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VAPORIZATION CHEMISTRY AND THERMODYNAMICS OF CONGRUENTLY VAPORIZING ZINC INDIUM SULFIDE

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ABSTRACT

The vaporization and thermodynamics of $ZnIn_2S_4(s)$ were investigated with the computer-automated simultaneous torsion–Knudsen-effusion method in the temperature range 1088–1218 K. The vaporization of $ZnIn_2S_4(s)$ was shown to be congruent in that range by the reaction

$ZnIn_2S_4(s) = Zn(g) + In_2S(g) + 3/2\ S_2(g)$

Least-squares straight lines relating the equilibrium constants to the temperature were, from torsion results, $\log(K_p/Pa^{7/2}) = -(5.505 \pm 0.050) \times 10^4\ K/T + 47.21 \pm 0.44$, and from Knudsen results, $\log(K_p/Pa^{7/2}) = -(5.634 \pm 0.081) \times 10^4\ K/T + 48.30 \pm 0.70$. The average third-law $\Delta H^0(298\ K)$ of the vaporization reaction of $ZnIn_2S_4(s)$ was 1050.1 ± 0.6 kJ mol^{-1} from torsion-effusion and 1050.4 ± 0.7 kJ mol^{-1} from Knudsen-effusion. The value 1050.3 ± 1.0 kJ mol^{-1} was selected. The $\Delta H^0(298\ K)$ of combination of $ZnIn_2S_4(s)$ from its constituent binary sulfides, ZnS(wz) and $In_2S_3(s)$, was -49.9 ± 1.4 kJ mol^{-1}.

INTRODUCTION

$ZnIn_2S_4$ is a ternary layered semiconductor which has been much studied because of its photoconductivity, luminescence, and electrical properties [1]. The large density of vacancies in the structure of $ZnIn_2S_4$ crystals make this structure intermediate between those of amorphous and crystalline semiconductors. $ZnIn_2S_4$ was first reported by Hahn and Klingler [2]. Two other ternary compounds of ZnS and In_2S_3, viz., $Zn_2In_2S_5$ and $Zn_3In_2S_6$, have been found to be stable at room temperature [3,4]. A multitude of compounds with compositions between those of ZnS and $ZnIn_2S_4$ have stability in temperature ranges higher than 1050 K [4,5].

Crystals of $ZnIn_2S_4$ have been prepared by chemical vapor transport [1]

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and thin films have been prepared by thermal evaporation [6]. No information is available on the vapor pressure, vaporization reaction, or thermodynamics of $ZnIn_2S_4$. Considerable information about these properties of ZnS and In_2S_3, the binary constituents of $ZnIn_2S_4$, is available and much of it has been tabulated by Mills [7].

ZnS(s) vaporizes in the temperature range 1074–1324 K by the reaction [7]

$$\mathrm{ZnS(wz)} = \mathrm{Zn(g)} + 1/2\ \mathrm{S_2(g)} \tag{1}$$

in which wz denotes the wurtzite form of the solid. Munir and Mitchell [8], among others [7], studied the vapor pressure and thermodynamics of vaporization of ZnS(s). Their work gives the equilibrium constant of reaction (1) as

$$\log\left(K_\mathrm{p}/\mathrm{Pa}^{3/2}\right) = -(1.921 \pm 0.016) \times 10^4\ K/T + 17.05 \pm 0.13 \tag{2}$$

Reanalysis of their data with the Gibbs energy functions of Mills gives ΔH^0(298 K) of reaction (1), 388.0 ± 0.2 kJ mol^{-1} by third-law analysis and 379.1 ± 3.0 kJ mol^{-1} by second-law analysis. Mills selected the value 387.0 kJ mol^{-1}.

In_2S_3(s) vaporizes in the temperature range 1000–1218 K by the reaction [7,9]

$$\mathrm{In_2S_3(s)} = \mathrm{In_2S(g)} + \mathrm{S_2(g)} \tag{3}$$

Haque et al. [10], among others [7], studied the vapor pressure and thermodynamics of vaporization of In_2S_3(s). They give ΔH^0(298 K) of reaction (3), 613.4 ± 1.0 kJ mol^{-1}.

