Equilibrium Vapor Concentrations in the Antimony + Iodine System. Molar Absorptivities of Antimony(III) Iodide Vapor

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Absorbances of vapors generated by various SbI_3 + Sb and SbI_3 + I_2 mixtures have been measured over the wavelength interval 210−510 nm. Concentrations calculated from SbI_3(l) vapor pressures published by various authors are compared and used to derive molar absorptivities of SbI_3(g). Values, at 10 nm intervals, have been assigned for the temperature range 390−850 K. Except for small irregularities at higher temperatures for SbI_3 + Sb mixtures (SbI?) and at the lowest temperatures for SbI_3 + I_2 mixtures (SbI_5?) absorbance data can be satisfactorily explained assuming SbI_3 to be the only compound of antimony in the vapor phase.

On heating a sample of SbI_3(g) at temperatures in the range 800−1100 K, Bakhyshov et al. (1972) and Kuniya et al. (1976), in independent studies, observed an increase in pressure over that expected from the perfect gas law. Bakhyshov et al. attributed the increase to, and derived equilibrium constants for, reaction 1. Kuniya et al. assumed the dissociation corresponded to, and derived equilibrium constants for, reaction 2. The Bakhyshov, et al. results, taken together with thermodynamic constants given by Knacke et al. (1991) for reaction 3, lead to the prediction that, at temperatures above 500 K and with a total concentration of antimony iodides in the vapor around 10 μmol·L^{-1}, SbI(g) should be the dominant species in equilibrium vapors generated by reaction 4. The Kuniya et al. results give equilibrium constants for reaction 2 which are more than an order of magnitude larger than those derived using Knacke et al. data.

$$SbI_3(g) \rightleftarrows SbI(g) + I_2(g) \qquad (1)$$

$$SbI_3(g) \rightleftarrows (1/4)Sb_4(g) + (3/2)I_2(g) \qquad (2)$$

$$SbI_3(g) \rightleftarrows Sb(s) + (3/2)I_2(g) \qquad (3)$$

$$SbI_3(g) + 2Sb(s) \rightleftarrows 3SbI(g) \qquad (4)$$

In the present paper a spectrophotometric study of equilibrium vapors formed by SbI_3 + Sb and SbI_3 + I_2 mixtures is reported. Absorbances have been examined for evidence for the presence of antimony iodide molecules other than SbI_3(g). Mixtures of antimony(III) iodide and iodine are of interest relative to the questioned existence of SbI_5. Melting and boiling points for SbI_5 have been listed in CRC Handbooks (e.g., 1955−56, 1990−91) for many years. The reported melting point is based on very early work and has been questioned as possibly that of a eutectic mixture of iodine and SbI_3; e.g., see Gmelins Handbook (1949). The *Encyclopedia of Inorganic Chemistry* (King, Ed.; 1994) states that SbI_5 is unknown. The boiling point of SbI_5 given in CRC Handbooks is virtually the same as that of SbI_3. In contrast, the boiling point of $SbCl_3$ is appreciably higher than that of $SbCl_5$. Lefkowitz et al. (1969) report the preparation of solid SbI_5, with identification based on chemical analysis and crystal structure; see also Macintyre (1992). On heating their crystals Lefkowitz et al. did not observe melting but report a change in color and the onset of decomposition, producing a red vapor, around 513 K. Qualitative tests were said to show that the vapor was not iodine.

Experimental Section

Vapor phase absorbances in the range 210−700 nm were measured with a Cary 14H spectrophotometer. Samples were isolated in cylindrical quartz cells, 2 cm diameter, with path length 1 or 10 cm. Samples were introduced through a side arm, attached at the center of the cell and perpendicular to the cell axis.

The mixtures examined were prepared from antimony metal and iodine (Baker-Adamson Reagent I_2, 99.8%). Two sources of antimony were used, initially a powder, from a lecture demonstration bottle which did not provide the supplier's analysis, and, for the final two samples, Aldrich Sb granules, 10 mesh, 99.9999%. Analysis of a sample of the powder, using an ICP atomic emission spectrometer, model 955, Plasmo Atomcorp, indicated a purity level of ~99.95%; the principal impurities found were As, 0.1%; Fe, 0.17%; Pb, 0.07%; and P, 0.06%. SbI_3, prepared from the two sources, gave absorbance results which were indistinguishable.

