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Vaporization chemistry in the gallium-sulfur system

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Abstract

Various attempts were made to reproduce the anomalous variation in vapor composition with decreasing temperature of gallium sulfide (Ga_2S_3), first observed by Roberts and Searcy (RS) as an increase in the partial pressure of $Ga_2S(g)$. The simultaneous Knudsen and torsion (Volmer) effusion method was applied in the range 1095-1284 K to stoichiometric, sulfur-rich, and gallium-rich samples prepared by two methods. In every case, effusion experiments resulted in room-temperature residues of α-Ga_2S_3. The anomalous phenomenon of RS was never observed in this work, but the results, along with a survey of the literature, made it possible to establish conditions necessary for its observation. With samples of normal size, of cross section of around 1 cm^2, the key factor is a small effective area of the effusion orifice, namely < 0.12 mm^2. The possibility is presented that the type of chemical reaction taking place during vaporization can depend on orifice area; the range of literature values of $\Delta H^{\ominus}(298\ K)$ for vaporization of $Ga_2S_3(s)$ (645-661 kJ mol^{-1}) may be related to such an effect.

INTRODUCTION

This work is from the MS Thesis of the first author [1]. It is part of a continuing effort to understand unusual vaporization and effusion phenomena in high-temperature materials. Metal sulfides appear to be especially fecund for this effort; gallium sulfide is an example of a much broader set of systems which exhibit unusual chemical phenomena during vaporization and effusion.

The structure and phase equilibria of gallium sulfide have been extensively studied. Goodyear and Steigmann [2] reported the crystal structure of α-$Ga_2S_3(s)$ to be monoclinic, with lattice constants $a = 11.14$ Å, $b = 6.41$ Å, and $c = 7.03$ Å, and $\beta = 121.22°$. Its structure belongs to space group *Cc*. Three different temperature-composition phase diagrams of the Ga-S system have been reported [3-5]. Lieth et al. [3] reported GaS(s) and $Ga_2S_3(s)$ with melting points of 962 ± 2°C and 1090 ± 2°C, respectively,

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and a eutectic point at 893 ± 7°C and 55% sulfur. Rustamov et al. [4] reported three types of $Ga_2S_3(s)$: α-$Ga_2S_3(s)$, stable from room temperature to its transition temperature between 550 and 600°C; β-$Ga_2S_3(s)$, stable from 550–600°C to 1020°C; and γ-$Ga_2S_3(s)$, stable from 1020°C to its melting point at 1120 ± 10°C. They also reported the phases GaS(s), which melts at 1015 ± 10°C, and $Ga_2S(s)$ and $Ga_4S_5(s)$ which are formed from peritectic reactions at 960 ± 10°C and 940 ± 10°C, respectively. Pardo et al. [5] described three crystalline forms of $Ga_2S_3(s)$: monoclinic α'-$Ga_2S_3(s)$, stable from room temperature to its melting point at 1100°C; and hexagonal α-$Ga_2S_3(s)$ and wurtzite-type β-Ga_2S_3, sulfur-deficient modifications formed in the presence of GaS(s) in the temperature range 885–1080°C.

The literature reports [2,4,5] of the names of the different crystalline forms of $Ga_2S_3(s)$ are not consistent with one another. The phase α-$Ga_2S_3(s)$ reported by Goodyear and Steigmann [2] and the phase α'-$Ga_2S_3(s)$ reported by Pardo et al. [5] are the same. It is not clear if any of the $Ga_2S_3(s)$ phases, (α, β, or γ) reported by Rustamov et al. [4] are the same as α-$Ga_2S_3(s)$ [2]. Also, it is possible that the phases β-$Ga_2S_3(s)$ reported by Rustamov et al. [4] and Pardo et al. [5] are the same. Throughout the remainder of this paper when reference is made to α-$Ga_2S_3(s)$, the phase reported by Goodyear and Steigmann [2] will be assumed.

The vaporization chemistry of $Ga_2S_3(s)$ has been studied by a variety of methods. The reported mode of vaporization of $Ga_2S_3(s)$ varied. The most unusual observation was that upon cooling Ga_2S_3 across a transition temperature in the range 1225–1245 K, the partial pressure of $Ga_2S(g)$ anomalously increased while that of $S_2(g)$ decreased. This observation will be referred to in this paper as the Anomalous Phenomenon.

Spandau and Klanberg [6] reported that above 950°C in a nitrogen atmosphere $Ga_2S_3(s)$ loses sulfur by the reaction

$$2Ga_2S_3(s) = Ga_4S_5(s) + 0.5S_2(g) \tag{1}$$

Uy et al. [7] studied the vaporization of $Ga_2S_3(s)$ by mass spectrometry in the temperature range 897–1028 K. They reported it to be congruent by the reaction

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

Kashkooli and Munir [8] (KM) measured the vapor pressure of $Ga_2S_3(s)$ by the torsion-effusion method in the temperature range 1129–1304 K. Their vapor pressures, in conjunction with free-energy functions from Mills [9], yielded a third-law $\Delta H^{\ominus}(298\ K)$ value of 661.4 ± 0.3 kJ mol^{-1} for the vaporization of $Ga_2S_3(s)$ by reaction (2) [10].

