J. Chem. Eng. Data **2007,** *52,* 1343−1346

Torsion Measurement of Orpiment Vapor Pressure

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Total vapor pressures of orpiment, As_2S_3, were measured by the torsion effusion method, and their dependence was found to fit the following equation: $\log(p/\mathrm{kPa}) = (14.14 \pm 0.20) - (9160 \pm 200)\cdot(T/\mathrm{K})$ in the temperature range (501 to 583) K. The vapor molecular weight, evaluated at some temperatures in the covered range using the Knudsen equation on the vapor pressure measurements, was found to be equal to 250 ± 20 g·mol^{-1}, which confirmed that, as reported in the literature, the primary sublimation processes of orpiment are $As_2S_3(s) = As_2S_3(g)$ and $As_2S_3(s) = (1/2)As_4S_4(g) + (1/2)S_2(g)$. Increasing the temperature does not change the importance of both reactions so that the second-law enthalpies associated with both reactions are comparable and equal to $\Delta H°(542\ \mathrm{K}) = 175 \pm 4$ kJ·mol^{-1}.

Introduction

Despite the importance of As_2S_3 (orpiment) in geochemistry and in pyrometallurgical fields, no reliable information is available in the literature on the sublimation process and, in particular, the vapor pressure of this compound. Richnow[1] measured heat of vaporization of this compound above the liquid phase using a calorimeter furnace and obtained $\Delta_{\mathrm{vap}}H°(T) = 350$ kJ·mol^{-1}. Mills[2] reported that the first pressure data, obtained by vapor density measurements at very high temperatures (1100 to 1370 K), were reported by Britzke and Kapustinskii.[3] Some vapor pressure values for this compound were determined by Hsiao and Schlechten[4] employing the Langmuir method. They used weight loss rate measurements considering congruent sublimation, although in their work the authors expressed doubt that the compound decomposes to As_2S_2 and sulfur, both of which volatilize. By a modified statistical method, Isakova and Nesterov[5] measured, in a closed vessel, the vapor pressure above the molten compound obtaining values decidedly higher than those reported by Hsiao and Schlechten.[4] Also Ustyugov et al.[6] using a static method that employed a quartz membrane manometer determined a new set of vapor pressures, and the obtained values are also higher than those obtained by Hsiao and Schlechten.[4] The saturated vapor pressures below the melting point were measured by Gospodinov and Pashinkin[7] using the Knudsen method and considering congruent sublimation and employing as the vapor molecular weight that of $As_2S_3(g)$. There are several studies on the composition of the vapor in equilibrium with As_2S_3,[8−11] but the results and conclusions of these investigations are not in agreement. Lu and Donohue,[8] from electron diffraction analysis, suggested that the only molecule in the vapor phase is As_4S_6. Kuadzhe et al.[9] from the density of the overheated vapor, concluded that at temperatures below the melting point the vapor is composed of $As_2S_3(g)$ and $As_4S_6(g)$. Ban and Knox,[10] from a mass spectrometric study of the laser-induced vaporization of the compound, concluded that the predominant species in the vapor were S_2 and molecules of the type As_3S_x (with x from 1 to 4), where As_3S and As_3S_4 were found to be particularly abundant. Faure et al.,[11] from the relative intensities of the ion species obtained by a mass spectrometer, employing different electron-accelerating voltages, deduced that the primary vaporization reaction is

$$As_2S_3(s) = 2AsS(g) + (1/2)S_2(g) \qquad (1)$$

Unfortunately, the appearance potentials of the observed ions necessary for their reliable identification were not determined. From the total weight loss rates of the As_2S_3 samples measured by a microbalance, the authors[11] calculated opportunely, using the Knudsen equation, the partial pressures of the gaseous species. By second- and third-law treatment of the partial pressures so obtained, two final standard vaporization enthalpies, according to reaction 1, were determined; however, the values are in disagreement by about 67 kJ·mol^{-1}, and in particular the third-law enthalpies present an evident temperature trend. Pashinkin et al.[12] investigated by mass spectrometry the vapor above As_2S_3, and the results obtained differ significantly from those of Faure et al.[11] In particular, they reported that in addition to $As_2S_3(g)$ other gaseous species As_nS_n (with n from 1 to 4) and S_2 were present in the vapor so that, in addition to the congruent vaporization, other vaporization processes occur that are defined by the reaction