Samples of metal and of iodine crystals were added to a Pyrex reaction tube, which was attached to a vacuum system and, by graded seal, to the side arm of a quartz absorbance cell. The reaction tube opening was closed by flame seal-off and the apparatus evacuated for several minutes before isolation of the assembly from the pumping system by a second seal-off. Reaction between antimony and iodine occurred rapidly when the metal was flamed gently. Some of the product was vaporized into the absorbance cell and condensed and the reaction tube removed by flame seal-off. The various mixtures studied are listed in Table 1.

The isolated cell and the attached section of the side arm were heated by separate clam-shell-type furnaces. The furnaces were in close contact, in a T arrangement. Temperatures of the cell and side arm were controlled separately, ±1 K, and were measured with chromel−alumel thermocouples. The thermocouples were calibrated at the boiling point of water and the melting point of tin. When a condensed phase was present, condensation on the windows was prevented by keeping the vapor temperature, T_g, in the cell body above that of the condensed phase, T_c, in the side arm tip. Temperatures are given in Table 1.

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Table 1. Temperatures, Derived Concentrations, and Spectral Fit

T_c/K	T_g/K	$c(SbI_3,g)$/ (μmol·L^{-1})	$c(I_2,g)$/ (mmol·L^{-1})	SF		T_c/K	T_g/K	$c(SbI_3,g)$/ (μmol·L^{-1})	$c(I_2,g)$/ (mmol·L^{-1})	SF
					SN 1. 1 cm cell $SbI_3(l) + Sb(s)$					
471	522	132.6	*a*	2		460	469	80.6	*a*	0
458	467	78.9		1		451	465	69.0		0
484	510	228.4		0		447	466	49.4		0
489	509	279.0		0		484	495	199.0		0
485	494	204.1		1		463	479	95.7		0
476	487	166.5		2		450	459	51.3		0
469	479	119.5		1		487	497	212.1		0
					SN 2. 1 cm cell $SbI_3(s) + Sb(s)$					
439	457	35.5	*a*	0						
					$SbI_3(l) + Sb(s)$					
448	466	56.5		0						
					$SbI_3(g) + Sb(s)$					
843	840	79.1		0		718	716	79.1	*a*	0
800	782	79.1		0		474	484	79.1		0
652	782	79.1		0						
					SN 3. 1 cm cell $SbI_3(l) + I_2(g)$					
456	495	76.6	~0.026	2		471	487	145.2	~0.026	1
445	470	46.4	~0.026	0		475	487	167.9	~0.026	0
					SN 4. 1 cm cell $SbI_3(s) + I_2(g)$					
434	456	27.1	~0.035	0		441	457	40.4	~0.035	0
					$SbI_3(g) + I_2(g)$					
581	576	40.7	~0.035	0		828	843	40.7	~0.035	0
757	765	40.7	~0.035	0		678	672	40.7	~0.035	0
					SN 5. 10 cm cell $SbI_3(s) + Sb(s)$					
407	429	5.26	*a*	2		417	448	9.14	*a*	1
					$SbI_3(g) + Sb(s)$					
479	471	10.6		1		676	715	13.8		2
795	811	17.3		4		620	626	13.4		2
769	766	17.2		4		522	519	12.8		1
					SN 6. 1 cm cell $SbI_3(s) + I_2(g)$					
418	442	10.4	3.46	2		411	423	8.48	2.85	1
434	448	27.0	5.22	1		387	393	1.73	1.45	0
					$SbI_3(l) + I_2(g)$					
451	458	54.8	7.58	0		486	493	204.7	12.9	0
465	478	90.4	9.37	2		481	486	167.1	12.0	1
					SN 7. 1 cm cell $SbI_3(l) + I_2(g)$					
484	497	240.2	1.12	0		490	502	291.7	1.16	0
453	464	69.5	0.728	0		444	453	46.5	0.669	0
464	473	110.8	0.864	0		484	491	235.1	1.15	0
473	480	154.6	0.960	0						
					SN 7. 1 cm cell $SbI_3(s) + I_2(g)$					
427	440	20.1	1.66	0		435	443	30.2	0.553	0
439	437	37.4	0.582	0		427	438	20.1	0.873	0
440	446	37.3	0.578	0		420	428	14.1	2.01	0
395	403	2.60	0.870	0		408	414	5.83	1.99	0
418	425	11.4	0.921	0		398	405	3.06	1.88	0
433	442	27.6	1.33	0		398	405	4.60	1.88	0
440	447	38.4	0.640	0		423	430	15.2	1.93	0

[a] $c(I_2)$ concentrations for SN 1, 2, and 5 were too small to give measurable absorbances. Values (not listed) were calculated from $c(SbI_3,g)$ and equilibrium constants (Knacke, 1991) for reaction 3.

