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THE ISOMOLECULAR EXCHANGE REACTION $Ga_2S(g) + In_2S(g) = 2\ InGaS(g)$

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ABSTRACT

Equilibria involving the molecules $Ga_2S(g)$, $In_2S(g)$, and $InGaS(g)$, by the reaction

$Ga_2S(g) + In_2S(g) = 2InGaS(g)$

were investigated between 1060–1350 K by the Knudsen-effusion, mass-spectrometric method. The reaction enthalpy at 298 K was calculated to be 0 ± 1 kJ mol^{-1}. The enthalpy of formation of InGaS at 298 K and the enthalpy of atomization of InGaS at 298 K were calculated to be 80 ± 18 kJ mol^{-1} and 710 ± 18 kJ mol^{-1}, respectively. The equilibrium constant and the enthalpy of reaction indicated that the three gaseous molecules have a bent triatomic structure in which S is a center atom and no bond between metals.

INTRODUCTION

Knudsen-cell mass spectrometry can be used to study isomolecular exchange reactions [1], in which all the participating substances are gases and the same number of moles of gas occur on both sides of the chemical equation. If the ionic intensities of all participants in the reaction are measured, several uncertain quantities such as ionization cross-sections, fragmentations, and instrumental sensitivities tend to cancel.

The purpose of this study was to investigate the reaction between $Ga_2S(g)$ and $In_2S(g)$. The isomolecular exchange reaction

$$Ga_2S(g) + In_2S(g) = 2GaInS(g) \qquad (1)$$

was proposed. The goals were to establish the reaction, to study it by Knudsen-cell mass spectrometry, to measure its equilibrium constant, and to consider, on the basis of the results, the molecular geometry of the molecules participating in the reaction.

Mills [2] reported the enthalpies of formation and the atomization energies of both $Ga_2S(g)$ and $In_2S(g)$. ΔH_f^0 (298 K) of $In_2S(g)$ is 21 ± 33 kJ

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mol^{-1} and of $Ga_2S(g)$ is 138 ± 13 kJ mol^{-1}; ΔH_a^0 (298 K) of $In_2S(g)$ is 624.3 kJ mol^{-1} and of Ga_2S is 804.6 kJ mol^{-1}, respectively. Gas-phase infrared spectroscopy by Shevel'kov et al. [3,4] indicated that these molecules possess C_{2v} symmetry. The apex angles of $In_2S(g)$ and $Ga_2S(g)$ were estimated to be 100 and 112°, respectively [5].

$S_2(g)$, $Ga_2S(g)$, and $In_2S(g)$ were found [6–8] to be the major species in the vapor phase above the corresponding heated sesquisulfides. In a study of In_2S_3 by the mass-spectrometric technique in the temperature range 1005–1220 K, Colin and Drowart [7] observed S^+, S_2^+, In^+, In_2S^+, InS^+, In_2^+, and $In_2S_2^+$ ions. The ions S_2^+, In_2S^+, and $In_2S_2^+$ were taken to be parent ions, and In^+ and InS^+ were said to be parent ions as well as fragment ions formed from In_2S^+. The ion In_2^+ was said to be a fragment ion formed from In_2S^+, and S^+ was considered to be formed by fragmentation from InS^+, In_2S^+, and $In_2S_2^+$. In a study by Knudsen-effusion, mass spectrometry in the temperature range 950–1130 K, Miller and Searcy [8] found the major ions S_2^+ and In_2S^+ along with the minor ions In^+, In_2^+, and InS^+. The latter were proposed to be ionic fragments of In_2S^+. On this basis they proposed the vaporization reaction

$$In_2S_3(s) = In_2S(g) + S_2(g) \tag{2}$$

In a similar study of Ga_2S_3 by Uy et al. [7] the ions S^+, S_2^+, Ga^+, Ga_2^+, GaS^+ and Ga_2S^+ were observed in the temperature range 897–1020 K. The ions Ga^+, Ga_2^+, and GaS^+ were taken to be fragment ions from Ga_2S^+ and S^+ to be fragmented from S_2^+ ion. They proposed the vaporization reaction

$$Ga_2S_3(s) = Ga_2S(g) + S_2(g) \tag{3}$$

Nothing is known about the proposed gaseous product, InGaS(g). Infrared spectroscopy of the similar system In_2O–Ga_2O–InGaO isolated in a N_2-matrix was reported [9,10]. The molecular structure and the molecular parameters of InGaO(g) were estimated from the observed vibrational frequencies and by comparison with those of $Ga_2O(g)$ and $In_2O(g)$.

