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Mass-spectrometric observation of a condensed-phase transition during effusion of gallium sesquisulfide

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Abstract

A theory of condensed-phase transitions during vaporization processes, i.e. a theory of triple points, was tested by mass-spectrometric observation of the effusing vapor of gallium sesquisulfide, Ga_2S_3(c), as the condensed phase underwent a phase transition both in the increasing-temperature direction and in the decreasing-temperature direction through 25 cycles. Theoretical prediction of the trajectory of partial-pressure ratios in pressure, temperature, composition space through a temperature-driven phase transition was tested by measuring ionic intensity ratios. The vapor species, principally Ga_2S(g) and S_2(g), had a ratio of partial pressures independent of temperature while either the low-temperature or the high-temperature condensed phase was effusing congruently, but the ratio showed strong predictable dependence on temperature and composition during a condensed-phase transition, in line with the theory. This work is the first direct test of these theoretical predictions. © 1997 Elsevier Science B.V.

Keywords: Gallium sulfide; Knudsen-cell mass spectrometry; Knudsen effusion; Phase transition; Triple point

1. Introduction

A congruently vaporizing condensed phase in equilibrium with its vapor might undergo a condensed-phase transition if the temperature is changed. For example[1], below 1293 K, wurzite, the hexagonal or α form of zinc sulfide, vaporizes congruently by

$$ZnS(\alpha) = Zn(g) + \tfrac{1}{2}S_2(g) \qquad (1)$$

and above 1293 K, sphalerite, the cubic or β form vaporizes congruently by

$$ZnS(\beta) = Zn(g) + \tfrac{1}{2}S_2(g) \qquad (2)$$

As the temperature is increased (or decreased) through 1293 K, the transition between condensed phases occurs, and during the transition all three phases, α, β and vapor are at equilibrium.

As demonstrated in recent theoretical papers [2,3], when a condensed-phase transition occurs in the presence of the vapor, i.e. at a triple point, the compositions of all three phases must be different; and vaporization must be incongruent, except in the special instance of the euatmotic composition [4]. The composition difference between ZnS(α) and ZnS(β) is small and unknown; in this example, we account for the unknown difference by writing the formulas $Zn_xS(\alpha)$ and $Zn_yS(\beta)$, with the arbitrary assumption that $x > y$. Then, during the condensed phase transi-

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tion the incongruent vaporization reaction is represented by the two equations

$$Zn_xS(\alpha) = Zn_yS(\beta) + (x-y)Zn(g) \qquad (3)$$

$$Zn_yS(\beta) = (y/x)Zn_xS(\alpha) + (x-y)/2xS_2(g) \qquad (4)$$

In general, for a binary system with two congruently vaporizing condensed phases $A_aB_b(\lambda)$, stable at high temperatures, and $A_eB_f(\rho)$, stable at low temperatures, the reactions equivalent to Eqs. (1) and (2) are

$$A_aB_b(\lambda) = aA(g) + bB(g) \qquad (5)$$

$$A_eB_f(\rho) = eA(g) + fB(g) \qquad (6)$$

We write the chemical formulas such that $a + b = 1$ and $e + f = 1$. For simplicity, we take λ and ρ to be line-phases, i.e. we take variations in their stoichiometry to be negligible, even though stoichiometry of condensed phases in reality vary slightly with temperature and with composition of the vapour phase [5]. Then the equilibrium constants of Eqs. (5) and (6) are, respectively,

$$K_p(\lambda) = (X_A^v)^a(X_B^v)^bP \qquad (7)$$

$$K_p(\rho) = (X_A^v)^e(X_B^v)^fP \qquad (8)$$

where P is the vapor pressure, and (X_A^v) and (X_B^v) are the mole fractions of species A(g) and B(g) in the vapor, respectively.

The incongruent vaporization reactions equivalent to reactions in Eqs. (3) and (4)

$$[a/(a-e)]A_eB_f(\rho) = [e/(a-e)]A_aB_b(\lambda) + B(g) \qquad (9)$$

$$[f/(f-b)]A_aB_b(\lambda) = [b/(f-b)]A_eB_f(\rho) + A(g) \qquad (10)$$

In terms of the Gibbs–Helmhotz equation, the equilibrium constants of reactions in Eqs. (9) and (10), $K_p(9)$ and $K_p(10)$, respectively, are expressed

$$\ln K_p(9) = -\Delta H^0(9)/RT + \Delta S^0(9)/R = \ln P_B \qquad (11)$$

$$\ln K_p(10) = -\Delta H^0(10)/RT + \Delta S^0(10)/R = \ln P_A \qquad (12)$$

where ΔH^0 (9), ΔH^0 (10), ΔS^0 (9) and ΔS^0 (10) are standard enthalpies and entropies of reactions (9) and (10), respectively.

