FOREWORD

ABSTRACT

Investigation of the saturated vapor above InS, In_2S_3 and

In_2S_3+In samples and of the superheated vapor has yielded

$In_2S(g)$ $2In(g)+1/2S_2(g)$ ΔH°_{298}=98.2±5.0 kcal/mole

$In_2S_2(g)$ $In_2S(g)+1/2S_2(g)$ ΔH°_{298}=26.5±6.0 "   "

$InS(g)$ $In(g)+1/2S_2(g)$ ΔH°_{298}=17.4±4.0 "   "
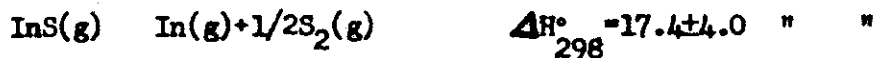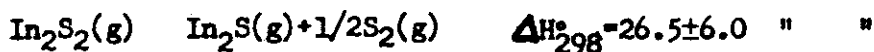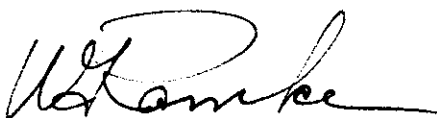
Combining these data with $D^\circ_{298}(S_2)$=102.0±2.0 kcal/mole one obtains:

ΔH°_{298}(at.In_2S)=149.2±5.5; D°_{298}(InS)=68.4±4.5;

ΔH°_{298}(at.In_2S_2)=226.7±8.0; D°_{298}(dim,InS)=89.9±11.0 kcal/mole.

This technical documentary report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Division
Air Force Materials Laboratory

INTRODUCTION

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

Indium oxide has been studied[1,11,11a] by mass spectrometric techniques and it has been shown **that in the gas phase above** $In_2O(s)$, In_2O and O_2 molecules and In atoms are the predominant species. A value of 119.6 ± 5.0 kcal/mole for the atomization energy of $In_2O(g)$ and an upper limit (most probably very close to the real value) for the dissociation energy of the InO molecules $D_0^0 \leqslant 75$ kcal/mole were obtained.

The indium-sulfur system has a complex phase diagram. Thermal, microscopic and **roentgenographic** studies[12,13] have shown the existence of several stoechiometric compounds: InS, In_4S_5 and In_2S_3. A thermal effect at 370°K was interpreted to indicate the decomposition of an unstable compound In_3S_4[12]. No evidence was found in the more recent study[12] for the existence of a compound In_2S previously assumed[14,15]. The free **energy** of formation has been measured by Thompson, Stubbs and Schufle[16] for In_2S_3, In_3S_4, InS and for an assumed compound

1

In_5S_6. Hahn and Burrow[17] have measured the enthalpy of formation of InS and In_2S_3. More recently, Spandau and Klanberg[18] have measured the vapor pressure above melts of InS+In and In_2S_3+4In. Assuming the vapor phase to be composed of gaseous In_2S molecules and using the enthalpies of formation **mentioned** above, the latter authors calculated for the atomization enthalpy of gaseous In_2S a value of $\Delta H_0^o(at, In_2S) = 162 \pm 12$ kcal/mole.

In this paper, a mass spectrometric investigation of the saturated vapor above InS, In_2S_3 and above a mixture of In_2S_3 and In and of superheated vapor is reported. The In-Se and In-Te systems have also been studied and will be the object of a forthcoming publication.

2

EXPERIMENTAL

The main features of the mass spectrometer and Knudsen effu-
sion cell have been described previously[19-21]

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

The superheated vapor was studied using 5cm long double
quartz cells placed inside a carbon oven surrounded by a thin
tantalum sheet (Fig.1). Each section of the double cell was heated
individually by radiation from a tungsten loop. When necessary
electron bombardment was applied. The upper section was always
maintained at a higher temperature than the lower one containing
the sample. A small quartz plug was placed in the bottle neck
connecting both sections as shown in Fig.1. Its main function
was to avoid vapor coming from the lower compartment to effuse

3

directly without impinging several times on the walls of the hotter section; it also aids in reading the temperature of the upper section by means of an optical pyrometer aiming the effusion hole.