$$As_2S_3(s) = (2/n)As_nS_n(g) + (1/2)S_2(g) \qquad (2)$$

Unfortunately, no molecular abundances or partial pressures were reported in the work, but it was inferred that the $As_nS_n(g)$ species and $As_2S_3(g)$ were present in comparable quantities. In another mass spectrometric work, Pashinkin et al.[13] reported that $As_4S_4(g)$ and $S_2(g)$ were the only major products from the sublimation of As_2S_3 and evaluated the enthalpy associated with the reaction

$$As_2S_3(s) = (1/2)As_4S_4(g) + (1/2)S_2(g) \qquad (3)$$

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10.1021/je700056e CCC: $37.00

Lau et al.[14] using a high-temperature mass spectrometer investigated the vaporization of As_2S_3(s). From accurate measurements of the appearance potential and the relative intensity of the ions observed in the vapor mass spectrum, the authors concluded that As_2S_3(g), As_4S_4(g), and S_2(g) were the principal gaseous species, with a minor amount of As_4S_5(g), so that the primary sublimation processes of As_2S_3(s) are reaction 3 and the congruent reaction

$$As_2S_3(s) = As_2S_3(g) \tag{4}$$

along with a small contribution from

$$As_2S_3(s) = (1/2)As_4S_5(g) + (1/4)S_2(g) \tag{5}$$

The ion intensity data indicated that reaction 3 predominates over reaction 4. Unfortunately, neither total nor partial pressures were reported in their work.

The aim of the present work was to perform measurements of the total vapor pressure of this compound by the torsion effusion method, a method which does not require knowledge of the vapor molecular weight. At some temperatures, measuring the torsion angles and at the same time the mass loss rate of the As_2S_3 sample, the vapor molecular weight was determined by the Knudsen effusion method.

Experimental and Results

Ultrapure synthesized As_2S_3 samples supplied by Alfa Aesar (code 041980, 99.999 % nominal purity) and by Acros Organics (code 192510250, 99.99 % pure) and two mineral samples (orpiment) from the Mineralogy Museum of this University (sample A) and from a private source (sample B) were studied. X-ray diffraction analysis showed that both synthesized samples were amorphous, whereas the mineral ones were crystalline. To minimize the oxidation, the samples were loaded into the torsion cell in a drybox and rapidly introduced into the assembly which was then quickly evacuated. The torsion assembly, the same as that described in a previous work,[15] was suspended from an arm of a vacuum balance, (Chan 1000) to evaluate the mass loss rates of the sample during the torsion pressure measurements. A pyrophyllite torsion cell having the effusion holes of the lodgings with different diameters (0.5 and 1.8 mm) was used. The use of this cell permits pressure measurements to be carried out over a large temperature range. In fact, by filling both lodgings with the sample (the lodging with the larger effusion hole was filled with a minor amount), in the first step of the experiment, at low temperature, the torsion of the assembly was due to the effusion of vapor from both lodgings (cell A). Proceeding the measurement further, the vaporization of the sample in the lodging with the larger hole was completed (considering the minor amount and the larger effusion hole) so that the torsion angle of the assembly, now due only to the effusion of vapor from the lodging with the smaller hole, decreases. The cell now behaves as a new cell (cell A_1), and the pressures, measured at higher temperatures, were taken under experimental conditions similar to the first step (only the temperature changes). The two corresponding instrument constants, $K\alpha$, necessary to convert the torsion angles into pressure values were determined and frequently checked by measuring the vapor of very pure standards having well-known vapor pressures,[16] cadmium and zinc in this study. The constant values referred to the cell as A and A_1 were found to be well reproducible with an associated uncertainty of about 5 % of their average and did not depend on the standard used. The cells A and A_1 were also used as a Knudsen cell so that, during the calibration runs, in addition to the torsion angles, the mass loss rates of the standard elements used were also measured under isothermal conditions to determine the Knudsen constants. The average values so obtained from the two standards were found to be practically equal. These constants were used to evaluate the vapor molecular weight, measuring simultaneously the mass loss rates of the As_2S_3 samples and the corresponding torsion angles.