Roberts and Searcy [11] (RS) discovered the Anomalous Phenomenon. They studied the vaporization of $Ga_2S_3(s)$ by mass spectrometry and reported that upon lowering the temperature from 1228 ± 3 to 1203 K, the partial pressure of one of the two principal vapor molecules, $Ga_2S(g)$, increased anomalously by about 50% instead of decreasing by 50%, as expected from their knowledge of the variation of partial pressure with temperature in other temperature ranges. During the same time the partial pressure of the other principal vapor molecule, $S_2(g)$, decreased. They attributed this anomaly to a transformation and to changes with temperature in the equilibrium compositions of two solid phases, a low-temperature form (l-Ga_2S_3) and a high-temperature form (h-Ga_2S_3) of $Ga_2S_3(s)$ that coexist with the vapor at 1228 ± 3 K.

Starzynski and Edwards [12] (SE) observed the Anomalous Phenomenon while measuring the difference between the vapor pressure over $Ga_2S_3(s)$ and the vapor pressure over the two-phase mixture $MnGa_2S_4(s)/Mn_3Ga_2S_6(s)$ during a differential torsion-effusion experiment in the temperature range 1098–1242 K. When the temperature was lowered from 1242 to 1194 K, the differential pressure dropped as expected, rose isothermally to a univariant plateau for a period of about 2 h, then decreased through a bivariant condition to a value expected from measurements of pressure in other temperature ranges. They also observed a change in the slope of $\log P(Ga_2S_3)$ versus $1/T$ at 1173 ± 5 K. They reported a third-law $\Delta H^{\ominus}(298\ \text{K})$ value of 644 ± 10 kJ mol^{-1} for the vaporization of $Ga_2S_3(s)$ by reaction (2).

Kshirsager and Edwards [10] (KE) measured the vapor pressure of residual $Ga_2S_3(s)$ in the temperature range 1130–1280 K while studying the vaporization chemistry in the $CdS–Ga_2S_3$ system. They observed the Anomalous Phenomenon after lowering the temperature from 1280 to 1240 K and after lowering the temperature from 1268 to 1228 K. They reported a third-law $\Delta H^{\ominus}(298\ \text{K})$ value of 663.4 ± 0.8 kJ mol^{-1} for the vaporization of $Ga_2S_3(s)$ by reaction (2).

Williamson and Edwards [13] (WE) measured the vapor pressure of residual $Ga_2S_3(s)$ in the temperature range 1116–1268 K while studying the vaporization chemistry in the $PbS–Ga_2S_3$ system but reported no observation of the Anomalous Phenomenon. They reported a third-law $\Delta H^{\ominus}(298\ \text{K})$ value of 654.8 ± 1.5 kJ mol^{-1} for vaporization of $Ga_2S_3(s)$ by reaction (2).

Weber [14] studied the vaporization of $Ga_2S_3(s)$ by mass spectrometry and found that upon cooling the sample from 1238 to 1190 K, the Anomalous Phenomenon was observed.

Recent work [15] has revealed the Anomalous Phenomenon several times when $Ga_2S_3(s)$ was studied by the simultaneous torsion-effusion and Knudsen-effusion method. The transition temperature was 1242 ± 2 K.

Among other Group IIIA chalcogenides, $Ga_2Se_3(s)$ and $In_2Se_3(s)$ were reported to vaporize congruently [7]. More recently, Grimes [16] and Srinivasa and Edwards [17] reported that $Ga_2Se_3(s)$ and $In_2Se_3(s)$, respectively, vaporize incongruently, with some characteristics similar to those of $Ga_2S_3(s)$.

Piacente et al. [18] studied the vaporization of GaS(s) by mass spectrometry, thermogravimetry, and torsion effusion in the temperature range 1026–1188 K. They reported it to be incongruent by the reaction

$$2Ga_2S_2(s) = Ga_2S_3(s) + Ga_2S(g) \tag{3}$$

We prefer to write eqn. (3) as

$$4GaS(s) = Ga_2S_3(s) + Ga_2S(g) \tag{4}$$

Their vapor pressures from torsion-effusion measurements in conjunction with free-energy functions from Mills [9] yielded a third-law $\Delta H^{\ominus}(298\ \mathrm{K})$ value of 303.9 ± 0.5 kJ mol^{-1}.

A feature common to experiments [10,12,14,15] that have yielded the Anomalous Phenomenon was a low effective area A_0W of the orifice in the cell [10] or a high ratio of sample surface area A_s to A_0W, where A_0 is the cross sectional area and W is the transmission probability [19,20]. A_s is a poorly defined concept and is rarely reported. For purposes of comparison, A_s was arbitrarily taken to be 100 mm^2 in all cases. In cases [10,12,14,15] where $A_0W \leq 0.115$ mm^2 or where the ratio of $A_s : A_0W \geqslant 870$, the Anomalous Phenomenon was observed. The orifices used by WE [13] had an A_0W value of ≤ 0.115 mm^2 and did not yield the Anomalous Phenomenon. This contradiction will be discussed below. The geometric properties of the cell used in the work of RS [11] were not available.

The vaporization behavior of other systems has been reported [21,22] to depend on A_0W or $A_s : A_0W$. Munir and Searcy [21] studied the vaporization of GaN(s) by the torsion-effusion method. They reported that GaN(s) vaporized congruently from a torsion-effusion cell when $A_s : A_0W \approx 30$ and incongruently when $A_s : A_0W \geq 100$. Myers et al. [22] studied the vaporization of $V_3P(s)$ by mass-loss effusion in the temperature range 1830–1900 K. They reported that $V_3P(s)$ vaporized congruently under non-equilibrium conditions when $A_0W \geqslant 1.32$ mm^2 and vaporized incongruently when $A_0W \leq 0.185$ mm^2.

