Thermochimica Acta, 59 (1982) 81–93
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

VAPORIZATION CHEMISTRY AND THERMODYNAMICS IN THE $CdGa_2S_4$–Ga_2S_3 SYSTEM

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(Received 21 April 1982)

ABSTRACT

The chemistry and thermodynamics of vaporization of $CdGa_2S_4(s)$, $CdGa_8S_{13}(s)$, and $Ga_2S_3(s)$ were studied by computer-automated, simultaneous Knudsen-effusion and torsion-effusion, vapor pressure measurements in the temperature range 967–1280 K. The vaporization was incongruent with loss of $Cd(g) + 1/2\ S_2(g)$ and production of $CdGa_8S_{13}(s)$, a previously unknown compound, in equilibrium with $CdGa_2S_4(s)$, until the solid became $CdGa_8S_{13}$ only. Then, incongruent vaporization continued with production of $Ga_2S_3(s)$ until the solid was Ga_2S_3 only. The latter vaporized congruently. The $\Delta H°(298\ K)$ of combination of one mole of CdS(s) with one mole of $Ga_2S_3(s)$ to give $CdGa_2S_4(s)$ was -22.6 ± 0.9 kJ mole^{-1}. The $\Delta H°(298\ K)$ of combination of one mole of CdS(s) with four moles of $Ga_2S_3(s)$ to give $CdGa_8S_{13}(s)$ was -25.5 ± 1.1 kJ mole^{-1}. The $\Delta H°(298\ K)$ of $CdGa_8S_{13}(s)$ with respect to disproportionation into $CdGa_2S_4(s)$ and $3\ Ga_2S_3(s)$ was -2.8 ± 0.6 kJ mole^{-1}. $CdGa_8S_{13}(s)$ was not observed at room temperature. The $\Delta H°(298\ K)$ of vaporization of the residual $Ga_2S_3(s)$ was 663.4 ± 0.8 kJ mole^{-1}, which compared well with a value of 661.4 ± 0.3 kJ mole^{-1} already available from the literature. Implications of small variations in stoichiometry of compounds in this study were observed and are discussed.

INTRODUCTION

Compounds of the type AB_2C_4, where A and B are divalent and trivalent metals, respectively, and C is a chalcogen, are of interest for semiconductor optoelectronic devices. Thermodynamic and high-temperature chemical properties, important in preparation techniques and in applications, are not available for most such compounds.

The compound $CdGa_2S_4$ displays large birefringence and is potentially interesting as a nonlinear optical material [1–3]. The crystal structure of $CdGa_2S_4$ was studied by Hahn et al. [4]. Crystal growth by chemical transport was reported by Nitsche et al. [5], and by melt growth was reported by Shand [6] and by Chedzey et al. [7]. However, none of these methods

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yielded stoichiometric crystals. High-temperature thermochemical properties, necessary for interpretation of such behavior, are lacking. This paper reports studies of the vaporization and thermodynamics of $CdGa_2S_4(s)$.

The vaporization of CdS(s) was studied by several investigators [8] including Goldfinger and Jeunehomme [9] who used mass spectrometry, Munir [10] who used torsion effusion, and Kshirsagar et al. [11] who used simultaneous Knudsen and torsion effusion. The vaporization reaction was found to be

$$CdS(s) = Cd(g) + 1/2\,S_2(g) \tag{1}$$

The vaporization of $Ga_2S_3(s)$ was studied by torsion effusion by Kashkooli and Munir [12] and by mass spectrometry by Uy et al. [13]. The vaporization reaction was

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

The $\Delta H°(298\ K)$ from Munir was 661.4 ± 0.3 kJ mole^{-1} with data from Mills [8]. An increase in vapor pressure of $Ga_2S_3(s)$ accompanied by an increase in the partial pressure of $Ga_2S(g)$ upon lowering the temperature across 1228 ± 3 K was reported by Roberts and Searcy [14] and Starzynski and Edwards [15].

The $ZnGa_2S_4$–Ga_2S_3 system was studied by Gates and Edwards [16]. They found the intermediate compound $ZnGa_8S_{13}(s)$. With respect to the binary sulfides, the $\Delta H°(298\ K)$ of $ZnGa_2S_4(s)$ was -38 ± 12 kJ mole^{-1} and of $ZnGa_8S_{13}(s)$ was -59 ± 19 kJ mole^{-1}.