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

The analysis of the In and S content gave for the InS sample 79.16% In and 19.53% S (calculated 78.16 and 21.84%) and for the In_2S_3 sample 74.34% In and 24.41% S (calculated 70.47 and 29.53%).
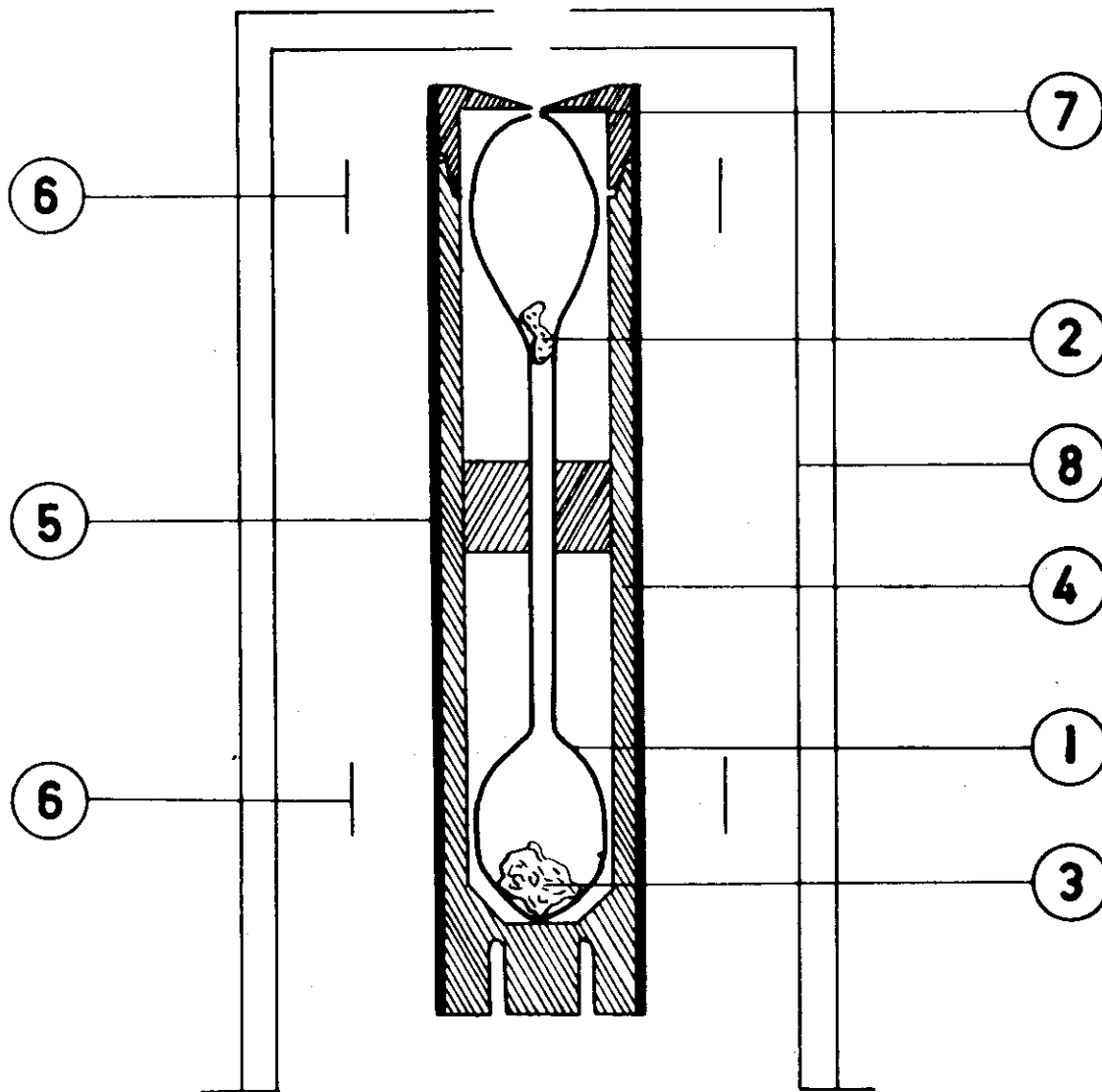
Fig.1: <u>Double cell:</u> ① quartz cell; ② quartz plug; ③ sample; ④ carbon crucible; ⑤ tantalum sheet; ⑥ tungsten loop; ⑦ effusion orifice; ⑧ radiation shields.