The purposes of this work were: (1) to prepare solid samples of $Ga_2S_3(s)$ and solid samples which were gallium-rich and sulfur-rich with respect to $Ga_2S_3(s)$; (2) to use the simultaneous torsion- and Knudsen-effusion method to study the vaporization reactions in the gallium–sulfur system; (3) to calculate equilibrium constants and thermodynamic properties of those vaporization reactions; and (4) to determine the conditions which produce the Anomalous Phenomenon.

EXPERIMENTAL

Six samples were made with the atomic ratios of gallium to sulfur of 2.00, 1.00, 0.80, 0.67, 0.56, and 0.37. They were labeled S1–S6, respectively.

TABLE 1

Geometric properties of cells C1 and C2. The symbols in column one are the following: d, moment arm; L, length of the orifice; L/r, length-to-minimum radius ratio; Θ, semiapex angle; W, transmission probability; F, recoil force correction factor; A_0 area of the orifice; A_0W effective orifice area

Cell dimension	Cell C1		Cell C2	
	Orifice 1	Orifice 2	Orifice 1	Orifice 2
d (mm)	8.20 ±0.11	8.33 ±0.08	7.86 ±0.03	8.08 ±0.03
L (mm)	2.07 ±0.33	2.07 ±0.03	1.55 ±0.03	1.88 ±0.07
L/r	6.39 ±0.11	6.53 ±0.17	3.16 ±0.07	3.84 ±0.15
Θ (deg)	29.9 ±0.5	29.8 ±0.5	32.9 ±0.5	31.2 ±0.5
W	0.906±0.003	0.904±0.003	0.930±0.002	0.918±0.003
F	1.105±0.004	1.105±0.004	1.104±0.003	1.099±0.004
A_0 (mm^2)	0.330±0.006	0.316±0.007	0.754±0.003	0.754±0.003
A_0W (mm^2)	0.299±0.006	0.286±0.006	0.701±0.003	0.692±0.004

All samples, with the exception of S5, were prepared by heating the elements and a small amount of iodine in evacuated sealed Vycor tubes at 800 ± 10°C for several days. The iodine functioned as a mineralizing agent and was later sublimed away. Sample S5 was prepared by mixing excess sulfur and Ga_2S_3(s) which had been previously made. Two other samples labeled S3* and S4* were prepared by the same method and with the same compositions as those of S3 and S4, respectively, with the difference that S3* and S4* were protected from air contamination by working in an argon-filled glovebox with NaK desiccant. The elements were 99.99% gallium from Atomergic Chemetals Corp. and 99.999% sulfur and 99.99% iodine from Johnson Matthey Chemicals Limited. Debye–Scherrer X-ray powder diffractograms were made of all samples.

Vapor pressures of samples were measured by the computer-automated simultaneous torsion- and Knudsen-effusion method. The design and use of the apparatus have been described elsewhere [23–26]. Temperature measurements ≥ 1035 K were made with an optical pyrometer. Lower temperatures were estimated from the furnace power. Two graphite torsion–Knudsen cells called C1 and C2 were used. The geometric properties of the cells are given in Table 1. Both cells had two compartments and the starting materials were proportioned between compartments according to the effective areas of the effusion orifices [10].

Seven sets of effusion experiments were done and will be referred to as E1–E7. In Table 2, column one gives the experiment number, column two gives the starting sample mass, column three gives the sample composition, column four gives the type of cell, and column five gives the temperature range of each experiment.

Vapor pressures were calculated with the Volmer equation [27,28]

$$P_t = 2k\Delta\theta/(d_1F_1A_{o1} + d_2F_2A_{o2}) \qquad (5)$$

TABLE 2

The starting sample masses, the sample compositions, the cell types, and the temperature ranges used in experiments E1–E7

Experiment	Amount of sample (mg)	Sample type	Cell type	Temperature range (K)
E1	685.7	S4	C1	1095–1236
E2	196.4	S4*	C1	1121–1274
E3	191.1	S3*	C1	1141–1266
E4	168.4	S3	C2	1051–1231
E5	223.1	S3	C2	1035–1284
E6	243.2	S5	C2	1109–1254
E7	289.9	S6	C2	1115–1252

and the Knudsen equation [27,28]

$$P_K = (dg/dt)(2\pi RT/M^*)^{1/2}/(W_1A_{01} + W_2A_{02}) \tag{6}$$

where P_t is the torsion (or Volmer) pressure, P_K is the Knudsen pressure, k is the torsion constant of the torsion fiber, $\Delta\theta$ is the angular displacement of the torsion pendulum due to vapor effusing from the orifices of the cell, d_1 and d_2 are the moment arms, F_1 and F_2 are the recoil force correction factors [19,20], A_{01} and A_{02} are the areas of the orifices, dg/dt is the rate of mass loss from the cell, T is the temperature of the cell, M^* is the assigned molecular weight of the effusing vapor, and W_1 and W_2 are the transmission probabilities [19,20] of the orifices. The assigned molecular weight M^* can be any positive real number. It was arbitrarily set equal to the average molecular weight M_K of the effusing vapor produced by reaction (2). M_K was calculated with the equation [27,29]

$$M_K = \sum_{j=1}^{J} \left(m_j M_j^{-1/2}\right)^{-2} \tag{7}$$

where m_j is the mass fraction and M_j is the chemical molecular weight of species j in an effusing vapor with J molecular species, in the present case, $J = 2$. A comparison between the Knudsen pressures and the torsion pressure can be made with the equation

$$M = M^*(P_K/P_t)^2 \tag{8}$$

where M is the apparent molecular weight of the vapor. Disagreement between M and M_K can arise from a variety of factors including use of the wrong vaporization equation to calculate M_K. Equation (8) can also be used to obtain estimates of vapor compositions and to monitor variations in vapor composition.