To prepare SbI_3 + Sb(s) mixtures, SN 1, 2, and 5 (SN, an abbreviation for sample number), a small amount of metal was added to the cell at the time the elements were added to the reaction tube. To prepare $SbI_3 + I_2$ mixtures, SN 3 and 6, the desired amount of iodine was vaporized into the cell, after sublimation of the SbI_3 but before the final seal-off.

After spectra were recorded for SN 3, for which a condensed phase of SbI_3 was present for all scans, the entire sample was condensed in the tip of the side arm. Then a small amount of the SbI_3, along with the iodine, was vaporized and condensed back into the cell. The cell and side arm tip were then immersed in separate liquid N_2 baths, and a portion of the tip, containing the remaining SbI_3, was sealed off. The mixture in the cell was then identified as SN 4.

SN 6 contained a relatively large amount of SbI_3, around 0.1 mmol in a cell volume of ~4 mL, with the iodine vapor concentration, $c(I_2,g)$, much higher than that in SN 3 or 4; see Table 1. After spectra were recorded, part of the iodine was condensed in the tip of the side arm. The cell and the sidearm tip were again immersed in separate liquid N_2 baths, and the side arm tip, with most of the iodine, was sealed off. The mixture remaining in the cell was then identified as SN 7.

Results and Discussion

Antimony iodide vapors did not absorb appreciably at wavelengths, λ, greater than 450 nm. The concentration of iodine in the $SbI_3 + I_2$ mixtures was calculated from iodine absorbances in the range $450 < \lambda < 520$ nm, using Beer's law and molar absorptivities reported by Sulzer and Wieland (1952). Then, for the wavelength range $340 < \lambda < 460$, the iodine absorbances were calculated from $c(I_2,g)$ and Sulzer and Wieland molar absorptivities. At wavelengths below 350 nm, molar absorptivities reported by Passchier (1968) were used. Iodine absorbances were subtracted from the total absorbances to obtain the antimony iodide contributions. In samples with Sb(s) present, iodine vapor absorbances were too small to measure. For these samples values of $c(I_{2,g})$ were calculated from equilibrium constants (Knacke et al., 1991) for reaction 3 and the antimony(III) iodide concentration, $c(SbI_3,g)$.

Molar absorptivities for $SbI_3(g)$, $\epsilon_{\lambda,T}(SbI_3,g) = A_{\lambda,T}(SbI_3,g)/c(SbI_3,g)$, where $A_{\lambda,T}$ represents the $SbI_3(g)$ absorbance divided by the cell path length, were initially assigned from the SN 3 absorbances. As discussed below, $c(SbI_3,g)$ values for SN 3 were derived from vapor pressure data. The iodine absorbance in SN 3 was negligible except for very small values, ~0.01, near the iodine absorbance maximum, 490−510 nm. These values were used to estimate $c(I_2,g)$; see Table 1. A thermodynamic argument, based on data compiled by Knacke et al. (1991) and the Bakhyshov et al. (1972) results, indicates that at the iodine concentration for SN 3, and with $c(SbI_3,g)$ fixed by equilibrium with SbI_3(liq), Sb(s) will not be present and $c(SbI,g)$ and $c(Sb_4,g)$ will be very small. And for the small value of $c(I_2,g)$, the concentration of $SbI_5(g)$, as may be generated by reaction 5, was also assumed negligible. Hence, for SN 3, the

$$SbI_3(g) + I_2(g) \rightleftarrows SbI_5(g) \qquad (5)$$

observed absorbances in the range $200 < \lambda < 460$ nm were attributed to $SbI_3(g)$. The corresponding spectrum is shown in Figure 1.

The vapor pressure of $SbI_3(l)$ has been measured by a number of authors; work prior to 1979 has been summarized by Ferro et al. (1979). Some of the results are shown in Figure 2. The diaphram gauge values of Bruner and Corbett (1961), range 533−678 K, by Sime (1963), range 510−629 K, and by Ustinov and Petrov (1970), range 456−674 K, are in close agreement. Bruner and Corbett (hereafter abbreviated BC) give the vapor pressure equation

$$\log P_{\mathrm{mm}} = -2504.5(T/\mathrm{K})^{-1} - 2.800 \times 10^{5}(T/\mathrm{K})^{-2} + 7.2120$$

If this equation is extrapolated, see solid line, Figure 2, to the temperature range of the Ferro et al. transpiration studies, 450−493 K, which is also the range of the SN 3 absorbance measurements, the projected pressures are larger than values given by the equation derived by Ferro et al., dotted line in Figure 2, by a nearly constant factor of 1.6. The vapor pressure equation given by Knacke et al. (1991), dashed line in Figure 2, includes a temperature dependence so as to fit the Ferro et al. result near the melting point and intersect the BC line at higher temperatures. When compared with the BC equation, vapor pressures reported by Bakhyshov et al. (1972) are unusually high at lower temperatures. Those of other researchers lie between the BC and the Ferro et al. results.