5

EXPERIMENTAL RESULTS

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

A. Composition of the vapor.

1. Single cell experiments.

The characteristic atomic and molecular ions observed were S$^+$, S$_2^+$, In$^+$, InS$^+$, In$_2^+$, In$_2$S$^+$, and In$_2$S$_2^+$. All of these ions were identified from their mass and isotopic distribution. The interception of the molecular beam[1] further showed these ions to be **formed from neutral species originating from the Knudsen cell. Ionization** efficiency curves were measured for each of these ions, except S$^+$, to define which molecules gave rise to their formation. For all the ions, except In$^+$ and InS$^+$, the ionization efficiency varied essentially linearly for several volts above the appearance potential. For In$^+$ and InS$^+$, it was the resultant of two essentially linear components. Approximate appearance potentials, assembled in Table I, were derived from these curves using the linear extrapolation method. The energy scale was first calibrated with the known appearance potentials of water[22] or mercury[23] to establish that In$^+$ was,

6

in the low energy part of its ionization efficiency curve, a
parent ion. The known ionization potential of In[23] was subse-
quently used as a reference for the other ions. The onsets of
the second process in the ionization curves of In^+ and InS^+ at
8.7±1.0 and 11.7±1.0 eV. respectively were attributed to the frag-
mentation of In_2S molecules. The appearance potential of S_2^+
measured here, 9.6 0.5 eV, is in agreement with a value obtained
previously[9] and confirmed in a recent study[24]. It shows the
presence of S_2 molecules in the vapor above the InS and In_2S_3
samples. The low appearance potentials of InS^+, In_2S^+ and $In_2S_2^+$
(7.0±0.5; 7.6±0.5 and 6.4±0.5 eV) indicate their formation from
the corresponding molecules by direct ionization. The high value
of the appearance potential of In_2^+, 10.8±1.0 eV, compared to
5.8±0.3 eV measured[25] for the approximate ionization potential,
shows this ion to be formed by fragmentation of the In_2S molecules.
It was finally concluded from thermodynamic considerations that
S^+ had to be a fragment ion.

The saturated vapor above InS and In_2S_3 is thus mainly
composed of In_2S and S_2 molecules with small amounts of In atoms,
InS and In_2S_2 molecules.

During the experiments with InS and In_2S_3 samples, the
S_2^+/In_2S^+ ratio did however not remain constant with temperature
nor time, thus indicating a variation in composition of the con-
densed phase. Values of this ratio varying from 10^{-3} to 2 were

7

observed. Temperatures where a variation of this ratio was oberved could be correlated with the known decomposition temperatures of the **various** indium-sulfur compounds[12]. Other ion intensity ratios for nominal 35 eV electrons are given in Table I.

The vapor in equilibrium with the mixture In_2S_3+12In contained only In_2S molecules with small concentrations of atomic indium; no S_2 molecules could be detected.

2. Double cell experiments.

When the double cell was used, the composition of the vapor could be varied gradually by increasing the temperature of the upper section, thus provoking dissociation of the molecules. The composition could be varied from **one** similar to that observed in the single cell experiments to one where mainly S_2 molecules and In atoms with small concentrations of InS and In_2S molecules were present. Maximum relative intensities obtained in the double cell **experiments** are also given in Table I. On superheating the vapor, the InS molecule became slightly more abundant relative to the In_2S molecule, whereas the concentration of the In_2S_2 molecule fell below the detection limit of the instrument. The In_2^+/In_2S^+ ratio had a constant value in both type of experiments, which is what one would expect for a fragment ion.

