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VAPORIZATION STUDY OF THE $SbBr_3$ SYSTEM BY THE TORSION–EFFUSION METHOD

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ABSTRACT

Vapor pressures of solid antimony tribromide were measured by the torsion–effusion technique. The values obtained can be expressed by the equation

$$\log P(\text{atm}) = (9.3 \pm 1.3) - (4.4 \pm 0.5)/T$$

in the temperature range 324–368 K.

The standard heat of vaporization was derived by second- and third-law treatment of the data and compared with values reported in the literature. The value ΔH^0_{vap} (298 K) = 19.5 ± 0.5 kcal mole^{-1} was derived.

INTRODUCTION

The vaporization process of antimony halides has been studied by several authors in connection with their utilization in the synthesis of semiconductor compounds[1, 2].

In our previous works[3, 4], the vapor pressures of the iodide and chloride of this element were measured. For the tribromide, in addition to the early vapor pressure data quoted by Stull[5], the data reported in the literature have been measured mainly by static methods[6, 9] and over the liquid phase. In view of the lack of experimental data on the vaporization of the solid phase, and in order to complete the series of the antimony halides, measurements of vapor pressure over $SbBr_3$ by using the torsion method were performed.

EXPERIMENTAL AND RESULTS

The $SbBr_3$ was supplied by Cerac/Pure as 99.7% pure (Sb_2O_3 as impurity) and was used without further purification. The vaporization cell was filled in a dry-box in order to avoid interaction with the atmosphere. The basis of the method is well known[10]; when the sample is heated at a given temperature, the corresponding vapor pressure is derived by measuring the torsion angle (α) using the relation

$$p = \frac{2K\alpha}{(a_1 l_1 f_1 + a_2 l_2 f_2)L}$$

where K is the constant of the torsion wire to which the Knudsen cell is suspended, a_1 and a_2 are the areas of the two effusion holes, l_1 and l_2 are the respective distances from the rotation axis, f_1 and f_2 are the corresponding geometrical correction factors, and L is the torsion wire length. The correction factors are derived from the equation[11]

$$\frac{1}{f} = 0.0147\left(\frac{L}{r}\right)^2 + 0.3490\left(\frac{L}{r}\right) + 0.9982$$

where r and L are the radius and the thickness of the effusion hole, respectively. The temperatures were measured by a calibrated chromel–alumel thermocouple inserted in a second cell below the torsion cell.

In this study, different cells and suspension wires were employed; their physical and geometrical constants are reported in Table 1. Some calibration experiments with very pure mercury were performed using the different cells in order to check the existence of thermodynamic equilibrium conditions, the reliability of the constants used and the absence of any substantial error in the temperature measurements. Good agreement between the ΔH^0_{vap} (298 K) of the mercury derived both by second- and third-law treatments of the vapor pressure data and the value selected by Hultgren et al.[12] can be considered as a successful check.

TABLE 1

CONSTANTS OF THE CELLS EMPLOYED

Cell	*Orifice area*		*Moment arm*		*Correction factors*[11]	
	$a_1(cm^2) \times 10^4$	$a_2(cm^2) \times 10^4$	($\pm$ 0.05 cm)		f_1	f_2
A	6.8 $\pm$ 0.5	6.8 $\pm$ 0.5	0.81	0.79	0.226	0.217
B	6.8 $\pm$ 0.5	7.1 $\pm$ 0.5	0.81_5	0.86	0.226	0.240
C	19.6 $\pm$ 0.8	19.6 $\pm$ 0.8	0.97_5	0.94_5	0.268	0.314

Torsion filament ($L = 35.0 \pm 0.2$ cm)	*Torsion constant (dyne cm rad^{-1})*
Tungsten wire 30 μm diam.	0.352 $\pm$ 0.04
Tungsten wire 50 μm diam.	2.44 $\pm$ 0.36
Fiber Ni–Pt 10% (150 $\times$ 50) μm	0.33 $\pm$ 0.05

TABLE 2

VAPOUR PRESSURE (Atm) AND THIRD-LAW $\Delta H^0_{298(VAP)}$ (KCAL MOLE^{-1}) VALUES OF $SbBr_3$.