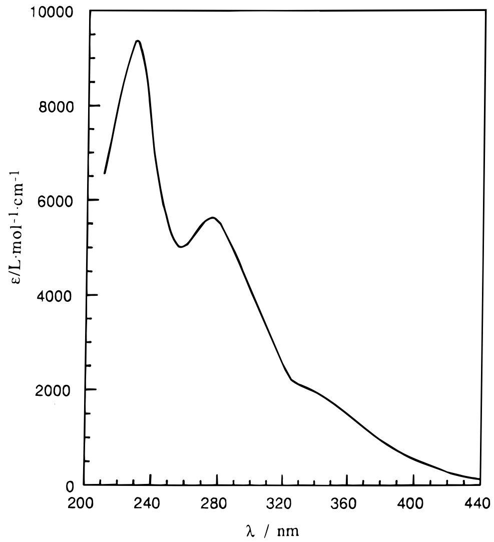

Figure 1. $SbI_3(g)$ molar absorptivities at 500 K, based on concentrations derived from Bruner and Corbett (1961) vapor pressure data.

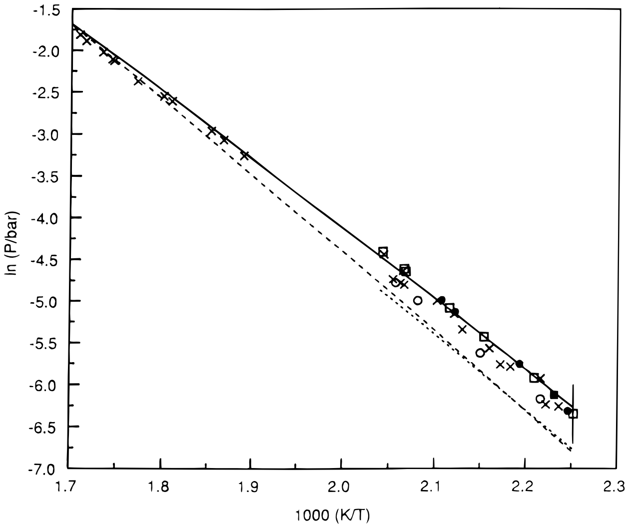

Figure 2. Derived vapor pressures. SbI_3 in equilibrium with condensed phases above the melting point (vertical line) of pure SbI_3. (—) Bruner and Corbett (1961) equation for pure SbI_3(liq). (···) Ferro et al. (1979) equation, transpiration data. (- - -) Knacke et al. (1991) equation. (×) above 525 K, Bruner and Corbett, Sb + SbI_3 solutions. (×) below 500 K, SN 1, this work. Samples: (■) SN 2, (●) Sn 3, (○) SN 6, (□) SN 7, this work.

The SN 3 absorbance data can be correlated equally well using concentrations derived from the Ferro et al. (1979) transpiration vapor pressures or, alternatively, with those given by the BC equation. To give the observed absorbances, molar absorptivities used with the Ferro et al. concentrations must be larger, by a factor of 1.6, than those used for concentrations based on the BC equation. Because, as discussed in some detail below, absorbance data at temperatures below the melting point give vapor pressures in somewhat better agreement with those projected from the BC equation than a corresponding treatment using Ferro et al. values, the molar absorptivities listed in

Table 2. Empirical Equations Derived for $\epsilon_{\lambda,T}(SbI_3,g)$ for the Temperature Range 390−850 K ($\epsilon/(L \cdot mol^{-1} \cdot cm^{-1}) = a + bT + c/T^2$)

λ/ nm	a/ ($L \cdot mol^{-1} \cdot cm^{-1}$)	b/ ($L \cdot mol^{-1} \cdot cm^{-1} \cdot K^{-1}$)	c/ ($L \cdot mol^{-1} \cdot cm^{-1} \cdot K^2$)	ϵ(500 K)
210	788	11.52		6549
220	6862	3.019		8372
230	7806	0.4728	0.3270×10^9	9350
240	6049	1.802		6950
250	3408	3.836		5326
260	3422	3.289		5067
270	5084	0.9187		5544
280	5890	−0.7854		5497
290	5328	−1.026		4815
300	4279	−0.5068		4025
310	3172	0.1507		3248
320	2118	0.7392		2487
330	1872	0.4603		2103
340	1932	0.0489		1957
350	1712	0.0617		1742
360	1390	0.1994		1490
370	979	0.4573		1208
380	694	0.5022		945
390	446	0.5725		732
400	265	0.5603		545
410	209	0.4127		415
420	−34	0.6144		273
430	−12	0.3850		181
440	−53	0.3523		123
450	67			67

Table 2 are those derived using saturated vapor concentrations given by the BC equation.