TABLE I. Appearance Potentials and Relative Intensities

		S_2^+	In^+	InS^+	In_2^+	In_2S^+	$In_2S_2^+$
Appearance potential (in eV.)	Parent ion	9.6 ± 0.5	5.8 ± 0.5	7.0 ± 0.5	-	7.6 ± 0.5	6.4 ± 0.5
	Fragment ion	-	8.7 ± 1.0	11.7 ± 0.5	10.8 ± 0.5	-	-
Relative Intensity (for 35 eV).	Single cell	see	2.10^{-1}	2.10^{-2}	9.10^{-2}	1	10^{-3}
	Double cell	texte	11	9.10^{-2}	9.10^{-2}	1	$<10^{-4}$

B. Pressure Determination

The partial pressure P_A of a neutral species A present in the evaporation cell is given by the relation [20]

$$k(\sigma\gamma)_A P_A = I_A T \qquad (1)$$

(I_A = ion intensity; T= absolute temperature; σ = ionization cross section; γ = secondary electron multiplier efficiency; k = geometric constant of the instrument). To derive absolute values of the pressures in both types of cells, the samples (either InS and In_2S_3) were weighted and vaporized completely[1], the ion intensities of the major species being integrated with time. The $k(\sigma\gamma)_A$ values for the major species were then readily obtained from the Hertz-Knudsen equation

$$G_A = P_A s \left[\frac{M_A}{2\pi RT} \right]^{1/2} \Delta t \qquad (2)$$

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

$$k(\sigma\gamma)_A = \frac{s}{G} \left(\frac{M_A}{2\pi R} \right)^{1/2} \Sigma I_A T^{1/2} \Delta t \left\{ 1 + \frac{(\sigma\gamma)_A}{(\sigma\gamma)_B} \frac{(M_B)^{1/2}}{(M_A)^{1/2}} \frac{\Sigma I_B T^{1/2} \Delta t}{\Sigma I_A T^{1/2} \Delta t} + \ldots \right\}$$

10

These integrations also yield a value of the ratio of the product of ionization cross section and multiplier efficiency for the major species; a constant value of $(\sigma\gamma)_{S_2}/(\sigma\gamma)_{In_2S} = 2.5\pm0.3$ both for 35 and 70 eV electrons was obtained in the single cell experiments.
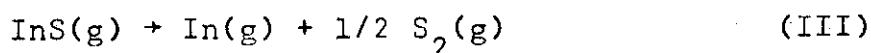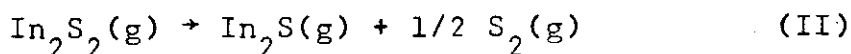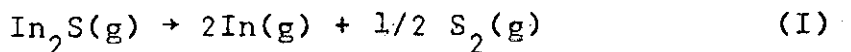
In order to obtain absolute pressures for the double cell experiments, where depending on the temperature of the upper section of the cell the major species were either In_2S and S_2 or In and S_2, as well as **to obtain the relative partial pressure of the minor** species in both types of experiments, the ionization cross sections and multiplier efficiencies in Table II were necessary. Ionization cross sections were estimated from Otvos and Stevenson's data[26], assuming by analogy with a number of dimeric molecules[27-30] that the ratio $\sigma_{X_2}/\sigma_X = 1.6$. Multiplier efficiencies were taken from a calibration curve[31] of a multiplier analogous to the one used here and which is similar to a curve given by Inghram, Hayden and Hess[32]. Molecular effects were taken into account as suggested by Stanton, Chupka and Inghram[33]. Whenever, in order to avoid fragmentation, the ion intensities of the minor species were measured at a low electron energy, the following relation was applied:

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

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

11

C. Gaseous Equilibria.

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

$$In_2S(g) \rightarrow 2In(g) + 1/2\ S_2(g) \qquad \text{(I)}$$

$$In_2S_2(g) \rightarrow In_2S(g) + 1/2\ S_2(g) \qquad \text{(II)}$$

$$InS(g) \rightarrow In(g) + 1/2\ S_2(g) \qquad \text{(III)}$$

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

$$\Delta G_T^o = -RT\ln K = -RT\ln \prod_i P_i^{\nu_i} = \Delta H_{298}^o - T\Delta\left\{-\left(\frac{G_T^o - H_{298}^o}{T}\right)\right\}$$

($\Delta G_T^o =$ free energy change; $R =$ gas constant; $K =$ equilibrium constant; $P_i =$ partial pressure; $\nu_i =$ stoechiometric coefficient; $\Delta H_{298}^o =$ enthalpy change at $298°K$; $-\left(\dfrac{G_T^o - H_{298}^o}{T}\right) =$ free energy function) were used, together with the known dissociation energy of the S_2 molecule $D_{298}^o = 102 \pm 20$ kcal/mole[5,34,35] to obtain the following thermochemical data.

