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THERMODYNAMICS AND VAPORIZATION CHEMISTRY IN THE $PbS-Ga_2S_3$ SYSTEM

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ABSTRACT

Vaporization chemistry in the $PbS-Ga_2S_3$ system was studied by the simultaneous torsion- and Knudsen-effusion methods. Vapor pressures and compositions were measured in the temperature range 898-1267 K. On a log(K) vs. $1/T$ plot the data fell into five regions of univariant vapor pressure and one region of solid solution. The vaporization reactions and their average third-law $\Delta H^0(298\text{ K})$ were:

Reaction	$\Delta H^0(298\text{ K})$ (kJ mol^{-1})
$3/2\ Pb_2Ga_2S_5(s) = PbS(g) + 1/2\ Pb_4Ga_6S_{13}(s)$	233.6 ± 0.4
$Pb_4Ga_6S_{13}(s) = PbS(g) + 3\ PbGa_2S_4(s)$	237.9 ± 1.0
$3\ PbGa_2S_4(s) = PbS(g) + Pb_2Ga_6S_{11}(s)$	256.6 ± 0.7
$1/2\ Pb_2Ga_6S_{11}(s) = PbS(g) + 3/2\ Ga_2S_3(ss)$	270.0 ± 0.7
$PbS(ss, \text{ in } Ga_2S_3) = PbS(g)$	269.6 ± 1.5
$Ga_2S_3(s) = Ga_2S(g) + S_2(g)$	654.8 ± 1.5

High-temperature mass spectrometry confirmed the vapor species within each region. Two new ternary compounds, $Pb_4Ga_6S_{13}$ and $Pb_2Ga_6S_{11}$, both high-temperature compounds, were detected. Enthalpies of ternary compounds with respect to those of the binary constituents PbS(s) and $Ga_2S_3(s)$ were, per mol of PbS:

Compound	$\Delta H^0(298\text{ K})$ (kJ mol^{-1})
$Pb_2Ga_2S_5(s)$	-20.18 ± 2.0
$Pb_4Ga_6S_{13}(s)$	-28.52 ± 3.0
$PbGa_2S_4(s)$	-35.43 ± 3.0
$Pb_2Ga_6S_{11}(s)$	-39.90 ± 4.0

A previously reported anomalous increase in vapor pressure with decreasing temperature in $Ga_2S_3(s)$ was not observed in this work.

INTRODUCTION

Ongoing interest in transition- and representative-metal chalcogenide compounds of the form $M'M''_xX_y$, where M′ is a divalent metal, M″ is a

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trivalent metal, and X is a chalcogenide, S, Se, or Te, stems from their potential use in solid-state electronic devices. Thermodynamic and high-temperature chemical properties, important in processes of CVD and crystal growth and which yield information about bonding strengths, are not known for many of these compounds.

Preparation and structural properties of $PbGa_2S_4$ were first reported by Eholie et al. [1] and later by Peters and Baglio [2] and Chilouet et al. [3]. The structure of $PbGa_2S_4$ is orthorhombic and of space group D_{2h}^{24}-*Fddd* with lattice constants $a = 20.44$ Å, $b = 20.64$ Å, and $c = 12.09$ Å [3]. Mazurier et al. [4] reported the preparation and structural properties of $Pb_2Ga_2S_5$. $Pb_2Ga_2S_5$ has an orthorhombic structure with lattice constants $a = 12.39$ Å, $b = 11.90$ Å, and $c = 11.03$ Å, and is of space group *Pbca*. The phase diagram of the pseudobinary system $PbS-Ga_2S_3$ was determined by differential thermal analysis [3]. Four intermediate phases were present: $Pb_2Ga_2S_5$, $PbGa_2S_4$, and two Ga_2S_3-rich solid solutions, one of wurtzite type at temperatures above 1273 K, and one of distorted blende type at temperatures below 1243 K. $Pb_2Ga_2S_5$ and $PbGa_2S_4$ were found to have peritectic decompositions at 1173 and 1203 K, respectively. Golovei et al. [5] studied the phase equilibria but reported only one intermediate compound, $PbGa_2S_4$.

The vaporization of PbS(s) has been studied by Hansen and Munir [6], Colin and Drowart [7], and numerous others [8]. The vaporization reaction was found to be

$$PbS(s) = PbS(g) \tag{1}$$

Mills [8] selected ΔH^0(298 K) of reaction (1) to be 230.1 ± 4.0 kJ mol^{-1}.

Studies of the vaporization of Ga_2S_3 by Kashkooli and Munir [9], Uy et al. [10], and Kshirsagar and Edwards [11] showed that vaporization was congruent by

$$Ga_2S_3(s) = Ga_2S(g) + S_2(g) \tag{2}$$

The ΔH^0 (298 K) was found to be 661.4 ± 0.3 kJ mol^{-1} [8,9], 673.6 ± 25 kJ mol^{-1} [10], and 663.4 ± 0.8 kJ mol^{-1} [11]. A differential torsion-effusion experiment by Starzynski and Edwards [12] gave a ΔH^0 (298 K) for reaction (2) of 644.0 ± 10 kJ mol^{-1}. They also reported that a discontinuity in the slope of a plot of log $P(Ga_2S_3)$ vs. $1/T$ occurred at 1173 ± 5 K. An anomalous increase in the vapor pressure of Ga_2S_3 upon lowering the temperature across 1228 ± 3 K was reported by Roberts and Searcy [13] and later by others [11,12].

The objectives of this study were to determine the composition of the vapor phase and the vaporization reactions of the ternary compounds and Ga_2S_3, to use the simultaneous Knudsen-effusion and torsion-effusion method to measure the vapor pressure as a function of temperature, and to calculate the equilibrium constant of each vaporization reaction as a function of temperature and the thermodynamic properties of each vaporization reaction and ternary compound.