For the other mixtures values of $c(SbI_3,g)$ were calculated from the relationship $c(SbI_3,g) = (A_{\lambda,T} - c(I_2,g)\epsilon_{\lambda,T}(I_2,g))/\epsilon_{\lambda,T}(SbI_3,g)$; see Table 1. With the exception of two high-temperature scans for SN 5, and slightly higher than expected absorbances at the lowest temperatures for SN 6 and SN 7, discussed below, no irregularities were observed which would suggest the presence of appreciable concentrations of other molecules. The temperatures cover a wide range, 390−850 K; the fit of observed and calculated spectra was improved by expression $\epsilon_{\lambda,T}(SbI_3,g)$ at various wavelengths as empirical functions of temperature; see Table 2. At some wavelengths the initial SN 3 assignments were adjusted slightly to improve the overall fit for all samples. The derived spectrum, Figure 1, shows maxima around 275 and 229 nm, with a shallow minimum around 257 nm, and a shoulder around 340 nm. These values agree well with those published by Kuniya et al. (1976), 228, 276, and 340 nm, the only previous report of the spectrum found in the literature; molar absorptivities were not given in the Kuniya et al. paper.

The spectral fit, SF, defined as the number of absolute values of ((A(obs) − A(calc))(path length) larger than the combined estimated uncertainties of the base line and the absorbance measurements, 0.016, is indicated for each scan in Table 1. For each equilibrium mixture observed and calculated absorbances were compared at 10 nm intervals, covering the range $200 < \lambda < 520$, a spectral scan. Hence, the SF value for a given scan may range from 0, the best possible fit, to 31. The overall fit, a total SF value of 34 for all scans (the maximum possible is over 2000), is seen to be very good. While the fit suggests the relative values of the molar absorptivities are valid within a few percent, the absolute values depend on the selection of vapor pressure data used to derive the concentrations. In Table 1 results for each mixture are listed in the order in which scans were taken.

Partial pressures, calculated from derived concentrations and the perfect gas law, are shown in Figures 2 and 3. As noted above an equally good fit with the Ferro et al. (1979) vapor pressures for equilibrium with $SbI_3(l)$, Figure 2, can be obtained by multiplying the molar absorptivities in Table 2, and concomitantly dividing the $c(SbI_3,g)$ values, Table 1, by a factor of 1.6.

