Torsion Vapor Pressures and Sublimation Enthalpies of Arsenic Triselenide and Tritelluride

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Total vapor pressures of As_2Se_3 and As_2Te_3 were measured by the torsion-effusion method, and their temperature dependences were found to fit the following equations: As_2Se_3(s), $\log(p/\text{kPa}) = (12.20 \pm 0.20)$ to $(9170 \pm 130)/(T/\text{K})$ and As_2Te_3(s), $\log(p/\text{kPa}) = (10.45 \pm 0.20)$ to $(8185 \pm 150)/(T/\text{K})$. Considering the complex mode of vaporizing of As_2Se_3, the mean second-law enthalpy and entropy values associated to the sublimation of 1 mol of the vapor mixture at the mid-point temperature, $\Delta H°(587\ \text{K}) = (175 \pm 3)\ \text{kJ·mol}^{-1}$ and $\Delta S°(587\ \text{K}) = (233 \pm 4)\ \text{J·K}^{-1}\text{·mol}^{-1}$, were calculated from the temperature dependence of its vapor pressure. As_2Te_3 dissociates upon sublimation yielding As_4(g) and Te(s). Both As_4(g) and Te_2(g) are present in the vapor over Te-saturated As_2Te_3, where the Te_2(g) partial pressures are considered equal to the vapor pressure of the pure element. On this basis, treating the pressure data by second- and third-law methods, the standard sublimation enthalpy associated to the sublimation reaction, $As_2Te_3(s) = 0.5\ As_4(g) + 3\ Te(s)$, $\Delta H°(298\ \text{K}) = 81 \pm 2\ \text{kJ·mol}^{-1}$, was determined.

Introduction

Apparently the first study on the vaporization of As_2Se_3 was carried out mass spectrometrically under non-equilibrium conditions by Knox and Ban,[1] who found that in addition to As_4(g) and Se(g) unusual molecules such as As_3Se and As_3Se_4 were present in the vapor. The same authors, in a subsequent mass spectrometric study[2] of the laser-induced vaporization of As_2Se_3 and As_2Te_3, found that for both compounds the most prominent species present in their vapor were the dimer chalcogen molecules, Se_2(g) and Te_2(g), and molecules of the type As_3X_n(g), where X = Se or Te and n = 1 to 4, and confirmed that among these As_3Se, As_3Se_4, and As_3Te were particularly abundant. Also Gorbov and Krestovnikov[3] used a mass spectrometer to study the vapor above As_2Se_3 and observed the ions As_4^+, As_2^+, $As_2Se_2^+$, and $As_2Se_3^+$, but they were not able to establish the composition of the neutral vapor. However, the authors reported a temperature dependence of the vapor pressures obtained by the Knudsen-effusion method assuming as the molecular weight that of As_2Se_3. At higher temperatures Ustyugov et al.[4] measured using the manometric method the total vapor pressures above the molten compound using a quartz Bourdon gauge. Some boiling points measured at elevated pressures by Baker[5] were expressed by a $p-T$ equation practically equal to that reported by Ustyugov et al.[4]

Besides the above-mentioned study by laser-induced vaporization,[2] the vaporization of arsenic telluride was studied by Ustyugov et al.[4] using a static method and measuring the saturated total vapor pressure at high temperatures. Gorbov and Krestovnikov[6] mass spectrometrically found that (i) in the range (473 to 600) K the spectra of the vapor above As_2Te_3 was constituted by As_2^+, As_4^+, and $As_2Te_2^+$; (ii) the $As_2Te_2^+$ amount is decidedly negligible at the highest temperatures; and (iii) the ratio $p(As_4)/p(As_2)$ is practically constant over the covered temperature range and is equal to 0.8. The authors, ignoring the mass spectrum, also made Knudsen-effusion measurements of the total vapor pressure considering as the vapor molecular weight that of As_2Te_3. From these values a log p versus $1/T$ equation was derived. The overall vaporization reaction and the sublimation pressures for As_2Te_3 have been determined by Northrop[7] using a mass spectrometer for qualitative identification of the vapor and a thermogravimetric apparatus. The author found that this compound dissociates to As_4(g) and solid tellurium, so that from thermogravimetric measurements the Knudsen-effusion As_4(g) pressures over Te-saturated As_2Te_3 were determined. In particular, Northrop[7] reports that (i) no $AsTe^+$ or other arsenic−tellurium species were observed in the mass spectrum; (ii) the ratios of the observed arsenic vapor species $As^+/As_2^+/As_3^+/As_4^+$ were constant, independent of temperature, and practically the same as those in the vapor over pure arsenic;[8] and (iii) the Te_2(g) pressures measured above pure Te and those above residual tellurium at the end of the experiments, when the pressures of the arsenic gaseous species were decidedly negligible, were found in agreement among themselves and with those selected for the pure element.[8] This implies that the solubility of arsenic in solid tellurium is negligible; therefore, this element originated from the decomposition of As_2Te_3 at nearly unity activity.

