_2S_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_2S_2 and Pb_2S_2 compensates
for an increase in the vibration frequencies. The entropy of
SnS-PbS was taken as the average of the preceding ones, cor-
rected 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 mo-
lecules are known from spectroscopic data[10,20]. In the case
of Sn_2S_2 and Pb_2S_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.

8

TABLE II. <u>Enthalpies of Sublimation</u>. ΔH^0_{298}

Experiment	Molecule	Temperature range	2d Law	3d Law	Best average
63.02	SnS	835-1005	$50.1^{+}_{-}3.0$	$52.4^{+}_{-}1.6$	
63.03		840-965	52.5	53.3	$52.6^{+}_{-}1.6$
63.04		815-970	52.1	52.0	
63.02	Sn_2S_2	835-1005	$56.4^{+}_{-}5.0$	$57.3^{+}_{-}5.0$	
63.03		885-965	57.0	58.2	$56.5^{+}_{-}5.0$
63.04		815-970	53.0	57.1	
63.13	PbS	985-1080	$52.5^{+}_{-}4.0$	$56.9^{+}_{-}1.6$	
63.14		915-1080	49.7	55.1	$55.7^{+}_{-}1.6$
63.15		865-1090	-	55.0	
63.18		995-1100	55.5	55.7	
63.18	Pb_2S_2	995-1100	$64.5^{+}_{-}5.0$	$67.8^{+}_{-}5.0$	
63.22		1129	-	66.7	$66.6^{+}_{-}5.0$
63.27		1140	-	67.5	

9

Dissociation energies of both SnS and PbS molecules were derived from the thermodynamic cycle:

$$\Delta H^o_{298} (\text{kcal/mole})$$

			Sn	Ref.	Pb	Ref.
MeS(g)	$\longrightarrow$	MeS(s)	-52.6 ± 1.6	this work	-55.7 ± 1.6	this work
MeS(s)	$\longrightarrow$	Me(s)+S(s)	$+25.1 \pm 1.2$	40	$+22.5 \pm 0.5$	41
Me(s)	$\longrightarrow$	Me(g)	$+72.0 \pm 0.6$	39	$+46.8 \pm 0.6$	39
S(s)	$\longrightarrow$	$1/2\ S_2(g)$	$+15.4 \pm 1.5$	39	$+15.4 \pm 1.5$	
$1/2\ S_2(g)$	$\longrightarrow$	S(g)	$+51.0 \pm 1.5$	39,42	$+51.0 \pm 1.5$	
MeS(g)	$\longrightarrow$	Me(g)+S(g)	$+110.9 \pm 3.0$		$+80.0 \pm 2.8$	

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

$$PbS \longrightarrow Pb(g) + 1/2\ S_2(g)$$
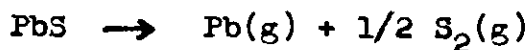
from the corresponding equilibrium constant. In those experiments where only Pb pressures were measured, the S_2 pressure (and vice versa) was deduced from the known fact that the sublimation is

10

stoichiometric and hence that

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

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

TABLE III. <u>Dissociation Enthalpy of the PbS Molecule.</u>

Experiment	T°K	log P(PbS)atm	log P(Pb)atm	log P(S_2)atm	D^0_{298}(PbS)kcal/mole
63.14	1002	-4.15	-	-5.98	79.6
63.14	1050	-3.60	-	-5.35	79.4
63.15	990	-4.30	-	-6.18	80.1
63.15	1040	-3.75	-	-5.54	79.6
63.18	1043	-3.70	-	-5.69	81.0
63.22	1007	-4.10	-5.20	-	78.6
63.22	1050	-3.62	-4.71	-	78.6
63.27	979	-4.45	-5.85	-	80.7
63.27	1118	-3.00	-4.12	-	79.2
63.27	1034	-3.80	-5.00	-5.74	79.8
63.27	1062	-3.50	-4.69	-5.36	79.0
63.27	1012	-4.02	-5.32	-6.05	80.4
63.27	1182	-2.60	-3.79	-4.72	81.4

$$\text{Average } D^0_{298} = 79.8 \pm 2.6$$
$$D^0_0 = 78.9 \pm 2.6$$

11

The agreement between the dissociation energy D_{298}^o 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

$$Sn_2S_2(g) \longrightarrow 2SnS(g) \qquad \Delta H_{298}^o = 48.7 \pm 5 \text{ kcal/mole}$$
$$Pb_2S_2(g) \longrightarrow 2PbS(g) \qquad \Delta H_{298}^o = 44.8 \pm 5$$
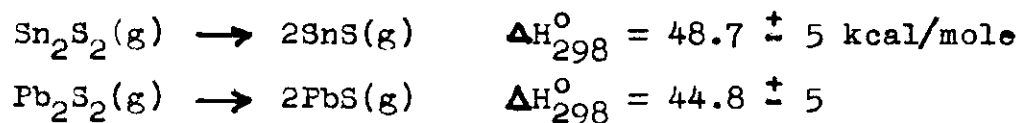
Finally, the dissociation enthalpy of the $SnPbS_2$ molecule given in Table IV, was obtained from the reaction

$$2SnPbS_2(g) \longrightarrow Sn_2S_2(g) + Pb_2S_2(g)$$
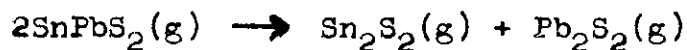
for which no pressure calibration is required and for which it was assumed that relative ionization cross sections and multiplier efficiencies compensate one another.

12

TABLE IV. Dissociation Enthalpy of the $SnPbS_2$ Molecule.

$$SnPbS_2 \longrightarrow SnS + PbS$$

Experiment	T°K	Relative Intensities (arbitrary units)			ΔH^O_{298} kcal/mole
		Sn_2S_2	Pb_2S_2	$SnPbS_2$	
63.25	1200	2380	100	1710	48.2
63.26	1062	3920	134	1050	46.2
	1090	4020	182	1135	46.6
	1098	947	254	614	45.8
	1115	150	1910	643	45.7
63.28	1043	1280	178	790	46.5
	1079	6060	401	2630	46.4

Average 46.5 ± 5.0

13

DISCUSSION.

In a study of the absorption spectrum of the SnS molecule, Barrow, Drummond and Rowlinson[16] derived the dissociation energy D_0'' 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 $D_0'' \approx 56.100 - 17.853 = 38.247$ 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 $D_0'' = 111 \pm 6$ 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

14

can not be decided, altough the best agreement between the two
spectroscopic values derived from the repulsive state, the con-
vergence limit of the E state and the thermochemical value might
favor the $S(^3P_0)$ sublevel. This agreement might be used to sug-
gest a selected dissociation energy $D_0^0(SnS) = 110.3 \pm 1.6$ 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 $D_0^0(PbS)$ of 81.4 kcal/mole is
obtained. This value is in good agreement with the value
$D_0^0(PbS) = 79.1 \pm 2.8$ 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
$D_0''(PbS) = 80.9$ kcal/mole is obtained. This implies however that
the excited E state of PbO and PbS do not correlate with the

15

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 Vesselowskii[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 spectroscopic value $D_0'' = 130.9$ 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 thermochemical and spectroscopic dissociation energies of both SnS and PbS constitutes another confirmation of the value $D_{298}^o = 102$ 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_2S_2, and Pb_2S_2 it is interesting 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

16

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 theses molecules, P_4 is indeed known to be tetrahedral[50].

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