The second-law sublimation enthalpies of these standards were determined by the slopes of the linear equations obtained plotting log(α) vs $1/T$, where α is the torsion angle measured at the corresponding temperatures T. The obtained values, $\Delta H°$(535 K) = (111 ± 3) $kJ \cdot mol^{-1}$ and $\Delta H°$(623 K) = (126 ± 4) $kJ \cdot mol^{-1}$ for cadmium and zinc, respectively, are in decidedly good agreement with those selected by Hultgren et al.[16] (110 and 128 $kJ \cdot mol^{-1}$ for cadmium and zinc, respectively). This agreement was taken as a check of the validity of the procedure used to obtain the second-law enthalpy associated with the production of 1 mol of vapor phase from As_2S_3 and as a check of the reliability of the temperature measurements.

The total vapor pressures above both synthesized samples could not be measured. In particular, in the first step of their vaporization, the torsion angles increased with temperature, but

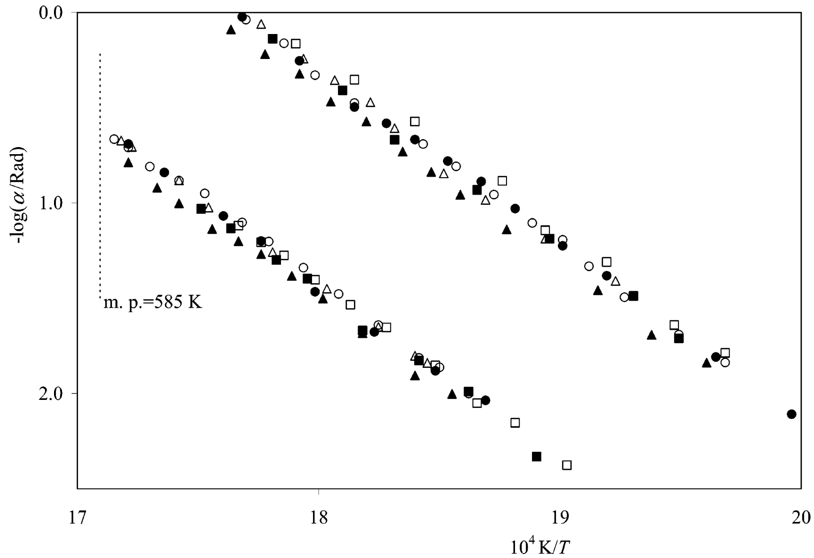

Figure 1. Torsion angles measured above solid orpiment: ●, run 1; ○, run 2; ■, run 3; □, run 4; ▲, run 5; △, run 6.

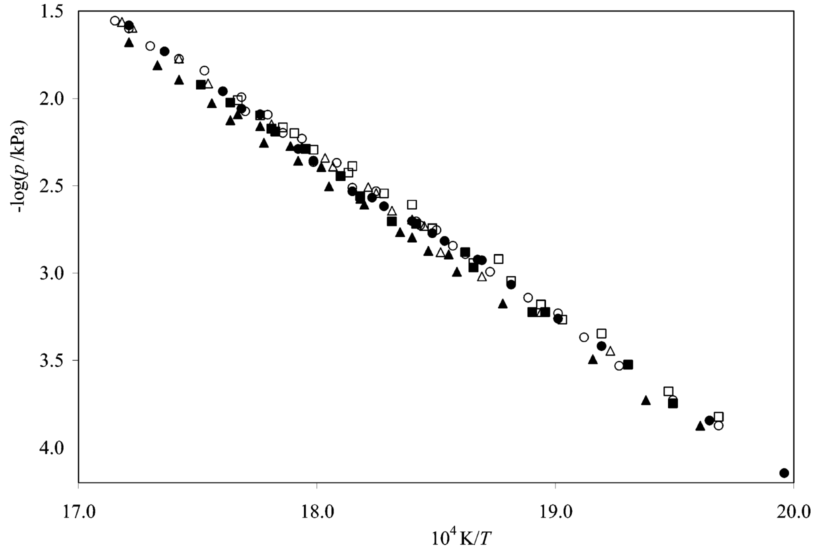

Figure 2. Total vapor pressures for orpiment: ●, run 1; ○, run 2; ■, run 3; □, run 4; ▲, run 5; Δ, run 6.