EXPERIMENTAL

Procedures

Samples were prepared by heating the elements in sealed, evacuated, Vycor tubes in a resistance furnace. The preparation procedure has been described [11]. The elements used were gallium and sulfur with stated purity greater than 99.99% from Johnson Matthey Chemicals and indium with stated purity of 99.99% from Indium Corporation of America. The instrument was a Nuclide 12-90-HT Knudsen-cell mass spectrometer.

Three sets of mass-spectrometric experiments designated E1, E2, and E3 were done, each with separately prepared samples. Two graphite effusion cells designated PC1 and PC2 were used, PC1 in E1 and E2, and PC2 in E3. Cell PC1 had a cylindrical orifice with length 0.603 cm, radius 0.038 cm, and transmission probability 0.132; the same orifice parameters, respectively, of PC2 were 0.687 cm, 0.037 cm, and 0.116.

Heating was by radiation from two resistively heated tungsten ribbons encircling the effusion cell, one near its top and one near its bottom. Radiaton shields above and on the sides were of tantalum and below were of molybdenum. Temperatures were measured in E1 and E2 by sighting a calibrated optical pyrometer through a prism and mirror into a black-body hole in the bottom of the effusion cell. In E3, temperatures were measured with a Pt, Pt–10%–Rh thermocouple inserted into a thermocouple well in the bottom of the effusion cell.

Ions were produced by bombardment with 75 V electrons. Ions were identified from their mass-to-charge ratios, isotopic distributions, and shutter effects. Each type of ion with shutter effect was scanned with the shutter open and with the shutter closed to obtain intensities. Special searches were made in regions where dimers, ternary species, and polymeric sulfur ions would appear.

In E1 and E2, samples which were initially 10 mol% Ga_2S_3 and 90 mol% In_2S_3 were used. In E3, a sample which was initially 90 mol% Ga_2S_3 and 10 mol% In_2S_3 was used.

Data treatment

Equilibrium constants of reaction (1) were calculated from the ion currents with

$$K_p = \frac{I^2_{\mathrm{InGaS}^+}}{\left(I_{\mathrm{In_2S}^+}\right)\left(I_{\mathrm{Ga_2S}^+}\right)} \tag{4}$$

standard enthalpy changes at 298 K, ΔH^0 (298 K) were calculated by the second-law and the third-law methods [12]. Gibbs-energy functions, $\phi^0(T)$, given by

$$\phi^0(T) = -\left[G^0(T) - H^0(298\ K)\right]/T \tag{5}$$

of Ga_2S(g) and In_2S(g), but not of InGaS(g), were available in the literature [2]. For InGaS(g), $\phi^0(T)$ was calculated from estimated molecular parameters with the rigid-rotor, harmonic-oscillator model [13]; for internal consistency the same procedures were used to calculate $\phi^0(T)$ for Ga_2S(g) and In_2S(g), and the literature values were not used.

In the absence of an experimentally established structure, the InGaS molecule was assumed to have a bent, C_s configuration. For Ga_2S(g) and

TABLE 1

Bases for theoretical thermodynamic calculations

Molecule	Symmetry	Apex angle (degrees)	Bond length (Å)	Vibrational frequency (cm^{-1})		
				$v1$	$v2$	$v3$
Ga_2O	C_{2v}	142	1.81	472	193	809
In_2O	C_{2v}	135	1.98	442	140	722
InGaO	C_s	138	1.81, 1.98	450	165	782
Ga_2S	C_{2v}	112	2.20	210	140	355
In_2S	C_{2v}	100	2.32	210	120	330
InGaS	C_s	106	2.20, 2.32	207	130	350

In_2S(g), force constants and bond angles were taken from the values estimated by Spoliti et al. [5], and the equations by Herschbach and Laurie [14] were used to obtain bond lengths from force constants. The vibrational frequencies reported by Shevel'kov et al. [3] were used. For InGaS, the In–S and Ga–S bond lengths were assumed to be the same as those in In_2S and Ga_2S molecules. The bond angles and vibrational frequencies were taken to have the same ratios as in the spectroscopically studied Ga_2O–In_2O–InGaO system; they were calculated with ratios involving Ga_2O and Ga_2S and with ratios involving In_2O and In_2S, and then the average of the two results was used.