From Eqs. (11) and (12) one obtains

$$\ln P_B/P_A = -[\Delta H^0(9) - \Delta H^0(10)]/RT + [\Delta S^0(9) - \Delta S^0(10)]/R \qquad (13)$$

or

$$\ln [X_B^v/X_A^v] = \Delta H^0(\mathrm{tr})/RT + \Delta S^0(\mathrm{tr})/R \qquad (14)$$

where $\Delta H^0(\mathrm{tr}) = \Delta H^0(9) - \Delta H^0(10)$ and $\Delta S^0(\mathrm{tr}) = \Delta S^0(9) - \Delta S^0(10)$, which quantities can be viewed as the enthalpy and entropy, respectively, of the phase transition.

The goal of this work was to use the relationship above, from a thermodynamic theory [3] that has been recently developed, to examine the 'anomalous phenomenon' of Roberts and Searcy [5,6] during the effusion of vapor over $Ga_2S_3(c)$ into a mass spectrometer. The procedures in the present experiments were based on predictions of the theory and were designed to test the theory. The theory distinguishes between equilibria in an effusion cell and equilibria in a transpiration system, but such differences are expected to be small [3] and not likely to be resolvable by mass spectrometry.

In the course of a Knudsen cell mass-spectrometric experiment, Roberts and Searcy [5] observed an increase in the partial pressure of $Ga_2S(g)$ and simultaneous decrease in the partial pressure of $S_2(g)$ over $Ga_2S_3(c)$ when the temperature of the cell was lowered from 1230 to 1203 K. They ascribed this anomaly to a phase transformation between two solid phases, a low temperature from (l-Ga_2S_3) and a high temperature form (h-Ga_2S_3) of Ga_2S_3 differing in composition by 0.4 atomic percent sulfur; their model had both phases coexisting with the vapor at 1228 ± 3 K. In the present work phase ρ corresponds to l-Ga_2S_3 and phase λ corresponds to h-Ga_2S_3. Since the discovery of the anomalous phenomenon by Roberts and Searcy [5], the same effect has been observed by others [6–9].

Previous work [3,5] shows that for gallium sulfide above 1200 K, the phases in Eqs. (5)–(14) can be written as ρ:$(Ga_2S)_{0.5}(S_2)_{0.5}(c)$; λ: $(Ga_2S)_{0.50378}(S_2)_{0.49622}(c)$; A: $Ga_2S(g)$; and B: $S_2(g)$. The formulas of the condensed phases carry no implications about structures; they correspond with the algebraically convenient formulations of Eqs. (9) and (10)[10].

In the present study, the ion intensities of S_2^+ and Ga_2S^+ (and other Ga-containing ions) were measured as functions of temperature in a Knudsen-cell mass spectrometer.

The partial pressure, P_i, within the Knudsen cell are related to the ion intensities measured with the mass spectrometer by equation

$$P_i = I_i^+ T / \kappa_i \sigma_i(E) \gamma_i \qquad (15)$$

where κ_i is a transmission constant which includes the effect of ionic fragmentation, $\sigma_i(E)$ is the ionization cross-section for electrons of energy E, and γ_i is the gain of the ion detector for species i. In a mass-spectrometric study, the mole fraction ratio of species A(g) and B(g) at a given temperature can be represented by

$$X_B^v / X_A^v = k I_B^+ / I_A^+ \qquad (16)$$

where $k = \kappa_A \sigma_A(E) \gamma_A / \kappa_B \sigma_B(E) \gamma_B$. In this work, k is taken to be independent of temperature.