Table 1. Temperature Dependence of the Total Vapor Pressure and Second-Law Sublimation Enthalpy of Orpiment[a]

				ΔT	$\log(p/\text{kPa}) = A - B/(T/\text{K})$		$\Delta_{\text{sub}}H°(T)$
sample	run	cell	no. of points	K	A	B	kJ·mol^{-1}
A	1	A	13	501−566	14.02 ± 0.20	9096 ± 109	174.1 ± 2.1
		A_1	8	535−581	14.29 ± 0.36	9233 ± 201	176.7 ± 3.8
A	2	A	14	508−565	14.00 ± 0.19	9082 ± 103	173.8 ± 2.0
		A_1	13	537−583	14.06 ± 0.22	9089 ± 126	174.0 ± 2.4
B	3	A	12	510−567	13.84 ± 0.16	9052 ± 87	173.3 ± 1.7
		A_1	11	539−581	13.87 ± 0.29	9041 ± 164	173.1 ± 3.1
A	4	A	9	520−563	14.54 ± 0.46	9378 ± 250	179.5 ± 4.8
		A_1	9	542−582	14.32 ± 0.13	9243 ± 73	176.9 ± 1.4
B	5	A	7	513−562	14.01 ± 0.37	9096 ± 200	174.1 ± 3.8
		A_1	8	529−571	14.16 ± 0.45	9178 ± 248	175.7 ± 4.7
B	6	A	8	508−559	14.59 ± 0.42	9359 ± 225	179.1 ± 4.3
		A_1	10	526−566	14.32 ± 0.21	9239 ± 114	176.8 ± 2.2

[a] The associated errors are standard deviations.

the values were not reproducible. With further heating, in isothermal conditions, the angle increased or decreased at random due to the decomposition of the compounds probably because it was amorphous or not well synthesized. On the contrary, the vapor pressures above both mineral samples were found to be decidedly measurable and very reproducible. The torsion angles measured above solid orpiment in six runs are reported in Figure 1. The vapor pressures measured at temperatures higher than the melting point (585 K) were not taken into account. The total vapor pressures, calculated from the torsion angles measured with cells A and A_1 using the corresponding instrument constants, are reported in Figure 2. Their

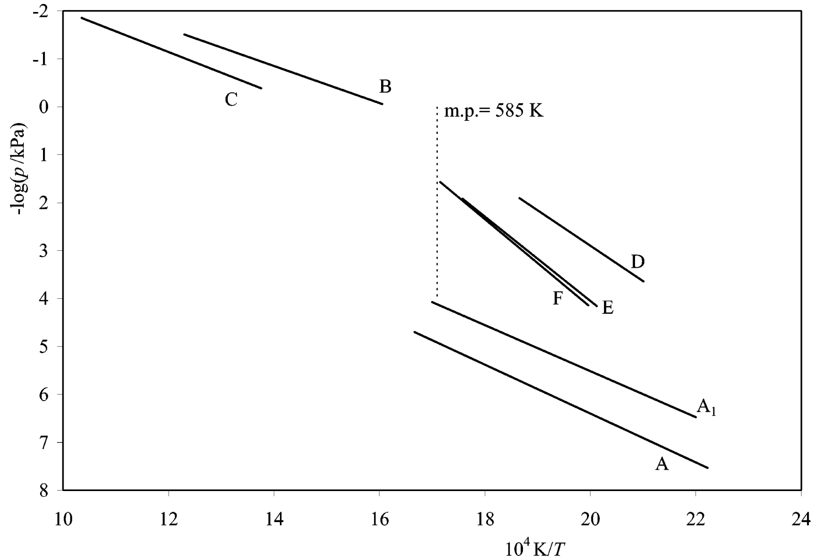

Figure 3. Comparison of the total vapor pressures of orpiment reported in the literature: A and A_1, Hsiao and Schlechten[4] (see footnote in Table 2); B, Isakova and Nesterov;[5] C, Ustyugov et al.;[6] D, Gospodinov and Pashinkin;[7] E, Faure et al.;[11] F, this work.