Table 1 lists the parameters used to calculate values of Gibbs-energy functions as well as parameters from the literature [9,10] of the oxides. Column 1 gives the formula of the molecule, column 2 the symmetry, column 3 the apex angle, column 4 the bond length, and columns 4–6 the vibrational frequencies.

Table 2 gives the resulting values of Gibbs-energy functions as well as values from the literature [2] for Ga_2S(g) and In_2S(g); column 1 gives the temperature, columns 2 and 3 the values for Ga_2S(g) from this work and the literature [2], respectively, columns 4 and 5 the values for In_2S(g) from this

TABLE 2

Gibbs-energy functions of gaseous Ga_2S, In_2S, and InGaS

T (K)	$-\phi^0$ (298 K) (J mol^{-1} K^{-1})					$-\Delta\phi^0$ (298 K) (J mol^{-1} K^{-1}) Reaction (1)
	Ga_2S		In_2S		InGaS	
1000	336.27	316.14	348.99	343.5	348.68	12.10
1100	340.19	319.82	352.91	347.1	352.59	12.08
1200	343.89	323.30	356.61	350.6	356.30	12.10
1300	347.39	326.64	360.12	354.2	359.80	12.09
1400	350.71	329.78	363.45	357.7	363.13	12.10

work and the literature [2], respectively, column 6 the value for InGaS(g) from this work, and column 7 the change in Gibbs-energy function of reaction (1).

RESULTS

Ions found in the temperature range 1060–1350 K were S^+, Ga^+, Ga_2S^+, In^+, S_2^+, $InGaS^+$, Ga_2^+, In_2S^+, GaS^+, $InGa^+$, InS^+, In_2^+, and $InGaS_2^+$. Relative intensities, of course, varied with temperature and sample composition. The list above gives the ions in order of decreasing intensity at 1165 K at an intermediate time in E3. In E1 and E2, but not E3, the ions $In_2S_2^+$ and $Ga_2S_2^+$ were observed. Ions sought but not found were GaS_2^+, InS_2^+, $Ga_4S_2^+$, $In_4S_2^+$, $In_2Ga_2S_2^+$, and S_3^+ and higher sulfur polymers up to S_8^+. Ions used in the thermodynamic calculations were In_2S^+, Ga_2S^+, and $InGaS^+$.

Choice of initial sample composition in E1 and E2 was based on the desire to maximize the information available from the sample; since In_2S_3 is

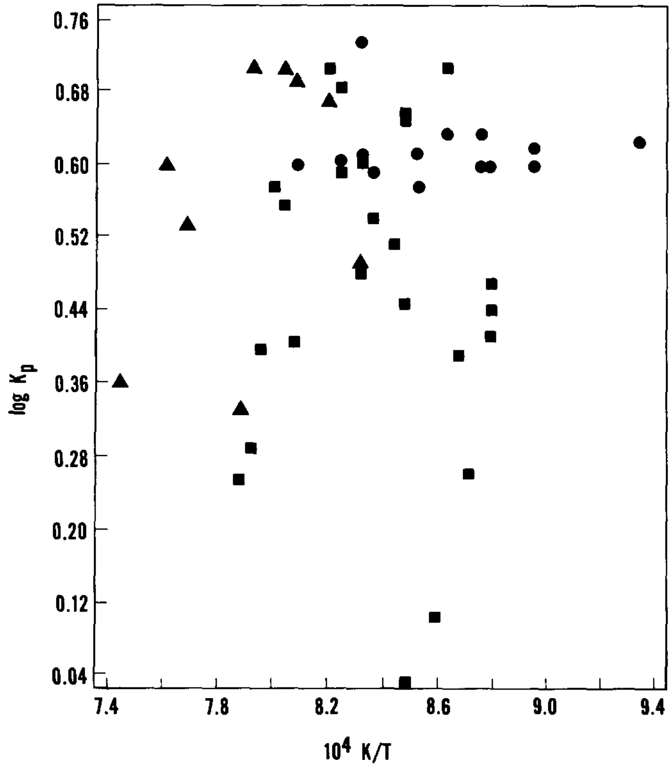

Fig. 1. Plot of logarithm of equilibrium constant of Reaction (1) as a function of inverse temperature. (▲) from E1, (■) from E2, (●) from E3.

