Vapor Pressure of Antimony (III) Bromide

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Transpiration measurements with argon as a carrier gas give heats of sublimation and vaporization of $SbBr_3$ of 19.7 and 13.8 kcal. per mole, respectively.

LIQUID-VAPOR and solid-vapor equilibria for antimony (III) bromide were determined between 323° and 403° K. with a transpiration apparatus similar to those described previously (*2*, *5*). This work is part of a study on the higher oxidation states of antimony, which required vapor pressures at fairly low temperatures. The vapor pressure of $SbBr_3$ (l) has already been measured (*4*) at high temperatures. Since both $SbCl_3$ and SbI_3 vaporize as simple, monomeric molecules (*1*, *4*), it has been assumed that $SbBr_3$ vaporizes similarly.

EXPERIMENTAL

A run with the transpiration apparatus consisted of passing argon gas at 746 mm. over a bed of $SbBr_3$ maintained at a constant temperature. The transported $SbBr_3$ condensed at the cold end of the transport tube, from which it was washed with 6*N* sulfuric acid and subsequently analyzed. Tank argon (99.998%) was passed through a flow meter and into the apparatus. The amount of argon transpired was determined by displacing water in a Mariott flask. The argon pressure was kept constant at 746 mm. by manually adjusting the hydrostatic pressure head with a laboratory jack placed under the water collection vessel.

The temperature of the $SbBr_3$ sample in the transpiration apparatus was held constant to ±0.2° K. by immersion in a water bath. The bath temperature was controlled electronically, using a thermister sensing element (Yellow Springs Instrument Co., Model 71). The temperature was measured with an ASTM mercury-in-glass thermometer which was accurate to ±0.1° K. Above 358° K., the sample was heated in a tube furnace, and the temperature was measured with calibrated thermocouples. The temperature was controlled electronically with a platinum resistance sensing element (Electronic Processes Corp., Model 7503A). The temperature of the sample was defined to about ±1° K., as indicated by thermocouples at each end and the middle of the sample.

Table I. Vapor Pressure of $SbBr_3$(s) and $SbBr_3$(l) by Argon Transpiration at 746 Mm.

Run	*T*° C.	Argon Flow Rate, Ml./Min.	Argon Transpired, Mmoles	Antimony Transported, μm.	$SbBr_3$ Pressure, Mm. Hg
1	60.0	6	44.8	2.90	0.048
2	60.0	9	59.8	4.15	0.051
3	60.0	13	63.3	4.12	0.049
4	60.0	18	39.6	2.55	0.048
5	60.0	18	64.6	4.32	0.050
6	60.0	23	65.8	4.67	0.053
7	60.0	30	43.2	2.57	0.044
8	60.0	31	47.0	3.10	0.049
9	60.0	39	61.7	4.63	0.056
10	60.0	49	63.9	4.93	0.057
11	50.0	18	133.3	3.51	0.019
12	52.5	19	156.8	5.07	0.024
13	55.0	18	108.9	4.31	0.029
14	57.4	20	104.2	5.74	0.041
15	60.0	20	69.7	5.07	0.054
16	62.5	19	47.2	4.11	0.065
17	65.0	19	42.3	4.36	0.077
18	67.6	19	38.5	4.46	0.086
19	70.0	20	36.9	5.86	0.118
20	72.5	21	37.7	7.25	0.143
21	75.0	19	35.3	8.55	0.180
22	77.7	17	38.0	11.45	0.224
23	80.0	20	32.8	11.71	0.266
24	82.5	17	29.8	13.58	0.337
25	85.0	18	31.8	17.15	0.402
26	87.6	18	25.3	15.95	0.470
27	102.5	23	40.8	60.5	1.11
28	103.0	19	26.9	45.5	1.26
29	104.5	19	22.9	34.8	1.13
30	108.0	18	22.2	46.2	1.56
31	112.0	17	21.0	52.7	1.88
32	115.0	18	28.4	83.0	2.18
33	116.0	23	28.0	73.0	1.95
34	119.0	20	27.8	89.0	2.39
35	122.0	21	29.2	107.0	2.74
36	123.0	18	21.8	84.5	2.89
37	126.5	20	24.0	112.6	3.51
38	130.0	21	25.5	143.7	4.21

The relative probable error in a single measurement of pressure is 5.4%.

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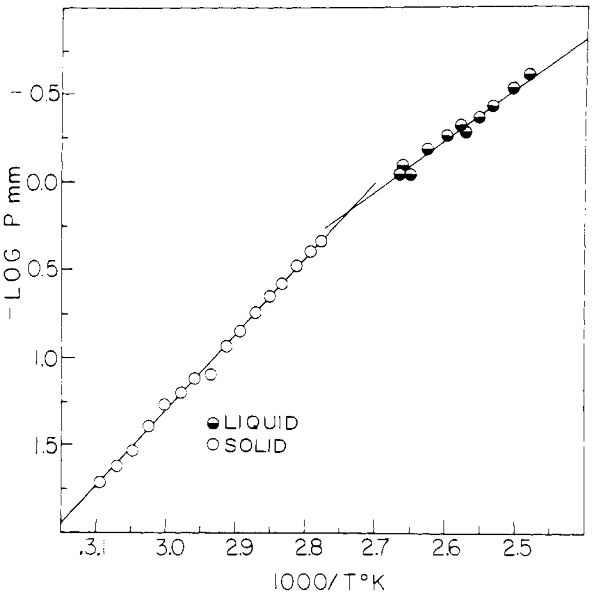

Figure 1. Vapor pressure of $SbBr_3$

RESULTS

If it is assumed that the gases are ideal, that the argon is saturated with antimony (III) bromide, and that transport of antimony (III) bromide by thermal diffusion is negligible, then the partial pressure of antimony (III) bromide is given directly by Dalton's law in the following form:

$$P = \frac{n_{Sb}}{n_{Sb} + n_{Ar}} P_{Ar}$$

or more simply

$$P = n_{Sb} P_{Ar} / n_{Ar}$$

since n_{Sb} is much smaller than n_{Ar} (Table I). Here P is the vapor pressure in millimeters of $SbBr_3$ (g), P_{Ar} is the measured pressure of argon (746 mm.), and n_{Sb} is the number of moles of of $SbBr_3$ transported by n_{Ar} moles of argon carrier gas. The preparation, purification, and analysis of $SbBr_3$ are described (*4*) in a previous paper. These data are summarized in Table I and Figure 1. The lines drawn through the experimental points were fit by least squares to equations of the form $\log P_{atm.} = -A/T + B$. The values are listed below in Table II (temperature range: 323° to 403° K., standard state: 1 atm.).

Table II. Calculated Thermodynamic Quantities

	A	B	$\Delta H°$, Kcal. $Mole^{-1}$	$\Delta S°$, Cal. $Deg.^{-1}$ $Mole^{-1}$
Sublimation	4302.2	8.7298	19.7 ± 0.3	39.9
Vaporization	3022.9	5.2197	13.8 ± 0.3	23.9

The intersection of the two lines in Figure 1, calculated with the data in Table II, permits determination of the melting point of antimony (III) bromide, 364.5° K., compared with a reported (*3*) value of 369.8° K. If ΔC_p for vaporization is estimated to be –3 cal. $deg.^{-1}$ $mole^{-1}$, then $\Delta H°_{vap}$ may be calculated for 298° K. for the data in this work and for the value previously reported (*4*) at higher temperatures. Taking the mean vaporization temperatures to be 388° and 771° K., respectively, one obtains values of 14.5 and 14.1 kcal. $mole^{-1}$, in good agreement.

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