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Vaporization chemistry and thermodynamics of the lead–indium–sulfur system by computer-automated Knudsen and torsion effusion methods

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Vaporization of $PbIn_2S_4(s)$ was studied by computer-automated simultaneous Knudsen and dynamic torsion effusion. Vapor pressures and the apparent molecular weight of the effusing vapor were displayed in real time. The vaporization reaction was $PbIn_2S_4(s) = In_2S_3(s) + PbS(g)$. The vapor pressure was measured 108 times in the temperature range 948–1086 K. For the vaporization reaction, third-law analyses gave $\Delta H°(298\ K) = 253.0 \pm 0.1$ kJ/mol. The enthalpy of $PbIn_2S_4(s)$ with respect to its constituents $PbS(s)$ and $In_2S_3(s)$ was -23 ± 4 kJ/mol. The apparent molecular weight showed stoichiometry changes in indium sulfide during the experiment. Residual indium sulfide, remaining after loss of all PbS, vaporized with some nonstoichiometry by $In_2S_3(s) = In_2S(g) + S_2(g)$. The vapor pressure of the residual indium sulfide was measured 57 times in the temperature range 1035–1121 K; third-law analyses yielded $\Delta H°(298\ K) = 613.4 \pm 0.4$ kJ/mol for the dissociative vaporization reaction. The compound $Pb_2In_6S_{11}(s)$, found at lower temperatures, had negligible stability at the temperatures of this investigation. The unit cell of $PbIn_2S_4(s)$ was orthorhombic with $a = 2.275$ nm, $b = 1.356$ nm, and $c = 1.953$ nm.

INTRODUCTION

The lead–indium–sulfur and similar systems have applications in solid-state devices.[1,2] A knowledge of the mode of vaporization, vapor pressure, and thermodynamics of the materials would be useful in their vapor deposition, crystal growth, and purification and in formulations of theoretical models.

The vaporization of $PbS(s)$ has been investigated by Colin and Drowart[3] and by Hansen and Munir.[4] The vaporization was congruent to molecules of $PbS(g)$. The $\Delta H°(298\ K)$ of sublimation was 230 ± 4 kJ/mol.[5] Mass spectrometric studies of the vaporization of $In_2S_3(s)$ by Miller and Searcy[6,7] and by Colin and Drowart[8] showed that the vaporization was congruent by

$$In_2S_3(s) = In_2S(g) + S_2(g)\ , \tag{1}$$

with $\Delta H°(298\ K)$ of sublimation of 617 ± 13 kJ/mol[6] and 602 ± 13 kJ/mol.[8]

A study of the phase diagram of the system $PbSe-Ga_2Se_3$ was reported by Eholie *et al.*[9] They reported a compound $PbGa_2Se_4$ of orthorhombic crystal symmetry with $a = 1.064$ nm, $b = 1.074$ nm, and $c = 0.636$ nm. Eholie *et al.*[10] later reported the synthesis, crystal symmetry, and magnetic properties for the compounds EuM_2X_4 and SrM_2X_4, where M = Al or Ga, X = S or Se. The latter compounds are isostructural with $PbGa_2Se_4$. Peters and Baglio[11] reported an orthorhombic crystal symmetry with a tentative space group of D_{2h}^{24}-*Fddd* for the compounds MGa_2S_4, where $M = Ca^{2+}$, Sr^{2+}, Pb^{2+}, Eu^{2+}, (Na^+, La^{3+}), or (Na^+, Ce^{3+}). The compound $BaGa_2S_4$ was found to be cubic.

The phase diagram of the $PbS-In_2S_3$ system was reported by Rustamov *et al.*[12] One compound $PbIn_2S_4$ was found and slight solid solution was shown. The compounds $PbIn_2S_4$ and $Pb_2In_6S_{11}$ were reported by Gates[13]; the Debye–Scherrer x-ray diffractogram of $PbIn_2S_4$ was indexed as orthorhombic in space group *Fddd* with parameters $a = 2.275$ nm, $b = 1.356$ nm, and $c = 1.953$ nm. Rustamov *et al.*[12,14] reported $PbIn_2S_4$ as monoclinic with parameters $a = 1.267$ nm, $b = 0.398$ nm, $c = 1.535$ nm, and $\beta = 95°$.

Recently, Krämer and Berroth[15] reported a study of the $PbS-In_2S_3$ system. The compound $PbIn_2S_4$ was found, and, in addition, $Pb_4In_9S_{17}$, $Pb_9In_{20}S_{39}$, and $Pb_6In_{10}S_{21}$ were observed; $Pb_4In_9S_{17}$ is sulfur deficient with respect to the $PbS-In_2S_3$ join. $PbIn_2S_4$ was orthorhombic in space group *Pnma* with $a = 1.1686$ nm, $b = 0.38528$ nm, and $c = 1.3763$ nm. The melting point of $PbIn_2S_4$ was 1168 K. Ginderow[16] published structures of $Pb_4In_9S_{17}$ and $Pb_9In_{20}S_{39}$, which were the same as those of Krämer and Berroth.