more volatile than Ga_2S_3, relatively more In_2S_3 was used. However, formation of solid solution along with the lower vapor pressure of Ga_2S_3(s) caused ions from Ga_2S(g) to have very low intensities in E1 and E2, an effect which

TABLE 3

Ion intensities, equilibrium constants, and standard enthalpies of Reaction (1)

T (K)	$I_i \times 10^{12}$ (A)			K_p	ΔH^0(298 K) (kJ mol^{-1})
	Ga_2S^+	In_2S^+	$InGaS^+$		
Set E1					
1248	6.4	31000	990	4.94	−1.48
1310	24	61000	2200	3.31	2.80
1263	5.7	24000	820	4.91	−1.44
1322	16.2	44100	1660	3.86	1.14
1349	8110	34000	25000	2.27	7.12
1272	49.5	20800	1480	2.12	7.43
1222	14.2	12900	915	4.57	−0.66
1238	26.8	13100	1290	4.74	−1.04
1205	42.8	11300	1210	3.03	3.47
average	3rd-law: ΔH^0 (298 K) $= 1.9 \pm 1.2$				
	2nd-law: ΔH^0 (298 K) $= -38.7 \pm 31.4$				
Set E2					
1176	1.61	2640	137	4.41	−0.29
1202	1.85	5900	181	3.00	3.56
1176	1.54	5860	198	4.34	−0.13
1217	1.34	12800	284	4.70	−0.94
1157	3.34	1270	144	4.89	−1.28
1186	5.08	1930	559	3.19	2.91
1150	3.60	3920	184	2.40	5.53
1145	2.45	684	55	1.81	8.19
1162	26.4	3860	358	1.26	11.82
1131	0.64	3500	77.6	2.69	4.37
1176	3.34	6040	148	1.09	13.38
1204	1.59	7720	219	3.91	0.92
1135	1.93	3560	132	2.54	4.92
1212	1.27	7850	195	3.81	1.18
1222	1.26	7990	223	4.94	−1.45
1198	1.38	9000	202	3.29	2.63
1238	3.16	28200	471	2.49	5.58
1255	6.01	30200	816	3.67	1.61
1243	4.88	29500	712	3.52	2.03
1274	18.5	70100	1520	1.78	9.30
1176	2.81	22300	415	2.75	4.33
1258	21.4	84000	2100	2.45	5.84
1263	19.0	73900	1640	1.92	8.43
1135	0.92	3750	99.7	2.90	3.67
average	3rd-law: ΔH^0 (298 K) $= 4.0 \pm 0.8$				
	2nd-law: ΔH^0 (298 K) $= 8.9 \pm 23.5$				

TABLE 3 (continued)

T (K)	$I_i \times 10^{12}$ (A)			K_p	ΔH^0 (298 K) (kJ mol^{-1})
	Ga_2S^+	In_2S^+	$InGaS^+$		
Set E3					
1203	5990	5330	12900	5.21	−1.95
1113	3290	1880	5000	4.04	0.53
1134	7330	2770	9180	4.15	0.29
1157	10300	3070	1150	4.18	0.23
1200	18100	5860	20600	4.00	0.69
1214	24900	43600	20700	3.95	0.82
1175	31500	5380	24900	3.66	1.54
1064	2710	561	2510	4.14	0.29
1195	29900	5690	25500	3.82	1.14
1137	23000	3020	16400	3.87	0.95
1170	33500	4760	25300	4.01	0.64
1242	27500	2360	15800	3.85	1.10
1132	42400	2410	19900	3.88	0.92
1112	12600	503	4940	3.85	0.97
average	3rd-law: ΔH^0 (298 K) = 0.6 ± 0.2				
	2nd-law: ΔH^0 (298 K) = 0.9 ± 5.4				

introduced significant uncertainty into the results. Consequently, in E3, the composition of 90 mol% In_2S_3 was chosen; fewer data could be obtained from a given amount of sample but they were less scattered. In E3, the intensities of In_2S^+, Ga_2S^+, and $InGaS^+$ were comparable.