The aims of the present investigation were threefold. (1) To determine the vaporization reaction of $ZnIn_2S_4$. In the temperature range 1088–1218 K the vapor pressure of In_2S_3(s) is 1.5–3.0 times that of ZnS(wz). In that range, would the stability of $ZnIn_2S_4$(s) with respect to its binary constituents be sufficient to cause congruent vaporization? (2) To measure the vapor pressure of $ZnIn_2S_4$(s) as a function of temperature by the method of simultaneous Knudsen-effusion and torsion-effusion [10]. (3) To evaluate the equilibrium constant and thermodynamics of the vaporization reaction and, thence, the thermodynamics of $ZnIn_2S_4$(s).

EXPERIMENTAL

Samples

Solid samples with compositions ranging from ZnS to In_2S_3 in increments of 5 mol % on the basis of these formulas were prepared by heating the elements in evacuated, sealed, Vycor tubes. Each sample was heated at 400°C for 3 days, then the temperature was increased by 25°C each day until it was 700°C. The temperature was kept at 700°C until sulfur vapor was no longer visible in the tube. The tube was quenched in air, and opened in a dry box with nitrogen atmosphere. The sample was removed, ground with an agate mortar and pestle, and placed in another Vycor tube which was then evacuated and sealed. The tube was heated to 700°C, then the temperature was increased by 25°C each day until it was 900°C. The tube was air quenched and opened in the dry box. Each sample was stored in a vial inside a desiccator over $CaSO_4$. A Debye–Scherrer X-ray diffractogram of each sample was made.

Bulk-effusion experiments

To establish the vaporization reaction of $ZnIn_2S_4(s)$, samples of seven of the compositions above were heated in a radio-induction furnace in graphite crucibles of a previously described design [11] at temperatures sufficiently high to cause measurable amounts of effusion. The experiment at one of the compositions was repeated, thus eight experiments were done. Each experiment consisted of several successive heatings, with examination of the sample residue after each heating. The details of the procedure in these experiments, compositions, temperatures, amounts, and times, can be found in Table 3.

Measurement of vapor pressures and thermodynamics

Vapor pressures of $ZnIn_2S_4(s)$ were measured in the temperature range 1088–1218 K by the simultaneous torsion-effusion and Knudsen-effusion method. The apparatus, procedure, and data analysis have been described previously [10,12,13]. Data acquisition was automated with a laboratory computer [12,13].

For interpretation of the vapor-pressure measurements and thermodynamics of vaporization, the vaporization of $ZnIn_2S_4(s)$ was assumed to be congruent by the reaction

$$ZnIn_2S_4(s) = Zn(g) + In_2S(g) + 3/2\ S_2(g) \tag{4}$$

Pertinent equations used in data analysis were the torsion equation

$$P_T = 2k\,\Delta\theta/(d_a F_a A_a + d_b F_b A_b) \tag{5}$$

and the Knudsen equation

$$P_K = (dg/dt)(2\pi RT/M^*)^{1/2}/(W_a A_a + W_b A_b) \tag{6}$$

in which P_T is torsion pressure, P_K is Knudsen pressure, k is the constant of the torsion fiber in the torsion apparatus, $\Delta\theta$ is the displacement of the torsion pendulum due to vapor streaming from the effusion cell, d_a and d_b are the moment arms, F_a and F_b are the recoil force correction factors [14], and A_a and A_b are the areas of the two effusion orifices, labelled a and b, dg/dt is the rate of mass loss of the sample by effusion, T is the temperature of the effusion cell, M^* is the assigned molecular weight of the effusing vapor, R is the gas constant, and W_a and W_b are the transmission probabilities [14] of the orifices.

The resulting vapor pressures were converted to equilibrium constants of reaction (4) with the equation

$$K_p = P_{Zn}P_{In_2S}P_{S_2}^{3/2} \tag{7}$$

$$= 1.894 \times 10^{-2}\, P^{7/2} \tag{8}$$

A least-squares, straight-line fit to the equation

$$\log K_p = -A/T + B \tag{9}$$

was accomplished with the equilibrium constants from eqn. (8).