For congruent vaporization reactions (5) and (6), the vapour composition is practically independent of temperature. If the composition of λ and ρ are practically identical, a graph of $\ln[(1 - X_A^v)/X_A^v]$ or $\ln[I_B^+/I_A^+]$ vs. $1/T$ is practically a single, horizontal straight line for both congruently vaporizing phases. On the same graph the incongruent vaporization reactions in Eq. (9) and Eq. (10) give slanting straight or slightly curved lines according to Eq. (14), because both $\Delta H^\circ(\mathrm{tr})$ and $\Delta S^\circ(\mathrm{tr})$ are functions of temperature in the vicinity of the phase transition [3]. Such graphs are schematically shown in Fig. 1. In Fig. 1 the vertical coordinate is the logarithm of the ratio of the ionic intensities of B^+ and A^+ and the horizontal coordinate is $1/T$. The slanting line labeled 3-P represents results to be expected from observations while both condensed phases and the vapor are at equilibrium within the effusion cell, i.e. while a transition between phases is occurring. Left of the slanting line, the horizontal line represents results to be expected while λ, the high-temperature phase, is effusing congruently. Right of the slanting line, the horizontal line represents results to be expected while ρ, the low-temperature phase, is effusing congruently. The two horizontal straight lines are shown at slightly different levels in recognition of the known small difference between the compositions of the high- and low-temperature congruently vaporizing phases [5,11].

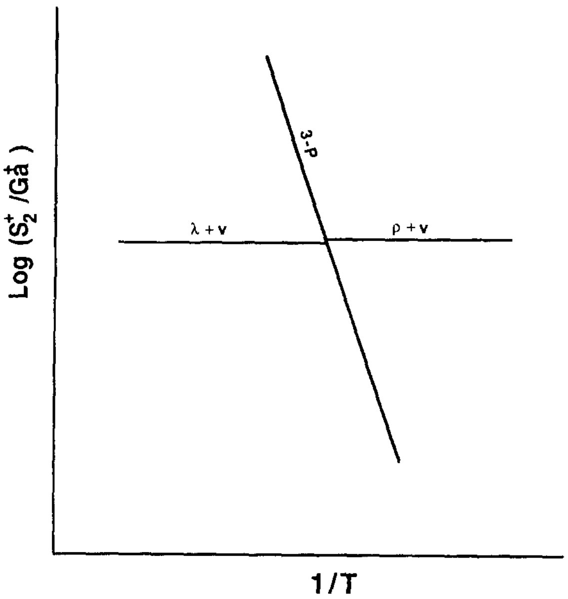

Fig. 1. Ideal relationship of logarithm of ionic intensity ratio to inverse temperature in the vicinity of a triple point.

When all three phases are at equilibrium in the effusion cell [11], the condensed phase will change as the unstable condensed phase transforms to the stable condensed phase through effusion of the excess vapor species. Upon exhaustion of the unstable condensed phase, the vapor composition, and hence the ionic intensity ratio in the mass spectrometer, will change as the composition of the stable phase changes to the congruently effusing one. In such cases, time-dependent ionic intensity ratios not on any of the lines represented in Fig. 1 will be observed.

2. Experimental

The Ga_2S_3 sample was prepared by heating together stoichiometric amounts of the elements and 1% by mass of iodine, as a mineralizing agent, at 1000°C for a week in an evacuated sealed Vycor tube. After heating, iodine was distilled to one end of the reaction tube, which end was cooled by liquid nitrogen. The reaction tube was broken, and the resulting sample was ground and stored in a closed vial. Samples were prepared and characterized at the University of Toledo, OH.

Mass spectrometric experiments were conducted at the Forschungszentrum, Jülich, Germany, with a quadrupole mass spectrometer, ELFS-Type, from ATOMIKA Tech. Physik GmbH, Munich. The sample was contained in a graphite Knudsen cell and the cell was enclosed in a cylindrical cavity in a molybdenum crucible. The crucible assembly was heated by radiation and electron bombardment. Temperatures were measured with an automatic infrared optical pyrometer, model TMR 85-d from Dr. George Maurer GmbH, sighted into a black-body hole in the side of and centered 1.5 mm below the bottom of the cavity in the molybdenum crucible; measurements were calibrated by observing, in a separate experiment, the triple point of silver in an effusion cell in the mass spectrometer.