The present investigation had the following objectives: (1) Ascertain the vaporization reactions of $PbIn_2S_4(s)$ and $Pb_2In_6S_{11}(s)$. The volatility of $PbS(s)$[4] is about two orders of magnitude higher than that of $In_2S_3(s)$.[5] The stability of $PbIn_2S_4(s)$ and $Pb_2In_6S_{11}(s)$ with respect to the constituent sulfides would determine the relative volatilities over the compounds. (2) Exploit the computer-automated simultaneous Knudsen-effusion, dynamic torsion–effusion method[17–19] to determine the vapor pressure and vapor composition over the system. (3) Use these results for an evaluation of equilibrium constants and thermodynamics of reactions in the system.

EXPERIMENTAL

Samples

Solid samples with compositions ranging from $PbS \cdot In_2S_3$ to In_2S_3 in increments of 10 mol% were prepared by heating the elements in evacuated, sealed Vycor tubes. In the vicinity of $2PbS \cdot 3In_2S_3$ samples were pre-

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pared at intervals of 2 mol%. One sample was made at $3PbS \cdot In_2S_3$. Debye–Scherrer x-ray diffractograms of each sample were obtained. Some samples were left exposed to check the effect of the atmosphere. The melting point of a $PbIn_2S_4$ sample placed in an evacuated sealed tube was determined by increasing the temperature by 5 °C every 30 to 60 min until the sample melted. The x-ray diffractogram of $PbIn_2S_4$ was indexed on the assumption that its unit cell was orthorhombic with space group *Fddd* as in $PbGa_2Se_4$,[9] after Gates.[13]

Preliminary experiments

To establish the vaporization reaction, 1.125 g of $PbIn_2S_4$ in a graphite Knudsen cell was heated by radio induction in vacuum at 1060 K. Four successive vaporization experiments were performed. Heating times ranged from 6 to 14 h. The surface and the bulk material of the residue were analyzed after each experiment by Debye–Scherrer x-ray diffractometry. The sublimates were analyzed in the same way.

To obtain preliminary values of vapor pressures, 1.175 g of $Pb_2In_6S_{11}(s)$ in a graphite cell was heated in a torsion–Knudsen-effusion apparatus.[20] Vapor pressures measured as a function of temperature served to define the suitable range of temperatures for later measurements.

Torsion-effusion apparatus

The torsion–effusion pendulum and vacuum balance by means of which simultaneous measurements of torsion and Knudsen vapor pressures were effected have been described.[20,21] Data from the pendulum and from the balance were acquired automatically by a laboratory computer.[17–19] Calibration of the torsion fiber,[22,23] measurements of the cell and orifice dimensions,[20] and calculations of transmission probabilities and recoil force factors[24] were by standard methods. The torsion-effusion cell was constructed of graphite from a previously described design.[20]

Temperature measurements

Temperatures of the effusion cells were measured in one of two ways. In the preliminary experiments, temperatures were measured by optical pyrometry. In experiments in which vapor pressures were measured, temperatures were measured indirectly by a Pt, Pt–10% Rh thermocouple in a dummy cell[22] identical in design and materials to the torsion–effusion cell. The two cells were placed symmetrically, the torsion–effusion cell above and the dummy cell below the center of the furnace, and separated by ~2 mm.

Data analysis

Vapor pressures and vapor compositions

Two independent determinations of vapor pressures could be made.

The torsion pressure P_T was obtained from[22]

$$P_T = 2Q_e/(f_1A_1d_1 + f_2A_2d_2) , \qquad (2)$$

where Q_e is torque exerted by the effusing vapor, f_1 and f_2 are recoil-force correction factors, A_1 and A_2 are orifice areas, d_1 and d_2 are moment arms of the orifices, and subscripts 1 and 2 refer to the two orifices. Q_e was obtained from the equation of motion of the torsion–effusion pendulum by the method of Gates and Edwards[20] applied to data obtained automatically by the laboratory computer.[17,19]

The Knudsen pressure P_K was obtained from measurements of rate of mass loss by

$$P_K = (dg/dt)(2\pi RT/M^*)^{1/2}/(W_1A_1 + W_2A_2) , \qquad (3)$$

where dg/dt is the rate of mass loss from the cell, W_1 and W_2 are the transmission probabilities of the two orifices, T is the temperature, and M^* is an assumed molecular weight of the effusing vapor species.

The apparent molecular weight during each vaporization experiment was calculated from

$$M = M^*(P_K/P_T)^2 . \qquad (4)$$

The average molecular weight $\bar{M}$ of the vapor species is given by[22]

$$\bar{M} = \left(\sum_{j=1}^{n} m_j M_j^{-1/2}\right)^{-2} , \qquad (5)$$

where m_j is the mass fraction and M_j is the molecular weight of the j species in the effusate.

For a congruently vaporizing solid producing only two vapor species a and b, with molecular weights M_a and M_b, respectively, a measurement of M by Eq. (4), combined with Eq. (5), yields the mole fraction of a in the solid X_a^s:

$$X_a^s = [M_b - (MM_b)^{1/2}]/[M_b - (MM_b)^{1/2} - M_a + (MM_a)^{1/2}] . \qquad (6)$$

The mole fraction X_b^s is obtained from $X_a^s + X_b^s = 1$.