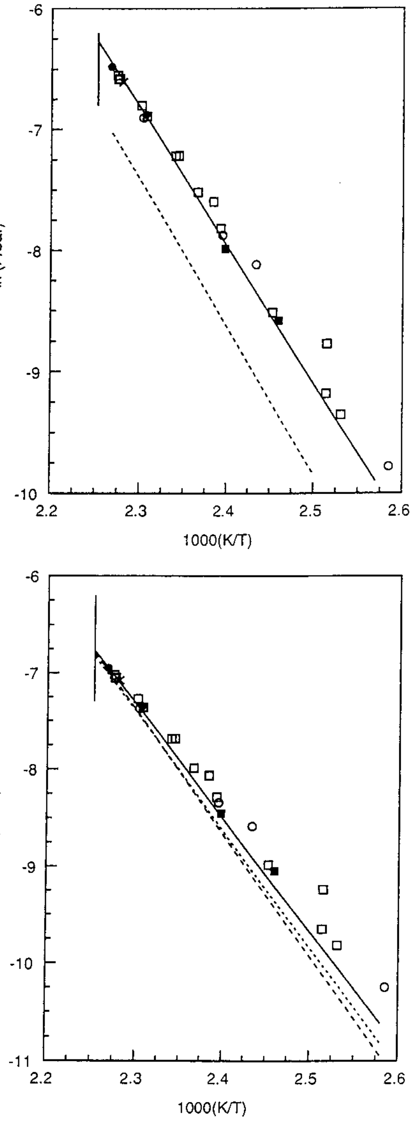

Figure 3. (A, top) Derived vapor pressures of SbI_3 below the melting point (vertical line) of SbI_3, using molar absorptivities from Table 2. (—) Values projected from $\Delta H°$ and $\Delta S°$ of vaporization, derived from the Bruner−Corbett equation, and $\Delta H°$ and $\Delta S°$ of fusion (Cubicciotti and Eding, 1965). (- - -) Ferro et al. (1979) equation, effusion data. Samples (×) SN 2, (●) SN 4, (■) Sn 5, (○) SN 6, (□) SN 7, this work. (B, bottom) Derived vapor pressures of SbI_3 below the melting point (vertical line) of pure SbI_3, using molar absorptivities (Table 2) multiplied by 1.6. (—) Values projected from $\Delta H°$ and $\Delta S°$ of vaporization, derived from the Ferro et al. (1979) transpiration equation, and $\Delta H°$ and $\Delta S°$ of fusion (Cubicciotti and Eding, 1965). (···) Ferro et al. (1979) equation, effusion data. (- - -) Knacke et al. (1991) equation for vapor pressure of $SbI_3(s)$. Samples: (×) SN 2, (●) SN 4, (■) SN 5, (○) SN 6, (□) SN 7, this work.

SbI_3 + Sb(s) Mixtures. Equilibrium pressures of SbI_3 derived for SN 1, Figure 2, generally lie below the BC line for pure SbI_3, and below values derived for SN 3 and 7. The displacement is similar to that observed for SbI_3 + Sb(s) mixtures by BC at higher temperatures, which they attribute to lowering of the SbI_3 vapor pressure by formation of a solution of Sb in $SbI_3(l)$.

For SN 2, the same derived concentration, see Table 1, gave a satisfactory fit for five scans with T_c between 475 and 840 K; i.e., all the SbI_3 appeared to be in the vapor phase with no change in concentration as the temperature was increased. With T_c at 448 K, Figure 2, and at 439 K, Figure 3, lower absorbances indicated condensation of some of the SbI_3.

SN 5 contained only a small amount of SbI_3 and a substantial amount of powdered Sb. With T_c between 479 and 795 K, essentially all the SbI_3 appeared to be in the vapor phase. However, derived concentrations increased regularly and reversibly as the temperature was increased; see Table 1. This suggests adsorption and desorption of SbI_3 on the metal powder. Appreciably lower absorbances with T_c at 407 and 417 K indicated condensation of some of the vapor; the corresponding pressures are shown in Figure 3.

At the two highest temperatures, 769 and 795 K, and at wavelengths below 270 nm, small extra absorbances, i.e., over that expected from $c(SbI_3,g)$, were observed with SN 5, resulting in SF values of 4 in each case. While the extra absorbances might be attributed to SbI(g), the source has not been identified. It may in part arise from vapors of the metal or metal oxide. In a separate experiment vapors formed by a sample of antimony metal, previously heated in air, were found to give measurable absorbances around 210 nm at temperatures above 800 K. This absorbance appeared to be associated with a sharply rising peak (with a maximum in the far ultraviolet); e.g., at 830 K, the absorbance was near zero with $\lambda > 270$ nm and increased as the wavelength was decreased, to ~0.1 at 210 nm.

The Bakhyshov et al. (1972) equation for the equilibrium constant of reaction 1, $\log(K_1/\mathrm{mmHg}) = -5058.6(T/\mathrm{K})^{-1} + 5.709$, together with Knacke et al. (1991) data for reaction 3, gives predicted ratios $c(SbI,g)/c(SbI_3,g)$ for SN 2 which range from 0.1 at 448 K to 44 at 840 K, and for SN 5 from 0.16 at 417 K to 350 at 795 K. $\Delta S°$ (for a standard state of 1 bar) for reaction 1, as calculated from the Bakhyshov et al. equation, is only 54 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, which is much smaller than expected. For example, $\Delta S°$ values (1000 K) from the JANAF Tables (Chase et al., 1986) for the corresponding reaction for chlorides and bromides of phosphorus, aluminum, titanium, and zirconium are all similar and much larger, in the range 138 ± 12 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. A recalculation, using the Bakhyshov et al. total pressures, but including the effect of the $I_2(g) \rightleftarrows 2I(g)$ equilibrium, gave an even smaller $\Delta S°$, 44 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. However, the result is found to be very sensitive to the value used for the sum $c(SbI_3(g)) + c(SbI(g))$ in their experiment. An increase in the sum of only 2% gave, in a least-squares treatment, the revised equation $\ln(K_1/\mathrm{bar}) = -21607(T/\mathrm{K})^{-1} + 16.14$; the corresponding $\Delta S°$ value is now 134 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$. This revised result seems more compatible with the absorbance observations, giving predicted ratios $c(SbI,g)/c(SbI_3,g)$ less than 0.03 in all but four of the absorbance equilibrium mixtures: SN 2, 0.21, T_c at 800 K, 0.56, T_c at 843 K (no unusual absorbance change was seen in SN 2 samples); SN 5, 0.28, T_c at 769 K, 0.54, T_c at 795 K.