EXPERIMENTAL

Samples

Samples at every 10 mol% PbS ranging from PbS to Ga_2S_3 were prepared by heating stoichiometric amounts of the elements in evacuated, sealed, Vycor tubes. The supplier and purity of the elements used in the preparation were: Pb, United Mineral and Chemical Corporation, 99.999%; Ga, Atomergic Chemetals Company, 99.999%; and S, United Mineral and Chemical Corporation, scientific grade. Samples with the stoichiometry $(PbS)_x(Ga_2S_3)_y$, where $0.10 \leqslant x \leqslant 0.90$ and $x + y = 1.0$, were heated at 1063 K and $PbGa_2S_4$ ($x = 0.50$) was heated at 1163 K for several days until sulfur vapor was no longer visible in the Vycor tube. $Pb_2Ga_2S_5$ was prepared by combining and heating stoichiometric amounts of previously prepared PbS and $PbGa_2S_4$ in evacuated, sealed, Vycor tubes at 1268 K for 60 min, then the temperature was lowered to 1123 K and held constant for 15 min. All preparation temperatures were uncertain by ± 5 K. In each case the sample was quenched in water and stored in a glass vial inside a desiccator which contained $CaSO_4$. Debye–Scherrer X-ray diffractograms of all the samples were obtained.

Mass spectrometry

Mass spectra of a sample with the composition of $Pb_4Ga_6S_{13}$ were obtained with a Nuclide 12-90 HT mass spectrometer. Vapor was introduced into the ion source by vaporization of the sample from a graphite Knudsen cell. Relative pressures of species emanating from the Knudsen cell in the range 963–1158 K were determined by measuring the intensity, at opened and closed shutter positions, of the ions corresponding to the species. Temperature measurements were made with a Pt/Pt–10% Rh thermocouple placed in the bottom of the Knudsen cell. Searches were made for ternary ions containing Pb, Ga, and S.

Knudsen-effusion and torsion-effusion

Vapor pressures of samples which initially were $Pb_2Ga_2S_5$ were measured by the computer-automated, simultaneous, Knudsen-effusion, torsion-effusion method [14–17].

Three graphite effusion cells were used and were labeled 1, 2, and 3; the same numbers label the experiments in which the cells were used. The design of the graphite cells has been previously described [18]. The diameters of the orifices, moment arms of the orifices, and the orifice lengths were measured with a traveling microscope. The transmission probability, W, and the recoil-force factors, F, were calculated with computer programs using equations of Freeman and Edwards [19]. Each graphite effusion cell was outgassed under vacuum at about 1500 K for 12–14 h before the sample was loaded.

Temperature measurements were made with a Pt/Pt–10% Rh thermocouple in a graphite dummy cell identical in design to the effusion cell. The two cells were placed vertically symmetrically with respect to each other above and below the center of the furnace and separated by ca. 2 mm. The thermocouple was calibrated by observing the temperature of the dummy cell with the thermocouple and a calibrated optical pyrometer. This procedure introduced uncertainties of ± 4 K into the temperature measurements.

The torsion constants, k, of the fibers were calibrated before and after each experiment by a standard method which has been previously described [18].

Data collection and treatment

Three experiments were done, each starting with a sample of $Pb_2Ga_2S_5$ but with different effusion cells. The experiments were labeled experiment 1, experiment 2, and experiment 3. In all experiments, the order in which the temperatures were set was determined by choosing preselected temperatures randomly within the temperature range of the experiment. In experiment 1, 324.30 mg of $Pb_2Ga_2S_5$ were loaded into effusion cell 1. The sample was divided equally between the two chambers of the effusion cell. Vapor pressure measurements were made in the temperature range 898–1267 K. The entire sample was vaporized.

In experiment 2, 359.70 mg of $Pb_2Ga_2S_5$ were loaded into effusion cell 2. The sample was divided equally between the two chambers of the effusion cell. The temperature range was 919–1288 K.

In experiment 3, 345.15 mg of $Pb_2Ga_2S_5$ were loaded into effusion cell 3. The sample was distributed between the two chambers in proportion to the effective orifice areas (area × transmission probability) [11]. The temperature range was 922–1250 K.

The data acquired in the course of an experiment were taken from measurements of: (1) the temperature of the effusion cell; (2) the mass of the pendulum and the time; and (3) the times at which the pendulum was at a number of preset positions.

The torque, Q_e, caused by the effusion of vapor from the effusion cell was calculated from the pendulum position vs. time measurements with a least-squares fit of the data to the equation of motion of an ideal torsion pendulum [18]. The vapor pressure, P_t, in the effusion cell was calculated from the torque, Q_e, exerted on the torsion pendulum by the effusing vapor with the Volmer equation [20]:

$$P_t = 2Q_e/[(FAd)_1 + (FAd)_2] \tag{3}$$

where the subscripts 1 and 2 identify the orifices, F is the recoil force correction factor, A is the area, and d is the moment arm of an orifice.

The Knudsen pressure, P_k, was calculated from the rate of mass loss, dg/dt, and the measured temperature, T, with the Knudsen equation [20]:

$$P_k = (dg/dt)(2\pi RT/M^*)^{1/2}/[(AW)_1 + (AW)_2] \tag{4}$$

in which the subscripts 1 and 2 identify the orifices, W is the transmission probability, A is the area, and M^* is the assigned molecular weight of the effusing vapor. The apparent molecular weight of the effusing vapor was calculated from [20]:

$$M = M^*(P_k/P_t)^2 \tag{5}$$

The assigned molecular weight of the effusing vapor was taken to be the average molecular weight [20]:

$$M^* = \left(\sum_{i=1}^{n} m_i M_i^{-1/2}\right)^{-2} \tag{6}$$

where m_i and M_i are the mass fraction and the molecular weight, respectively, of molecular constituent i in an effusing vapor of n molecular constituents. Use of eqn. (6) requires detailed knowledge of the vaporization process. The result for PbS vapor was 239.3 g mol^{-1} and for Ga_2S_3 vapor was 124.7 g mol^{-1}, on the basis of eqns. (1) and (2), respectively.