Table 2. Comparison of the Temperature Dependence of the Total Vapor Pressures of Orpiment

		ΔT	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
ref	method	K	A	B
4	Langmuir	433−603	3.80[a]	5098[a]
5	static	623−813	6.26[b]	3865[b]
6	static	727−966	6.31	4307
7	Knudsen	476−536	11.86 ± 0.56	7382 ± 911
11	Knudsen	497−569	13.53[c]	8793[c]
this work	torsion	501−583	14.14 ± 0.20	9160 ± 200

[a] As reported in Table 3 of the work. [b] Evaluated in this work using the experimental points reported in Figure 2 of the work. [c] Evaluated in this work using the experimental mass loss rates reported in the work (see text).

temperature dependence was expressed for each run by a log p vs $1/T$ equation obtained by treating the data using a least-squares method. The equations so obtained are reported in Table 1. In the same table, the corresponding second-law sublimation enthalpies are also reported. Weighting slopes and intercepts of these equations proportionally to the experimental points, the following expression is representative of the total vapor pressure of orpiment over the temperature range (501 to 583) K

$$\log(p/\mathrm{kPa}) = (14.14 \pm 0.20) - (9120 \pm 200)\cdot(T/\mathrm{K}) \quad (6)$$

where the associated errors were estimated. This equation is compared in Table 2 and Figure 3 with those found in the literature. In particular, a set of Knudsen vapor pressure values were calculated by us from the total weight loss rates reported by Faure et al.[11] and the vapor molecular weight taken equal to 250 g·mol^{-1}, and their linear fit is reported in Table 2. The vapor molecular weight was determined in some runs of the present work. At low temperatures using the cell as A and at higher temperatures as A_1, in addition to the torsion angles, α, the mass loss rates of the compound ($\Delta m/\Delta t$) were also measured at fixed temperatures, T, so that the vapor molecular weight was determined by using the well-known Knudsen equation [17] in the form $M = T[K(\Delta m/\Delta t)/\alpha]^2$ The constant K was evaluated during the vaporization of the pure standards employing the same experimental procedure knowing, of course, their vapor molecular weight. The molecular weight values obtained at different temperatures are comparable, and their average value, equal to 250 ± 20 g·mol^{-1}, is equal, within the error, to that of As_2S_3 (246 g·mol^{-1}). In accord with the findings of Lau et al.,[14] this result confirms that reactions 3 and 4 are the primary sublimation processes of As_2S_3 and that other processes involving As_nS_n gaseous species ($n = 1$ to 3) as reported by Faure et al.[11] and by Pashinkin et al.[12] are most likely minor.

It is interesting to note that our torsion vapor pressures, though the corresponding log p vs $1/T$ equation gives a slightly higher slope, are in good agreement with those calculated using the weight loss rates reported by Faure,[11] and this can be taken as a check of the vapor molecular weight value.

Considering that the temperature dependence of the intensities of all ions observed in the mass spectrometric work[10−14] above As_2S_3 is practically equal, we are persuaded to believe that the importance of both of the sublimation reactions 3 and 4, though with different weights, does not change with temperature. On this basis, the temperature dependence of the As_2S_3(g), As_4S_4(g), and S_2(g) partial pressures is comparable so that the second-law enthalpies of both the sublimation processes of As_2S_3, according to eqs 3 and 4 and calculated from the slope of eq 6, are comparable and equal to $\Delta H°(542\ \mathrm{K}) = 175 \pm 5\ \mathrm{kJ\cdot mol^{-1}}$ at the midpoint of the experimental temperature range.