1) the atomization energy of gaseous In_2S: $\Delta H_{298}^o(at, In_2S)$

2) the dissociation energy of gaseous InS: $D_{298}^o(InS)$

3) the atomization energy of gaseous In_2S_2: $\Delta H_{298}^o(at, In_2S_2)$

4) the dimerization energy of gaseous InS: $\Delta H_{298}^o(dim, InS)$

12

TABLE II. Ionization Cross Sections and Multiplier
Efficiencies

Species	Cross section	Multiplier Efficiency
In	24.8	0.58
S_2	20.5	0.91
InS	30.0	0.42
In_2S	20.0	0.38
In_2S_2	48.0	0.38

The free energy functions for gaseous In and S_2 were taken from Stull and Sinke's compilations[36]. Those for InS, In_2S and In_2S_2 were estimated. For InS, the free energy function was calculated assuming an internuclear distance of 2.5 Å. The vibration frequency ω was estimated at 420 cm^{-1} from the empirical realtion $\omega(M-O)/\omega(M-S) = 1.68 \pm 0.10$ which holds for M=C, Si, Ge, Pb and Al[37,39]. The value of $\omega(In-O) = 703.08$ cm^{-1} was taken from the spectroscopic data of Watson and Shambon[38]. By analogy with gaseous AlO and AlS[39] the ground state of InS was assumed to be $^2\Sigma$. The In_2S molecule (as previously Al_2O[42] and In_2O[11]) was assumed to have a In-S-In bent structure with a bond angle of 100° by analogy with H_2S, SO_2, $(CH_2)_2S$ and SCl_2[40]. The translational and rotational entropy and free energy function were readily obtained from statistical mechanical formulae[40] The frequencies of the three normal vibrations were calculated to be $\omega_1 = 535$ cm^{-1}, $\omega_2 = 500$ cm^{-1} and $\omega_3 = 133$ cm^{-1} by assuming the stretching force constant k_1 of the In-S bond to be identical to the one in the InS molecule; the bending force constant k_δ was estimated on the basis that $\dfrac{k_\delta}{1^2 k_1} = 0.094$ which holds for SO_2 and H_2S[40] (1 = internuclear distance) It is difficult to estimate the electronic contribution to the free energy function for this molecule. There are no spectroscopic data available for any triatomic molecule of this type in the III_B-VI group. Moreover In_2S being a heavy molecule little can be predicted for the configuration and relative positions of the

ground and excited electronic states. Due to the lack of data
it was assumed that the ground state was a singlet. Although
there is some spectroscopic evidence[41,45] for a linear
structure of the B_2O_2 molecule it is difficult to say whether
this structure is maintained when both B and O are replaced
by heavier atoms of the same groups. In any case, the free
energy function is not very sensitive to a change of struc-
ture as was shown for Al_2O_2[42]. The free energy function of
In_2S_2 was taken identical to that of As_4[36], a tetratomic
molecule of approximately the same mass, the uncertainty
being estimated at ± 5 cal/mole/°. The different free energy
functions used are summarized in Table III.

Table IV gives the enthalpy change for reaction (I). The
average value $\Delta H^o_{298}(I) = 98.2 \pm 4.0$ kcal/mole combined with
$D^o_{298}(S_2) = 102.0 \pm 2.0$ kcal/mole yields a value for the atomi-
zation energy of In_2S of:

$$\Delta H^o_{298}(at.In_2S) = 149.2 \pm 5.5 \text{ kcal/mole}$$

Table V gives the enthalpy change for reaction (II).
The average value $\Delta H^o_{298}(II) = 26.5 \pm 6.0$ kcal/mole combined
with $D^o_{298}(S_2)$ leads to $\Delta H^o_{298}(at.In_2S_2) = 226.7 \pm 8.0$ kcal/mole.