TABLE 3

Standard molar Gibbs energy functions $G^{\ominus}(T)-H^{\ominus}(298\ \mathrm{K})/T$ (J $\mathrm{mol}^{-1}\mathrm{K}^{-1}$)

Temperature (K)	Ga_2S_3(s)	Ga_2S(g)	S_2(g)	GaS(s)
1000	−200.0	−316.1	−245.7	−82.6
1100	−208.3	−319.8	−248.2	−86.2
1200	−216.3	−323.3	−250.5	−89.6
1300	−224.1	−326.6	−252.6	

Least-squares fits of pressures as functions of temperature were made to the equation

$$\log(P/P_a) = -B(K/T - K/T') + C \tag{9}$$

where $1/T'$ is the mean of the experimental values of $1/T$, B is the slope and C is the intercept at $1/T = 1/T'$ from the least-squares fit.

Values of $\Delta H^{\ominus}(298\ \mathrm{K})$ for vaporization reactions were calculated from experimental data and Gibbs energy functions $\phi^{\ominus}(T)$ by the second-law [30] and third-law [9,30] methods. Standard Gibbs energy functions [9] for Ga_2S_3(s), GaS(s), Ga_2S(g), and S_2(g) at several temperatures are given in Table 3. At intermediate temperatures, values for $\Delta\phi^{\ominus}(T)$ were obtained by linear interpolation.

Because no sulfur-rich (with respect to Ga_2S_3) phases have been reported in the literature and no evidence for such phases was found in the data obtained here, the assumption was made that sulfur in the form of S_2(g) was lost from samples S5 and S6 in experiments E6 and E7, respectively, until the composition of Ga_2S_3(s) was reached. The theoretical amounts of excess sulfur in samples S5 and S6 were calculated to be 59.0 and 20.8 mg, respectively.

RESULTS

Sample analysis

Sample S1 was an inhomogeneous mixture of a dark green material with inclusions of metallic gallium and sample S2 was greenish-yellow; the X-ray powder diffractograms of S1 and S2 contained only lines of GaS(s). Sample S3 was yellow and yielded an X-ray diffractogram which contained lines of α-Ga_2S_3(s) and GaS(s). Sample S4 was ivory colored and yielded an X-ray diffractogram which contained only lines of α-Ga_2S_3(s). Samples S5 and S6 were yellow and yielded X-ray powder diffractograms which contained the lines of α-Ga_2S_3(s) and the most intense line of rhombic sulfur.

Vapor pressure measurements

Values of pressures and temperatures from experiments E1–E7 are given elsewhere [1]. Figures 1 and 2 contain straight lines which represent

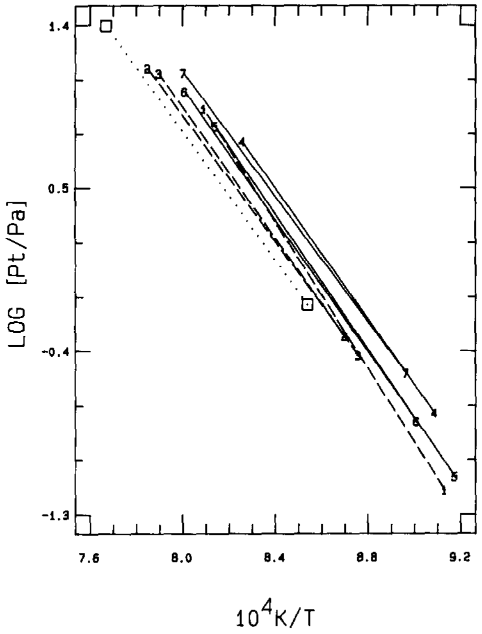

Fig. 1. Comparative straight lines which represent $\log[P_t/P_a]$ vs. K/T data from torsion measurements in experiments E1–E7. The broken lines marked 1–3 represent experiments E1–E3, respectively, where the sample effused from cell C1, and the solid lines marked 4–7 represent experiments E4–E7, respectively, where the sample effused from cell C2. The dotted line marked by open squares represents the results obtained by KM [8].

$\log(P/P_a)$ versus K/T data from torsion and Knudsen measurements, respectively, in experiments E1–E7. In addition, a straight line representing the results obtained by KM [8] is included. The log P versus $1/T$ lines in Figs. 1 and 2 resulted from the vaporization of Ga_2S_3(s) according to reaction (2). In both figures, the dashed lines represent experiments E1–E3 where the sample effused from cell C1, and the solid lines represent experiments E4–E7 where the sample effused from C2.

Table 4 gives parameters from least-squares fits of pressure and temperature data from experiments E1–E7 to eqn. (7). Column one gives the experiment number and the group number (for experiments E4 and E5). Group I data and group II data were fitted separately to a straight line. Column two gives the method by which pressures were measured. Columns three and four give the parameters B and C, respectively, and column five gives the mean value of $1/T$ from each experiment.

