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Sublimation study of $BiBr_3$

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Steady-state sublimation vapour pressures of anhydrous bismuth tribromide have been measured by the continuous gravimetric Knudsen–effusion method from 369.3 to 478.8 K. Additional effusion measurements have also been made from 435.4 to 478.6 K by the torsion–effusion method. Based on a correlation of $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$, a recommended $p(T)$ equation has been obtained for $BiBr_3(s)$

$$\alpha\text{-BiBr}_3\text{:}\ \log p = -C\alpha/T - 12.294 \log T + 5.79112 \times 10^{-3}\, T + 47.173$$

with $C\alpha = (\Delta_{sub}H^0_{298} + 20.6168)/1.9146 \times 10^{-2}$

$$\beta\text{-BiBr}_3\text{:}\ \log p = -C\beta/T - 23.251 \log T + 1.0492 \times 10^{-2}\, T + 77.116$$

with $C\beta = (\Delta_{sub}H^0_{298} + 46.2642)/1.9146 \times 10^{-2}$

where p is in Pa, T in Kelvin, $\Delta_{sub}H^0_{298}$ in kJ mol^{-1}. Condensation coefficients and their temperature dependence have been derived from the effusion measurements.

1. Introduction

Vapour pressures of $BiBr_3$ have been reported by Evnevich and Sukhodski [1] using the boiling point method in the temperature range from 615 to 767 K. Cubicciotti and Keneshea [2] determined vapour pressures of liquid $BiBr_3$ by the transportation method from 523 to 698 K. The only sublimation pressure measurement of $BiBr_3$ using the torsion and Knudsen method was found in the temperature range from 400 to 478 K [3].

Vapour and sublimation pressures are generally in good agreement. Standard sublimation enthalpies of α-and β-$BiBr_3$ at 298.15 K derived from these studies range from (105.12 ± 2.87) to (97.65 ± 2.87) kJ mol^{-1}. The present study has been undertaken to obtain new sublimation vapour pressures for $BiBr_3$ using the continuous gravimetric Knudsen and torsion–effusion techniques.

2. Experimental procedure and results

Anhydrous $BiBr_3$ of Puratronic grade (10 p.p.m. total metal impurities) was used in this study. Effusion cells, based essentially on a design by Blairs *et al.* [4] and fabricated from type-304 stainless steel, were filled inside a nitrogen dry box (moisture level $\leq$ 20 v.p.m.). A series of interchangeable push-fit effusion cell lids, each carrying an orifice of different size and having right-circular cylindrical geometry were used in the measurements. Provision was made via a port in the dry box wall, to attach loaded gravimetric effusion cells directly to a calibrated Ni-Span-C 902 spring balance (11.222 ± 0.012 cm mg^{-1}) inside the effusion apparatus. Spring contractions during effusion runs were measured by cathetometer (± 0.001 cm). Steady-state effusion rates at each temperature, W (mg h^{-1}), were derived from linear least squares plots of spring contraction versus time data. Effusion cells were maintained in a fixed position in the constant zone (± 0.5 K) of laboratory tube furnaces. Dynamic vacua better than 1.33×10^{-5} Pa were maintained during effusion runs. Effusion cell temperatures (± 0.25 K) were measured with calibrated NiCr/NiAl thermocouples with their hot junctions located in close proximity to the effusion cells. Actual cell temperatures were determined in separate dummy runs in which fine calibrated NiCr/NiAl thermocouples were inserted into the effusion cell bodies via the orifices and measured concurrently with the measurement thermocouples. All temperatures reported are in terms of the International Practical Temperature Scale of 1968 (IPTS-68).

Orifice area a and length L were measured using a Leitz Wetzlar metallograph at known magnification. Orifice Clausing factor [5] W_B and recoil force factors [6] f were derived from their length to radius ratios (L/r). Moment arms of the torsion–effusion cells were measured by cathetometer as (0.843 ± 0.001) cm. Effusion orifice parameters used in the gravimetric and torsion–effusion measurements are reported in Tables I and II. The smallest effusion orifice, No. 1, used in

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TABLE I Knudsen–effusion orifice parameters. a,r, L and W_B are the orifice area, radius, length and Clausing factor [6] respectively

Orifice No.	a (mm^2)	r (mm)	L (mm)	Clausing factors W_B[5]
1	—	—	—	0.0152[a]
2	0.1031	0.1812	0.238	0.6123
3	0.2125	0.2601	0.234	0.6871
4	0.4491	0.3781	0.243	0.7591
5	0.8498	0.5201	0.246	0.8501

[a] $aW_B(\text{mm}^2) = (1.2373 \times 10^{-5} \pm 2.194 \times 10^{-7})T + (1.1506 \times 10^{-2} \pm 0.06 \times 10^{-4})$

the gravimetric effusion measurements had complex geometry and its effective orifice area aW_B was determined using 99.999 mass per cent cadmium and 99.9 mass per cent benzoic acid as sublimation vapour pressure standards. Orifice dimensions were remeasured between runs and found to be unchanged.