Ionic intensities, equilibrium constants, and third-law heats of reaction (1) are presented in Table 3. Column 1 gives the crucible temperature, columns 2–4 the ionic intensities, and columns 5 and 6 the equilibrium constant and the third-law ΔH^0 (298 K), respectively, of reaction (1). The average third-law value and the second-law value of ΔH^0 (298 K) are given at the bottom in each set of experiments.

Figure 1 is a plot of log K_p of reaction (1) vs $1/T$. Results from E1 are represented by triangles, those from E2 by squares, and those from E3 by circles.

DISCUSSION

The mass spectra of the vapor over the sulfide mixtures show that InGaS(g) is formed by metal exchange between In_2S(g) and Ga_2S(g) with a low enthalpy of reaction. An equilibrium constant of 4 for equation (1) would be predicted if the reaction enthalpy were zero. Indeed, the values of K_p were always near 4 ($\log 4 = 0.6$) and the third-law values of ΔH^0 (298 K) were near zero.

The scatter of the results from E1 and E2 was high. This scatter arose largely from the very low partial pressures of $Ga_2S(g)$ in these experiments, though there may have been a contribution to the scatter from the method of temperature measurement. The low partial pressures of $Ga_2S(g)$ were due to three factors: (1) the vapor pressure of $Ga_2S_3(s)$ is lower than that of $In_2S_3(s)$ by a factor of about 15 in the temperature range of these experiments; (2) solid solution formed and since $Ga_2S_3(s)$ was only 10 mol% of the sample its vapor pressure was consequently lower; (3) the effective volatility of $Ga_2S_3(s)$ was lowered further through mass action, since $S_2(g)$ was produced by vaporization of the more active $In_2S_3(s)$ as well as by vaporization of $Ga_2S_3(s)$.

The large scatter in the results in E1 and E2 make the second-law values of ΔH^0 (298 K) from those sets of experiments useless in deciding if the enthalpy of reaction (1) is zero, although in each case the uncertainty range contains zero. However, in E3, where the scatter is low, the second-law and third-law values are in good agreement and, together, show that the enthalpy of reaction (1) is negligible. We conclude that ΔH^0 (298 K) $= 0 \pm 1$ kJ mol^{-1}.

With the ΔH^0 (298 K) of reaction (1) and the ΔH^0 (298 K) of formation of $In_2S(g)$ and $Ga_2S(g)$ [2], we obtain the ΔH^0 (298 K) of formation of InGaS(g) to be 80 ± 18 kJ mol^{-1}. This ΔH^0 (298 K) of formation and values of ΔH^0 (298 K) of formation of the gaseous elements from Hultgren et al. [15] (In(g), 243 ± 1 kJ mol^{-1}; Ga(g), 272 ± 2 kJ mol^{-1}; and S(g), 275.2 ± 0.0 kJ mol^{-1}) yield the ΔH^0 (298 K) of atomization of InGaS(g), 710 ± 18 kJ mol^{-1}. This result compares well with the value 714 ± 1 kJ mol^{-1}, calculated with atomization enthalpies from Mills [2] and the ΔH^0 (298 K) of reaction (1). Mills gives no uncertainties in the values of these atomization enthalpies. A realistic uncertainty in the atomization enthalpy of InGaS(g) is the ± 18 kJ mol^{-1} given on the first value above.

The negligibly small enthalpy of reaction (1) tends to eliminate the possibility of metal–metal bonds and, for that matter, any strong interaction between the two metal–sulfur bonds within the gaseous molecules of the three sulfides involved. It is not likely that the bond enthalpies of putative Ga–Ga and In–In bonds in the sulfide molecules would add together to be within 2 kJ mol^{-1} of twice that of a putative Ga–In bond in InGaS. Moreover, asymmetric and symmetric linear structures of Ga_2S and In_2S molecules are ruled out by spectroscopic evidence. The conclusion is that each of the three dimetallic sulfide molecules are bent and have no metal–metal bond.

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