The aim of the present work was to perform extensive measurements of the total vapor pressure of As_2Se_3 and As_2Te_3 by a torsion-effusion apparatus that does not imply explicit knowledge of the molecular weight of the vapor. The data so obtained were compared with those reported in the literature.

Experimental Section

As_2Se_3 and As_2Te_3 used in the present work have a nominal purity of 99.99 % and 99 %, respectively, as certified by the supplier (Aldrich Chemical Co.). The samples were loaded into the effusion cells in a dray box and rapidly transferred into the torsion assembly, which was evacuated at low pressure. The torsion assembly is shown in Figure 1. The torsion angles were

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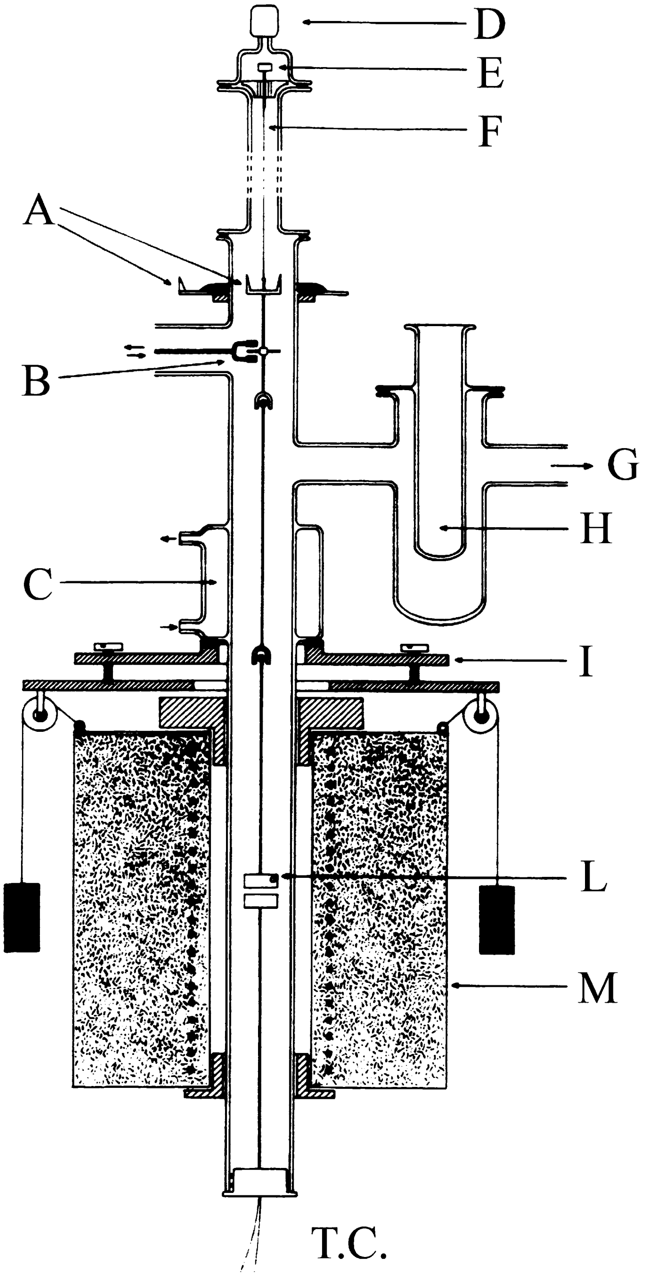

Figure 1. Torsion-effusion assembly: A, assembly for torsion-angle measurement; B, magnetic damping apparatus; C, water cooling; D, Penning gauge; E, height regulator of the torsion equipment; F, torsion tungsten wire; G, vacuum system; H, liquid nitrogen trap; I, support and alignment system of the torsion assembly; L, torsion cell; M, furnace; TC, thermocouple.