In experiments E1 and E2, the vapor pressures of samples S4 and S4*, respectively, were univariant with temperature in the range 1095–1274 K until the samples were exhausted from their cells.

In experiment E3, sample S3* was initially heated to 1182 ± 5 K. During the first 125 min, the pressure rose to a maximum value of 12.5 Pa and then

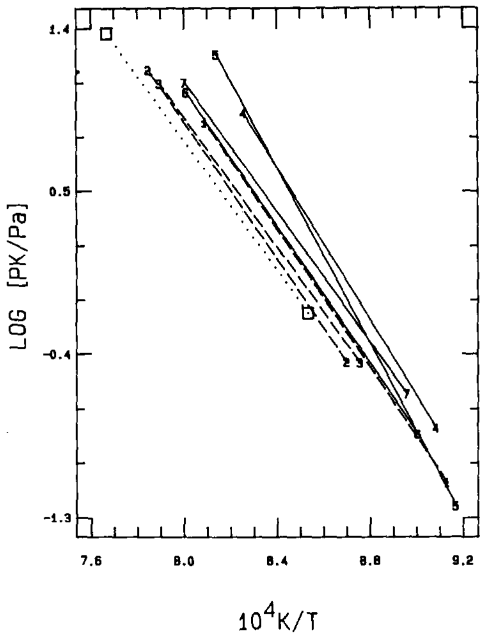

Fig. 2. Comparative straight lines which represent log[P_K/P_a] vs. K/T data from Knudsen measurements in experiments E1–E7. The broken lines marked 1–3 represent experiments E1–E3, respectively, where the sample effused from cell C1, and the solid lines marked 4–7 represent experiments E4–E7, respectively, where the sample effused from cell C2. The dotted line marked by open squares represents the results obtained by KM [8].

TABLE 4

Parameters in eqn. (9) derived by least-squares analysis

Experiment	Method	$10^{-4}(B \pm \sigma_B)$	$(C \pm \sigma_C)$	$10^4K/T'$
E1	Torsion	2.018 ± 0.043	−0.030 ± 0.013	8.570
	Knudsen	1.910 ± 0.030	−0.034 ± 0.009	8.570
E2	Torsion	1.730 ± 0.037	0.590 ± 0.010	8.180
	Knudsen	1.898 ± 0.034	0.406 ± 0.011	8.253
E3	Torsion	1.802 ± 0.055	0.370 ± 0.015	8.319
	Knudsen	1.779 ± 0.061	0.352 ± 0.017	8.319
E4 (I)	Torsion	1.902 ± 0.259	−0.287 ± 0.035	9.350
(I)	Knudsen	2.004 ± 0.237	−0.287 ± 0.032	9.350
(II)	Torsion	1.790 ± 0.059	−0.048 ± 0.017	8.705
(II)	Knudsen	1.782 ± 0.046	−0.056 ± 0.014	8.681
E5 (I)	Torsion	1.776 ± 0.140	−0.205 ± 0.040	9.245
(I)	Knudsen	1.786 ± 0.121	−0.170 ± 0.034	9.245
(II)	Torsion	1.855 ± 0.032	−0.038 ± 0.010	8.613
(II)	Knudsen	1.808 ± 0.026	−0.082 ± 0.010	8.532
E6	Torsion	1.810 ± 0.040	0.164 ± 0.012	8.486
	Knudsen	1.800 ± 0.034	0.176 ± 0.010	8.462
E7	Torsion	1.725 ± 0.023	0.254 ± 0.006	8.510
	Knudsen	1.742 ± 0.026	0.270 ± 0.008	8.470

decreased slowly but continuously to 1.3 Pa. During that same time, 32.1 mg (or 16.8% by mass) of sample effused from the cell and $M = 143.6 \pm 1.5$ g mol^{-1}. Afterwards, the pressure became univariant with temperature in the range 1141–1266 K and $M = 115.0 \pm 1.9$ g mol^{-1} until the experiment was completed. The residue, which was a yellow solid, was removed and examined by X-ray powder diffraction. The diffractogram was that of α-Ga_2S_3(s) [2]. The ratio of values of M during the initial 32.1 mg of mass lost and when the pressure was univariant in E3 was 1.25 ± 0.02.

In experiments E4 and E5, 8.5 mg (or 5.0% by mass) and 12.3 mg (or 5.5% by mass) were lost from samples of S3 while they were heated in the range from 490 ± 25 K and 1020 ± 25 K. The value of M during this time varied between 400 and 600 g mol^{-1}. Subsequently, the pressure versus temperature data divided themselves naturally into two groups. Data acquired during the loss of the next 32.5 mg (or 20.3% by mass) in E4 and the next 43.9 mg (20.8% by mass) in E5 were called group I; the temperature ranges were 1051–1106 K in E4 and 1035–1141 K in E5. Data acquired after group I in each experiment were called group II. Temperature ranges for group II data were 1100–1231 K in E4 and 1089–1284 K in E5. Pressures in group I were univariant with temperature until the pressure decreased precipitously to that of group II. Group II pressures were univariant with temperature until the samples were exhausted. The last three data from E4 were eliminated from the least-squares and thermodynamic analyses because they represent a drop in vapor pressure by about 50% due to the cell's having been misloaded [1]. (One chamber became empty before the other did.) The average values of M with group I data were 126.7 ± 4.2 and 147.9 ± 5.4 g mol^{-1}, and with group II data were 102.1 ± 2.6 and 110.2 ± 2.3 g mol^{-1} for experiments E4 and E5, respectively. The ratios between the average values of M calculated with group I data and the average values of M calculated with group II data were 1.24 ± 0.06 and 1.34 ± 0.06, respectively.