For the purpose of checking the congruency of the vaporization, the reaction quotient $P_{Zn}P_{S_2}^{1/2}$ was calculated at each temperature from

$$P_{Zn}P_{S_2}^{1/2} = 0.1283\, P^{3/2} \tag{10}$$

and related to the temperature by a least-squares fit to an equation of the form of eqn. (9). Then the temperature at which the product from eqn. (10) equals K_p from eqn. (2) was calculated.

The apparent molecular weight M of the effusing vapor was calculated from

$$M = M^*(P_K/P_T)^2 \tag{11}$$

The assigned molecular weight can be any positive real number, but in order to produce accurate Knudsen pressures, M^* was set equal to the average molecular weight $\overline{M}$ of congruently effusing $ZnIn_2S_4$ vapor. $\overline{M}$ was calculated from the equation [15]

$$\overline{M} = \left(\sum_{j=1}^{n} m_j M_j^{-1/2} \right)^{-2} \tag{12}$$

in which n is the number of species effusing and m_j is the mass fraction and M_j is the molecular weight of species j in the effusing vapor. The result was $\overline{M} = 136.2$.

The effusion cell was of graphite and was machined to a previously described design [11]. Its pertinent geometric properties are given in Table 1.

The sample for the vapor-pressure measurements was $ZnIn_2S_4$. A portion was kept for X-ray diffraction analysis and for analyses for Zn and In by atomic absorption. The mass of the sample added to each chamber of the effusion cell was measured. At the end of the vapor-pressure measurements, the sample residue in each chamber in the effusion cell was analyzed by X-ray diffraction and for Zn and In by atomic absorption.

Thermodynamic calculations were by previously described second-law and

TABLE 1

Geometric parameters of the torsion-effusion cell (The orifice is a frustum of a right, circular cone)

Orifice	Length/ min. radius	Semiapex angle (deg)	Area (mm^2)	Transmission probability	Recoil-force correction	Moment arm (cm)
1	4.38 ± 0.04	30.6 ± 0.5	0.673 ± 0.010	0.913 ± 0.003	1.098 ± 0.004	0.803 ± 0.001
2	4.70 ± 0.04	30.6 ± 0.5	0.606 ± 0.010	0.913 ± 0.003	1.101 ± 0.004	0.803 ± 0.001

TABLE 2

Gibbs-energy functions, $-[G^0(T)-H^0(298\ \mathrm{K})]/T$ in J mol^{-1} K^{-1}

T(K)	ZnS(s)	In_2S_3(s)	Zn(g)	In_2S(g)	S_2(g)	Reaction (4) (±2.0)
1000	83.14	228.40	171.46	343.5	245.73	572.4
1100	86.90	237.73	172.84	347.1	248.15	567.5
1200	90.50	247.02	174.18	350.6	250.45	562.9
1300	93.55	255.94	175.48	354.2	252.63	559.1

third-law methods [13,16,17]. Gibbs energy functions used in these calculations are given in Table 2. The Gibbs energy function of $ZnIn_2S_4$(s) was taken to be the sum of those of ZnS(s) and In_2S_3(s); ZnS(wz) was assumed [11]. The sources of these values were Mills [7] for sulfur-containing species

TABLE 3

Results of bulk-effusion experiments

Experiment	Initial mol % ZnS	Initial mass (mg)	Successive heating	T(K) (±20)	Time (min)	Mass loss (mg)	Phases present after heating
1	25	349.0	1	1173	50	85.5	α, β
			2	1173	60	95.3	α, β
2	65	290.3	1	1171	64	34.0	γ, δ
			2	1230	71	135.6	δ, ZnS
			3	1251	60	96.7	ZnS
3	65	126.6	1	1108	1410	40.0	
			2	1108	1500	45.3	δ, ZnS
4	35	180.0	1	1073	277	6.3	
			2	1073	670	27.8	
			3	1073	2665	98.3	
			4	1073	270	5.9	β
			5	1108	220	7.2	
			6	1108	180	10.2	β
5	45	303.0	1	1281	41	278.8	δ, ZnS
6	55	225.1	1	1108	1380	34.5	β
			2	1108	2460	70.1	β
			3	1108	2100	64.3	β
7	85	187.9	1	1108	1440	35.2	δ, ZnS
			2	1108	2880	65.7	δ, ZnS
			3	1108	1290	31.7	ZnS
8	70	327.1	1	1178	23	45.9	
			2	1176	40	51.4	
			3	1188	100	88.3	δ, ZnS