Least-squares straight-line fits of pressures or equilibrium constants as functions of temperature were made to the equation

$$\log_{10} X = C/T + D \tag{7}$$

where X is pressure or equilibrium constant for a vaporization reaction and C and D are parameters from the fit.

Vapor pressure at a given temperature was observed to vary as a function of orifice area in comparing results from experiments 1, 2, and 3. Measured vapor pressures, P_m, were related to vapor pressures, P_0, in a hypothetical cell with orifice area of zero by [21]:

$$P_0 = P_m(1 + WA/\alpha A_s) \tag{8}$$

where α is the condensation coefficient, A is the orifice area, W is the transmission probability, and A_s is the area of the vaporizing sample.

For each type of measurement, Knudsen-effusion or torsion-effusion, values of P_m and its uncertainty were obtained from least-squares fits of $\log_{10} P_m$ vs. $1/T$ at eleven equally spaced temperatures within the temperature range of the experiments. Values of P_0 at a given temperature were obtained by extrapolation of a straight line through the three points from experiments 1, 2, and 3 on a plot of P_m vs. $(P_m AW)$. The uncertainty in P_0 was calculated from the weighted least-squares fit of P_m vs. $(P_m AW)$. The weighting factor used in this least-squares treatment was the square of the inverse of the uncertainty in the measured pressure. Average ratios of P_0/P_m were calculated from both Knudsen-effusion and torsion-effusion results. The measured pressure of each type from experiment 1 was multiplied by the P_0/P_m ratio and the resulting pressure was assumed to be the equilibrium vapor pressure. In the case of PbS vapor with only one important vapor species, this assumption is accurate. In the case of Ga_2S_3 vapor with two equally important vapor species of different molecular weights, the equilibrium pressure would be $0.97P_0$, a factor which is unimportant in the thermodynamic results in this paper and within the uncertainties in the vapor pressure measurements.

Third-law values of $\Delta H^0(298\ \text{K})$ of the vaporization reactions were calculated from the equilibrium vapor pressures and the standard Gibbs energy function $\phi^0(T)$ in which

$$\phi^0(T) = -\left[G^0(T) - H^0(298\ \text{K})\right]/T \tag{9}$$

with the equation [22]:

$$\Delta H^0(298\ \text{K}) = T\Delta\phi^0(T) - RT\ \log_e\left(K_p/\text{Pa}^m\right) + 11.526mRT \tag{10}$$

where the last term corrects the pressure to the standard pressure of 1 atm. The third-law method is preferred to the second-law method because results from the former are less affected by temperature-dependent effects [22,23].

The values of the Gibbs energy functions of PbS(s), PbS(g), Ga_2S_3(s), Ga_2S(g), and S_2(g) were obtained from the literature [8]. Gibbs energy functions of ternary compounds were calculated as the sums of the Gibbs energy functions of the binary constituents.

Tables 1 and 2 give values of the Gibbs energy functions used in this work. In Table 1 the first column gives the temperature, and subsequent columns give the values of the Gibbs energy functions of PbS(s), PbS(g),

TABLE 1

Gibbs energy functions of binary constituents, S_2, and reaction (16)

T (K)	$-[G^0(T) - H^0(298\ \text{K})]/T$ (J mol^{-1} K^{-1})					Reaction (16)
	PbS(s)	PbS(g)	Ga_2S_3(s)	Ga_2S(g)	S_2(g)	
800	265.01	109.50	182.30	308.24	240.58	366.52
900	267.82	113.47	191.25	312.29	243.09	364.13
1000	270.45	117.24	199.95	316.14	245.68	361.87
1100	272.96	120.88	208.28	319.82	248.19	359.73
1200	275.04	124.31	216.31	323.30	250.50	357.49
1300	277.56	127.57	224.05	326.65	252.59	355.19

TABLE 2

Gibbs energy functions of $Pb_2Ga_2S_5$ and related ternary compounds

T (K)	$-[G^0(T) - H^0(298\ K)]/T$ (J mol^{-1} K^{-1})				Reactions (11)-(15)
	$Pb_2Ga_2S_5$	$Pb_4Ga_6S_{13}$	$PbGa_2S_4$	$Pb_2Ga_6S_{11}$	
800	401.29	984.87	291.79	765.88	155.52
900	418.19	1027.63	304.72	800.69	154.35
1000	434.42	1068.80	317.19	834.33	153.22
1100	450.03	1108.34	329.16	866.59	152.09
1200	464.93	1146.16	340.62	897.55	151.00

Ga_2S_3(s), Ga_2S(g), S_2(g), and reaction (16), respectively, at the temperatures in the first column. In Table 2 the first column gives the temperatures, and the subsequent columns give the corresponding values of the Gibbs energy functions of $Pb_2Ga_2S_5$(s), $Pb_4Ga_6S_{13}$(s), $PbGa_2S_4$(s), $Pb_2Ga_6S_{11}$(s), and reactions (11)–(15), respectively.

RESULTS

Preliminary experiments

The Debye–Scherrer X-ray diffractograms of the samples showed them to be mixtures of $Pb_2Ga_2S_5$ and $PbGa_2S_4$ for compositions between $Pb_2Ga_2S_5$ and $PbGa_2S_4$, and mixtures of $PbGa_2S_4$ and Ga_2S_3 for compositions between those of $PbGa_2S_4$ and Ga_2S_3. The *d*-spacings calculated from the X-ray diffractogram of $PbGa_2S_4$ matched those listed in the JCPDS file 23-348 for $PbGa_2S_4$.