Table 1. Torsion Vapor Pressure of As_2Se_3

run 2		run 4		run 6	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
cell A		cell C		cell C	
574	3.73	553	4.43	554	4.43
586	3.39	558	4.26	563	4.13
593	3.21	564	4.08	569	3.92
596	3.11	573	3.83	571	3.89
601	3.01	580	3.62	576	3.75
607	2.89	586	3.42	580	3.62
612	2.79	590	3.35	588	3.45
616	2.64	597	3.19	594	3.29
623	2.45	605	2.95	600	3.11
		613	2.78	606	2.98
				610	2.84

run 7		run 10		run 11	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
cell C		cell D1		cell D1	
538	4.73	538	4.73	537	4.86
544	4.56	544	4.56	541	4.76
551	4.43	551	4.43	548	4.51
559	4.19	559	4.19	549	4.46
562	4.08	562	4.08	555	4.29
571	3.75	571	3.75	560	4.16
579	3.50	579	3.50	567	3.93
598	3.06	598	3.06	570	3.91
603	2.97	603	2.97	576	3.67
		cell D2		582	3.56
		573	3.73	589	3.36
		592	3.23	595	3.17
		603	2.97	600	3.08
		609	2.85	cell D2	
		614	2.72	576	3.64
		620	2.53	590	3.29
		628	2.30	610	2.80
		636	2.20	616	2.66
				622	2.53
				630	2.34
				639	2.15

opportunely measured by comparing the alignment of two needles (welded in opposition on the assembly) with an index fixed on a large goniometer. The sample was heated by a furnace having a large isothermal zone (~8 cm). For rapid cooling of the system, the furnace can be rapidly let down. The temperatures were measured by a calibrated chromel−alumel thermocouple inserted in a cell equal to the torsion cell and placed beneath it. Two conventional pyrophyllite cells (A and C), having the effusion holes of both the lodgings with equal diameters (0.8 and 1.5 mm, respectively) and a cell (D) having the two effusion holes with different diameters (0.5 and 1.8) mm, were used. The use of cell D permits, in a single experiment, the measurement of pressure over a large temperature range. In fact, by filling both lodgings of this cell with a compound (the lodging with the larger effusion hole with a small amount), the torsion of the assembly and the pressure measurement are due to the effusion of vapor from both lodgings (cell D1). During the vaporization, the sample in the lodging with the larger hole vaporizes completely (since the sample amount is small and because the effusion hole is larger) so that the torsion of the assembly, now due to the effusion of the vapor only from the lodging with the smaller hole, decreases. The cell now behaves as a new cell (cell D2), and the pressures measured at higher temperatures are taken at the same experimental condition as the first step of the experiment. For each cell and in particular for the cell D used as D1 and D2, the corresponding instrument constants necessary to convert the torsion data into pressure values were determined and checked by vaporizing in separate experiments carried out before and/or during the study of each compound, very pure standards having well-known vapor pressure. Lead and cadmium were used in this study. The calibration constants were found to be reproducible to within about 10 % of their average values.

As_2Se_3. In the first step of the vaporization of a fresh sample of this compound, the pressures were quite reproducible. However, going on the vaporization of the sample, when the residue in the cell was about 20 % of the original amount, the pressures were not reproducible, and their values showed a decreasing trend. This is evident in run 11 in which a large amount of sample was vaporized employing the cell D as D1. When the cell D was used as D2, the residue gave vapor pressure values that were not very reproducible and gave a log p versus $1/T$ line (see Table 2) having a slope lower than those obtained from other runs with fresh samples. At present, we do not have