and Hultgren et al. [18] for Zn(g). The vaporization of $ZnIn_2S_4(s)$ was assumed to follow eqn. (4).

RESULTS

Phase content vs. composition

Examination of X-ray diffractograms of the samples with compositions ranging from ZnS to In_2S_3 by increments of 5 mol % revealed six phases in the system: (1) $In_2S_3(s)$ saturated with 20 ± 5 mol % ZnS; (2) a ternary compound at 0.3 ZnS–0.7 In_2S_3; (3) a ternary compound at 0.5 ZnS–0.5 In_2S_3; (4) a ternary compound at 0.6 ZnS–0.4 In_2S_3; (5) a ternary compound at 0.7 ZnS–0.3 In_2S_3; and (6) ZnS(s) saturated with less than 5 mol % In_2S_3. Uncertainty in each of the compositions was ±5 mol %. The ternary compounds were denoted α, β, γ, and δ, respectively. Compounds β, γ, and δ have been reported by others [5] with ZnS contents of 49.6 ± 1, 59.78 ± 0.9, and 70.08 ± 1.2 mol %, respectively, compound β is $ZnIn_2S_4$, the subject of the present study. Compound α has not been reported previously.

Bulk-effusion experiments

The results of the bulk-effusion experiments are found in Table 3. These results show that the pressure–composition relationships in the ZnS–In_2S_3 system are temperature dependent; experiment (5), at 1281 ± 20 K, gave a result different from that of the others. In the other experiments, samples containing less than 50 mol % ZnS vaporized with net loss of In_2S_3 and the solid approached phase β, $ZnIn_2S_4$, in composition. In experiment (6) with 55 mol % ZnS, the sample vaporized with net loss of ZnS and the solid approached β in composition. Samples with more than 60 mol % ZnS vaporized with net loss of In_2S_3 and approached ZnS in composition. A minimum or stable congruently vaporizing point in the vapor pressure vs.

TABLE 4

Amounts of Zn and In in the sample before and after the vapor-pressure experiment with $ZnIn_2S_4(s)$

	Theoretical $ZnIn_2S_4$	Before experiment	After experiment	
			Chamber a	Chamber b
% Zn	15.44	15 ± 1	14 ± 1	15 ± 1
% In	54.25	54 ± 3.3	56 ± 2.3	56 ± 1.9

composition curve occurs at $ZnIn_2S_4$; a maximum or metastable congruently vaporizing point occurs at 60 ± 5 mol % ZnS. At the high temperature, 1281 ± 20 K, of experiment (5), $ZnIn_2S_4$ does not vaporize congruently. Experiments (1) and (5) indicate that the highest temperature at which $ZnIn_2S_4$(s) vaporizes congruently is in the range (1173 ± 20)–(1281 ± 20) K.

Vapor pressures and thermodynamics

The initial mass of the sample was 1.1006 g distributed approximately equally between the two chambers of the effusion cell. In the course of the vapor-pressure experiment, 572 mg or 52.0% of the sample effused. X-Ray diffractograms of the sample before and after the vapor-pressure experiment were the same and matched that given in the literature [2]. Atomic absorption analyses for zinc and indium in the sample before and after the vapor-pressure experiment, along with theoretical amounts in $ZnIn_2S_4$, are given in Table 4; uncertainties in indium analyses are standard deviations in several measurements; uncertainties in zinc analyses are estimated. Within the limits of error, the sample composition did not change during the experiment.