Mass spectrometry of a sample with the composition $Pb_4Ga_6S_{13}$ in the temperature range 963–1158 K gave the following ions: PbS^+, Pb^+, S^+, Ga_2S^+, S_2^+, Ga^+, and Ga_2^+. Comparison of the relative pressures of the ions revealed that at the onset of the experiment and until all the PbS was vaporized from the sample, the predominant vapor species was PbS. After the PbS was exhausted from the sample, the vapor species were Ga_2S(g) and S_2(g). Thus, the vaporization process is incongruent with loss of PbS(g) up to the composition of Ga_2S_3. No ternary vapor species containing Pb, Ga, and S was observed.

Effusion cells and apparatus

The dimensions of the effusion cells are given in Table 3. The first column gives the cell designation and the second column gives the orifice designation. The third to ninth columns give, respectively, the orifice area, the

TABLE 3

Effusion cell dimensions

Experiment	Orifice	Orifice area (10^{-3} cm^2)	Orifice length (cm)	$\frac{\text{Length}}{\text{radius}}$	Moment arm (cm)	W	F	θ (deg)
1	I	2.790 ± 0.131	0.128 ± 0.001	4.295 ± 0.011	0.800 ± 0.001	0.3415 ± 0.0010	0.3859 ± 0.0011	–
	II	2.850 ± 0.113	0.128 ± 0.001	4.252 ± 0.008	0.805 ± 0.001	0.3437 ± 0.0011	0.3883 ± 0.0010	–
2	I	8.820 ± 0.330	0.218 ± 0.001	4.110 ± 0.080	0.790 ± 0.003	0.3508 ± 0.0033	0.3961 ± 0.0038	–
	II	8.820 ± 0.330	0.213 ± 0.001	4.020 ± 0.080	0.800 ± 0.003	0.3555 ± 0.0035	0.4013 ± 0.0039	–
3	I	5.360 ± 0.100	0.209 ± 0.003	5.061 ± 0.375	0.798 ± 0.003	0.9032 ± 0.0022	1.0930 ± 0.0033	29.39 ± 0.35
	II	5.190 ± 0.100	0.208 ± 0.003	5.117 ± 0.385	0.798 ± 0.003	0.9032 ± 0.0022	1.0933 ± 0.0034	29.33 ± 0.35

orifice length, the length-to-radius ratio, the moment arm, the transmission probability, the recoil-force correction factor, and the semiapex angles of the conical orifices used in experiment 3 (in the other two experiments, the orifices were cylindrical).

The torsion constant of the fiber used in experiment 1 was 0.308 ± 0.010 dyne × cm rad^{-1} before and after experiment 1, that used in experiment 2 was 0.304 ± 0.002 dyne × cm rad^{-1} before and after experiment 2, and that used in experiment 3 was 0.302 ± 0.006 dyne × cm rad^{-1} before and after experiment 3.

Vapor pressures and thermodynamics

At the start of experiment 1 and until 73.7 ± 0.2 mg (22.7 ± 0.1%) of sample had been lost, the vapor pressure was univariant. This composition region was named region 1. When the sample composition changed by vapor loss past region 1, the vapor pressure at a given temperature decreased by 45–60%. Following this decrease, the vapor pressure again became univariant until a total of 107.7 ± 0.2 mg (33.2 ± 0.1%) of sample had been lost. This second composition region, from 22.7 to 33.2% sample lost, was named region 2. The vapor pressure at a given temperature then decreased by 80–95% relative to that in region 2, and once again the vapor pressure became univariant until a total of 148.8 ± 0.2 mg (45.9 ± 0.1%) of sample had been lost. This composition region, from 33.2 to 45.9% sample lost, was named region 3. Then the vapor pressure at a given temperature decreased by 80–90% relative to that in region 3, and the vapor pressure again became univariant until a total of 174.0 ± 0.2 mg (53.6 ± 0.1%) of sample had been lost. This fourth composition region, from 45.9 to 53.6% sample lost, was named region 4. Then the vapor pressure became bivariant, i.e., depended on temperature and composition. This bivariance lasted until 216.8 ± 0.2 mg (66.9 ± 0.1%) of the sample had been lost. This composition region, from 53.6 to 66.9% sample lost, was a solid-solution region. The vapor pressure then became univariant and remained so until the sample was exhausted from the effusion cell. This last composition region, from 66.9 to 100% sample lost, was named region 5. Several data that were obtained while the sample was changing phase (region 1–2, region 2–3, region 3–4) were omitted from the subsequent analyses. The total mass lost during the collection of these data was less than 1% of the total sample mass.

From the mass spectrometry results, viz., that PbS is the predominant vapor species as long as it is present in the sample, the initial sample composition, and the total mass loss, the sample composition at the changes between regions was calculated. The sample compositions at the beginning of each region in experiment 1 were: region 1, $Pb_2Ga_2S_5$; region 2, $Pb_{3.97 \pm 0.07}Ga_{6.00}S_{12.97 \pm 0.07}$; region 3, $Pb_{1.01 \pm 0.01}Ga_{2.00}S_{4.01 \pm 0.01}$; region 4, $Pb_{1.89 \pm 0.06}Ga_{6.00}S_{10.89 \pm 0.06}$; and region 5, $Ga_{2.00 \pm 0.01}S_{3.00 \pm 0.01}$. The formulas of the corresponding compounds were taken to be: region 1, $Pb_2Ga_2S_5$; region 2, $Pb_4Ga_6S_{13}$; region 3, $PbGa_2S_4$; region 4, $Pb_2Ga_6S_{11}$; and region 5, Ga_2S_3. The solid-solution was taken to be PbS in Ga_2S_3. Thus, the vaporization reactions for this system are:

$$3/2\ Pb_2Ga_2S_5(s) = PbS(g) + 1/2\ Pb_4Ga_6S_{13}(s) \tag{11}$$

$$Pb_4Ga_6S_{13}(s) = PbS(g) + 3\ PbGa_2S_4(s) \tag{12}$$

$$3\ PbGa_2S_4(s) = PbS(g) + Pb_2Ga_6S_{11}(s) \tag{13}$$

$$1/2\ Pb_2Ga_6S_{11}(s) = PbS(g) + 3/2\ Ga_2S_3(ss) \tag{14}$$

$$PbS(ss, in\ Ga_2S_3) = PbS(g) \tag{15}$$

$$Ga_2S_3(s) = Ga_2S(g) + S_2(g) \tag{16}$$

In experiments 2 and 3, the same five regions of univariant vapor pressures and the region of bivariant vapor pressures between regions 4 and 5 were observed. In experiment 2, the sample compositions at the beginning of each region were: region 1, $Pb_2Ga_2S_5$; region 2, $Pb_{3.92 \pm 0.05}Ga_{6.00}S_{12.92 \pm 0.05}$; region 3, $Pb_{1.02 \pm 0.01}Ga_{2.00}S_{4.02 \pm 0.01}$; region 4, $Pb_{1.86 \pm 0.07}Ga_{6.00}S_{10.86 \pm 0.07}$; and region 5, $Ga_{2.00 \pm 0.01}S_{3.00 \pm 0.01}$. The transition between regions 3 and 4 was not as distinct in this experiment as it was in experiment 1. In experiment 3, the sample compositions at the beginning of each region were: region 1, $Pb_2Ga_2S_5$; region 2, $Pb_{3.90 \pm 0.10}Ga_{6.00}S_{12.90 \pm 0.10}$; region 3, $Pb_{1.00 \pm 0.02}Ga_{2.00}S_{4.00 \pm 0.02}$; region 4, $Pb_{1.86 \pm 0.06}Ga_{6.00}S_{10.86 \pm 0.06}$; and region 5, $Ga_{2.00 \pm 0.01}S_{3.00 \pm 0.01}$. The transitions between the regions were not as distinct as in experiment 1.

Table 4 gives the parameters from the least-squares treatment of $\log_{10}(P/\mathrm{Pa})$ vs. $1/T$ by eqn. (7). The first column gives the experiment and region designation, the second column gives the type of measurement, torsion, t, or Knudsen, K, the third and fourth columns give the value of C and its standard deviation, respectively, the fifth and sixth columns give the value of D and its standard deviation, respectively, and the seventh column gives the covariance between C and D.

The results from the weighted least-squares treatment of the data with eqn. (8) are given in Table 5. The composition region is given in the first column, the type of measurement is given in column two, the ratio of the vapor pressure at zero orifice area to the measured vapor pressure in experiment 1 and its standard deviation are given in column three, and the average condensation coefficient and its standard deviation are given in column four. The average condensation coefficients were calculated on the basis of a sample area of 2.38 cm^2.

Tables 6 through 10 give the equilibrium results in the order in which they were obtained after correction to zero orifice area with eqn. (8). In each table the first column gives the order in which the data were obtained, the second column gives the temperature, the third column gives the vapor

TABLE 4

Parameters in eqn. (7) for $\log_{10}(P/\mathrm{Pa})$ vs. $1/T$

Expt.	Region	Type	$-C$	σ_C	D	σ_D	$-\mathrm{cov}(C, D)$
1	1	t	11472.2	295.5	12.20	0.30	88.68
		K	11757.9	429.4	12.46	0.43	186.28
	2	t	9725.6	527.4	10.19	0.54	281.85
		K	8439.6	1029.9	8.93	1.02	1048.80
	3	t	12670.4	466.9	12.28	0.43	202.25
		K	13192.0	721.2	12.74	0.66	477.07
	4	t	13434.9	647.4	12.42	0.58	380.14
		K	12362.4	800.6	11.40	0.73	581.61
	5	t	14013.1	869.6	12.13	0.72	624.56
		K	14095.5	851.6	12.22	0.70	595.03
2	1	t	10523.3	704.2	11.04	0.71	501.42
		K	11537.1	1052.0	12.02	1.06	1110.14
	2	t	11442.2	1207.6	11.69	1.17	1416.94
		K	11460.9	1039.9	11.69	1.01	1050.24
	3	t	13591.9	730.8	13.01	0.68	493.65
		K	12712.1	930.5	12.18	0.86	795.65
	4	t	13247.4	1007.1	12.56	0.92	922.20
		K	12020.8	1395.1	11.41	1.26	1761.40
	5	t	16548.2	422.0	14.07	0.36	159.52
		K	16708.4	400.8	14.15	0.32	130.70
3	1	t	9581.4	969.6	10.08	0.99	959.91
		K	8930.6	1454.7	9.42	1.47	2139.12
	2	t	10441.5	1289.8	10.61	1.25	1616.28
		K	10882.7	1478.8	11.02	1.44	2124.84
	3	t	12473.9	658.0	11.99	0.61	402.86
		K	12183.7	768.2	11.70	0.71	546.65
	4	t	13426.0	1198.2	12.61	1.09	1308.09
		K	12728.8	1941.1	11.94	1.76	3415.96
	5	t	17115.8	270.1	14.54	0.22	60.10
		K	17185.4	334.3	14.56	0.27	91.76

TABLE 5

Vapor pressures at zero orifice area relative to measured vapor pressures in experiment 1, and condensation coefficients