The purposes of this study were: (1) to learn the vaporization reactions of $CdGa_2S_4$; (2) to use the simultaneous Knudsen-effusion and torsion-effusion method to measure the vapor pressure as a function of temperature; (3) from the vapor pressures, calculate equilibrium constants of the vaporization reactions as functions of temperature, and thence calculate the thermodynamic properties of the vaporization reactions and the reactants and products therein.

EXPERIMENTAL

Samples were prepared by heating the high-purity elements in evacuated sealed Vycor ampoules. The heating program described earlier [17] was followed. The compound $CdGa_2S_4$ and other samples of $(1-x)CdS \cdot xGa_2S_3$ with x ranging from 0.0 to 1.0 by increments of 0.1 were prepared. Each sample was analyzed for phase content by X-ray powder diffractometry.

Vapor pressures of a sample which initially was 1.0000 g of $CdGa_2S_4$ were measured by the simultaneous Knudsen-effusion, torsion-effusion method [18–22] with procedures already described [11]. Vapor pressures were obtained automatically with a laboratory computer. Temperature measurements were made with a Pt, Pt–10% Rh thermocouple in a dummy cell identical to and symmetrically placed with respect to the torsion-effusion cell [11]. The torsion-effusion cell was of graphite machined to a standard design [16]; its geometric properties are given in Table 1.

Vapor pressures were calculated with the torsion equation [23]

$$P_{\mathrm{T}} = \frac{k\Delta\theta}{d_{\mathrm{a}}F_{\mathrm{a}}A_{\mathrm{a}} + d_{\mathrm{b}}F_{\mathrm{b}}A_{\mathrm{b}}} \tag{3}$$

and the Knudsen equation [23]

$$P_{\mathrm{K}} = \frac{(\mathrm{d}g/\mathrm{d}t)(2\pi RT/M^*)^{1/2}}{W_{\mathrm{a}}A_{\mathrm{a}} + W_{\mathrm{b}}A_{\mathrm{b}}} \tag{4}$$

in which P_{T} is torsion pressure, P_{K} is Knudsen pressure, k is the constant of the torsion fiber, $\Delta\theta$ is the displacement of the torsion pendulum due to vapor effusing from the cell, d_{a} and d_{b} are the moment arms, F_{a} and F_{b} are the recoil force correction factors [23], and A_{a} and A_{b} are the areas of the two effusion orifices, labelled a and b, $\mathrm{d}g/\mathrm{d}t$ 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_{a} and W_{b} are the transmission probabilities [23] of the orifices. The apparent molecular weight, M, of the effusing vapor was calculated from

$$M = M^*(P_{\mathrm{K}}/P_{\mathrm{T}})^2 \tag{5}$$

The average molecular weight, $\bar{M}$, of an effusing vapor with n molecular species in the vapor is given by [21]

$$\bar{M} = \left(\sum_{j=1}^{n} m_j M_j^{-1/2} \right)^{-2} \tag{6}$$

in which m_j is the mass fraction and M_j is the molecular weight of species j in the effusing vapor.

Gibbs energy functions of elements and binary compounds involved in vaporization reactions were obtained from the literature [8,24]. Those of ternary solid compounds were obtained as the sum of those of the con-

TABLE 1

Geometric properties of the effusion cell

Parameter	Orifice a	Orifice b
Area/mm^2	0.256	0.285
Length/radius	3.85	4.09
Transmission probability	0.366	0.353
Recoil force factor	0.414	0.393
Moment arm/mm	8.11	8.11

TABLE 2

Standard molar Gibbs energy functions, $\mathcal{G}^{\circ\prime}(T)$

T/K	$-[G^{\circ}(T)-H^{\circ}(298\ \mathrm{K})]/T$ (J mole^{-1} K^{-1})						
	$CdS(s)$	$Ga_2S_3(s)$	$CdGa_2S_4(s)$	$CdGa_8S_{13}(s)$	$Cd(g)$	$Ga_2S(g)$	$S_2(g)$
900	91.3	191.3	282.6	856.5	176.7		243.1
1000	95.1	200.0	295.1	895.1	178.2		245.7
1100	98.8	208.3	307.1	932.0	179.6	319.8	248.2
1200	102.3	216.3	318.6	967.5	181.0	323.3	250.5
1300		224.1				326.6	252.6

stituent binary sulfides [16]. The Gibbs energy functions used in this work are given as functions of temperature in Table 2. Those at temperatures not given in the table were obtained by linear interpolation.