In both of the proposed reactions for the vaporization of $PbIn_2S_4(s)$ (*vide infra*), $In_2S_3(s)$ is a product. In order to find the pressure due to $PbS(g)$ alone, the vapor pressure due to species from $In_2S_3(s)$ was subtracted. For P_T,

$$P_{PbS(g)} = P_{total} - P_{In_2S(g)} - P_{S_2(g)} . \qquad (7)$$

For P_K, the corrected rates of mass loss were found by

$$(dg/dt)_{PbS(g)} = (dg/dt)_{total} - (dg/dt)_{In_2S(g)} - (dg/dt)_{S_2(g)} \qquad (8)$$

and used in Eq. (3).

Thermodynamics

The standard enthalpy change $\Delta H^\circ(298\ K)$ of the vaporization reactions was determined at each experimental temperature by the third-law method[25]:

$$\Delta H^\circ(298\ K) = -RT\ln(K_p/Pa^m) + T\Delta\phi^\circ + 11.526mRT , \qquad (9)$$

in which K_p is the equilibrium constant of a vaporization reaction with apparent units of Pa^m, and $\Delta\phi^\circ$ is the change in Gibbs energy function of the vaporization reaction, and the Gibbs energy function of a substance is

$$\phi^\circ = -[G^\circ(T) - H^\circ(298\ K)]/T . \qquad (10)$$

TABLE I. Standard molar Gibbs energy functions $-[G^\circ(T) - H^\circ(298\ \mathrm{K})]/T$ in J/(mol K).

T/(K)	PbS (s)	PbS (g)	In_2S_3 (s)	In_2S (g)	S_2 (g)	$PbIn_2S_4$ (s)
900	113.47	267.82	218.70	339.74	243.13	332.17
1000	117.24	270.45	228.40	343.51	245.73	345.64
1100	120.88	272.96	237.73	347.27	248.15	358.61
1200	124.30	275.31	247.02	350.62	250.45	371.32

Second-law values of $\Delta H^\circ(298\ \mathrm{K})$ were obtained from the slopes of plots of Σ vs $1/T$,[25,26] where

$$\Sigma = -R\ln(K_p/\mathrm{Pa}^m) + \Delta\phi^\circ + 11.526mR\ . \tag{11}$$

Values of Gibbs energy functions for PbS(s), PbS(g), In_2S_3(s), In_2S(g), and S_2(g) were taken from Mills.[5] The Gibbs energy functions of $PbIn_2S_4$(s) were calculated as the sum of those for PbS(s) and In_2S_3(s). Values of Gibbs energy functions are given in Table I.

The enthalpy of vaporization of PbS(g) from $PbIn_2S_4$(s) was used with the enthalpy of vaporization of PbS(s)[5] to obtain the combination enthalpy of the reaction

$$\mathrm{PbS}(s) + \mathrm{In_2S_3}(s) = \mathrm{PbIn_2S_4}(s)\ . \tag{12}$$

Procedure

The torsion–effusion cell was outgassed at 1280 °C for 48 h. 1.290 g of a sample $PbIn_2S_4$(s) was put into a torsion–Knudsen cell with equal amounts in each of the two compartments. To minimize the exposure of the sample to the atmosphere, a flow of nitrogen gas was maintained while installing the cell into the torsion–Knudsen-effusion apparatus.

A typical set of P_T and P_K was obtained in the following manner: At least once each day, the pendulum rest point[23] and the balance-computer calibration factor[18] were measured. The furnace current for a desired temperature was set. Time was allowed for the temperature to stabilize. The computer was instructed to observe the motion of the pendulum and, simultaneously, the rate of mass loss. The computer used the data and stored properties of the pendulum and the cell to calculate and display P_T, P_K, and apparent molecular weight M of the effusing vapor species. Temperature was noted several times during an experiment. Several measurements of P_T, P_K, and M were done at a given furnace current. Sometimes the temperature changed slightly while the current setting was constant. Thus, several data over a close range of temperature were obtained. Then the furnace current was changed for experiments at another temperature. The order in which the current settings were chosen was scattered so as to avoid any temperature trend in the measurements. The temperatures and the values of P_T, P_K, and M measured at temperatures within a close range were averaged.

The residues of the sample from each cell chamber were examined by x-ray diffractometry and were analyzed chemically for Pb and In by atomic absorption.

RESULTS

Samples

Debye–Scherrer x-ray diffractograms of the samples established that the only ternary compounds stable at room temperature were $PbIn_2S_4$(s) and $Pb_2In_6S_{11}$(s). The melting point of $PbIn_2S_4$ was 1153 ± 15 K. The results of indexing the diffractogram of $PbIn_2S_4$(s) are shown in Table II, where the observed d spacings, theoretical d spacings, Miller indices, and relative intensities are listed in columns 1 through 4, respectively. The unit cell was orthorhombic with $a = 2.275$ nm, $b = 1.356$ nm, and $c = 1.953$ nm. The observed d spacings of $Pb_2In_6S_{11}$(s) are shown in Table III. Attempts to index its powder pattern as cubic, hexagonal, tetragonal, and orthorhombic were unsuccessful. Diffractograms of samples of $PbIn_2S_4$ exposed to air showed no change in samples exposed for up to 14 h.

TABLE II. Comparison of observed and theoretical d spacings of $PbIn_2S_4$.