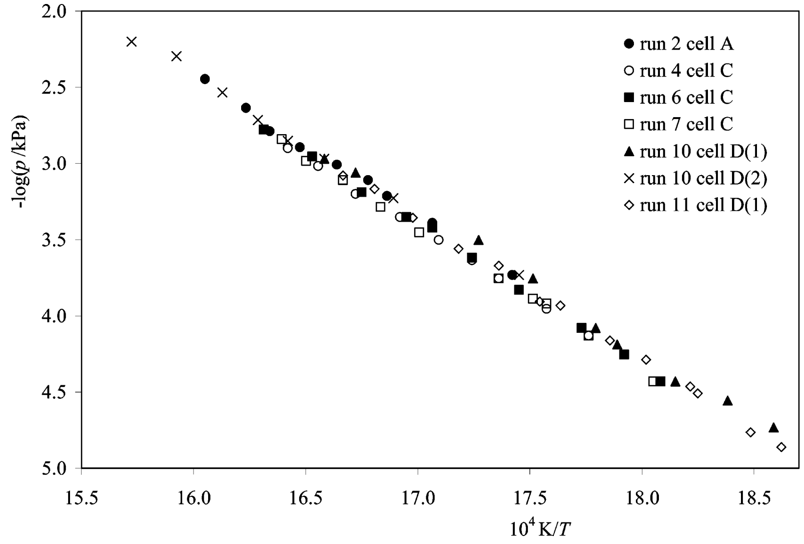

Figure 2. Experimental vapor pressure above As_2Se_3.

Table 2. Temperature Dependence of the Vapor Pressure above As_2Se_3 and As_2Te_3

				ΔT	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$[a]	
compd	cell	run	no. of points	K	A	B
As_2Se_3	A	2	9	574−623	12.12 ± 0.38	9094 ± 227
	C	4	10	558−609	11.99 ± 0.14	9068 ± 80
	C	6	10	553−613	12.45 ± 0.19	9327 ± 109
	C	7	11	554−610	12.36 ± 0.24	9282 ± 142
	D1	10	9	538−603	12.20 ± 0.44	9131 ± 247
	D2	10	8	573−636	12.07 ± 0.40	9062 ± 241
	D1	11	13	537−600	12.25 ± 0.19	9188 ± 107
	D2	11	7	576−639	11.49 ± 0.05	8712 ± 30[b]
As_2Te_3	A	2	6	589−628	10.50 ± 0.63	8252 ± 384
	C	3	9	551−615	10.57 ± 0.20	8248 ± 116
	C	6	8	581−633	10.46 ± 0.27	8235 ± 164
	A	7	9	535−626	10.09 ± 0.45	7974 ± 260
	D1	10	10	531−603	10.58 ± 0.22	8231 ± 124
	D2	10	7	585−638	10.37 ± 0.45	8152 ± 276
	C	12	6	554−618	10.53 ± 0.49	8251 ± 286

[a] The errors associated with slopes and intercepts are standard deviations. [b] This run was not taken into account in evaluating the final selected equation (see text).

Table 3. Total Vapor Pressure Measured above As_2Se_3 and As_2Te_3

			ΔT	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
compd	method (ref)	no. of points	K	A	B
As_2Se_3	Knudsen (3)		541−626	12.55	9092
	static (4)	19	926−1132	9.02	5682.7
	boiling point (5)	16	907−1191	9.028	5620
	this work	70	537−636	12.22 ± 0.23	9172 ± 133
As_2Te_3	static (4)	15	1052−1200	6.675	6074
	Knudsen (6)	28	521−631	9.203	7079 ± 130
	Knudsen (7)[a]	39	567−626	9.64	7590 ± 90
	this work	55	531−633	10.50 ± 0.25	8200 ± 150

[a] The equation is referred to As_4(g) partial pressure.

a clear explanation for this vaporization behavior, so we have taken into account only the pressure data measured in the first step of each vaporization run when the solid compound was at unit activity. On this basis only the total vapor pressures measured when about 50 wt % of the sample was vaporized were retained for thermodynamic analysis. They are reported in Table 1and plotted in Figure 2. The temperature dependence of the total pressure, linearized by least-squares treatment of the data, is expressed for each run by a log p versus $1/T$ equation and reported in Table 2. Weighting slopes and intercepts of these equations proportional to the number of experimental points (the data of the run 11 obtained by cell D2 were not taken into account), the following equation, representative of the total vapor pressure of As_2Se_3 in the temperature range (537 to 636) K, was selected:

$$\log(p/\mathrm{kPa}) = (12.20 \pm 0.20) - (9170 \pm 130)/(T/\mathrm{K}) \qquad (1)$$

where the associated errors were estimated. The slope of this equation substantially agrees with that of the only previous study above the solid compound[3] (see Table 3 and Figure 3), but the absolute pressure data are lower. The Knudsen-effusion data reported by Gorbov and Krestovnikov[3] were obtained, assuming that the vapor molecular weight was that of As_2Se_3. However, the actual composition of the vapor is more complex and changes with temperature. Thus, we believe that our results should be considered more reliable.