Region	Type	P_0/P_m	Cond. coeff.
1	K	1.2367 ± 0.0554	$(3.216 \pm 0.435) \times 10^{-3}$
1	t	1.2248 ± 0.0545	$(3.723 \pm 0.966) \times 10^{-3}$
2	K	1.2802 ± 0.0548	$(2.741 \pm 0.570) \times 10^{-3}$
2	t	1.2917 ± 0.0284	$(2.815 \pm 0.291) \times 10^{-3}$
3	K	1.0161 ± 0.0169	$(1.567 \pm 0.591) \times 10^{-2}$
3	t	1.0440 ± 0.0205	$(9.980 \pm 0.314) \times 10^{-3}$
4	K	0.8652 ± 0.0033	$(5.968 \pm 0.079) \times 10^{-3}$
4	t	0.8869 ± 0.0100	$(6.980 \pm 0.206) \times 10^{-3}$
5	K	0.8887 ± 0.0224	$(2.136 \pm 0.716) \times 10^{-2}$
5	t	0.9346 ± 0.0123	$(2.899 \pm 1.479) \times 10^{-2}$

TABLE 6

Equilibrium vapor pressures in region 1 and third-law ΔH^0(298 K) of reaction (11)

Order	Temp. (K)	P_k (Pa)	P_t (Pa)	ΔH^0(298 K) (kJ mol^{-1})	
				Knudsen	Torsion
1	985.8		5.49		231.7
2	1055.0		30.56		232.1
3	960.0	2.69	2.16	231.6	233.4
4	1008.3	11.55	11.53	230.5	230.5
5	938.5		0.99		234.4
6	942.0	1.17	1.32	234.0	233.0
7	976.6	3.17	3.37	234.1	233.6
8	1029.0	13.65	13.45	233.6	233.7
9	1008.0	8.19	7.49	233.3	234.1
10	913.0	0.41	0.57	235.1	232.5
11	981.0	3.46	3.85	234.4	233.5
12	924.1		0.83		232.4
13	986.0	4.16	4.40	234.0	233.6
14	1020.0	11.36	11.03	233.2	233.4
15	977.0	3.25	3.16	234.0	234.2
16	1001.2	7.01	7.16	233.1	232.9
17	945.4	1.31	1.31	233.9	233.9
18	1033.4	14.91	14.78	233.8	233.8
19	1023.0	10.86	11.84	234.2	233.5
20	943.6		1.22		234.1
21	972.4	2.80	2.99	234.1	233.6
22	1049.3	18.93	18.63	235.1	235.2
23	1015.8	7.43	7.80	235.9	235.5
			Average:	233.8 ± 0.3	233.4 ± 0.2
			Selected:	233.6 ± 0.4	

TABLE 7

Equilibrium vapor pressures in region 2 and third-law ΔH^0(298 K) of reaction (12)

Order	Temp. (K)	P_k (Pa)	P_t (Pa)	ΔH^0(298 K) (kJ mol^{-1})	
				Knudsen	Torsion
1	987.0	3.00	2.93	236.9	237.1
2	1013.0	5.89	5.80	237.2	237.3
3	968.8		1.71		237.3
4	999.0	3.94	3.82	237.4	237.7
5	1031.0		8.67		237.9
6	950.9		0.93		237.9
7	953.3		1.43		235.1
8	920.0		0.55		234.5
9	1010.0	4.29	4.68	239.2	238.5
10	1051.2	10.04	8.90	241.0	242.1
			Average:	238.3 ± 0.8	237.5 ± 0.6
			Selected:	237.9 ± 1.0	

TABLE 8

Equilibrium vapor pressures in region 3 and third-law $\Delta H^0(298\ \mathrm{K})$ of reaction (13)

Order	Temp. (K)	P_k (Pa)	P_t (Pa)	$\Delta H^0(298\ \mathrm{K})$ (kJ mol^{-1})	
				Knudsen	Torsion
1	1086.2	4.31	4.20	256.3	256.5
2	1042.0	1.09	1.33	258.3	256.5
3	1099.2	5.83	6.14	256.4	255.9
4	1131.0	12.74	13.39	256.1	255.6
5	1113.2	8.18	8.47	256.4	256.1
6	968.0		0.17		255.5
7	1023.4	0.85	0.82	256.0	256.2
8	1086.6	4.13	4.18	256.7	256.6
9	1076.4	3.16	3.19	256.8	256.8
10	1152.8	23.06	25.23	255.1	254.2
11	1104.0	4.30	4.45	260.3	260.0
			Average:	256.8 ± 0.5	256.4 ± 0.4
			Selected:	256.6 ± 0.7	

pressure from Knudsen-effusion measurements, the fourth column gives the vapor pressure from torsion-effusion measurements, and the fifth and sixth columns give the third-law $\Delta H^0(298\ \mathrm{K})$ of the reaction listed in the heading

TABLE 9

Equilibrium vapor pressures in region 4 and third-law $\Delta H^0(298\ \mathrm{K})$ of reaction (14)

Order	Temp. (K)	P_k (Pa)	P_t (Pa)	$\Delta H^0(298\ \mathrm{K})$ (kJ mol^{-1})	
				Knudsen	Torsion
1	1129.0		4.46		265.5
2	1143.2		6.00		265.9
3	1083.2	1.04	0.96	268.4	269.1
4	1091.0	1.13	1.15	269.5	269.3
5	1003.2		0.09		270.0
6	1056.7	0.41	0.47	270.4	269.1
7	1033.6	0.25	0.25	269.0	268.9
8	1115.7	2.06	2.30	269.7	268.7
9	1145.5	4.39	4.67	269.3	268.7
10	1108.0	1.71	1.62	269.7	270.1
11	1111.5	1.46	1.65	271.9	270.8
12	1151.0	4.35	4.42	270.6	270.4
13	1124.8	2.52	2.50	269.9	270.0
14	1153.8	3.37	3.63	273.7	273.0
15	1111.8	1.15	1.52	274.2	271.6
16	1059.8	0.47		269.9	
17	1096.8	0.83		273.6	
			Average:	270.7 ± 0.5	269.4 ± 0.5
			Selected:	270.0 ± 0.7	