Observed d spacing/nm	Theoretical d spacing/nm	h,k,l	Relative intensity
1.115	⋯	⋯	0.5
0.905	⋯	⋯	1(b)[a]
0.495	0.500	2, 2, 2	0.5
0.461	0.464	3, 1, 3	0.5
0.377	0.374	2, 2, 4	5
0.360	0.360	5, 1, 3	1
0.339	0.339	0, 4, 0	10
0.328	0.331	6, 2, 0	1
0.317	0.316	5, 3, 1	2
0.288	0.288	5, 3, 3	2
0.282	0.284	2, 2, 6	0.5
0.274	0.274	6, 2, 4	6
0.269	0.270	2, 2, 4	2
0.265	0.267	1, 5, 1	2
0.254	0.253	8, 2, 2	3
0.245	0.244	7, 3, 3	<0.5
0.232	0.232	6, 2, 6	0.5
0.212	0.213	8, 4, 2	1.5
0.208	0.209	9, 3, 3	4
0.204	0.204	8, 2, 6	1.5
0.1947	0.1951	11, 1, 3	2
0.1921	0.1921	9, 3, 5	3.5
0.1895	0.1896	12, 0, 0	0.5
0.1846	0.1850	1, 7, 3	1
0.1826	0.1832	2, 6, 6	0.5
0.1698	0.1695	0, 8, 0	1.5
0.1676	0.1677	13, 1, 3	1.5
0.1645	0.1639	11, 5, 1	1.5
0.1589	0.1587	1, 7, 7	0.5
0.1564	0.1567	12, 4, 4	<0.5
0.1536	0.1533	9, 7, 1	<0.5
0.1413	0.1410	11, 7, 1	1
0.1395	0.1395	8, 8, 4	0.5
0.1369	0.1365	16, 0, 4	0.5
0.1356	0.1349	15, 3, 5	0.5
0.1324	0.1323	1, 9, 7	0.5(b)[a]
0.1303	0.1305	17, 1, 3	<0.5(b)[a]
0.1280	0.1280	16, 2, 6	<0.5
0.1264	0.1264	12, 8, 0	<0.5
0.1222	0.1222	4, 10, 6	1
0.1161	0.1161	18, 2, 6	1
0.1140	0.1140	19, 3, 3; 13, 9, 1	1
0.0980	0.0982	7, 13, 3	<0.5
0.0964	0.0964	0, 14, 2	<0.5
0.0884	0.0884	25, 3, 3	0.5
0.0875	0.0875	3, 15, 5	0.5

[a] b = broad.

TABLE III. *d* spacing and relative intensities in $Pb_2In_6S_{11}$.

Observed *d* spacing/nm	Relative intensity	Observed *d* spacing/nm	Relative intensity
0.456	<0.5	0.1949	<0.5
0.443	<0.5	0.1926	6
0.409	5	0.1906	0.5
0.394	<0.5	0.1886	<0.5
0.383	5	0.1870	4
0.365	0.5	0.1843	0.5
0.338	10	0.1819	<0.5
0.333	10	0.1793	<0.5
0.324	<0.5	0.1773	<0.5
0.316	<0.5	0.1748	0.5
0.309	<0.5	0.1731	<0.5
0.300	<0.5	0.1713	0.5
0.295	<0.5	0.1702	<0.5
0.284	10	0.1669	5
0.280	0.5	0.1653	3
0.271	<0.5	0.1572	<0.5
0.261	<0.5	0.1544	<0.5
0.257	9	0.1510	<0.5
0.254	<0.5	0.1422	3
0.243	<0.5	0.1401	<0.5
0.230	<0.5	0.1384	<0.5
0.224	<0.5	0.1370	<0.5
0.221	4	0.1349	2
0.218	<0.5	0.1323	3
0.211	6	0.1296	<0.5
0.209	6	0.1272	<0.5
0.207	0.5	0.1255	<0.5
0.206	0.5	0.1227	4
0.203	<0.5	0.1208	<0.5
0.1991	<0.5	0.1194	<0.5
0.1970	<0.5	0.1158	3

Vaporization reactions

The residue of the first vaporization of the sample $PbIn_2S_4(s)$ in the induction furnace was identified as $Pb_2In_6S_{11}(s)$. The residues from the subsequent vaporizations at room temperature were found to consist of $Pb_2In_6S_{11}(s)$ and $In_2S_3(s)$. The sublimates from all four vaporizations were PbS.

In view of these findings, two alternative modes of vaporization were proposed:

$$3PbIn_2S_4(s) = Pb_2In_6S_{11}(s) + PbS(g)\ , \tag{13}$$

$$Pb_2In_6S_{11}(s) = 3In_2S_3(s) + 2PbS(g) \tag{14}$$

or

$$PbIn_2S_4(s) = In_2S_3(s) + PbS(g)\ . \tag{15}$$

Later results (*vide infra*) showed that the stability of $Pb_2In_6S_{11}(s)$ was insignificant at the temperatures of the measurements, and hence the vapor pressure measurements were interpreted in terms of Reaction (15).

Vapor pressures and enthalpy increments

As PbS evaporated from $PbIn_2S_4(s)$, the composition of the sample approached that of pure indium sulfide. After a mass loss that approximated the loss of all PbS in accordance with Reaction (15), the vapor pressure and the apparent molecular weight of the vapor decreased. The vapor pressures stabilized at values that were lower by a factor of about 10 at a given temperature. The apparent molecular weight decreased from 236 ± 2 to 189 ± 4. The mass range over which the transition occurred was about 40 mg.