A calculation using Bakhyshov et al. total pressures with the assumption that the dissociation corresponds to reaction 2 gave partial pressures of $Sb_4(g)$ larger than the Knacke et al. (1991) values for the equilibrium $4Sb(s) \rightleftarrows Sb_4(g)$. When the dissociation is assumed to correspond to reaction 3, derived equilibrium constants are around 50 times larger than those predicted from the Knacke et al. compilation.

$SbI_3 + I_2$ Mixtures. Derived partial pressures for SN 3, discussed above, are shown in Figure 2. SN 4 appeared fully vaporized with no change in composition as the temperature was increased from 580 to 828 K; see Table 1. For scans with T_c at 434 and 441 K, the SN 4 absorbance was smaller (some of the SbI_3 condensed); derived pressures are shown in Figure 3. The slightly larger values of $c(I_2,g)$ in SN 4, as compared with SN 3, reflect the volume change as a result of the seal-off procedure. In SN 4 $c(I_2,g)$ is still too small to give measurable iodine absorbances in the 210−450 nm range.

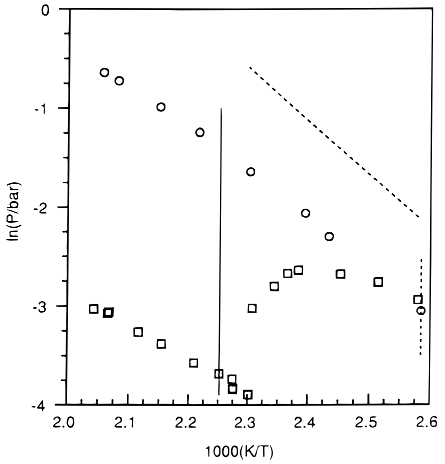

Figure 4. Derived partial pressures of I_2. (—) vertical line, melting point of pure SbI_3. (···) vertical line, melting point of pure I_2. (- - -) sloping line, vapor pressure of pure $I_2(l)$. Samples: (○) SN 6, (□) SN 7, this work.

SN 6 contained a relatively large amount of condensed SbI_3 and, of the seven samples, had the highest concentration of iodine (e.g., $P(I_2) = 0.53$ bar with T_g at 493 K). However, except for the very lowest temperatures, the spectral fit of vapor spectra from SN 6 was satisfactory when only $SbI_3(g)$ and $I_2(g)$ were assumed present; i.e., nothing to indicate the presence of appreciable concentrations of SbI_5 was observed. $SbCl_3(g)$ and $SbCl_5(g)$ have been found (Gregory, 1995) to have quite different absorption spectra. Derived partial pressures of $SbI_3(g)$ are shown in Figures 2 and 3 and of $I_2(g)$ in Figure 4. The behavior of both components indicates formation of liquid solutions of SbI_3 and I_2. Above 444 K, the ratios $P(SbI_3)/P°(SbI_3)$, where $P°(SbI_3)$ is the extrapolated BC pressure, for the four scans are similar, 0.8 ± 0.03. The ratios $P(I_2)/P°(I_2)$, where $P°(I_2)$ is the vapor pressure of pure $I_2(l)$, decrease from 0.35 at $T_c = 451$ K to 0.28 at $T_c = 486$ K. The sums of these ratios, assumed to approximate the respective mole fractions in the liquid phase, were 1.15, 1.11, 1.11, and 1.10, close to the ideal solution value of 1. As T_c values decrease below 444 K, the melting point of pure SbI_3, $P(I_2)$ shows a continued regular fall-off; see Figure 4. The $P/P°$ ratios for iodine rise as the temperature is reduced, to 0.43 at the lowest temperature. Thus, for SN 6, $I_2(g)$ appears to be in equilibrium with a liquid solution over the entire temperature range and $SbI_3(s)$ separates from the solution at the lower temperatures. Values derived for $P(SbI_3)$ at the two lowest temperatures, $T_c = 389$ and 411 K, although slightly high, are generally consistent with results from SN 2, 4, 5, and 7 (see Figure 3A) as would be expected if the vapor, in each case, is in equilibrium with $SbI_3(s)$.