Values of $\Delta H^{\circ}(298\ \mathrm{K})$ for vaporization reactions were calculated from experimental data and Gibbs energy functions $\mathcal{G}^{\circ\prime}(T)$ by the third-law method with [25]

$$\Delta H^{\circ}(298\ K) = RT\left[\Delta\mathcal{G}^{\circ\prime}(T)/R - \ln\left(K_{\mathrm{p}}/\mathrm{Pa}^{m}\right) + 11.526m\right] \tag{7}$$

in which $\mathcal{G}^{\circ\prime}(T)$ of a substance is given by

$$\mathcal{G}^{\circ\prime}(T) = -\left[G^{\circ}(T) - H^{\circ}(298\ K)\right]/T \tag{8}$$

and K_{p} is the equilibrium constant with apparent units of Pa^{m}. The last term in eqn. (7) accounts for the fact that the standard pressure is 1 atm. Second-law values of $\Delta H^{\circ}(298\ \mathrm{K})$ were obtained from slopes of Σ plots [25,26].

In the temperature range of these experiments, the vapor pressure of CdS(s) is more than 100 times that of $Ga_2S_3(s)$. Furthermore, presence of the vapor of CdS(s) by reaction (1) suppresses vaporization of $Ga_2S_3(s)$ by reaction (2). Consequently, the assumption was made that only CdS was lost from the sample until the composition of Ga_2S_3 was reached. Thus, the elemental composition of the sample could be calculated at any time from the initial mass and composition of the sample and the mass lost since the beginning of the experiment. The vapor was assumed to be that of CdS(s), viz. Cd(g) and $S_2(g)$, by reaction (1). With knowledge of the one or two solid phases present, the vaporization reaction of the sample could be deduced at any composition.

Identification of chemical changes resulting from the disappearance of one solid compound and the appearance of another as the composition of the sample changed was accomplished by observing changes in the temperature dependence of the vapor pressure. Across a miscibility gap, such a change is discontinuous. Any discontinuous change would occur in two steps in a two-chamber torsion-effusion cell. The same amount of sample was put in each chamber of the cell, but the effective areas of the effusion orifices were not exactly the same. Thus, any transition would occur first in the chamber with the larger effective orifice area (area × transmission probability), which we shall call chamber b, and later in the other chamber, which we shall call chamber a.

Let the pressure before the transition be P and after the transition be P'. We define

$$X=\frac{\mathrm{P}'}{\mathrm{P}} \tag{9}$$

Let the effective area of the larger orifice be A_b and of the smaller orifice be A_a. We assume that the difference between the areas of the orifices is small and define

$$\alpha=\frac{\mathrm{A}_b-\mathrm{A}_a}{\mathrm{A}} \tag{10}$$

where A is the average area of the orifices.

Let w be the mass of effusate (CdS) which must be lost from either chamber before the occurrence of the transition. At the time of the transition in chamber b, let Δg_a be the mass of effusate still to be lost from chamber a before the transition there. Let Δg_b be the mass of effusate lost from chamber b after the transition, while Δg_a is being lost from chamber a, i.e. until completion of the transition in chamber a. The following equations result

$$\Delta g_a = w\alpha \tag{11}$$

$$\Delta g_b = Xw\alpha \tag{12}$$

$$\frac{\Delta g_a}{\Delta g_a+\Delta g_b}=\frac{1}{1+X} \tag{13}$$

From measurements of the sample masses and the pressures at the onset and at the completion of a transition in a two-chamber effusion cell, the sample composition at the transition can be calculated.