The residue of the sample after the vaporization experiments was identified as In_2S_3 from its x-ray diffractogram. Atomic absorption analyses of the residues from the two chambers of the effusion cell gave the following results: chamber 1, $Pb < 0.01\%$, $In = 71 \pm 4.8\%$; chamber 2, $Pb < 0.01\%$, $In = 71 \pm 3.6\%$. These results correspond to a residue with the formula $In_2S_{2.9\pm0.5}$.

P_T and P_K over the system before it had attained the composition of $In_2S_3(s)$ were analyzed in terms of Reaction (15). To obtain the partial pressures of $PbS(g)$ from total pressures by Eqs. (7) and (8) our vapor pressures of residual $In_2S_3(s)$ were used.

Tables IV and V give results from study of $PbIn_2S_4(s)$ and from study of the residual $In_2S_3(s)$, respectively. In each table, columns 1, 2, 3, 4, and 5 give average temperature of measurements, number of measurements, P_T, P_K, and M, respectively. Columns 6 and 7 give third-law $\Delta H°(298\ K)$ values derived from P_T and P_K, respectively. Second-law results are given at the bottom of columns 6 and 7 in each table. The second-law results were not used subsequently because of the greater dependability of the third-law results.

The average third-law value of $\Delta H°(298\ K)$ of Reaction (15) from Table IV was 252.96 ± 0.08 kJ/mol by torsion effusion and 253.07 ± 0.09 kJ/mol by Knudsen effusion, where the uncertainties are standard deviations of the mean. A value of 253.0 ± 0.1 kJ/mol was chosen. The average third-law value of $\Delta H°(298\ K)$ of Reaction (1) from Table V was 613.56 ± 0.30 kJ/mol by torsion effusion and 613.29 ± 0.29 kJ/mol by Knudsen effusion. A value of 613.4 ± 0.4 kJ/mol was chosen. Combination of the chosen $\Delta H°(298\ K)$ of Reaction (15) with the enthalpy of vaporization of $PbS(s)^5$ of 230 ± 4 kJ/mol yields $\Delta H°(298\ K)$ of combination of $PbIn_2S_4(s)$ by Reaction (12) of −23 ± 4 kJ/mol.

Plots of $\log P_T$ vs $1/T$ for Reactions (15) and (1) are shown in Fig. 1. Least-squares straight lines are drawn through the points and are given by

$$\log(P/\mathrm{Pa}) = -(12\,060 \pm 104)\ \mathrm{K}/T + 11.60 \pm 0.10 \tag{16}$$

for Reaction (15) and

$$\log(P/\mathrm{Pa}) = -(16\,724 \pm 206)\ \mathrm{K}/T + 15.34 \pm 0.19 \tag{17}$$

for the vapor pressure of residual indium sulfide.

The apparent molecular weights of the vapors over $PbIn_2S_4(s)/In_2S_3(s)$ and over $In_2S_3(s)$ are plotted as functions of T in Fig. 2. The solid line in each case represents a cubic equation in T fitted through the points. Below 1045 K the apparent molecular weight of the vapor over $PbIn_2S_4(s)/In_2S_3(s)$ was independent of temperature and equal to 244.1 ± 2.5; that of $PbS(g)$ is 239.3. Above 1045 K, M decreased with increasing temperature. Below 1080 K, M over $In_2S_3(s)$ was independent of temperature and equal to 195.2 ± 3.9; the average molecular weight of $In_2S(g)$ and $S_2(g)$ in Reaction (1) by Eq. (5) is

TABLE IV. Vapor pressures and thermodynamics of Reaction (15): $PbIn_2S_4(s) = In_2S_3(s) + PbS(g)$.