The effusion orifice was cylindrical with diameter of 0.60 mm and length of 2.0 mm. These dimensions yielded a cross-sectional area of 0.28 mm^2 and a transmission probability (Clausing factor) [12] of 0.26 and thus the effective orifice area of the sample within the cell was 0.073 mm^2. The horizontal cross-sectional area of the sample within the cell was 0.785 cm^2. The ratio of these areas was 1100, which met the criterion of Uram and Edwards [6] that it be greater than 870 if the anomalous phenomenon is to be observed.

The experiments included measurements of the shutterable intensities of ions at *m/e* values of $^{64}(S_2^+)$, $^{65}(S_2^+)$, $^{66}(S_2^+)$, $^{69}(Ga^+)$, $^{71}(Ga^+)$, $^{76}(CS_2^+)$, $^{101}(GaS^+)$, $^{156}(Ga_2O^+)$, and $^{172}(Ga_2S^+)$ as functions of crucible temperature and time in the 1169–1255 K range. Some of the ions were observed only occasionally, but at every experimental temperature the intensity of $^{69}Ga^+$ and the intensity of an S_2^+ peak of appropriate intensity were measured. Moreover, scans of the mass spectrum were made regularly, especially at the beginning of the study, to identify ions from background and impurity species.

Natural isotopic abundances were used to convert measured intensities of S_2^+ at *m/e* of 65 and 66 to their equivalents at *m/e* of 64. The intensity of $^{69}Ga^+$ was the highest of any Ga-bearing ion and was used to track the partial pressure of $Ga_2S(g)$. This procedure required the assumption that all Ga^+ resulted from electron impact on $Ga_2S(g)$, an assumption justified by the known vaporization chemistry of Ga_2S_3 [5] and by the fact that in the present experiments the temperature coefficient of the ionic intensities of Ga_2S^+ and Ga^+ were the same. The latter fact was checked frequently throughout by observing the ratio of intensities of ions Ga_2S^+ and Ga^+.

3. Results

X-ray characterization of the gallium sulfide starting samples showed them to be α-Ga_2S_3 [6]. Ions with shutter effects observed in the mass spectrometer during congruent effusion of α-Ga_2S_3 were S^+, S_2^+, GaS^+, Ga_2^+, Ga_2S^+ and CS_2^+. Typical relative intensities, measured with 40 eV ionizing electrons, are reported in Table 1. In Table 1, the first column gives the date of the observation, the second column gives the temperature, the third through seventh columns give the relative intensities of Ga^+, GsS^+, Ga_2S^+, S_2^+ and CS_2^+, respectively, with that of Ga^+ adjusted to 100. Ions I^+, GaI^+, GaI_2^+ and Ga_2O^+ were observed with low relative intensities early in the study, but their intensities diminished rapidly and became unobser-

Table 1
Relative ionic intensities at 40 eV ionizing electrons

Date	*T*/K	Ga^+	GaS^+	Ga_2S^+	S_2^+	CS_2^+
March 10, 1994	1235	100	13.3	10.2	379	42.7
March 10, 1994	1225	100	12.4	9.5	314	31.4
March 18, 1994	1172	100	12.5	13.1	80	10.7
March 21, 1994	1170	100	12.1	16.0	164	14.5
March 22, 1994	1238	100	12.9	10.8	311	34.8
March 23, 1994	1248	100	13.7	9.5	342	39.0
March 23, 1994	1178	100	—	—	103	9.5
March 24, 1994	1237	100	13.8	9.6	290	33.4

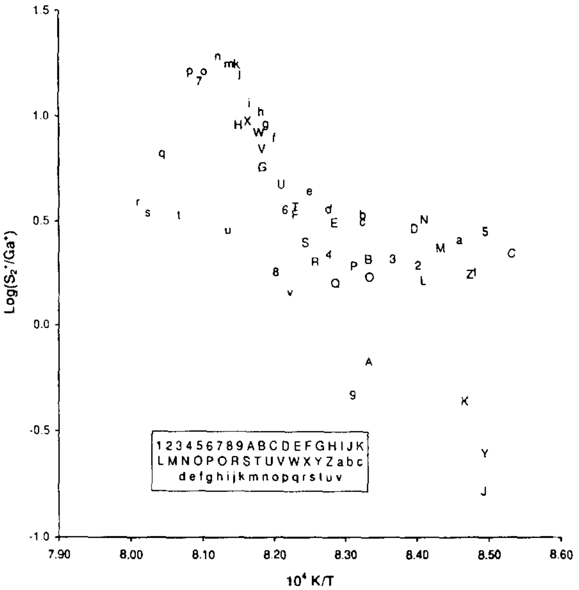

Fig. 2. Log (S_2^+/Ga^+) vs. $1/T$, Group I, March 4–8, 1994.