Table VI gives the enthalpy change for reaction(III).
The average value $\Delta H^o_{298}(III) = 17.4 \pm 4.0$ kcal/mole combined
with $D^o_{298}(S_2)$ leads to $D^o_{298}(InS) = 68.4 \pm 4.5$ kcal/mole.

Finally, using the above data one may calculate the dime-
rization energy of InS: $\Delta H^o_{298}(dim.InS) = 89.9 \pm 11.0$ kcal/mole.

15

TABLE III. Free Energy Function $-(G_T - H_{298})/T$

(in cal/mole/°)

T°K Specie	800	1000	1200	1400	1600
In[37]	43.4	44.2	45.0	45.7	46.3
S_2[37]	57.5	58.7	59.9	60.9	61.8
InS	62.8	64.3	65.4	66.4	67.5
In_2S	79.7	81.6	83.3	84.9	86.7
In_2S_2	81.9	84.8	87.4	89.6	91.8

16

TABLE IV. Enthalpy Change ΔH^{o}_{298} for the reaction

$$In_2S(g) \rightarrow 2In(g) + 1/2S_2(g)$$
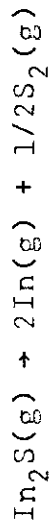
Experiment n°	Sample	Cell	T°K	$-\log p(In)$ (atm)	$-\log p(S_2)$ (atm)	$-\log p(In_2S)$ (atm)	ΔH^{o}_{298} kcal/mole
6503 A	In_2S_3	Double cell	1390	5.01	5.19	5.00	99.9
6503 B	In_2S_3	Double cell	1297	5.74	6.20	6.14	98.1
			1396	4.96	5.49	5.48	97.5
			1412	4.84	5.31	5.35	97.4
			1437	4.69	4.90	5.25	96.3
			1506	4.57	4.46	5.37	97.0
			1492	4.60	4.61	5.38	97.1
			1527	4.56	4.74	5.37	99.3
			1502	4.54	4.82	5.40	97.5
			1532	4.50	4.83	5.36	99.2
			1537	4.52	5.03	5.37	100.5
							98.2

17

TABLE V. Enthalpy Change ΔH^o_{298} for the Reaction

$$In_2S_2(g) \rightarrow In_2S(g) + 1/2S_2(g)$$

Experiment N°	Sample	Cell	T°K	$-\log p(In_2S)$ (atm)	$-\log p(S_2)$ (atm)	$-\log p(In_2S_2)$ (atm)	ΔH^o_{298} kcal/mole
6305	InS	Single cell	1170	4.27	4.34	7.36	25.6
			1208	4.88	4.20	6.56	28.2
			1226	3.78	4.10	6.57	27.7
6329	In_2S_3	Single cell	1185	4.10	4.09	6.85	27.0
			1117	4.25	4.97	7.37	25.9
			1149	4.08	4.25	7.05	25.5
			1218	3.55	4.06	6.53	26.4
			1119	4.25	4.97	7.38	25.8
			1180	3.72	4.32	6.82	25.6
			1201	3.59	4.15	6.65	25.9
6332	InS	Single cell	1141	3.82	5.62	7.38	25.8
			1205	3.72	5.26	6.88	28.4
6503$_B$	In_2S_3	Double cell	1206	3.93	4.61	7.07	26.8
			1206	3.81	4.47	6.96	26.4
							$\overline{26.5}$

TABLE VI. Enthalpy Change ΔH^o_{298} for the Reaction

$$InS(g) \rightarrow In(g) + 1/2S_2(g)$$

Exper. N°	Samples	Cell	T°K	$-\log p(In)$ (atm)	$-\log p(S_2)$ (atm)	$-\log p(InS)$ (atm)	ΔH^o_{298} kcal/mole
6332	InS	Single cell	1203	4.79	4.26	5.77	17.9
			1203	4.99	4.26	6.01	17.7
			1173	5.03	4.90	6.20	18.1
			1213	4.93	5.34	6.27	18.8
6503B	In$_2$S$_3$	Double cell	1437	4.69	4.90	6.76	16.4
			1506	4.57	4.46	6.70	15.5
							$\overline{17.4}$