RESULTS

The X-ray diffractograms of samples with compositions $(1-x)\mathrm{CdS}\cdot x\mathrm{Ga_2S_3}$, $x=0.5-1.0$, contained only lines of $\mathrm{CdGa_2S_4}$ and $\mathrm{Ga_2S_3}$, i.e. no compound of composition between these two was found in the samples.

The results of the vaporization experiment are presented in Table 3. The first column contains the indexes representing the order in which the data were acquired, the second column gives the Group assignments, vide infra, of the data, the third column gives the temperature, the fourth column gives the torsion pressure, the fifth column gives the Knudsen pressure, the sixth column gives apparent molecular weight from eqn. (5), and the seventh and eighth columns contain third-law $\Delta H°(298\ \mathrm{K})$ of the vaporization reaction from torsion and Knudsen measurements, respectively.

The results of the vapor pressure measurements by either torsion or Knudsen effusion can be divided into six groups, represented by Roman numerals in Table 3, column 2, viz.

Group I. The first 28 data. The torsion data in this group fit the straight line represented by eqn. (18), and the Knudsen data fit the straight line represented by eqn. (19).

Group II. Data numbered 29–31 in Table 3. These data were obtained while the transition from Group I to Group III was occurring.

Group III. Data numbered 32–42 in Table 3. The torsion data in this group fit the straight line represented by eqn. (20), and the Knudsen data fit the straight line represented by eqn. (21).

Group IV. Data numbered 43–48 in Table 3. These data were obtained while the transition from Group III to Group V was occurring.

Group V. Data numbered 49–52, 56–58, and 61–64 in Table 3. The

TABLE 3

Vapor pressures, apparent molecular weights, and thermodynamic results from torsion-effusion and Knudsen-effusion measurements

Index	Group and reaction no.	T/K	P_T/Pa	P_K/Pa	M	3rd law $\Delta H°(298\ \mathrm{K})$/kJ mole^{-1}	
						Torsion	Knudsen
1	I, 14	1083.0	6.40	6.74	108.5	361.43	360.73
2	I, 14	1072.0	4.95	5.09	103.4	361.32	360.95
3	I, 14	999.0	0.66	0.67	100.8	362.62	362.44
4	I, 14	1158.0	44.75	46.83	107.1	357.48	356.83
5	I, 14	1118.0	16.60	17.50	108.7	359.41	358.67
6	I, 14	1021.0	1.28	1.20	86.0	361.93	362.75
7	I, 14	1073.0	5.00	5.19	105.4	361.51	361.01
8	I, 14	1057.0	3.52	3.60	102.3	360.93	360.64
9	I, 14	967.0	0.24	0.20	67.9	363.52	365.72
10	I, 14	1139.0	28.30	29.98	109.8	358.34	357.52
11	I, 14	1105.0	11.33	11.70	104.3	360.64	360.19
12	I, 14	1011.0	0.90	0.86	89.3	362.94	363.51
13	I, 14	1133.0	22.26	22.94	103.9	359.92	359.49
14	I, 14	1043.0	2.35	2.38	100.3	361.57	361.41
15	I, 14	1107.0	12.31	12.81	105.9	360.12	359.57
16	I, 14	1017.0	1.21	1.12	83.8	361.27	362.25
17	I, 14	1080.0	6.00	6.10	101.1	361.33	361.11
18	I, 14	1063.0	4.26	4.35	102.0	360.38	360.11
19	I, 14	1143.0	26.58	27.23	102.7	360.45	360.10

TABLE 3 (continued)