	Number of				Third-law $\Delta H°$ (298 K) · mol/kJ	
T/K	measurements	P_T/Pa	P_K/Pa	M	Torsion	Knudsen
998.0 ± 1.6	4	0.643 ± 0.023	0.631 ± 0.014	231.4 ± 9.2	252.30 ± 0.33	252.46 ± 0.27
1021.0 ± 4.1	3	1.302 ± 0.064	1.310 ± 0.048	243.1 ± 6.3	252.01 ± 0.54	251.96 ± 0.67
960.0	1	0.210	0.216	256.9	252.04	251.79
995.0	1	0.491	0.441	193.4	253.80	254.72
987.0	2	0.509 ± 0.009	0.502 ± 0.011	233.7 ± 1.4	251.54 ± 0.15	251.67 ± 0.18
973.9 ± 1.7	8	0.313 ± 0.012	0.319 ± 0.019	249.0 ± 25.3	252.25 ± 0.21	252.13 ± 0.50
950.0 ± 1.8	4	0.154 ± 0.007	0.149 ± 0.010	225.7 ± 16.0	252.00 ± 0.21	252.25 ± 0.18
1002.4 ± 4.3	5	0.768 ± 0.059	0.757 ± 0.057	231.0 ± 10.0	251.88 ± 0.41	252.08 ± 0.54
1014.0	1	1.117	1.232	267.6	251.12	250.66
1024.0 ± 1.4	2	1.358 ± 0.039	1.407 ± 0.009	257.7 ± 10.6	251.92 ± 0.10	251.92 ± 0.27
1045.0 ± 2.2	4	2.473 ± 0.098	2.490 ± 0.110	243.6 ± 13.6	251.87 ± 0.15	251.88 ± 0.30
1018.5 ± 0.7	2	1.062 ± 0.019	1.064 ± 0.026	240.6 ± 3.3	253.00 ± 0.02	253.00 ± 0.06
1073.0 ± 1.0	3	4.617 ± 0.031	4.293 ± 0.018	207.4 ± 2.1	252.76 ± 0.28	253.42 ± 0.23
1027.9 ± 3.1	17	1.355 ± 0.059	1.350 ± 0.042	239.0 ± 15.7	253.13 ± 0.59	253.09 ± 0.79
1066.3 ± 1.5	8	3.626 ± 0.170	3.463 ± 0.161	219.4 ± 14.7	253.38 ± 0.27	253.80 ± 0.39
1084.1 ± 0.8	8	5.976 ± 0.016	5.531 ± 0.115	205.7 ± 8.1	252.92 ± 0.17	253.63 ± 0.21
1046.3 ± 1.2	3	2.093 ± 0.069	2.096 ± 0.033	240.9 ± 11.4	253.68 ± 0.04	253.68 ± 0.18
972.8 ± 1.0	4	0.253 ± 0.009	0.262 ± 0.012	259.0 ± 39.2	253.55 ± 0.04	253.47 ± 0.61
1007.6 ± 0.9	5	0.709 ± 0.015	0.737 ± 0.018	260.4 ± 20.0	253.80 ± 0.25	253.47 ± 0.19
1026.7 ± 1.2	3	1.248 ± 0.006	1.240 ± 0.017	237.1 ± 5.7	253.55 ± 0.25	253.63 ± 0.33
1065.0 ± 2.6	3	3.180 ± 0.158	3.166 ± 0.133	238.1 ± 8.1	254.26 ± 0.17	254.30 ± 0.25
1085.3 ± 0.8	6	5.468 ± 0.128	5.104 ± 0.258	209.3 ± 17.7	254.07 ± 0.35	254.64 ± 0.52
1017.0 ± 1.4	2	0.909 ± 0.041	0.963 ± 0.058	269.3 ± 8.0	253.97 ± 0.03	253.47 ± 0.18
971.0 ± 5.6	3	0.247 ± 0.020	0.256 ± 0.027	259.1 ± 20.0	253.50 ± 0.80	253.22 ± 0.80
1032.0	4	1.404 ± 0.054	1.436 ± 0.047	251.7 ± 17.9	253.80 ± 0.33	253.63 ± 0.29
970.0	1	0.327	0.341	258.7	250.95	249.99
			Average:	236.2 ± 2.3	252.96 ± 0.08	253.07 ± 0.09
					Second-law $\Delta H°$ (298 K) 244.59 ± 1.93 kJ/mol	Second-law $\Delta H°$ (298 K) 239.10 ± 1.98 kJ/mol

TABLE V. Vapor pressures and thermodynamics of Reaction (1): $In_2S_3(s) = In_2S(g) + S_2(g)$.

	Number of				Third-law $\Delta H°$ (298 K) · mol/kJ	
T/K	measurements	P_T/Pa	P_K/Pa	M	Torsion	Knudsen
1113.7 ± 4.9	7	2.01 ± 0.39	1.86 ± 0.26	158.0 ± 28.9	612.63 ± 1.99	614.03 ± 2.00
1098.5 ± 1.3	4	1.30 ± 0.15	1.29 ± 0.13	180.5 ± 21.8	612.65 ± 1.73	612.73 ± 1.13
1078.0 ± 0.0	4	0.63 ± 0.05	0.67 ± 0.03	207.0 ± 19.4	614.88 ± 1.32	613.71 ± 0.79
1097.0 ± 1.2	4	1.31 ± 0.07	1.38 ± 0.07	200.4 ± 5.7	611.65 ± 0.94	610.78 ± 1.03
1068.8 ± 0.5	5	0.44 ± 0.01	0.46 ± 0.01	199.2 ± 9.6	616.34 ± 0.33	615.51 ± 0.62
1032.0 ± 3.5	4	0.14 ± 0.01	0.15 ± 0.01	202.3 ± 41.3	615.82 ± 0.74	615.00 ± 2.30
1077.0 ± 0.0	2	0.61 ± 0.02	0.59 ± 0.06	172.9 ± 28.4	614.99 ± 0.52	615.47 ± 2.00
1037.8 ± 1.0	4	0.18 ± 0.01	0.19 ± 0.01	202.9 ± 20.1	615.00 ± 0.19	614.04 ± 0.67
1063.7 ± 3.5	3	0.40 ± 0.05	0.42 ± 0.03	204.0 ± 25.0	615.29 ± 0.20	614.29 ± 0.89
1049.4 ± 2.2	5	0.26 ± 0.02	0.27 ± 0.03	187.6 ± 20.6	614.79 ± 0.35	614.54 ± 1.26
1109.0 ± 2.8	5	2.02 ± 0.34	2.03 ± 0.38	184.2 ± 19.3	610.18 ± 1.90	610.06 ± 2.42
1121.0	1	2.74	2.68	173.0	610.24	610.67
1100.0 ± 0.0	2	1.35 ± 0.04	1.41 ± 0.06	199.0 ± 7.1	612.62 ± 0.53	611.77 ± 0.85
1066.0 ± 0.0	2	0.43 ± 0.01	0.44 ± 0.02	190.6 ± 14.7	615.26 ± 0.09	614.84 ± 0.59
1086.0 ± 1.4	2	0.93 ± 0.06	0.97 ± 0.02	195.3 ± 18.0	612.01 ± 0.40	611.39 ± 0.39
1099.0	1	1.48	1.44	170.0	610.36	609.95
1120.0 ± 1.4	2	2.59 ± 0.25	2.55 ± 0.11	177.0 ± 19.8	610.86 ± 1.83	611.09 ± 0.78
			Average:	188.7 ± 3.6	613.56 ± 0.30	613.29 ± 0.29
					Second-law $\Delta H°$ (298 K) 676.4 ± 7.9 kJ/mol	Second-law $\Delta H°$ (298 K) 656.7 ± 9.6 kJ/mol