As_2Te_3. Previous studies on the sublimation of this compound showed that the process is not congruent and occurs either according to

$$As_2Te_3(s) \rightarrow 0.385As_2(g) + 0.308As_4(g) + 3Te(s) \qquad (2)$$

as reported by Gorbov and Krestovnikov[6] or to

$$As_2Te_3(s) = 0.5As_4(g) + 3Te(s) \qquad (3)$$

as reported by Northrop.[7] In both reactions the original sample shifts quickly to two condensed phases (As_2Te_3 and Te). Even though the composition of the condensed phase continuously changes during the vaporization due to the accumulation of the less volatile condensed phase (Te), at a given temperature the total vapor pressure must be constant as required by the phase rule. In the present work, the vapor pressures were found to be reproducible only in the first part of the experiment. Vaporization of the sample subsequently indicated that the pressure values were slightly lower than those measured in the first part. In particular, a vaporization experiment was carried out by heating a sample at a fixed temperature (630 K) and measuring the vapor pressure during the isothermal vaporization. It was observed that the pressure value was constant ($2.5 \cdot 10^{-3}$ kPa) as long as

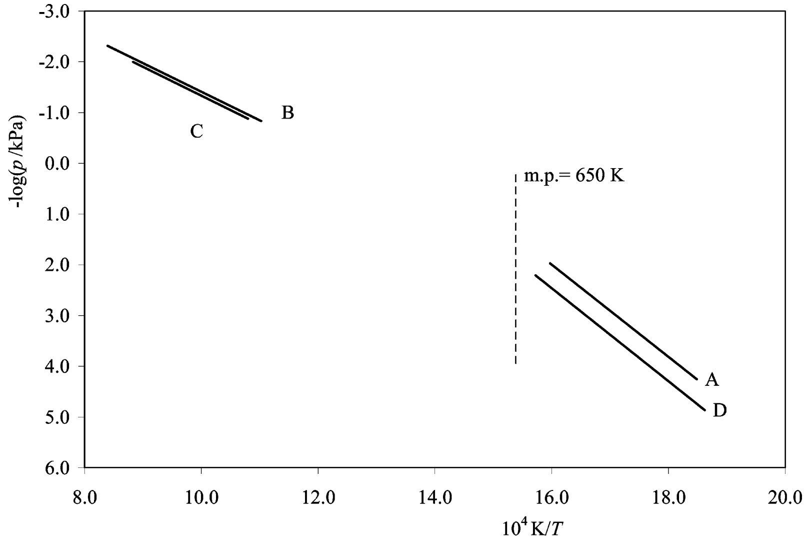

Figure 3. Comparison of total pressures for As_2Se_3: A, ref 3; B, ref 4; C, ref 5; D, this work.

Table 4. Torsion Vapor Pressure of As_2Te_3

run 2		run 3		run 6	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
cell A		cell C		cell C	
589	3.50	551	4.40	581	3.73
598	3.30	554	4.33	591	3.48
605	3.14	560	4.17	599	3.27
612	3.02	568	3.97	605	3.11
619	2.88	577	3.73	614	2.95
628	2.60	584	3.55	621	2.80
		595	3.25	627	2.69
		605	3.07	633	2.55
		615	2.87		

run 7		run 10		run 12	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
cell A		cell D1		cell C	
535	4.86	531	4.95	554	4.38
559	4.14	541	4.65	559	4.26
566	3.93	550	4.35	583	3.58
577	3.67	558	4.14	592	3.35
587	3.55	564	4.05	602	3.20
595	3.32	573	3.79	618	2.87
610	3.07	582	3.55		
613	2.94	588	3.40		
626	2.57	597	3.23		
		603	3.10		
		cell D2			
		585	3.59		
		601	3.17		
		609	2.99		
		616	2.89		
		624	2.65		
		633	2.52		
		638	2.43		

less than (60 to 70) % of the original sample was vaporized. Going on the vaporization of residue, the pressure decreased slowly. This behavior could be due to a small reduction of the activity of the residue solid arsenide when it is covered by a more compact tellurium shell produced as the vaporization proceeded. The pressures measured above As_2Te_3 in the first step are reported in Table 4 and plotted in Figure 4. For each run the temperature dependence of the pressure, obtained by linear least-squares treatment of the experimental data, is reported in Table 2. As usual, weighting slopes and intercepts of these equations proportional to the number of points, the following log p versus $1/T$ equation representative of the total vapor pressure above As_2Te_3 in the temperature range (531 to 633) K was selected:

$$\log(p/\mathrm{kPa}) = (10.45 \pm 0.20) - (8185 \pm 150)/(T/\mathrm{K}) \quad (4)$$

where the errors were estimated. Our pressure data are compared in Figure 5 and Table 3 with the Knudsen data reported in literature[6,7] and are found to be lower and present a slightly higher slope. It is interesting to note that if all the points of one experiment (run 3) were taken into account, considering also those measured at the end of the vaporization at high temperatures above a small amount of arsenide in the presence of large amount of tellurium (data not reported in Table 4), the obtained pressure−temperature equation give a slope (7609 K) lower than that selected (eq 4) and practically equal to that proposed by Northrop.[7] The disagreement between the absolute pressure values can be partially due to the value of the molecular weight value used to obtain the Knudsen data considering the vapor was constituted by only arsenic gaseous species.

Discussion

In previous mass spectrometric studies[1−3] on the vapor composition above As_2Se_3, it was observed that the vaporization of this compound is not congruent and complex. On this basis from the slope and intercept of eq 1 were calculated the second-law enthalpy and entropy values associated to the sublimation of 1 mol at the vapor mixture at the middle of the experimental temperature range, $\Delta H°(587\ \mathrm{K}) = (175 \pm 3)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta S°(587\ \mathrm{K}) = (233 \pm 4)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

Concerning the vaporization of As_2Te_3, this compound dissociates completely according to reaction 2 or reaction 3. Considering the temperature dependence of the equilibrium constant of the dissociation reaction: $As_4(g) = 2\ As_2(g)$ evaluated from the data selected in the IVTANTHERMO data base:[9]

$$\log(K_p/\mathrm{kPa}) = -51.25 + 0.106/(T/\mathrm{K}) - 6.1{\cdot}10^{-5}/(T/\mathrm{K})^2 \quad (5)$$

under the conditions of this and other studies[6,7] practically only the arsenic gaseous species As_4 would be present in the vapor as reported by Northrop.[7] The As_2^+ ion observed in the mass spectrum given by Gorbov and Krestovnikov[6] is not a parent ion, and the complex analysis made by the authors on the

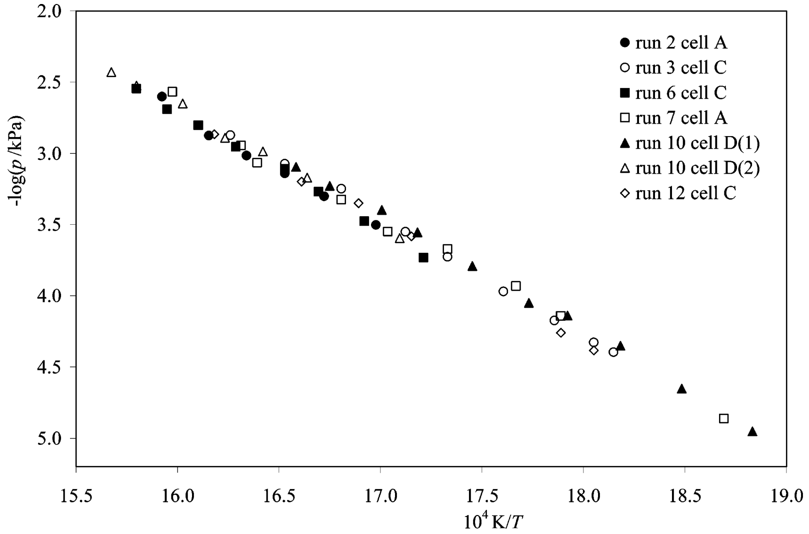

Figure 4. Experimental vapor pressure above As_2Te_3.