Index	Group and reaction no.	T/K	P_T/Pa	P_K/Pa	M	3rd law $\Delta H°(298\text{ K})/\text{kJ mole}^{-1}$	
						Torsion	Knudsen
20	I, 14	1163.0	42.73	43.91	103.3	359.64	359.24
21	I, 14	993.0	0.54	0.48	77.3	362.99	364.45
22	I, 14	1041.0	2.34	2.42	104.6	360.96	360.52
23	I, 14	1185.0	70.95	72.26	101.5	358.69	358.42
24	I, 14	1076.0	5.12	5.64	118.7	362.17	360.87
25	I, 14	1053.0	2.75	2.89	108.0	362.86	362.21
26	I, 14	1034.0	1.92	1.98	104.0	361.16	360.76
27	I, 14	1104.0	11.16	11.34	101.0	360.53	360.31
28	I, 14	1068.0	4.10	4.12	98.8	362.53	362.47
29	II	1134.0	18.60	21.02	124.9		
30	II	1140.0	18.64	20.04	113.1		
31	II	1063.0	3.92	3.82	92.9		
32	III, 15	1098.0	7.34	7.42	95.2	364.38	364.56
33	III, 15	1116.0	11.42	12.00	108.0	363.99	363.30
34	III, 15	1043.0	1.83	1.95	111.1	364.82	364.00
35	III, 15	999.0	0.58	0.57	94.5	364.23	364.45
36	III, 15	1127.0	14.14	15.09	111.4	364.45	363.54
37	III, 15	1149.0	21.68	22.72	107.5	365.19	364.52
38	III, 15	1062.0	2.86	3.02	109.1	365.33	364.61
39	III, 15	1119.0	11.14	11.53	104.8	365.29	364.81
40	III, 15	1092.0	5.36	5.48	102.3	366.74	366.44
41	III, 15	1038.0	1.60	1.60	97.8	364.87	364.87
42	III, 15	1003.0	0.58	0.62	111.8	365.65	364.81
43	IV	1153.0	20.63	21.62	107.4		
44	IV	1138.0	13.58	13.91	102.6		
45	IV	1043.0	1.38	1.46	109.5		
46	IV	1169.0	21.06	21.38	100.8		
47	IV	1106.0	4.61	4.74	103.4		
48	IV	1087.0	2.14	2.19	102.5		
49	V, 2	1133.0	0.22	0.24	116.4	666.21	664.57
50	V, 2	1183.0	0.96	0.90	101.9	665.09	664.69
51	V, 2	1237.0	4.51	4.44	94.8	662.07	662.40
52	V, 2	1280.0	13.42	13.11	93.4	660.67	661.16
53	VI	1240.0	6.91	9.03	167.1		
54	VI	1184.0	4.93	6.84	188.3		
55	VI	1105.0	0.81	1.07	170.7		
56	V, 2	1184.0	1.09	1.17	112.7	663.12	661.73
57	V, 2	1244.0	5.16	5.41	107.5	662.84	661.86
58	V, 2	1268.0	8.25	8.64	107.3	665.07	664.09
59	VI	1228.0	6.26	7.41	137.1		
60	VI	1204.0	2.84	3.50	148.6		
61	V, 2	1165.0	0.65	0.62	89.0	663.07	663.99
62	V, 2	1130.0	0.21	0.22	107.4	665.41	664.54
63	V, 2	1151.0	0.39	0.43	118.9	665.30	663.43
64	V, 2	1203.0	1.78	1.94	116.2	663.37	661.65

torsion data in this group fit the straight line represented by eqn. (22), and the Knudsen data fit the straight line represented by eqn. (23).

Group VI. Data numbered 53–55, 59, and 60 in Table 3. These data were acquired during anomalous vapor pressure increases [14,15] due to decreasing the temperature below a transition temperature after experiments above that temperature. These data were not used to obtain thermodynamic results in this work.

Of the original 1.0000 g of $CdGa_2S_4$, 0.268 ± 0.002 g had been lost at the beginning of the transition associated with Group II and 0.300 ± 0.002 g had been lost at the end of it. Across the transition, X in eqn. (9) was 0.75 ± 0.04. Then, via eqn. (13), the composition of the solid sample at the time of the transition was found to be $(CdS)(Ga_2S_3)_{4.03 \pm 0.10}$; the formula $CdGa_8S_{13}$ was assigned.

The vaporization reaction of $CdGa_2S_4$ during collection of data in Group I, was taken to be

$$\tfrac{4}{3}\ CdGa_2S_4(s) = \tfrac{1}{3}\ CdGa_8S_{13}(s) + Cd(g) + \tfrac{1}{2}\ S_2(g) \qquad (14)$$

The vaporization reaction after the composition of the solid sample reached that of $CdGa_8S_{13}$, i.e., during collection of data in Group III, was taken to be

$$CdGa_8S_{13}(s) = 4\,Ga_2S_3(s) + Cd(g) + \tfrac{1}{2}\ S_2(g) \qquad (15)$$

At the end of the next transition in the solid sample, i.e. immediately after collection of data in Group IV, 381 mg of mass had been lost. The 1.000 g of $CdGa_2S_4$ at the beginning of the experiment contained 380.1 g of CdS. The composition of the solid sample at this stage was assigned as that of Ga_2S_3, and the vaporization reaction during collection of data in Group V was taken to be that of $Ga_2S_3(s)$ [reaction (2)].