## DISCUSSION

The heat of atomization of In_2S, $\Delta H^o_{298}(at.In_2S) = 150 \pm 5.2$ kcal/mole obtained in this work using the third law can be compared with the value obtained by Spandau and Klanberg[18] using the second law, $\Delta H^o(at.In_2S) = 162 \pm 12$ kcal/mole. The present investigation showed the total pressure to be practically entirely due to In_2S molecules as concluded by Spandau and Klanberg. The latter authors seem however to have assumed that the heat of mixing of liquid $InS + In$ or $In_2S + 4In$ compensated the difference between the evaporation enthalpy at 298^oK and at the mean temperature of their measurements (1360^oK). When estimating the heat capacity of liquid InS and In_2S by using approximation formulae[43] and then calculating the change in heat content $H^o_{1960} - H^o_{298}$ for the evaporation reaction one finds 12.6 kcal/mole. It would seem improbable that the heat of mixing has such a high value; it is probably 0 ± 2 kcal/mole. The value $\Delta H^o_{298}(at.In_2S)$ deduced from Spandau and Klanberg's measurements is then reduced to 150 kcal/mole in agreement with the result obtained here.

Little can be said concerning the molecular structure of In_2S_2. The high value of the dimerization energy (89.9 ± 12 kcal/mole) compared to the value of the S-S bond of approximately 70 kcal/mole[44] and to the In-In bond such as in In_2[25] (22.4 ± 2.5 kcal/mole) would suggest, as in the case of Al_2O_2[42], a closed structure of the type

$$\begin{array}{ccc} & \text{In} & \\ \diagup & & \diagdown \\ \text{S} & & \text{S} \\ \diagdown & & \diagup \\ & \text{In} & \end{array}$$
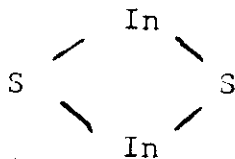
rather than a linear S= In - In= S or In-S-S-In structure. The value of the dissociation energy of InS can be used to confirm that the upper limit of the dissociation energy of InO[11a] is probably very near the real value: the ratio $\Delta H^{o}(\text{at.In}_2 X)/D^{o}(\text{InX})$ has a value of 2.18 for X=S and of 2.39 for X=O when the upper limit $D^{o} \leqslant 75$ kcal is used.

A more complete discussion of these considerations will be given in the In-Se and In-Te paper where all known group II_B- group VI molecules will be considered.

21

REFERENCES

(1) M.G. **Inghram** and J. Drowart, "Proceedings of Symposium on High Temperature Technology", p.219, McGraw Hill-Book Co. N.Y. (1960).

(2) L. Brewer and G.M. Rosenblatt, Chem. Revs. $\underline{61}$, 257(1961).

(3) R.J. Ackermann and R.J. Thorn, "Progress in Ceramic Science", Vol.1, p.39 (1961).

(4) P. Goldfinger and M. Jeunehomme, "Advances in Mass Spectrometry", p.534, Pergamon Press (1959).

(4a) P. Goldfinger, M. Ackerman and M. Jeunehomme, Final Technical Report, EOARDC, contract **no.** AF 61(052)-19 (1959).

(5) R. Colin, P. Goldfinger and M. Jeunehomme, Nature $\underline{187}$, 408 (1960).

(6) A. Sommer, P.N. Walsh and D. White, J. Chem. Phys. $\underline{33}$, 296 (1960).

(7) E.D. Carter, E.G. Rauh and R.J. Thorn, J. Chem. Phys., $\underline{35}$, 619 (1961).

(8) R. Colin, P. Goldfinger and M. Jeunehomme, Nature $\underline{194}$, 282 (1962).

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

(9) R. Colin and J. Drowart, J. Chem. Phys., $\underline{37}$, 1120 (1962).

(10) F.T. Greene and P.W. Gilles, J. Am. Chem. Soc., $\underline{84}$, 3598 (1962).

(11) S.A. Schukarev, G.A. Semenov and I.A. Ratkovski, Zhurn. Prikhadn. Khim., $\underline{35}$, 1455 (1962).