TABLE 10

Equilibrium vapor pressures in region 5 and third-law ΔH^0(298 K) of reaction (16)

Order	Temp. (K)	P_k (Pa)	P_t (Pa)	ΔH^0(298 K) (kJ mol^{-1})	
				Knudsen	Torsion
1	1238.1	6.23	7.36	656.0	652.6
2	1210.5	4.02	4.13	650.9	650.4
3	1206.3	3.53	3.48	651.4	651.7
4	1240.5	8.99	8.43	649.6	650.9
5	1256.1	11.86	10.47	651.6	654.2
6	1233.1	5.76	6.10	655.1	653.9
7	1261.4	11.55	11.40	654.7	655.0
8	1267.4	13.92	13.22	653.7	654.8
9	1116.3		1.20		625.1
10	1173.2	2.57	2.52	640.6	640.9
11	1197.0		3.00		649.8
12	1221.5	5.31	4.99	650.9	652.1
13	1213.0	4.28	3.72	650.9	653.8
14	1138.3	1.16	0.99	637.4	640.4
15	1170.8	1.83	1.81	645.9	646.1
16	1224.8	5.44	5.25	652.1	652.8
17	1267.7	12.79	13.17	655.7	655.0
18	1240.2	6.13	6.94	657.4	654.8
19	1252.2	8.93	9.42	655.6	654.4
20	1160.1		0.94		653.1
21	1204.7	3.10	3.02	653.1	653.7
22	1195.1	1.93	2.04	657.6	656.5
23	1241.9	6.18	6.18	658.1	658.1
24	1261.1	10.22	9.75	657.1	658.1
25	1223.9	3.59	3.72	660.1	659.3
26	1245.4	5.90	6.07	660.8	660.2
27	1231.0	4.21	3.99	660.4	661.5
28	1197.6	1.76	1.69	660.8	661.6
29	1124.1	0.39	0.21	650.2	662.2
30	1181.6	1.16	1.10	660.6	661.5
31	1153.5		0.60		658.3
32	1212.3	2.72	2.80	659.7	659.1
33	1240.4	5.35	6.16	660.3	657.4
34	1223.2	3.50	3.80	660.2	658.5
35	1259.7	9.01	9.47	659.1	658.0
36	1180.3		1.14		660.2
37	1226.4	3.75	3.83	660.4	660.0
38	1158.9	0.52	0.56	664.1	662.4
39	1259.7	8.37	9.26	660.6	658.5
			Average:	655.1 ± 1.0	654.5 ± 1.1
			Selected:	654.8 ± 1.5	

TABLE 11

Parameters in eqn. (7) for $\log_{10}K_p$ vs. $1/T$, Experiment 1

In regions 1–4 apparent units of K_p are Pa and in region 5 are Pa^2

Region	Type	$-C$	σ_C	D	σ_D	$-\mathrm{cov}(C, D)$
1	t	11470.1	295.5	12.26	0.30	88.65
	K	11755.6	429.3	12.51	0.43	186.21
2	t	9728.5	527.2	10.30	0.53	281.58
	K	8441.3	1030.2	9.05	1.02	1049.11
3	t	12667.9	466.8	12.28	0.43	202.17
	K	13190.6	721.1	12.75	0.66	476.94
4	t	13431.3	647.3	12.36	0.59	380.06
	K	12359.1	800.4	11.33	0.72	581.35
5	t	28124.8	1712.9	23.66	1.41	2421.67
	K	28201.1	1670.1	23.72	1.37	2287.21

of the table from the measurements by the Knudsen and torsion methods, respectively. At the bottoms of the fifth and sixth columns are given the average third-law $\Delta H^0(298\ \mathrm{K})$. Finally, at the bottom of column 6 the selected value of $\Delta H^0(298\ \mathrm{K})$ is given.

Table 11 gives the parameters from the least-squares treatment of the straight-line fit of equilibrium data to eqn. (7). The first column gives the experiment and region designation, the second column gives the type of measurement, the third and fourth columns give the value of C and its standard deviation, respectively, the fifth and sixth columns give the value of D and its standard deviation, respectively, and the seventh column gives the covariance between C and D.

The average $\Delta H^0(298\ \mathrm{K})$ of vaporization of PbS from Mills [8] combined with the selected $\Delta H^0(298\ \mathrm{K})$ of reactions (11)–(14) yields $\Delta H^0(298\ \mathrm{K})$ of the combination reaction per mol of PbS,

$$x\ \mathrm{PbS(s)} + y\ \mathrm{Ga_2S_3(s)} = \mathrm{Pb}_x\mathrm{Ga}_{2y}\mathrm{S}_{x+3y}\mathrm{(s)} \tag{17}$$

of -39.90 ± 4.0 kJ $\mathrm{mol^{-1}}$ for $Pb_2Ga_6S_{11}$, -35.43 ± 3.0 kJ $\mathrm{mol^{-1}}$ for $PbGa_2S_4$, -28.52 ± 3.0 kJ $\mathrm{mol^{-1}}$ for $Pb_4Ga_6S_{13}$, and -20.18 ± 2.0 kJ $\mathrm{mol^{-1}}$ for $Pb_2Ga_2S_5$.