In experiments E3–E5, the working hypothesis was that only Ga_2S(g) was present in the vapor during the initial 32.1 mg of mass lost in E3 and during the collection of group I data in E4 and E5, and that the remaining sample in all three cases vaporized congruently according to reaction (2). The average molecular weight of a vapor consisting of only Ga_2S(g) is 171.5 g mol^{-1} and the average molecular weight of the vapor produced by reaction (2) is 124.7 g mol^{-1}. Consequently, the ratio of 1.38 was expected for the changes in values of M as the vaporization reaction changed from reaction (4) to reaction (2). In Table 5, column one gives the experiment and columns two and three give the measured and theoretical amounts of mass losses, respectively, in E3–E5, if only Ga_2S(g) was present in the vapor.

In experiment E6, when sample S5 was heated to an estimated temperature of 325 ± 25 K, 59.3 mg of mass loss was recorded in a period of about

TABLE 5

Comparison between measured and theoretical amounts of mass loss in experiments E3–E7 if only $Ga_2S(g)$ was present in the vapor

Experiment	Measured	Theoretical ($Ga_2S(g)$ only)
E3	32.1 mg	37.3 mg
E4	32.5 mg	31.2 mg
E5	43.9 mg	41.2 mg

seven minutes. Subsequently, the pressure was univariant with temperature in the range 1109–1254 K until 90% by mass of the sample had effused from the cell. At this point the vapor pressure decreased by 20 ± 3%. After 93% by mass of sample was lost, the pressure dropped again by 15 ± 2%.

The working hypothesis was that the decreases in vapor pressure were due to the cell's having been misloaded. Confirmation of this hypothesis was found in E7, see below. Moreover, values for M with data measured before and after the vapor pressure decreases were the same [1].

In E7, when sample S6 was heated to an estimated temperature of 495 ± 25 K, 20.9 mg of mass loss was recorded in a period of 105 min. Subsequently, the pressure was univariant with temperature in the range 1115–1252 K until 90% by mass of the sample had effused from the cell. Then the pressure dropped by 24 ± 3%. The experiment was stopped and the residue was examined and weighed. The cell contained 12.3 mg of residue in one chamber and 0.5 mg of residue in the other chamber. X-ray powder diffraction of the residue in both cell chambers revealed α-Ga_2S_3 [2].

The vapor pressure decrease observed after the loss of 90% by mass of the sample in E7 was similar to the vapor pressure drop observed in E6. A comparison between the average values of M before and after the drop in vapor pressure showed no arguable difference [1]. The observations above are in line with the working hypothesis proposed to explain similar results in E6. Hence, data obtained after the loss of 90% by mass of sample in both E6 and E7 were not included in the least-squares and thermodynamic analyses.

The average values of M from experiments E1–E7 were 119.4 ± 4.0 (E1), 106 ± 3.5 (E2), 115.0 ± 1.9 (E3), 126.7 ± 4.2 with group I data and 102.1 ± 2.6 with group II data (E4), 147.9 ± 5.4 with group I data and 110.2 ± 2.3 with group II data (E5), 108.6 ± 1.5 (E6), and 100.1 ± 2.2 g mol^{-1} (E7), respectively. The uncertainties are standard deviations of the means. For comparison, we note that the Knudsen molecular weight of the vapor from reaction (2) is 124.7 g mol^{-1}.

For the purpose of data analysis, the following working assumptions about vaporization reactions were made. Vaporization occurred by reaction

TABLE 6

Standard molar enthalpies of vaporization reactions (2) and (4)

Experiment	Reaction	Average second-law $\Delta H^\ominus$(298 K) (kJ mol^{-1})		Average third-law $\Delta H^\ominus$(298 K) (kJ mol^{-1})	
		Torsion	Knudsen	Torsion	Knudsen
E1	2	768.2 ± 11.5	750.9 ± 9.7	655.8 ± 0.5	656.0 ± 0.4
E2	2	696.8 ± 14.3	760.0 ± 12.8	657.6 ± 0.5	660.5 ± 1.0
E3	2	723.6 ± 21.0	714.5 ± 23.4	657.4 ± 1.0	658.2 ± 1.0
E4 (I)	4	391.5 ± 49.7	411.2 ± 45.4	305.2 ± 0.8	305.2 ± 0.9
E4 (II)	2	714.6 ± 22.6	712.2 ± 17.5	643.7 ± 0.9	645.1 ± 0.8
E5 (I)	4	367.2 ± 26.8	369.0 ± 23.2	306.6 ± 1.0	305.9 ± 0.9
E5 (II)	2	740.4 ± 12.2	723.5 ± 9.8	654.1 ± 0.8	654.6 ± 0.7
E6	2	724.2 ± 15.4	720.7 ± 13.1	654.4 ± 0.7	655.5 ± 0.7
E7	2	691.9 ± 8.8	698.9 ± 10.0	648.5 ± 0.4	650.7 ± 0.5

(2) during acquistion of: (1) all of the data in E1 and E2; (2) data obtained after 16.8% by mass of sample effused from the cell in E3; (3) group II data in E4 and E5; and (4) data obtained after the initial 59.3 mg and 20.9 mg of mass loss in experiments E6 and E7, respectively. Vaporization occurred by reaction (4) during acquisition of group I data in experiments E4 and E5.