Table 5 gives the results of the vapor-pressure measurements and thermodynamic calculations. The first column gives the order in which the data were acquired, the second column gives the temperature, the third and fourth columns give the torsion and Knudsen pressures, the fifth column gives the apparent molecular weight from eqn. (11), and the sixth and seventh columns give the third-law ΔH^0(298 K) of reaction (4) from torsion and Knudsen data. In measurements 10, 13, 14, 19, 22–26, 28, and 53, no Knudsen measurement was made. The average third-law ΔH^0(298 K) by torsion is 1050.1 ± 0.6 kJ mol^{-1} and by Knudsen is 1050.4 ± 0.7 kJ mol^{-1}, where the uncertainties are standard deviations of the mean. The corresponding second-law results are, by torsion, 1114.0 ± 9.6 kJ mol^{-1} and, by Knudsen, 1138.2 ± 15.5 kJ mol^{-1}. The value 1050.3 ± 1.0 kJ mol^{-1}, based on the third-law results, is selected.

Reanalysis of the data on vaporization of ZnS(s) by Munir and Mitchell[8], with Gibbs energy functions from Mills [7], yielded ΔH^0(298 K) of reaction (1). The results were 388.0 ± 0.2 kJ mol^{-1} by third-law analysis, and 379.1 ± 3.0 kJ mol^{-1} by second-law analysis. The value selected by Mills was 387.0 kJ mol^{-1}. Combination of the latter value, the value from Haque et al. [10] for vaporization of In_2S_3(s) by reaction (3), 613.4 ± 1.0 kJ mol^{-1}, and our selected value for $ZnIn_2S_4$, gives ΔH^0(298 K) of the combination reaction

$$\mathrm{ZnS(wz)} + \mathrm{In_2S_3(s)} = \mathrm{ZnIn_2S_4(s)} \qquad (13)$$

The result is −49.9 ± 1.4 kJ mol^{-1}.

Least-squares straight lines relating the equilibrium constants of eqn. (4) to the temperatures in the range of the experiments were, from torsion

TABLE 5

Vapor pressures, apparent molecular weights, and third-law standard enthalpies of vaporization of $ZnIn_2S_4(s)$

Index	T(K) ($\pm 0.2\%$)	P_T(Pa) ($\pm 0.02 \pm 0.02\ P_T/\mathrm{Pa}$)	P_K(Pa) ($\pm 0.02 \pm 0.02\ P_K/\mathrm{Pa}$)	M	(3rd-law ΔH^0(298 K) (± 3.2)(kJ mol^{-1})	
					Torsion	Knudsen
1	1120	1.01	0.97	126 ± 8	1046.9	1048.3
2	1127	1.12	1.08	127 ± 7	1049.6	1050.9
3	1120	0.82	0.81	133 ± 10	1053.5	1054.2
4	1116	0.82	0.83	139 ± 10	1049.9	1049.9
5	1122	0.87	0.78	109 ± 10	1053.6	1057.3
6	1160	2.92	2.70	116 ± 3	1046.2	1049.2
7	1173	3.96	3.84	128 ± 3	1046.9	1048.2
8	1153	2.49	2.49	136 ± 4	1045.6	1045.8
9	1157	2.57	2.54	133 ± 4	1048.0	1048.6
10	1136	1.41			1049.8	
11	1139	1.51	1.54	142 ± 6	1050.2	1049.9
12	1143	1.65	1.59	126 ± 5	1050.9	1052.3
13	1135	1.23			1053.5	
14	1177	4.32			1047.2	
15	1179	4.28	4.30	137 ± 3	1049.3	1049.3
16	1181	4.73	4.62	130 ± 3	1047.5	1048.5
17	1177	4.28	4.44	147 ± 3	1047.6	1046.5
18	1183	4.97	4.87	131 ± 3	1047.5	1048.4
19	1166	2.98			1050.7	
20	1157	2.36	2.29	128 ± 4	1050.8	1052.2
21	1142	1.58	1.49	121 ± 6	1051.5	1053.5
22	1119	0.85			1051.6	
23	1116	0.77			1051.9	
24	1114	0.73			1052.2	
25	1111	0.67			1052.4	
26	1092	0.38			1053.3	
27	1093	0.38	0.35	116 ± 22	1054.2	1056.9
28	1099	0.46			1053.2	
29	1103	0.51	0.48	121 ± 16	1054.0	1056.1
30	1168	3.14	2.98	123 ± 3	1050.6	1052.6
31	1164	2.96	2.90	131 ± 3	1049.2	1050.2
32	1168	3.09	3.03	131 ± 3	1051.1	1052.0
33	1215	10.42	10.58	140 ± 3	1048.0	1048.7
34	1190	5.77	5.62	129 ± 3	1048.1	1049.2
35	1184	4.92	4.98	139 ± 3	1048.7	1048.5
36	1180	4.15	4.15	136 ± 3	1051.2	1051.4
37	1194	6.36	6.58	146 ± 3	1048.0	1047.0
38	1201	7.49	7.51	137 ± 3	1048.1	1048.2
39	1218	12.56	12.23	129 ± 3	1043.8	1045.0
40	1213	10.42	10.35	134 ± 3	1046.3	1046.8
41	1174	3.51	3.54	138 ± 3	1051.9	1051.8
42	1104	0.44	0.38	102 ± 19	1059.7	1064.2