(11a) R.P. Burns, G. DeMaria, J. Drowart and M.G. Inghram, J. Chem. Phys., $\underline{38}$, 1035 (1963).

(12) M.F. Stubbs, J.A. Schuffle, A.J. Thompson and J.M. Duncan, J. Am. Chem. Soc., $\underline{74}$, 1441-1443 (1952).

(13) K. Schubert, E. Dörre and E. Günzel, Naturwis., $\underline{41}$, 448 (1954).

(14) A. Thiel, Z. anorg. Chem., 40, 324 (1904); A. Thiel and H. Koelsch, Z. anorg. Chem., 66, 313 (1910); A. Thiel and H. Luckmann, Z. anorg. Chem., 172, 353-371 (1928).

(15) W. Klemm and H.U. v. Vogel, Z. anorg. Chem., 219, 45 (1934).

(16) A.J. Thompson, M.F. Stubbs and J.A. Schufle, J. Am. Chem. Soc., 76, 341 (1954).

(17) H. Hahn and F. Burrow, Angew. Chem., 68, 382 (1956).

(18) F. Klanberg and H. Spandau, J. Inorg. Nucl. Chem., 19, 180 (1961).

(19) J. Drowart and R.E. Honig, J. Phys. Chem., 61, 980 (1957).

(20) J. Drowart and P. Goldfinger, J. Chem. Phys., 55, 721 (1958).

(21) M. Ackerman, F.E. Stafford and J. Drowart, J. Chem. Phys., 33, 1784 (1960).

(22) F.H. Field and J.L. Franklin, Electron Impact Phenomena, Academic Press Inc., New York (1957).

(23) C.E. Moore, Natl. Bur. Standards, Circ.no.467 (1949).

(24) R. Haegeman, Compt. Rend., 255, 1102 (1962).

(25) G. DeMaria, J. Drowart and M.G. Inghram, J. Chem. Phys., 31, 1076 (1959).

(26) J.W. Otvos and D.P. Stevenson, J. Am. Chem. Soc., 78, 546 (1956)

(27) R. Colin, Ind. Chim. Belg., 26, 51 (1961).

(28) W.L. Fite and R.T. Brackman, Phys. Rev., 112, 1141 (1958).

(29) E.W. Rothe, L.L. Marino, R.H. Neynaber and S.M. Trujillo, Bull. Am. Phys. Soc., II, 6, 357 (1961).

(30) J. Berkowitz, H.A. Tasman and W.A. Chupka, J. Chem. Phys., 36, 2170 (1962).

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

(32) M.G. Inghram, R.J. Hayden and D.C. Hess, Natl. Bur. Standards (U.S.) Circ.**no.** 522, 257 (1953).

(33) H.E. Stanton, W.A. Chupka and M.G. Inghram, Rev. Sci. Inst., 27, 109 (1956).

(34) L. Brewer, J. Chem. Phys., 31, 1143 (1959).

(35) D.G.H. Marsden, J. Chem. Phys., 31, 1144 (1959).

(36) D.R. Stull and G.C. Sinke, Advances in Chemistry, Series 18, (1956).

(37) G. Herzberg, "Spectra of Diatomic Molecules", D. Van Nostrand Company Inc., Princeton, New Jersey (1945).

(38) W.W. Watson and A. Shambon, Phys. rev., 50, 607 (1936).

(39) C.N. Mc Kinney and K.K. Innes, J. Molec. Spectr., 3, 235 (1959).

(40) G. Herzberg, Infrared and Raman Spectra , D. Van Nostrand Company Inc., Princeton, New Jersey (1945).

(41) D. White, D.E. Mann, P.N. Walsh and A. Sommer, J. Chem. Phys., 32, 481 (1960).

(42) J. Drowart, G. DeMaria, R.P. Burns and M.G. Inghram, J. Chem. Phys., 32, 1366 (1960).

(43) O. Kubaschewski and Ll. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York (1958).

(44) T. L.Cottrell, "The Strengths of Chemical Bonds", Butterworths, London (1954).

(45) A. Sommer, D. White, M.J. Linevsky and D.E. Mann, J. Chem. Phys., 38, 87 (1963).