Acknowledgment

Particular thanks to Dr. Burli Maurizio for the orpiment sample.

Literature Cited

(1) Richnow, M. Determination of heat consumption in the vaporization of metals or metal compounds. *Metall. und. Erz* **1941**, *38*, 32−35.

(2) Mills, K. C. *Thermodynamic data for inorganic sulphides, selenides and tellurides*; Butterworths: London, 1974.

(3) Britzke, E. V.; Kapustinskii, A. F.; Tschenzowa, L. G. Affinity of metals for sulfur. III. Heats of combustion and formation of the sulfides of arsenic and the compounds $As_2O_3{\cdot}As_2O_5$ and $As_2O_3{\cdot}SO_3$. *Z. Anorg. Allg. Chem.* **1933**, *213*, 58−64.

(4) Hsiao, C. M.; Schlechten, A. W. Volatility and stability of metallic sulfides. *J. Metals* **1952**, *4*, 65−69.

(5) Isakova, R. A.; Nesterov, V. N. Vapor pressure of arsenic and thallium sulfides. *Tr. Inst. Metall. Obogashch., Akad. Nauk Kaz. SSR* **1962**, *5*, 29−33.

(6) Ustyugov, G. P.; Kudryavtsev, A. A.; Kuadzhe, B. M. Saturated vapor pressure of arsenic sulfides. *Izv. Akad. Nauk SSSR, Neorg. Mat.* **1968**, *48*, 1338−1339.

(7) Gospodinov, G. G.; Pashinkin, A. S. Saturated vapor pressure of solid arsenous sulfide. *Izv. Akad. Nauk SSSR, Neorg. Mat.* **1974**, *1011*, 2074−2075.

(8) Lu, C. S.; Donohue, J. An electron-diffraction investigation of S_4N_4, As_4S_4 realgar, As_4S_6 orpiment and S. *J. Am. Chem. Soc*. **1944**, *66*, 818−827.

(9) Kuadzhe, B. M.; Ustyugov, G. P.; Kudryavtsev, A. A. Vapor pressure and thermal stability of arsenic chalcogenides. *Tr. Inst. Mosk. Khim. Tekhnol. Inst. im. D. I. Mendeleeva* **1968**, *58*, 29−32.

(10) Ban, V. S.; Knox, B.e E. Mass-spectrometric study of the laser-induced vaporization of compounds of arsenic and antimony with the elements of Group VIa. *J. Chem. Phys.* **1970**, *521*, 248−253.

(11) Faure, F. M.; Mitchell, M. J.; Bartlett, R. W. Vapor pressure study of arsenic trisulfide. *High Temp. Sci.* **1973**, *5*, 128−137.

(12) Pashinkin, A. S.; Molodyk, A. D.; Belousov, V. I.; Strel'chenko, S. S.; Fedorov, V. A. Composition of arsenicIII sulfide vapor. *Izv. Akad. Nauk. SSSR, Neorg. Mat.* **1974**, *10*, 1600−1602.

(13) Pashinkin, A. S.; Malkova, A. S.; Chervonnyi, A. D. Thermodynamics of sublimation of arsenicIII sulfide. *Izv. Akad. Nauk. SSSR, Neorg. Mat.* **1976**, *12*, 814−817.

(14) Lau, K. H.; Brittain, R. D.; Hildenbrand, D. L. Vaporization of arsenic trisulfide and the dissociation energy of arsenic monosulfide. *J. Phys. Chem*. **1982**, *86*, 4429−4432.

(15) Brunetti, B.; Piacente, V.; Scardala, P. Torsion Vapor Pressures and Sublimation Enthalpies of Arsenic Triselenide and Tritelluride. *J. Chem. Eng. Data* **2007**, *52*, 24−29.

(16) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metals Park, OH, 1973.

(17) Knudsen, M. Effusion and the Molecular Flow of Gases Through Openings. *Ann. Phys.* **1909**, *29*, 179.

Received for review February 1, 2007. Accepted May 18, 2007.

JE700056E