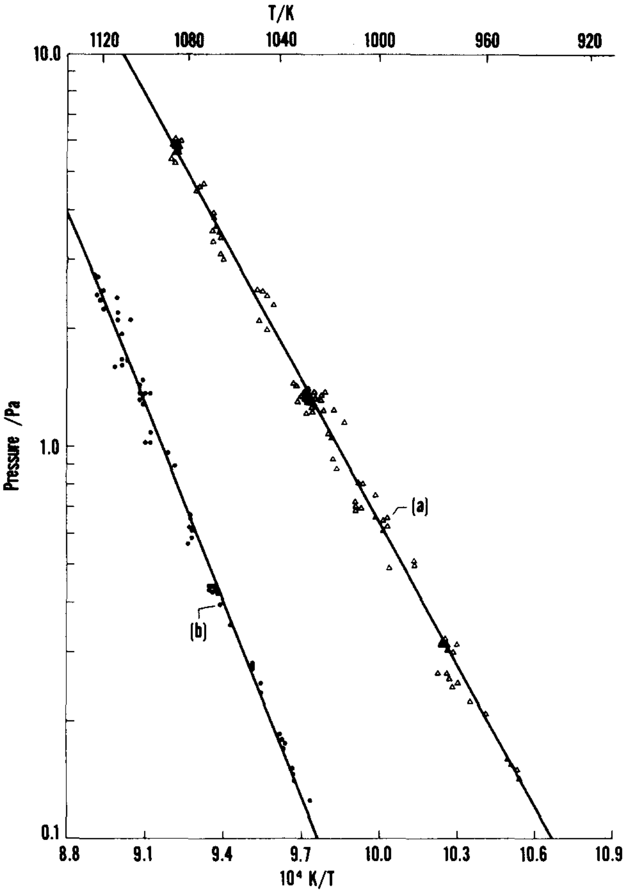

FIG. 1. Vapor pressures as functions of temperature: (a) over the two-solid-phase system $PbIn_2S_4(s)/In_2S_3(s)$; (b) over residual solid indium sulfide.

181.5. Above 1080 K, M decreased with increasing temperature.

The residual indium sulfide was taken to have the congruently vaporizing composition, and the solid composition was calculated with Eq. (6) from the vapor composition as reflected in the apparent molecular weight. The result, for $M = 195.2 \pm 3.9$, was a solid composition of $In_2S_{2.49\pm0.13}$, to compare with the composition $In_2S_{2.9\pm0.5}$ from analysis of the residual solid by atomic absorption. Miller and Searcy[7] give the composition of congruently vaporizing solid indium sulfide as $In_2S_{2.90\pm0.03}$.

In view of the large experimental uncertainties involved, these results can be considered consistent. However, the possibility exists that the sulfur deficiency in the vapor implied by the high value of M occurred because the residual indium sulfide vaporized incongruently below 1100 K. Finally, the fact that $M = 244.1 \pm 2.5$ was found below 1045 K for the $PbS(g)$ from Reaction (15) indicates that the measurements of M might be high by 2%. If M of the vapor from the residual indium sulfide below 1080 K is reduced by 2%, then the implied formula becomes $In_2S_{2.65\pm0.14}$.

DISCUSSION

Lead indium sulfide $PbIn_2S_4$ was found to vaporize incongruently by Reaction (15) in the temperature range 948–1045 K. No effect on the vapor pressure from Reactions (13) or (14) was observed; therefore, $Pb_2In_6S_{11}$ was taken to be unstable above 948 K. After PbS was exhausted only indium sulfide remained, and vaporization proceeded by Reaction (1).

The compound $Pb_2In_6S_{11}$ was found in the residues from all sealed tube experiments and vaporization experiments in which the final overall composition was between 50% and 100% In_2S_3. Since $Pb_2In_6S_{11}$ was not stable at the temperatures of the vaporization experiments, we conclude that it formed when the temperature was below its decomposition temperature. Other workers[12,15] did not observe $Pb_2In_6S_{11}$ or any compound near 60% In_2S_3. The reason for this difference is not apparent.