T (K)	$-log\ P$	$-\Delta H^0_{298}$	T (K)	$-log\ P$	$-\Delta H^0_{298}$
Expt. I: Cell A, torsion filament: tungsten wire (30 μm in diameter)					
337	3.925	19.51	363	3.080	19.59
342	3.681	19.42	363	3.080	19.59
345	3.603	19.46	363	3.090	19.60
345	3.703	19.62	364	2.960	19.44
347	3.524	19.45	364	3.040	19.58
348	3.557	19.55	364	3.080	19.64
350	3.427	19.46	366	3.040	19.68
351	3.399	19.47	366	2.931	19.49
352	3.373	19.48	367	2.922	19.53
352	3.457	19.61	367	2.987	19.64
353	3.348	19.49	368	2.879	19.51
353	3.373	19.53	368	2.755	19.30
353	3.361	19.51	369	2.718	19.29
353	3.402	19.58	369	2.840	19.49
354	3.302	19.47	369	2.840	19.52
355	3.288	19.50	370	2.683	19.28
355	3.361	19.62	371	2.658	19.28
356	3.323	19.61	371	2.748	19.44
356	3.323	19.61	372	2.634	19.28
357	3.256	19.56	372	2.752	19.49
357	3.223	19.51	372	2.702	19.40
358	3.188	19.50	373	2.569	19.22
358	3.272	19.64	373	2.716	19.47
359	3.141	19.48	374	2.549	19.22
359	3.223	19.64	375	2.630	19.40
360	3.072	19.42	375	2.639	19.40
360	3.226	19.67	376	2.554	19.31
360	3.226	19.67	376	2.495	19.21
361	3.147	19.59	376	2.519	19.31
361	3.172	19.64	377	2.493	19.25
361	3.023	19.39	377	2.437	19.15
362	3.001	19.40	378	2.416	19.15
362	3.126	19.61	379	2.371	19.12
362	3.123	19.60	380	2.347	19.11
			381	2.356	19.17
				Average:	19.5 ± 0.1[a]

Exp. II: Cell C, torsion filament: tungsten wire (30 μm in diameter)

334	4.154	19.69	362	3.186	19.71
335	4.055	19.59	363	3.091	19.61
343	3.851	19.74	363	3.082	19.59
346	3.754	19.76	367	2.991	19.65
348	3.675	19.74	372	2.754	19.49
349	3.640	19.74	374	2.748	19.56
352	3.524	19.72	375	2.741	19.59
353	3.475	19.69	376	2.725	19.61
353	3.464	19.68	377	2.709	19.62
356	3.392	19.73	379	2.640	19.58
358	3.323	19.72	379	2.539	19.41
360	3.249	19.71	386	2.277	19.22
360	3.263	19.73	391	2.191	19.26
				Average:	19.6 ± 0.1[a]

Expt. III: Cell C, torsion filament: tungsten wire (50 μm in diameter)

338	3.804	19.38	377	2.415	19.11
339	3.804	19.44	379	2.398	19.16
348	3.503	19.46	381	2.349	19.16
352	3.327	19.40	385	2.225	19.09
355	3.202	19.36	387	2.128	18.99
356	3.151	19.33	389	2.060	18.95
358	3.064	19.29	391	2.012	18.94
359	3.026	19.29	393	1.947	18.89
362	2.901	19.24	394	1.912	18.87
366	2.743	19.18	394	1.966	18.96
368	2.744	19.28	395	1.848	18.79
369	2.674	19.22	396	1.845	18.82
375	2.443	19.08	399	1.822	18.91
376	2.443	19.12	400	1.809	18.93
				Average:	19.1 ± 0.1[a]