A substantial part of the iodine in SN 6 was removed to generate SN 7. $P(I_2)$ values derived from the SN 7 absorbance data are also shown in Figure 4. With T_c between 433 and 490 K, $P(I_2)/P°(I_2)$ ratios are very small, between 0.03 and 0.04. Correspondingly the mole fraction of SbI_3 in the liquid phase is expected to be near unity; as seen in Figure 2, the derived $P(SbI_3)$ values for SN 7 agree well with those from SN 3, and with the BC line. As temperatures are reduced to values below 433 K, derived

SN 7 $P(I_2)$ values rise sharply; see Figure 4. $P(I_2)/P°(I_2)$ is 0.22 at T_c = 420 K; at the lowest temperature the ratio has increased to 0.47. Such an increase suggests that, as the temperature is reduced below 433 K, $SbI_3(s)$ condenses out of the solution, with a concomitant increase in the mole fraction of I_2 in the liquid phase. And, if true, values derived for $P(SbI_3)$ should correspond to those for vapors in equilibrium with $SbI_3(s)$, as seen in Figure 3A.

Vapor Pressures of $SbI_3(s)$. The solid line, Figure 3A, represents vapor pressures projected for $SbI_3(s)$ by combining the enthalpy and entropy of fusion, determined by drop calorimetry (Cubicciotti and Eding, 1965) with corresponding values for vaporization of the liquid, as derived from the Bruner−Corbett (1961) equation. The plotted points represent vapor pressures derived from the absorbance data. At T_c values above 435 K, derived pressures for all samples are close to the line. At 417 and 407 K values from Sn 5, in which Sb(s) was present, are also close to the projected values. At lower temperatures values from SN 6 and 7, which have appreciably higher iodine concentrations than the other samples (see Table 1), are generally somewhat above the line, particularly for $T_c < 400$ K. The absorbances for both samples below 400 K were small, with the uncertainty a relatively large fraction of the derived pressure.

While the slightly larger than expected absorbances for SN 6 and SN 7 at low temperatures may indicate the presence of small concentrations of SbI_5, this has not been clearly demonstrated. The spectral fits are satisfactory when $SbI_3(g)$ is assumed to be the only antimony compound in the vapor. Although at higher temperatures iodine vapor concentrations in SN 6 are much higher than those in SN 7, solubility effects (see Figure 4) result in very similar values of $c(I_2,g)$ for the two samples at the lowest temperatures; see Table 1. Thus, at low temperatures, where SbI_5 may be sufficiently stable to detect, the two samples do not provide for a test of the dependence of any "extra absorbance" on the iodine concentration. At slightly higher temperatures, derived pressures for SN 6, with T_c = 418 K and $c(I_2,g) = 3.46$ mmol·L^{-1}, and SN 5 at 417 K, with a calculated $c(I_2,g)$ of 9×10^{-11} mol·L^{-1}, are both very near the projected line; i.e., nothing is seen to indicate the presence of significant concentrations of SbI_5 in SN 6.

The dotted line, Figure 3A, represents the equation derived by Ferro et al. (1979) from their effusion data (range 382−441 K). The Ferro et al. result is also shown in Figure 3B, as a dotted line, where it may be compared with values derived from the absorbance data when molar absorptivities in Table 2 are multiplied by 1.6. The comparison is satisfactory at temperatures close to the melting point but not at lower temperatures. The solid line represents pressures projected by using Ferro et al. $\Delta H°$ and $\Delta S°$ of vaporization from their transpiration data together with the corresponding fusion values (Cubicciotti and Eding, 1965) to calculate sublimation values. This line is in better agreement with the absorbance values, but the fit is not quite as good as that shown in Figure 3A. In Figure 3B the sublimation vapor pressure equation given in the Knacke et al. (1991) compilation is shown as a dashed line.

Comparison of Vapor Pressures. In this work vapor pressures derived from absorbance data depend on the selection of the calibrating vapor pressure equation. Results for vapors in equilibrium with $SbI_3(1)$ correlate equally well using concentrations derived from the Bruner−Corbett equation (1961) or, alternatively, by using molar absorptivities larger by a factor of 1.6, with the Ferro et al. (1979) transpiration data. Absorbance vapor pressures for equilibrium with $SbI_3(s)$ are compared with values predicted by combining enthalpies and entropies of vaporization with calorimetrically determined (Cubicciotti and Eding, 1965) values for fusion. While the correlation for sublimation data is somewhat better using Brunner−Corbett values, the comparison with the result based on the Ferro et al. transpiration data, and larger molar absorptivities, does not provide clear evidence favoring one over the other. At lower temperature Ferro et al. effusion pressures, and those derived from the equation given by Knacke et al., are appreciably lower than values based on absorbance data.

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