Equation (6) applied to reactions (14) and (15) gives $\overline{M} = 97.8$, and applied to reaction (2) gives $\overline{M} = 124.7$. The average value of M from Table 3 for Group I data, reaction (14), is 100.4 ± 10.5, for Group III data, reaction (15), 104.9 ± 6.5, and for Group V data, reaction (2), 106.0 ± 10.1; from Group VI data, $M = 162.4 \pm 20.0$. The differences between the values of M and the values of $\overline{M}$ predicted from the vaporization reactions and the large variations among values of M are discussed subsequently.

Equilibrium constants of reactions (14) and (15) were calculated from measured pressures with the equation

$$K_p = 0.3800\ P^{3/2} \qquad (16)$$

and of reaction (2) with the equation

$$K_p = 0.2355\ P^2 \qquad (17)$$

After application of eqn. (16), the torsion data of Group I followed the straight line represented by

$$\log(K_p/\mathrm{Pa}^{3/2}) = -(1.947 \pm 0.015) \times 10^4\ \mathrm{K}/T + (18.79 \pm 0.14) \qquad (18)$$

and the Knudsen data of Group I followed

$$\log(K_p/\mathrm{Pa}^{3/2}) = -(1.999 \pm 0.018) \times 10^4\ \mathrm{K}/T + (19.29 \pm 0.17) \qquad (19)$$

The torsion data of Group III followed

$$\log(K_p/\mathrm{Pa}^{3/2}) = -(1.843 \pm 0.028) \times 10^4\mathrm{K}/T + (17.64 \pm 0.26) \qquad (20)$$

and the Knudsen data of Group III followed

$$\log(K_p/\mathrm{Pa}^{3/2}) = -(1.853 \pm 0.029) \times 10^4\ \mathrm{K}/T + (17.75 \pm 0.27) \qquad (21)$$

After application of eqn. (17), the torsion data of Group V followed the straight line represented by

$$\log(K_p/\mathrm{Pa}^2) = -(3.427 \pm 0.048) \times 10^4\ \mathrm{K}/T + (28.35 \pm 0.41) \qquad (22)$$

and the Knudsen data of Group V followed

$$\log(K_p/\mathrm{Pa}^2) = -(3.383 \pm 0.042) \times 10^4\ \mathrm{K}/T + (28.01 \pm 0.36) \qquad (23)$$

The average third-law value of $\Delta H°(298\ \mathrm{K})$ of reaction (14) from Group I data by torsion effusion was 361.0 ± 0.3 kJ mole^{-1} and by Knudsen effusion was 360.9 ± 0.4 kJ mole^{-1}, in which the uncertainties are standard deviations of the means. The corresponding second-law values were 385.0 ± 2.9 kJ mole^{-1} and 395.0 ± 3.5 kJ mole^{-1}, respectively. The value 361.0 ± 0.5 kJ mole^{-1}, based on the third-law results, was selected.

The average third-law value of $\Delta H°(298\ \mathrm{K})$ of reaction (15) from Group III data by torsion effusion was 365.0 ± 0.2 kJ mole^{-1} and by Knudsen effusion was 364.5 ± 0.2 kJ mole^{-1}. The corresponding second-law values were 365.2 ± 5.3 and 367.1 ± 5.5 kJ mole^{-1}, respectively. The value 364.8 ± 0.5 kJ mole^{-1}, based on the third-law results, was selected.

The average third-law value of $\Delta H°(298\ \mathrm{K})$ of reaction (2) from Group V data by torsion effusion was 663.8 ± 0.5 kJ mole^{-1} and by Knudsen effusion was 663.1 ± 0.4 kJ mole^{-1}. The corresponding second-law values were 690.5 ± 9.3 and 681.9 ± 8.2 kJ mole^{-1}, respectively. The value 663.4 ± 0.8, based on the third-law results, was selected.