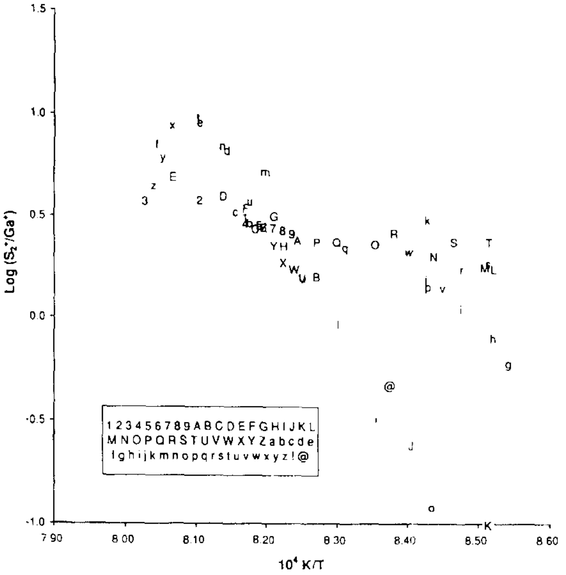

Fig. 3. Log (S_2^+/Ga^+) vs. $1/T$, Group II, March 10–15, 1994.

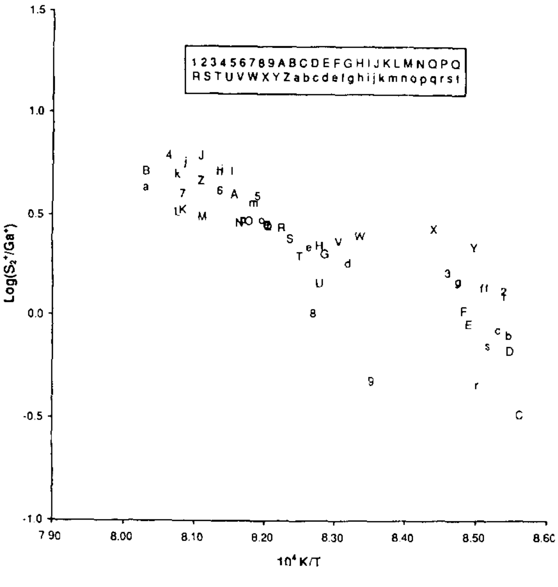

Fig. 4. Log (S_2^+/Ga^+) vs. $1/T$, Group III, March 16–18, 1994.

vable. Ions $Ga_2S_2^+$ and GaO^+ were sought but not found.

Observations on a single sample of 543.3 mg of α-Ga_2S_3 were made over a period of three weeks during which time 68.2% of the sample effused. The chemistry of the effusion process remained the same throughout, but details of the observations changed during the course of the experiments owing to decreased amount of sample. The results, then, are presented in four groups identified by their dates of acquisitions: Group I, 4–8 March 1994; Group II, 10–15 March 1994, Group III, 16–18 March 1994; Group IV, 21–24 March 1994. Groups I–III are shown in Figs. 2–4, respectively; the vertical axes are $\log(S_2^+/Ga^+)$ where the symbols S_2^+ and and Ga^+, in this context, represent the corresponding observed intensities of the ions. Group IV is given in Table 2, because the observations were not suitable for graphical presentation. The data in Group IV fell in tight clusters, because several long isothermal runs were included, and because the amount of sample remaining was insufficient to maintain the three-phase equilibrium at extreme temperatures long enough for accurate observations.