Exp. IV: Cell B, torsion filament: Ni-Pt (10%) fiber

339	3.889	19.57	365	2.875	19.36
342	3.764	19.55	367	2.848	19.40
346	3.668	19.62	367	2.986	19.64
346	3.667	19.62	368	2.844	19.45
352	3.463	19.62	368	2.835	19.44
352	3.463	19.62	369	2.798	19.48
353	3.365	19.52	370	2.764	19.42
355	3.366	19.63	370	2.775	19.44
355	3.366	19.63	370	2.753	19.40
356	3.365	19.63	372	2.723	19.44
357	3.190	19.45	373	2.676	19.39
357	3.252	19.55	373	2.676	19.39
358	3.136	19.42	374	2.650	19.39
358	3.162	19.46	375	2.595	19.34
359	3.190	19.56	376	2.540	19.29
360	3.136	19.52	378	2.486	19.28
360	3.087	19.44	379	2.469	19.29
360	3.111	19.48	380	2.497	19.37
361	3.065	19.46	383	2.442	19.39
361	3.065	19.46	385	2.353	19.31
363	3.024	19.49	387	2.337	19.36
364	3.024	19.55	389	2.269	19.32
364	2.919	19.37			
				Average:	19.5 ± 0.1[a]

Expt. V: Cell C, torsion filament: fiber Ni–Pt (10%)					
324	4.571	19.73	353	3.346	19.49
329	4.367	19.72	353	3.492	19.72
339	4.015	19.77	354	3.413	19.65
341	3.890	19.69	356	3.326	19.61
341	3.992	19.85	358	3.221	19.55
343	3.765	19.60	358	3.170	19.47
343	3.890	19.80	362	3.024	19.44
344	3.823	19.75	362	3.040	19.47
345	3.690	19.59	364	2.973	19.46
345	3.793	19.76	365	2.912	19.41
346	3.647	19.59	367	2.876	19.45
346	3.739	19.73	368	2.820	19.41
348	3.647	19.69	369	2.811	19.45
348	3.823	19.75	370	2.777	19.44
348	3.690	19.76	370	2.759	19.40
349	3.522	19.55	371	2.736	19.42
350	3.464	19.51	371	2.713	19.38
351	3.538	19.69	372	2.693	19.38
				Average:	19.6 ± 0.1[a]
Expt. VI: Cell A, torsion filament: Ni–Pt (10%) fiber					
342	3.619	19.32	367	2.726	19.20
349	3.539	19.58	368	2.645	19.12
353	3.317	19.44	370	2.593	19.13
353	3.238	19.31	370	2.684	19.28
354	3.171	19.26	373	2.403	18.93
355	3.141	19.27	374	2.203	18.63
356	3.113	19.29	374	2.601	19.32
357	3.113	19.33	375	2.569	19.29
357	3.141	19.37	375	2.398	19.01
358	3.062	19.29	375	2.188	18.64
358	3.113	19.38	376	2.378	19.01
359	3.087	19.39	378	2.358	19.08
360	3.038	19.36	378	2.339	19.02
360	3.038	19.36	379	2.330	19.04
361	2.937	19.25	379	2.313	19.01
362	2.902	19.24	380	2.292	19.01
363	2.919	19.32	380	2.288	19.01
364	2.826	19.22	381	2.256	18.99
365	2.919	19.16	381	2.249	18.98
366	2.812	19.29	382	2.206	18.94
				Average:	19.2 ± 0.1[a]

[a] Standard deviation.

The vapor pressure values of $SbBr_3$ measured in the temperature range by different cells and suspension filaments are given in Table 2. In the same table are also reported at each different experimental temperature the ΔH^0_{vap} (298 K) derived by the third-law treatment of the vapor pressure data.

As with the other halides[13, 14], it has been assumed that $SbBr_3$ vaporizes as the monomeric species. The necessary free-energy functions, $-(G^0_T - H^0_{298})/T$, for

TABLE 3

FREE-ENERGY FUNCTION (e.u.) AND HEAT CONTENT (KCAL MOLE^{-1}) OF $SbBr_3$ (M.P. 370 K)

T (K)	Condensed phase		Vapour phase	
	$-\left(\frac{G_T^0 - H_{298}^0}{T}\right)$	$H_T^0 - H_{298}^0$	$-\left(\frac{G_T^0 - H_{298}^0}{T}\right)$	$H_T^0 - H_{298}^0$
298	49.50		89.49	
310	49.52	0.31	89.52	0.19
330	49.63	0.84	89.60	0.58
350	49.82	1.39	89.73	1.00
370	50.08	1.94	89.92	1.40
390	50.88	6.20	90.13	1.78
410	51.70	6.88	90.38	2.15
420	52.10	7.19	90.50	2.34
440	52.91	7.89	90.78	2.73
460	53.73	8.59	91.08	3.13
480	54.54	9.29	91.38	3.51
500	55.33	9.97	91.68	3.92