TABLE 5 (continued)

Index	T(K) ($\pm0.2\%$)	P_T(Pa) ($\pm0.02\pm$ $0.02\ P_T$/Pa)	P_K(Pa) ($\pm0.02\pm$ $0.02\ P_K$/Pa)	M	(3rd-law ΔH^0(298 K) (±3.2)(kJ mol^{-1}))	
					Torsion	Knudsen
43	1167	2.86	2.92	142 ± 3	1053.0	1052.5
44	1162	2.61	2.57	132 ± 4	1051.8	1052.6
45	1180	4.27	4.43	147 ± 3	1050.1	1049.1
46	1184	4.63	4.76	144 ± 3	1050.7	1050.0
47	1137	1.43	1.40	130 ± 6	1050.3	1051.2
48	1165	3.07	3.07	136 ± 3	1048.9	1049.0
49	1182	4.66	4.71	139 ± 3	1048.8	1048.7
50	1174	3.99	4.05	140 ± 3	1047.4	1047.1
51	1116	0.81	0.80	133 ± 10	1050.4	1051.1
52	1155	2.23	2.44	163 ± 4	1051.1	1048.3
53	1088	0.34			1053.1	
54	1145	1.89	1.93	142 ± 5	1048.1	1047.4
55	1136	1.45	1.43	132 ± 6	1049.0	1049.6
			Ave.	132.6 ±2.0	1050.12 ±0.56	1050.39 ±0.70

results

$$\log\left(K_p/\text{Pa}^{7/2}\right) = -(5.505 \pm 0.050) \times 10^4\ K/T + 47.21 \pm 0.44 \qquad (14)$$

and from Knudsen results

$$\log\left(K_p/\text{Pa}^{7/2}\right) = -(5.634 \pm 0.081) \times 10^4\ K/T + 48.30 \pm 0.70 \qquad (15)$$

The relationship between temperature and the product in eqn. (10) was, from torsion results

$$\log\left(P_{\text{Zn}}P_{\text{S}_2}^{1/2}/\text{Pa}^{3/2}\right) = -(2.395 \pm 0.022) \times 10^4\ K/T + 20.08 \pm 0.019 \qquad (16)$$

and from Knudsen results

$$\log\left(P_{\text{Zn}}P_{\text{S}_2}^{1/2}/\text{Pa}^{3/2}\right) = -(2.414 \pm 0.035) \times 10^4\ K/T + 20.55 \pm 0.30 \qquad (17)$$

Simultaneous solutions of eqn. (16) with (2) and (17) with (2) yield $T = 1420 \pm 150$ K; above that temperature, ZnIn_2S_4 would not vaporize congruently.