From the results above and the $\Delta H°(298\ \mathrm{K})$ of vaporization of CdS(s) from Kshirsagar et al. [11], 339.3 ± 1.0 kJ mole^{-1}, we find $\Delta H°(298\ \mathrm{K})$ of the combination reaction

$$\mathrm{CdS(s)} + 4\,\mathrm{Ga_2S_3(s)} = \mathrm{CdGa_8S_{13}(s)} \qquad (24)$$

to be -25.5 ± 1.1 kJ mole^{-1}. With $\Delta H°(298\ \mathrm{K})$ of formation of CdS(s) and $\mathrm{Ga_2S_3}$(s) from Mills [8], -149.4 ± 2.1 and -516.3 ± 12.5 kJ mole^{-1}, respectively, we obtain $\Delta H°(298\ \mathrm{K})$ of formation of $\mathrm{CdGa_8S_{13}}$(s) to be -2240 ± 25 kJ mole^{-1}.

With the results above, we obtain from treating eqn. (14) the $\Delta H°(298\ \mathrm{K})$ of the combination reaction

$$3\,CdS(s) + CdGa_8S_{13}(s) = 4\,CdGa_2S_4(s) \tag{25}$$

to be -65.1 ± 3.4 kJ mole^{-1}, and of the combination reaction

$$CdS(s) + Ga_2S_3(s) = CdGa_2S_4(s) \tag{26}$$

to be -22.6 ± 0.9 kJ mole^{-1}. The $\Delta H°$(298 K) of formation of $CdGa_2S_4(s)$ is found to be -688.3 ± 6.5 kJ mole^{-1}.

The $\Delta H°$(298 K) of the disproportionation reaction

$$CdGa_8S_{13}(s) \rightarrow CdGa_2S_4(s) + 3\,Ga_2S_3(s) \tag{27}$$

is 2.8 ± 0.6 kJ mole^{-1}.

DISCUSSION

This work provided the vapor pressures over 2-phase solids of $CdGa_2S_4(s)$ with $CdGa_8S_{13}(s)$ and of $CdGa_8S_{13}(s)$ with $Ga_2S_3(s)$ as functions of temperature. The enthalpies of the vaporization reactions were obtained, the $\Delta H°$(298 K) of combination of one mole of CdS(s) with one mole of $Ga_2S_3(s)$ to give $CdGa_2S_4(s)$ was shown to be -22.6 ± 0.9 kJ mole^{-1}, and the $\Delta H°$(298 K) of combination of one mole of CdS(s) with four moles of $Ga_2S_3(s)$ to give $CdGa_8S_{13}(s)$ was shown to be -25.5 ± 1.1 kJ mole^{-1}. The $\Delta H°$(298 K) of $CdGa_8S_{13}(s)$ with respect to disproportionation into $CdGa_2S_4(s)$ and $3\,Ga_2S_3(s)$ was -2.8 ± 0.6 kJ mole^{-1}.

The compound $CdGa_8S_{13}(s)$ was discovered. Its $\Delta H°$(298 K) with respect to those of its constituent binary sulfides was less than that of the analogous compound $ZnGa_8S_{13}(s)$ [16], viz. -25.5 ± 1.1 kJ mole^{-1} vs. -59 ± 19 kJ mole^{-1}, respectively. The $\Delta H°$(298 K) of $CdGa_2S_4(s)$ with respect to its binary constituents was somewhat less than that of $ZnGa_2S_4$, viz. -22.6 ± 0.9 kJ mole^{-1} vs. -38 ± 12 kJ mole^{-1}, respectively. The compound $CdGa_8S_{13}(s)$ was not observed at room temperature. Its limited stability with respect to $CdGa_2S_4(s)$ and $Ga_2S_3(s)$ is expressed only at higher temperatures, including those in this work. The compound $ZnGa_8S_{13}(s)$ was observed at room temperature [16]. The binding of CdS(s) into $Ga_2S_3(s)$ is less energetic than that of ZnS(s).