With all three phases, λ, ρ and vapor, in the effusion cell, very large variations of the intensity of S_2^+ with temperature were observed. In order to remain within the sensitivity range of the mass spectrometric detector at all temperatures, observations were made on S_2^+ containing the various natural isotopes ^{32}S, ^{33}S and ^{34}S whose natural relative abundances are 0.9502,

Table 2

Temperature and logarithm of ionic intensity ratio of S_2^+ and Ga^+, Group IV

March 21, 1994		March 22, 1994		March 23, 1994		March 24, 1994			
T/K	Log (S_2^+/Ga^+)	*T*/K	Log (S_2^+/Ga^+)	*T*/K	Log (S_2^+/Ga^+)	T/K	Log (S_2^+/Ga^+)	T/K	Log (S_2^+/Ga^+)
1170	0.15	1243	0.50	1248	0.53	1237	0.43	1183	0.04
1174	0.22	1242	0.49	1246	0.52	1237	0.45	1181	0.05
1199	0.38	1242	0.48	1252	0.55	1237	0.46	1180	0.08
1206	0.39	1210	0.28	1181	−0.27	1237	0.47	1179	0.12
1231	0.80	1208	0.08	1179	−0.11	1249	0.49	1179	0.16
1231	0.67	1208	0.25	1179	−0.08	1234	0.46	1179	0.17
1233	0.62	1208	0.34	1178	0.01	1254	0.50	1179	0.18
1234	0.60	1207	0.38	1177	0.13	1252	0.48	1179	0.23
1234	0.59	1207	0.38	1177	0.23	1253	0.50	1179	0.24
1235	0.55	1207	0.41	1177	0.26	1252	0.49	1178	0.26
1236	0.54	1207	0.41	1252	0.65	1235	0.46		
1235	0.54	1206	0.43	1253	0.57	1236	0.45		
1236	0.53	1206	0.43	1253	0.54	1236	0.46		
1236	0.52	1181	0.48	1253	0.51	1196	−0.05		
1236	0.51	1233	0.78	1253	0.51	1195	0.08		
1236	0.51	1236	0.63	1255	0.47	1194	0.17		
1237	0.49	1237	0.59	1255	0.51	1193	0.17		
1236	0.51	1237	0.57	1196	−0.45	1194	0.23		
1236	0.50	1238	0.54	1191	−0.15	1193	0.24		
1236	0.50	1238	0.51	1190	−0.02	1194	0.29		
1236	0.50	1238	0.51	1190	0.03	1193	0.28		
1236	0.49	1238	0.50	1190	0.05	1182	0.20		
1236	0.49	1239	0.48	1247	0.62	1180	0.21		
1237	0.49			1246	0.57	1181	0.22		
1237	0.49			1246	0.54	1178	0.24		
1236	0.48			1246	0.51	1178	0.25		
1237	0.50			1246	0.51	1224	0.51		
1237	0.47			1247	0.49	1235	0.87		
1237	0.48			1235	0.46	1245	0.74		
1237	0.49					1178	−0.02		
1237	0.49					1188	0.00		
1244	0.52					1189	0.04		
1244	0.49					1205	0.27		

7.50×10^{-3} and 4.21×10^{-2}, respectively. Relative intensities of S_2^+ at masses 64, 65 and 66 (with a low-resolution mass spectrometer) are 0.903, 1.43×10^{-2} and 8.01×10^{-2}. At the lowest intensities of S_2^+ observations usually were made at *m/e* of 64 and at the highest intensities usually at *m/e* of 66, though in a few cases, *m/e* of 65 was observed. Then appropriate abundance corrections were applied.

Fig. 2 shows results obtained during the first four-day period. The data are represented on the plot by symbols that also give the order of acquisition of the data, as shown at the bottom of the figure. The first datum is represented by symbol '1' and the last by 'v'.

The ideal pattern shown in Fig. 1 is seen in the data in Fig. 2. Data 1–5 were obtained while the low-temperature phase, ρ, was in equilibrium with the vapor. The initial composition of the sample apparently was slightly Ga-rich relative to that of ρ, and the intensity ratio, S_2^+/Ga^+, increased slightly but monotonically during the series. Datum 6 was measured at a temperature above the transition temperature, and the series of data, 6–9, was obtained while three phases, λ, ρ and the vapor, were present within the effusion cell. After datum 9, at a temperature below the transition temperature, λ was exhausted, and during acquisition of data A and B the system returned to the initial state with ρ and vapor present. Data B–E were obtained with ρ and vapor present, but a slight monotonic change in the composition of ρ as it approached the congruently effusing composition can be seen from the intensity ratios in this series. The temperature of the phase transition can be seen to be near that of datum F, 1216 K. The series F–J was obtained with three phases present, and K and L were obtained during and after exhaustion of λ as the composition adjusted to that of the low-temperature, two-phase equilibrium. After datum M was obtained, ρ and vapor only were present until the temperature was raised to that of datum R. The intensity ratios in the sequence P–X show that the transition temperature is near the temperature of datum R, 1212 K. After acquisition of datum Y, the system again returned to the low-temperature, 2-phase equilibrium. The sequence a–u brought the system, for the first time, to the high-temperature, 2-phase equilibrium with λ and vapor present. In the sequence c–f, the transition temperature is seen to be near that of datum e, 1213 K. Datum v, the last in Fig. 2, was obtained with three phases present, below the temperature of the transition. After acquisition of datum v, the furnace was turned off, and the sample cooled to room temperature.