DISCUSSION

That ZnIn_2S_4(s) vaporizes congruently in the range 1088–1218 K was established in four ways: (i) bulk-effusion experiments numbered 1, 4, and 6 in Table 3 which began with samples with ZnS contents on either side of that of ZnIn_2S_4 caused the compositions of the samples to approach or reach that of $ZnIn_2S_4$; (ii) in the vapor-pressure experiment with $ZnIn_2S_4(s)$, in the temperature range 1088–1218 K, the fractions of Zn and In and the X-ray diffractograms of the sample were the same within experimental error before and after the experiment; (iii) in the vapor-pressure experiment with $ZnIn_2S_4(s)$, the vapor pressure at a given temperature and the apparent molecular weight of the effusing vapor were constant within experimental error throughout the experiment; and (iv) the reaction quotient $P_{Zn}P_{S_2}^{1/2}/Pa^{3/2}$ from the vapor pressure experiment with $ZnIn_2S_4(s)$ became equal to the equilibrium constant of the vaporization reaction of ZnS(wz), reaction (1), at 1420 ± 150. Within its large uncertainty, this temperature is in line with the result from the bulk effusion experiments that the highest temperature of congruent vaporization of $ZnIn_2S_4(s)$ is in the range 1173–1281 (±20) K. The vapor-pressure experiment indicated that the highest temperature of congruent vaporization is greater than 1218 K, the highest temperature in the experiment; the last temperature, too, is in line with the result in (iv).

The $\Delta H^0(298\ K)$ of vaporization of $ZnIn_2S_4(s)$ was shown to be 1050.3 ± 1.0 kJ mol^{-1}. The $\Delta H^0(298\ K)$ of $ZnIn_2S_4(s)$ with respect to those of its constituent binary sulfides, ZnS(wz) and $In_2S_3(s)$, was − 49.9 ± 1.4 kJ mol^{-1}. This enthalpy of combination is larger than that for most other ternary sulfides involving neither first-row nor alkali-family metals [10,11]. No other such sulfide is known to vaporize congruently. The combination enthalpies of such sulfides are usually between −15 and −42 kJ mol^{-1}. Its large enthalpy of combination along with the fact that the vapor pressures of ZnS(s) and $In_2S_3(s)$ differ by factors of only 1.5–3.0 in the temperature range of the present experiments accounts for the congruency of the vaporization of $ZnIn_2S_4(s)$.

A multitude of solid compounds with compositions between those of $ZnIn_2S_4(s)$ and ZnS are known to exist in the temperature range of the present experiments [4]. A sufficient increase in the partial pressures of ZnS vapor species over $ZnIn_2S_4(s)$ from an external source of ZnS vapor would cause the condensation of some compound ZnS-rich with respect to $ZnIn_2S_4$. The present results, particularly the results in (iii) and (iv) above, indicate that that compound would be ZnS(s) itself. In other words, the composition at the metastable maximum in the vapor-pressure vs. composition relationship of the $ZnS–In_2S_3$ system is between that of $ZnIn_2S_4$ and any other relatively ZnS-rich compound. Any such compound which violates this rule must have slight stability with respect to that of ZnS(s) and $ZnIn_2S_4(s)$. The present results place the metastable maximum at a composition of 60 ± 5 mol % ZnS. Two ternary compounds, γ, at 60 mol % ZnS, and another [4], at ca. 56 mol % ZnS and stable only above 1050 K, lie within this range and might violate the above rule.

The average of the molecular weights, M, in Table 5 is 132.6 ± 2.0, where the uncertainty is the standard deviation of the mean. The average molecular weight of congruently vaporizing $ZnIn_2S_4$(s) by eqn. (12) is 136.2. Thus, the data contain a small bias making the Knudsen pressures too high (by 1.3 ± 0.7%) or the torsion pressures too low or both. The alternative explanation, that the vapor contains a higher fraction of Zn(g) or S_2(g) than expected and the average M is correct, is not likely for two reasons. First, incongruent vaporization would be required, and second, the less volatile of the two constituent sulfides, ZnS, would be required to compose the higher fraction of the vapor. The reason for the bias is unknown, but the bias is sufficiently small and uncertain to be ignored.

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