Thermodynamics

Equilibrium constants K_p of reactions (2) and (4), respectively, were calculated from measured pressures with the equations

$$K_P = 0.2354P^2 \tag{10}$$

$$K_P = P \tag{11}$$

Plots of the logarithms of K_P from torsion and Knudsen pressures as functions of inverse temperature are given elsewhere [1].

Standard enthalpies of reactions (2) and (4) at 298 K obtained from experimental data and Gibbs energy functions are given in Table 6. In Table 6, column one gives the experiment and the group number (in the cases of E4 and E5), column two gives the reaction, columns three and four give values of the average second-law $\Delta H^\ominus$(298 K) with torsion and Knudsen pressures, respectively, and columns five and six give average third-law $\Delta H^\ominus$(298 K) values with torsion and Knudsen pressures, respectively.

DISCUSSION

α-Ga_2S_3(s) and GaS(s) were successfully prepared by sealed-tube methods and identified by X-ray powder diffraction at room temperature.

Attempts at preparation of the reported [4] Ga_4S_5(s) and Ga_2S(s) phases resulted in a mixture of α-Ga_2S_3(s) and GaS(s) in the case of Ga_4S_5(s), and GaS(s) with inclusions of metallic gallium in the case of Ga_2S(s). The phases Ga_4S_5(s) and Ga_2S(s) apparently are unstable at room temperature and require other pressure and temperature conditions for their formation.

Comparison of the X-ray powder diffractograms of the starting materials used in experiments E1–E7 and the X-ray powder diffractograms of α-Ga_2S_3(s), GaS(s), and rhombic sulfur showed that the compositions of the starting samples were (1) α-Ga_2S_3(s) for E1–E2; (2) a mixture of GaS(s) and α-Ga_2S_3(s) for E3–E5; and (3) a mixture of α-Ga_2S_3(s) and sulfur(rh) for E6–E7. X-ray diffractograms of the residues from E3 and E7 revealed only the presence of α-Ga_2S_3(s).

The vapor pressures over solid samples of Ga_2S_3(s) in the temperature range 1095–1284 K and of equilibrium mixtures of GaS(s) and Ga_2S_3(s) in the temperature range 1035–1141 K were determined. Results from experiments E1–E7 indicated that Ga_2S_3(s) vaporized congruently by reaction (2) in agreement with Uy et al. [7] and KM [8]. In E3–E5 where the starting samples were mixtures of GaS(s) and Ga_2S_3(s), the vaporization reactions proceeded as follows: the sample first vaporized incongruently according to reaction (4) and then the residue, which was Ga_2S_3(s), vaporized congruently according to reaction (2).

The hypothesis that reaction (4) occurred during acquisitions of the initial 32.1 mg of mass lost in E3 and of group I data in E4 and E5, was supported by the following: (1) the starting materials were GaS(s) and α-Ga_2S_3(s); (2) the apparent molecular weight of the vapor changed in the correct proportion as would be the case for a vapor consisting first solely of Ga_2S(g) and then of equimolar amounts of Ga_2S(g) and S_2(g); (3) gravimetric analyses of the residues from E3–E5 supported predictions based on the assumption that only Ga_2S(g) was in the vapor during the vaporization of GaS(s).

The 8.5 mg of sample and the 12.3 mg of sample that effused at the beginning of E4 and E5, respectively, in the temperature range estimated to be 490–1030 K, was most likely due to iodine or gallium–iodine species. However, the possibility of more elaborate molecules exists. The apparent molecular weight of the vapor during this time varied between 400 and 600 g mol^{-1}.

In this work, no sulfur-rich (with respect to Ga_2S_3) phases were found in the gallium–sulfur system. In experiments E6 and E7, the theoretical amount of excess sulfur that vaporized in the form of S_2(g) from the starting material was in good agreement with the actual amount of sample that effused from the cell at estimated temperatures of 325 ± 25 K and 495 ± 25 K, respectively. Also, the X-ray powder diffractogram of the residue from experiment E7 showed lines corresponding only to α-Ga_2S_3(s) which indicated that only S_2(g) was lost preferentially from the starting material until the composition of $Ga_2S_3(s)$ was reached. The drops in pressure observed in E6 after 90% and 93% by mass of sample were lost and the drop in pressure observed in E7 after 90% by mass of sample was lost, were due to the cell's having been misloaded.

In experiments E1–E3, the third-law $\Delta H^{\ominus}(298\ \text{K})$ values of reaction (2) were in good agreement with one another; however, they were in poor agreement with their corresponding second-law values. The poor agreement was likely due to variation with temperature of the composition of the condensed phase. The third-law values are more dependable because they are a weak function of temperature. The average of the three third-law $\Delta H^{\ominus}(298\ \text{K})$ values from E1–E3 was 656.9 ± 1.1 kJ mol^{-1} with torsion pressures and 658.2 ± 2.0 kJ mol^{-1} with Knudsen pressures.