The ideal pattern of Fig. 1 is seen in the data of Fig. 3 as well. Between acquisition of datum v of Fig. 2 and datum 1 of Fig. 3, the sample was left at room temperature under vacuum for a weekend. In sequence then, datum 1 of Fig. 3 followed datum v of Fig. 2.

Data 1–7 in Fig. 3 were obtained while the high-temperature phase effused congruently. Data 4-B revealed appearance of the low-temperature phase, probably in the temperature range 1217–1214, where data 8-A were obtained. The phase transition occurred near the temperature of datum 9, 1215 K. Data A and B represent the 3-phase equilibrium. The short time at the temperature of datum A resulted in generation of a small amount of the low temperature phase, and data C–F gave intensity ratios lower than those expected for the 3-phase equilibrium; these data represent the high-temperature, 2-phase equilibrium between vapor and the sulfur-rich high-temperature condensed phase. The transition occurred near the temperature of datum H, 1217 K.

Data H–K in Fig. 3 gave intensity ratios corresponding to the 3-phase equilibrium and data L–N were obtained while the composition of the sample adjusted to that of the low-temperature phase. Data O–T were obtained while the low-temperature phase effused congruently, data U–e while three phases were present, and datum f during transition to the high-temperature, 2-phase equilibrium. The transition occurred in the temperature range of data U–W, 1213–1215 K, near the temperature of datum W, 1215 K. During observation of data X–e, the system was in 3-phase equilibrium. Between measurements f and g the sample was cooled to ca. 1070 K and kept there overnight, then data g–j represent composition change, and datum k was obtained while ρ was effusing congruently. Data m–o represent 3-phase equilibria, datum p composition change, and data q–s congruent effusion of ρ. Data t and u were obtained during the 3-phase equilibrium, and between data u and v considerable time passed and effusion occurred but no measurement was made. Datum v was obtained during composition change, and datum w at or very near to congruent effusion of ρ. Data x–z represent composition change toward congruent effusion of λ. In the sequence from X–z no observation was made at a temperature near the phase transition.

Failure to observe data during the 3-phase equilibrium between observations u and v and between w and x showed that a significant fraction of the sample had effused in the previous parts of the experiment and that the 3-phase equilibrium could be maintained for only a short time. With care, datum ! was observed during the 3-phase equilibrium. Datum @ was obtained just after disappearance of λ.

The trends among data presented in Figs. 2 and 3 were observed also in data presented in Fig. 4. However, the fraction of sample remaining had become so small that it was difficult to observe the sample while three phases were present. The sequences 7–9 and Q–U placed the system in the 3-phase equilibrium, but all other observations given in Fig. 4 were of the system during 2-phase composition change or during 2-phase congruent equilibrium. The phase transition was observed in the sequence Q–S, near the temperature of datum R, 1217 K.

Observations of the sample were continued for four days more after the data given in Fig. 4 were acquired, but in only a few cases was the 3-phase equilibrium observed sufficiently long after thermal stabilization to obtain consistent measurements on both Ga^+ and S_2^+. The data obtained during these last four days are given in Table 2 in the order in which they were acquired. In Table 2, column 1 gives the date, column 2 gives the temperature, and column 3 gives the ratio of the intensity of S_2^+ to that of Ga^+. Several long isothermal runs are shown to establish that the ultimate $\log(S_2^+/Ga^+)$ under congruent effusion was near 0.5 as seen in Figs. 2–4. At the end of each day, the temperature was lowered below 700 K. In total, in Groups I–IV, the sample had been been cycled twenty five times from low-temperature phase to at least partly high-temperature phase to at least partly low-temperature phase.