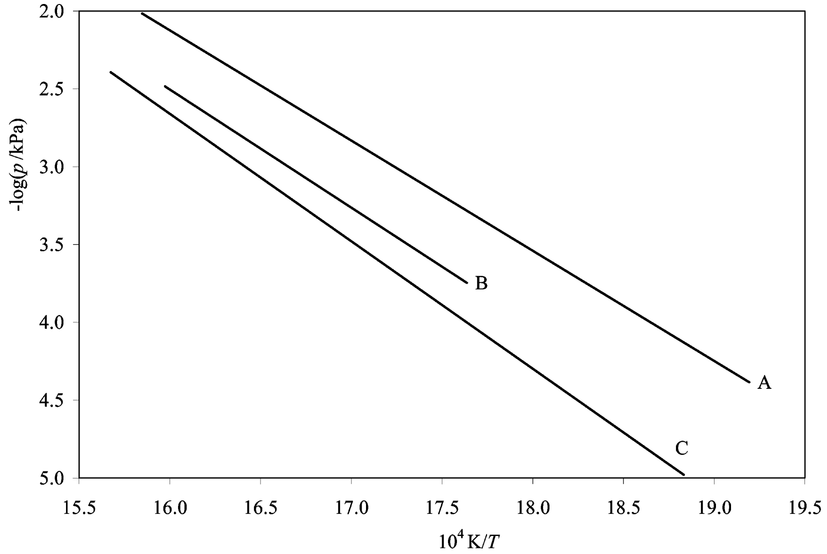

Figure 5. Comparison of total pressures for As_2Te_3: A, ref 6; B, ref 7; C, this work.

sublimation of this compound involving $As_2(g)$ is not correct. On this basis, in addition to $As_4(g)$, $Te_2(g)$ will also be present in the vapor in equilibrium with tellurium resulting from the non congruency of the sublimation (eq 3) and practically considered always at unit activity. The $Te_2(g)$ partial pressures were then considered equal to vapor pressure of pure element. Some sublimation runs with pure tellurium were carried out employing cell A in order to measure the vapor pressure of this element. The values obtained and their temperature dependence are given by

$$\log(p/\text{kPa}) = (10.30 \pm 0.15) - (8580 \pm 100)/(T/\text{K}) \quad (6)$$

and are in very good agreement with those selected by Hultgren et al.[8] This agreement was taken as a check of the value used for the instrument constant. Equations 6 and 4 were used to evaluate the $As_4(g)$ partial pressure represented by

$$\log(p/\text{kPa}) = (10.25 \pm 10.20) - (8125 \pm 150)/(T/\text{K}) \quad (7)$$

The second law sublimation enthalpy according to

$$2As_2Te_3(s) \rightarrow As_4(g) + 6Te(s) \quad (8)$$

was derived at the mid-point temperature from the slope of the eq 7, $\Delta H°(580\ \text{K}) = 155 \pm 3\ \text{kJ·mol}^{-1}$. This enthalpy value was reported at 298 K, by the enthalpy increments [$H°(580\ \text{K}) - H°(298\ \text{K})$] selected by Hultgren[8] for Te(s) ($8.2\ \text{kJ·mol}^{-1}$), by IVTANTHERMO data base[9] for $As_4(g)$ ($22.6\ \text{kJ·mol}^{-1}$), and by the calorimetric value measured by Blachnik and Schneider[10] for $As_2Te_3(s)$ ($40.3\ \text{kJ·mol}^{-1}$). The obtained value is $\Delta H°(298\ \text{K}) = 164 \pm 3\ \text{kJ·mol}^{-1}$. From two $As_4(g)$ partial pressures values calculated at the two extreme experimental temperatures, (530 and 630) K, from eq 7, the third-law standard sublimation enthalpies of the reaction 8 at these temperatures were also calculated. The Gibbs energy functions, $[G°(T) - H°(298\ \text{K})]/(T/\text{K})$, necessary in this calculation were taken from the same source as the enthalpy increments. In particular the Gibbs energy functions for $As_2Te_3(s)$ were evaluated using the standard entropy, $S°(298\ \text{K}) = 226\ \text{kJ·mol}^{-1}$, selected by Mills[11] and the calorimetric enthalpy increments reported by Blachmik and Shneider.[10] Considering the uncertainties in the As_4 pressure values and in the auxiliary thermodynamic data, the third-law standard sublimation enthalpy values, calculated at (530 and 630) K equal to (160.2 and 161.4) kJ·mol^{-1}, respectively, present a decidedly negligible temperature trend and the average value is in agreement with the value derived from the second law. On this basis, we propose as the standard enthalpy change associated to the sublimation of As_2Te_3(s) according to reaction 8 the value of 162 kJ·mol^{-1} with an estimated error limit of ±4 kJ·mol^{-1}.

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