In experiments E4–E7, the third-law $\Delta H^{\ominus}(298\ \text{K})$ values for reaction (2) were at variance with one another. The values ranged from 643.7 ± 0.9 kJ mol^{-1}, which agrees with the value obtained by SE [12], to 655.5 ± 0.7 kJ mol^{-1} which agrees with the value obtained by WE [13]. In a system such as gallium sulfide which may contain more than one phase or a phase possessing a wide range of homogeneity, the equilibrium reaction may not be uniquely defined throughout the experimental temperature range. The recorded pressure values at two different temperatures could refer to two different compositions of the same phase. More than one phase, each with a different dependence of vapor pressure on temperature, may have been present through some or all of the vaporization experiments. Evidence that $Ga_2S_3(s)$ is a complicated system has been given by others [4,5,11,14,15]. The most recent investigation [15] has indicated at least two phases close in composition. One phase is more stable at low temperatures (room temperature–1240 ± 2 K) and the other phase is more stable at higher temperatures.

A correlation was observed between the effective orifice areas of the cells used in experiments E1–E7 and the corresponding third-law $\Delta H^{\ominus}(298\ \text{K})$ values. In experiments E1–E3, the samples were contained in cell C1 which had a smaller effective orifice area A_0W than did C2, and yielded results which were consistent with one another. However, in experiments E4–E7 the samples were contained in cell C2 which had a larger effective orifice area than C1 by a factor of 2.4, and yielded variable results. The variation of results from the latter experiments is likely due to kinetic phenomena promoted by the larger effective orifice area.

In experiments E4–E5, the third-law $\Delta H^{\ominus}(298\ \text{K})$ values of the vaporization of GaS(s) by reaction (4) were in good agreement with each other; however, they did not agree with the second-law values. The poor agreement between second- and third-law values of $\Delta H^{\ominus}(298\ \text{K})$ is probably due to temperature measurements made at the sensitivity limit of the optical pyrometer when the effusion cell had just reached red heat. In most cases, the blackbody hole was barely or not visible through the pyrometer.

The third-law values are more dependable because they are less sensitive to such temperature effects. The average third-law values of $\Delta H^{\ominus}(298\ \text{K})$ were 305.9 ± 1.0 kJ mol^{-1} from torsion pressures and 305.6 ± 1.0 kJ mol^{-1} from Knudsen pressures; the torsion pressures of Piacente et al. [18] yielded 303.9 ± 0.5 kJ mol^{-1}.

The Anomalous Phenomenon [10–12,14,15] was not observed in this work. Comparison of the results of others [8,10–15] reveals a correlation between occurrence of the Anomalous Phenomenon and the size of A_0W. Experiments with cells having $A_0W \leq 0.115$ mm^2 or with a ratio of $A_s : A_0W \geq 870$ produced the Anomalous Phenomenon. Experiments in this work were done with cells having $A_0W > 0.115$ mm^2 and $A_s : A_0W < 870$; hence, this would explain, in part, the absence of the Anomalous Phenomenon.

The work of WE [13] did not yield the Anomalous Phenomenon and contradicts the correlation. However, closer examination of their data from set 1 for the vaporization of residual Ga_2S_3(s), reveals vapor pressures that are as much as 80% higher than expected (from other measurements in the same temperature range) when the sample was cooled from above 1240 K. Those results in addition to more recent ones [15] indicate that during the time the higher vapor pressures were measured, Ga_2S_3(s) did not vaporize according to reaction (2). It is conceivable that WE could have reproduced the Anomalous Phenomenon if they had treated their residue (Ga_2S_3) with the appropriate heating cycle.

Myers et al. [22] reported that the mode of vaporization of V_3P(s) was kinetically inhibited and depended on the size of the effective orifice area. Munir and Searcy [21] reported similar results in the gallium nitride system and found that the mode of vaporization of GaN(s) depended on the ratio of sample surface area to orifice area. The mechanistic details of kinetic phenomena promoted by orifices that contribute to the vaporization and condensation processes inside a Knudsen cell are not well understood, but clearly such phenomena play a major role.

Chemical system such as V–P, Ga–N, and Ga–S cannot sustain equilibrium conditions within an effusion cell with small ratios of $A_s : A_0W$. The sharpness of phase transitions observed from changes of vapor pressures with small composition changes would be dulled by such effects.

CONCLUSIONS

GaS(s) and Ga_2S_3(s) were the only condensed phases in the Ga–S system observed in this work. No sulfur-rich (with respect to Ga_2S_3) phases were discovered from effusion experiments or sealed-tube methods.

Several effusion experiments indicated that Ga_2S_3(s) vaporized congruently by reaction (2) in agreement with others [7,8]. However, differences (on the order of 16 kJ mol^{-1}) in the third-law $\Delta H^{\ominus}(298\ \text{K})$ values from the literature and from results obtained here imply chemical variability of the vaporization reaction of Ga_2S_3(s). The Ga–S system has been reported to be a complex system [4,5], especially at or near the composition of Ga_2S_3(s) [4,5,10–12,14,15]. It is probable that more than one phase (each with a composition different from Ga_2S_3 by less than 1 at.% [11]) was present in various reported effusion studies.

It is now known that the Anomalous Phenomenon was not reproduced in this work because the effective areas of the cell orifices were too large. The large orifices could not promote conditions in the cell for the subtle, but necessary composition changes needed for the Anomalous Phenomenon to occur. Work now under way, where the Anomalous Phenomenon has been reproduced several times and under a variety of conditions with sufficiently small orifices [15], has revealed phase transitions that are sharp and distinct. The transitions require small composition (< 1 at.%) changes in the condensed phase accompanied by large changes in vapor composition.

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