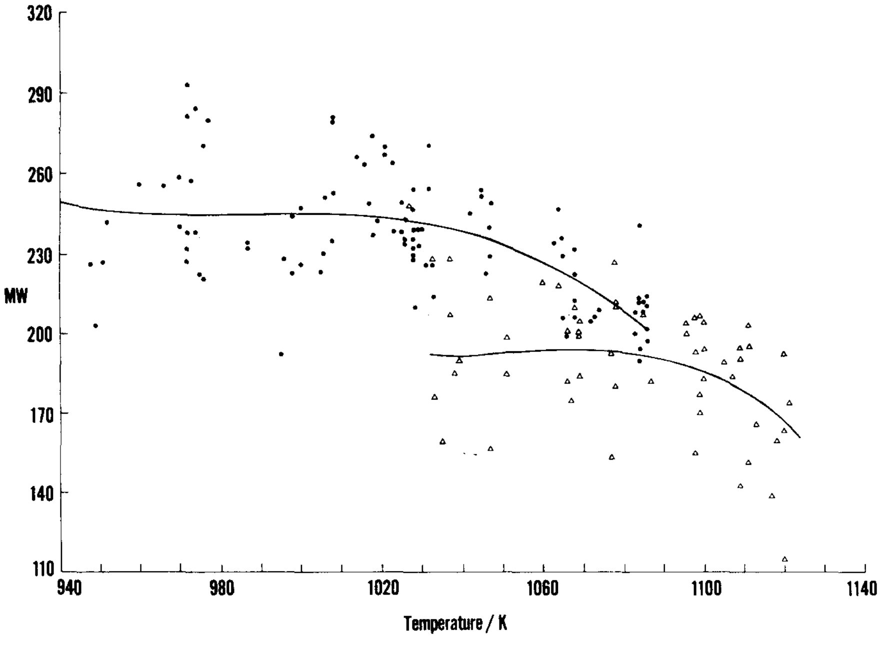

FIG. 2. Apparent molecular weights of vapors as functions of temperature: Dots are for the vapor over the two-solid-phase system $PbIn_2S_4(s)/In_2S_3(s)$. Triangles are for the vapor over residual solid indium sulfide.

The enthalpy of combination of $PbIn_2S_4(s)$, i.e., $\Delta H°(298\ K)$ of Reaction (12), is -23 ± 4 kJ/mol. Enthalpies of combination of other similar ternary sulfides[20] range from -15 to -42 kJ/mol.

The computer-automated dynamic torsion–effusion method yielded vapor pressures given by Eq. (16) over the $PbIn_2S_4/In_2S_3$ two-phase solid and vapor pressures given by Eq. (17) over $In_2S_3(s)$. In combination with simultaneous computer-automated Knudsen-effusion measurements, the method yielded vapor composition via the apparent molecular weight. The apparent molecular weight of 244.1 ± 2.5 of the vapor over the $PbIn_2S_4/In_2S_3$ two-phase solid below 1045 K showed that the vapor was composed of PbS molecules and confirmed Reaction (15) as the vaporization reaction up to 1045 K. At higher temperatures the apparent molecular weight decreased. The plot of $\log P$ vs $1/T$ showed no effect near 1045 K, as seen in Fig. 1; third-law values of $\Delta H°(298\ K)$ for Reaction (15) from data obtained below 1045 K averaged 1.2 ± 0.1 kJ/mol below values from data obtained above 1045 K. The changes at 1045 K imply that possibly another vaporization reaction was important above that temperature.

At temperatures above 1080 K, the average molecular weight of the effusing indium sulfide vapor was lower and decreased with increasing temperature. Third-law values of $\Delta H°(298\ K)$ for Reaction (1) from data below 1080 K averaged 3.2 ± 0.6 kJ/mol higher than those from above 1080 K. The change at 1080 K may be related to the known $\beta \rightarrow \gamma$ phase transition in $In_2S_3(s)$ at 1100 K[5] or to incongruent melting of one of the known sulfur-deficient indium sulfides.[27] Our average value of $\Delta H°(298\ K)$ of vaporization of residual indium sulfide of 613.4 ± 0.4 kJ/mol agrees well with the results of Miller and Searcy[6] of 617 ± 13 kJ/mol and of Colin and Drowart[8] of 602 ± 13 kJ/mol.

Dissolved $PbS(s)$ in the residual $In_2S_3(s)$ would contribute $PbS(g)$ molecules to increase the apparent molecular weight of the vapor, and would have some effect on any melting reaction. To bring about an apparent molecular weight of 195, 22 mol% of $PbS(g)$ in the vapor would be required. The solubility of $PbS(s)$ in $In_2S_3(s)$ is 2 mol%.[15] If so much $PbS(g)$ were in the vapor, the solid would quickly be depleted and an apparent molecular weight dependent on time would be found, in contradiction to observation. Furthermore, atomic absorption analysis of the residue showed $< 0.01\%$ Pb at the finish. Thus, it is unlikely that $PbS(g)$ was important during the study of residual indium sulfide.

The melting point of $PbIn_2S_4$ of 1153 ± 15 K was slightly lower than the reported[15] value of 1168 K. These results, when compared with the $PbS–In_2S_3$ phase diagram,[15] indicate that our melting point was that of the saturated solution of ~ 0.75 mol% of In_2S_3 in $PbIn_2S_4$.

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