The average apparent molecular weight of the vapor was: 229.7 ± 6.0 g $\mathrm{mol^{-1}}$ for region 1; 223.5 ± 8.8 g $\mathrm{mol^{-1}}$ for region 2; 220.1 ± 8.1 g $\mathrm{mol^{-1}}$ for region 3; 224.7 ± 12.8 g $\mathrm{mol^{-1}}$ for region 4; and 125.9 ± 6.5 g $\mathrm{mol^{-1}}$ for region 5.

A Raoult's law correction was applied to several data chosen from the solid-solution region, between the fourth and fifth regions, in experiment 1. The standard state chosen for this calculation was the saturated solid solution of PbS in Ga_2S_3. The vaporization reaction is given by eqn. (15). The equilibrium constant of this reaction is the product of the equilibrium pressure and the ratio of the equivalent fraction of PbS in the standard state to the equivalent fraction of PbS in the solid solution. The third-law ΔH^0(298 K) of reaction (15) was 269.6 ± 1.5 kJ mol^{-1}, which leads to ΔH^0(298 K) of the saturated solution of -39.5 ± 4.3 kJ mol^{-1} of PbS.

Throughout the three vaporization experiments no anomalous vapor pressure increase similar to that observed by Kshirsagar and Edwards [11], Starzynski and Edwards [12], and Roberts and Searcy [13] was observed during the vaporization of Ga_2S_3.

DISCUSSION

The vapor pressure over the PbS–Ga_2S_3 system was measured by the Knudsen-effusion and torsion-effusion methods in the temperature range of 898–1267 K. The four ternary Pb–Ga–S-containing compounds were found to vaporize incongruently. The compounds and corresponding vaporization reactions were: $Pb_2Ga_2S_5$, reaction (11); $Pb_4Ga_6S_{13}$, reaction (12); $PbGa_2S_4$, reaction (13); and $Pb_2Ga_6S_{11}$, reaction (14). This investigation revealed ΔH^0(298 K) of reaction (11) to be 233.6 ± 0.4 kJ mol^{-1}, of reaction (12) to be 237.9 ± 1.0 kJ mol^{-1}, of reaction (13) to be 256.6 ± 0.7 kJ mol^{-1}, and of reaction (14) to be 270.0 ± 0.7 kJ mol^{-1}. The vaporization of PbS by reaction (15) was treated as vaporization from an ideal solution with a ΔH_v^0(298 K) of 269.6 ± 1.5 kJ mol^{-1}. The uncertainty in this value arises from the uncertainty of the equivalent fraction of PbS remaining in the solution. The vaporization of Ga_2S_3 was found to be congruent by reaction (16) and the ΔH^0(298 K) of Ga_2S_3 by reaction (16) was 654.8 ± 1.5 kJ mol^{-1}.

The compounds $Pb_4Ga_6S_{13}$ and $Pb_2Ga_6S_{11}$ have not previously been reported [3–5]. These compounds existed only at the high temperatures of the experiments. They were not found at room temperature because, as the samples were quenched, the compounds disproportionated into $Pb_2Ga_2S_5$ and $PbGa_2S_4$ in the case of $Pb_4Ga_6S_{13}$, and $PbGa_2S_4$ and Ga_2S_3 in the case of $Pb_2Ga_6S_{11}$.

The values obtained for the ΔH^0(298 K) of combination per mole of PbS by reaction (17), -20 to -40 kJ mol^{-1}, were intermediate among those of other ternary metal sulfides, which range from -15 to -50 kJ mol^{-1} [24,25].

The quality of agreement between the average apparent molecular weight and the calculated average molecular weight of the effusing vapor for reactions (11) through (14) was only moderate. The values of the average apparent molecular weights were too low by approximately 10 to 20 g mol^{-1} when compared to the molecular weight of PbS(g), 239.3 g mol^{-1}. If approximately 1–2% of lead and/or sulfur were in the vapor phase, then the value of the average apparent molecular weight of the effusing vapor would be lower than that of a vapor consisting of only lead sulfide by the amount observed. Such could arise if lead sulfide molecules in the vapor phase dissociate to a small extent into lead atoms and S_2 molecules. Good agreement was found between the average apparent molecular weight of the effusing vapor from residual Ga_2S_3 and the calculated average molecular weight of gallium sulfide vapor by reaction (16), 125.9 ± 6.5 g mol^{-1} compared to 124.7 g mol^{-1}.

During the second and third experiments, the transitions between the regions were not as distinct as those in the first experiment. This behavior was due to kinetic factors occurring within the solid sample and leading to momentary nonequilibrium vaporization conditions within the effusion cell. The total effective orifice area of the effusion cell used in experiment 3 was ca. 5 times larger than the total effective orifice area of the effusion cell used in experiment 1, and that in experiment 2 was ca. 3 times larger. These larger effective orifice areas altered the equilibrium within the effusion cell, which made it more difficult to distinguish phase changes that occurred within the solid sample.

The vapor pressure over Ga_2S_3 observed in this experiment at a given temperature was between that observed by Edwards and Kshirsagar [11] and that observed by Starzynski and Edwards [12] at the same temperature. During the vaporization of Ga_2S_3, no anomalous vapor pressure increase was observed upon lowering the temperature across 1228 ± 3 K [11–13]. Also, no "break" or discontinuity in the slope of the log P vs. $1/T$ line at 1173 ± 5 K as reported by Starzynski and Edwards [12] was observed in this work. Starzynski and Edwards [12] discuss the possibility that more than one form of "Ga_2S_3" exists. In a recent study of In_2Se_3, Srinivasa and Edwards [26] found several condensed phases involved in the vaporization processes at various stages of evaporation of the material. They note similarities between the vaporization behavior of In_2Se_3 and that of Ga_2S_3. It is likely that Ga_2S_3 is a complicated vaporizing system and that several phases must be taken into account to explain all of the known results on the system.

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