The Knudsen-cell furnace was disassembled and the sample was weighed and examined. The entire remaining sample was found tightly attached to the under side of the lid of the cell. The mass of the remaining sample was 173.5 mg, i.e. 31.8% of the original mass, but 2–5 mg of carbon was introduced into the sample when it was scraped from the lid, so this reported mass is slightly too high.

4. Discussion

The 'anomalous phenomenon' of Roberts and Searcy [5,6] was observed in a large number and variety of decreasing temperature programs, and the corresponding increasing-temperature effect was observed an equal number of times. The temperature cycles showed that excess sulfur in the form of $S_2(g)$ was vaporized from the sample on the increasing-temperature side, and that excess gallium in the form of $Ga_2S(g)$ was vaporized on the decreasing-temperature side.

A recent theory was used to predict the form of the relationship among intensity ratio S_2^+/Ga^+, the temperature, and the composition of the sample. That prediction, illustrated in Fig. 1, proved to be correct as demonstrated by data in Figs. 2–4 and information and discussion in the text.

According to theory, the phase transition underlying the observed phenomenon is hysteretic in any of the three variables, temperature, pressure and composition [3]. The onset of the transition in the increasing temperature direction is at a higher temperature (by a fraction of a Kelvin), higher pressure and more sulfur-rich composition than in the decreasing temperature direction. The small difference in the temperatures of the increasing- and decreasing-temperature transitions could not be resolved experimentally in this work because of various uncertainties in the measurements of temperatures and pressures and in assignment of the sample composition.

The temperature of the phase transition was measurable in seven temperature sequences in these experiments; it was seen to be 1216, 1212, 1213, 1215, 1217, 1215 and 1217 K. The first three were seen in increasing-temperature sequences, and the last four in decreasing-temperature sequences. The average of these values, 1215 ± 2 K, is a reasonable measurement of the temperature of the phase transition in these experiments.

A few unexplained, small but significant variations of the observations from theoretical predictions can be noted. It is not understood why the data sequence 7–9 and datum v in Fig. 2, during which the sample was composed of three phases, fell at temperature 9–12 K above those in the sequence F–J, during which the sample was composed of three phases. Nor is it understood why in sequences M–Q in Fig. 2 and R–W in

Fig. 3, the intensity ratio S_2^+/Ga^+ decreased by 30–40% just before the onset of the phase transition in the decreasing temperature direction. These unexplained variations might be due to strong dependence on temperature of the composition of the low-temperature phase near the phase transition [13]. However, the experiments did not provide enough data to allow such complex interpretations. Moreover, these effects were not consistent; similar temperature programs at other times during the experiment did not produce them. Thus are they unexplained.

The remainder of the sample 31.8% was found to have transferred to the bottom side of the lid to which it was tightly bound at the end of the experiments. Such observation is not unusual in effusion experiments and indicates only that the lid might have been slightly cooler than the bottom of the cell. A temperature gradient of 2–3 K can produce such an effect. Any such temperature gradient is unrelated to the temperature range of 25 ± 3 K over which the 'anomalous phenomenon' has been observed in three laboratories. Roberts and Searcy [5] observed the phenomenon treated here at 1228 ± 3 K, Uram and Edwards [6,11] observed it at 1240 ± 2 K, and we observed it in this work at 1215 ± 2 K. In the present experiment, the optical pyrometer was sighted near the bottom of the sample cavity in the cell, which would mean that the temperature of the sample after it had transferred to the lid was even lower than the temperature read by the optical pyrometer. The principal contribution to uncertainty in the temperatures in the present experiment was the manner of calibration of the optical pyrometer used in the measurements. Its calibration with the triple point of silver in a separate experiment in a different effusion cell could have introduced a sizable systematic temperature mistake. The authors recommend the high value, that of Uram and Edwards [6], 1240 ± 2 K, as the temperature of the transition in question.

The present results confirm the predictions of a thermodynamic theory [3] that accounts for phenomena during phase transitions in the condensed phases of binary systems during vaporization. In high temperature effusion experiments such transitions typically cannot be observed directly and must be implied, as was done originally by Roberts and Searcy [5]. The phase transition in this work is not found in the published phase diagram [14], but its occurrence is confirmed by the phenomena observed in the present work and by their correlation with the theory.

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