TABLE 4

VAPOUR PRESSURE–TEMPERATURE EQUATIONS OF THE $SbBr_3$ SOLID

Exp.	*No. of points*	*ΔT (K)*	*log P (atm) = A − B/T*	
			A	*B × 10*$^{-3}$
I	45	337–368	7.63 ± 0.24	3.88 ± 0.08
II	17	334–367	8.66 ± 0.20	4.28 ± 0.07
III	11	338–368	10.04 ± 0.36	4.69 ± 0.13
IV	26	339–367	10.14 ± 0.33	4.77 ± 0.12
V	29	324–367	10.54 ± 0.29	4.92 ± 0.10
VI	21	342–367	10.21 ± 0.47	4.75 ± 0.17

solid and liquid phases were derived from the absolute standard entropy, $S_{298}^0 = 49.5$ e.u. (ref. 15), the solid heat capacity $Cp_s = 17.2 \pm 29.3 \times 10^{-3}\ T$ (ref. 13), the $\Delta H_m^0 = 3.51$ kcal mole^{-1} (ref. 16), and the heat capacity of the liquid reported by Takeyama and Atoda[17]. The free-energy functions used for the vapor phase are those reported by Clark and Rippon[18]. Their values and the corresponding heat content functions are summarized in Table 3.

The derived $SbBr_3$ ΔH_{vap}^0 (298 K) values are in very good agreement and therefore we selected the average value ΔH_{vap}^0 (298 K) = 19.5 kcal mole^{-1} with an error that should not exceed 1.0 kcal, taking into account the overall errors in the measurements.

TABLE 5

HEATS OF VAPORIZATION OF $SbBr_3$ AT 298 K

Method	*Phase*	$\bar{T}$ *(K)*	ΔH^0_T *(kcal mole⁻¹)*	ΔH^0_{298} *(kcal mole⁻¹)*	*Ref.*
Static	Liquid	490	13.1 ± 0.2	19.0 ± 0.2	7
Transpiration	Solid	347	19.7 ± 0.3	20.1 ± 0.3	8
	Liquid	389	13.8 ± 0.3	18.2 ± 0.3	8
Static	Liquid	468	13.2 ± 0.2	18.8 ± 0.2	6
Static	Liquid	478	12.8 ± 0.2	18.6 ± 0.2	9
Torsion	Solid and liquid (III law)	362	—	19.5 ± 1.0	Present work
	Solid (II law)	351	20.1 ± 2.3	20.5 ± 2.3	Present work

Considering the small experimental temperature range covered, which also includes the melting point[6], only the vapor pressures measured over the solid phase were used in order to determine pressure–temperature equations in the form

$$\log P(\mathrm{atm}) = \frac{A - B}{T}$$

The values of the constants relative to each experiment were determined by the least-squares method and are listed in Table 4. From these values, the equation

$$\log P(\mathrm{atm} = (9.3 \pm 1.3) - (4.4 \pm 0.5)/T$$

is proposed for the temperature dependence of the vapor pressure of $SbBr_3$(s). The constants are derived from the weighted mean of the corresponding constants reported in Table 4. The associated errors represent the semidispersion of the data and should reflect the estimated uncertainties in the temperature measurements and the calibration constants. From the slope, the second-law sublimation energy, $\Delta H^0_{\mathrm{vap}}$ (298 K) = 20.5 ± 2.3 kcal mole^{-1}, corrected at 298 K using the heat content functions reported in Table 3, was derived in spite of the relatively small temperature range covered. This value is in agreement with the third-law $\Delta H^0_{\mathrm{vap}}$ (298 K). In Table 5 our $\Delta H^0_{\mathrm{vap}}$ (298 K) values are compared with those reported in the literature corrected at 298 K by the heat contents of Table 3. This comparison shows an acceptable agreement; on this basis we propose the value $\Delta H^0_{\mathrm{vap}}$ (298 K) = 19.5 ± 0.5 kcal mole^{-1} for the standard vaporization enthalpy of antimony tribromide, giving more weight to our third-law results.

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