The agreement between third-law and second-law values of $\Delta H°$(298 K) was good for reaction (15), moderately good for reaction (2), and poor for reaction (14). Group I data, those involving reaction (14), produced a definite trend in $\Delta H°$(298 K) with experimental temperature. No significant trend was evident in Group III or Group V data involving reactions (15) and (2), respectively. The trend found in Group I data might be due to the use of incorrect Gibbs energy functions in the third-law calculations or to a temperature dependence of the composition of one of the compounds in the vaporization reaction.

The method of estimating Gibbs energy functions was the same for both ternary compounds, thus errors in these quantities, if present, should affect results for both reactions (14) and (15). The effect might be explained by a temperature-dependent valence of gallium in $CdGa_2S_4$(s), but not in $CdGa_8S_{13}$(s), since the latter is present in both reactions. An alternate explanation would be temperature-dependent solid solution of Ga_2S_3(s) in $CdGa_2S_4$(s) or of CdS(s) in $CdGa_8S_{13}$(s).

Some consistencies, which may be related to the effects above, are noticeable in the values of M in Table 3. In Group I data, when an observation at a relatively low temperature followed an observation at a relatively high temperature, an unusually low apparent molecular weight, M, of the vapor was obtained; cf. data pairs 5 and 6, 8 and 9, 11 and 12, 15 and 16, and 20 and 21. One sees a less distinct tendency toward higher values of M at higher temperatures and in experiments immediately following experiments at low temperatures. The latter tendency decreases with time as the amount of $CdGa_2S_4$(s) decreases. The indication is that the preferred composition of the vapor at lower temperatures following experiments at high temperatures is sulfur-rich, since the molecular weight of S_2(g), 64.1, is lower than that of Cd(g), 112.4. This preference would be due to one of the solid compounds in reaction (14), probably $CdGa_2S_4$, being sulfur-rich at high temperatures relative to its composition at the lower temperatures in these experiments. The possibility that a temperature bias in the equipment caused the trend above should not be ignored, but no such trend was seen in other studies with the same equipment at similar temperatures [11,27].

The average value of M from Group I was 100.4 ± 10.5, which is reasonably close to the predicted $\overline{M} = 97.8$. However, if the five unusually low values above are not considered, then the average M becomes 104.6 ± 4.3. The average M from Group III, where no consistent variations in M are seen, was 104.9 ± 6.5. The average M from Group IV, where reaction (15) was occurring in one chamber while relatively nothing ($< 1\%$) was occurring in the other, was 104.4 ± 3.4. Possibly the vapor during acquisition of the data discussed in this paragraph was sulfur-deficient. However, a conclusion cannot be drawn on the basis of such a small effect.

A clear and predictable difference is seen between the values of M in Group V data and those in Group VI data. Roberts and Searcy [14] showed by mass spectrometry that data obtained during an anomalous increase in vapor pressure involve an excess of Ga_2S(g), M.W. = 172, in the vapor. Thus values of M higher than $\overline{M} = 124.7$ predicted on the basis of reaction (2) are obtained in Group VI and values of M lower than 124.7 are obtained during Group V where the vapor is Ga_2S-deficient or sulfur-rich.

The vapor pressure as a function of temperature of the residual Ga_2S_3(s) in this work was in agreement with that of Ga_2S_3(s) reported by Kashkooli and Munir [12], but was less than that reported by Starzyński and Edwards [15]. The latter discuss the possibility that 'Ga_2S_3' exists in more than one form each with a different dependence of vapor pressure on temperature.

The range of temperatures in this work included the temperature at which Starzynski and Edwards saw a change in slope of the log P vs. $1/T$ plot, but no such break was seen in this work. The indication is that the gallium sulfide studied in this work and that studied by Kashkooli and Munir were the same, but that studied by Starzynski and Edwards was different, as they proposed.

The anomalous vapor pressure increase with decreasing temperature [14] was seen in data 53 and 59 in Table 3, though both were at temperatures at or above the reported transition temperature of 1228 ± 3 K. These observations indicate that the reported transition temperature may be too low.

ACKNOWLEDGEMENTS

The National Science Foundation through grant ENG77-22576 provided financial support for this work. Valuable discussions with Dr. H.B. Thompson are acknowledged.

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