A null point torsion–effusion apparatus employing a geared stepper motor and electronic driver was also used to measure sublimation vapour pressures. Each stepper motor pulse corresponded to a torsion angle of 0.05° and a deflection of 2.88 ± 0.09 mm as measured using an optical lever and a He–Ne laser. The torsion constant $k = 2.1504 \pm 0.1486 \times 10^{-7}$ N m^{-1} rad^{-1} of a 0.005 cm diameter tungsten wire was determined from changes of oscillation period after addition of inertia masses of known moments of inertia. A laser switch and interfaced computer were used as a precision timer for this purpose (± 0.0001 s). The design of the torsion–effusion apparatus precluded direct mounting of loaded effusion cells from the dry box. Instead, a procedure suggested by McCreary and Thorn [7] was used. Orifices of matched pairs of torsion cells were sealed with drops of naphthalene inside the dry box. On solidification, naphthalene sealed the orifices and protected the halide from hydrolysis during transfer to the torsion–effusion apparatus. On evacuation, naphthalene sublimed from and cleared the orifices.

Prior to measurements on $BiBr_3$, the sublimation vapour pressure of 99.999 mass per cent cadmium was measured by both effusion methods in the interval 529.6 to 592.1 K. Cadmium sublimation vapour pressures showed good agreement with the equation recommended by Iwu and Blairs [8]. Steady-state Knudsen–effusion sublimation vapour pressures for solid $BiBr_3$ in the range 369.3 to 478.8 K are reported in Table III and are plotted in Fig. 1 for five different effective orifice areas. Steady-state torsion–effusion

TABLE III Steady-state sublimation vapour pressure p and third-law sublimation enthalpy $\Delta_{sub}H^0_{298}$ for $BiBr_3$(s) determined by Knudsen–effusion method. W = steady-state effusion rate (mg h^{-1}). (p^0 = 101325 Pa)

Orifice No.		T (K)	W (mg h^{-1})	p (Pa)	$\Delta_{sub}H^0_{298}$ (kJ mol^{-1})
1		399.9	0.2504	0.916578	122.24
		415.7	0.2860	1.049767	123.42
	α	420.3	0.7044	2.590893	121.57
		426.0	1.1655	4.297740	121.34
		431.0	1.4691	5.428886	121.86
		436.3	2.0209	7.487388	122.12
		440.4	2.6227	9.728400	122.26
		442.8	3.1944	11.866103	122.14
		447.5	3.8740	14.417173	122.66
	β	450.4	5.1955	19.351247	122.30
		453.0	5.8325	21.749169	122.54
		458.7	9.9126	37.041377	121.97
		462.2	11.4863	42.963877	122.29
		468.4	15.6876	52.828917	122.61
		473.6	22.6501	85.062918	122.44
		478.8	40.5625	152.648420	121.40
2		399.5	0.2984	0.282044	123.18
		404.5	0.4968	0.472441	122.91
		409.6	0.7173	0.686237	123.13
	α	415.0	1.0295	0.991278	123.41
		419.5	1.6083	1.556765	123.12
		423.6	2.3264	2.262454	122.96
		424.8	2.6568	2.586280	122.81
		429.3	3.4984	3.424491	123.05
		430.5	3.7045	3.630928	123.16
		434.4	5.2561	5.174467	122.94
		436.8	6.0715	5.992827	123.05
		441.2	8.6329	8.562762	122.92
	β	446.1	11.8217	11.788643	123.03
		451.5	18.0807	18.136253	122.84
		455.3	25.3130	25.494381	122.54
		461.3	35.4892	35.967532	122.73
		466.2	52.0815	53.057832	122.47
3		390.6	0.2479	0.100272	123.89
		395.2	0.4508	0.183358	123.33
		399.9	0.6349	0.259779	123.59
		404.9	0.9557	0.393369	123.63
	α	409.4	1.2703	0.525690	123.99
		414.7	1.8494	0.770070	124.19
		420.8	3.0246	1.268362	124.19
		422.5	4.1972	1.763548	123.51
		426.9	5.8602	2.474890	123.55
		431.0	7.4842	3.175259	123.77
		436.0	10.5826	4.515028	123.86
		441.4	17.5649	7.539296	123.45
	β	446.1	24.8029	10.699945	123.38
		451.1	33.9783	14.737866	123.50
		455.8	47.7509	20.816020	123.41

TABLE II Torsion–effusion orifice parameters. a_1, a_2, r_1, r_2, L_1 and L_2 are the effusion orifice areas, radii and lengths respectively. f_1 and f_2 are the corresponding recoil force factors [6]

Cell No.	a_1	a_2	r_1	r_2	L_1	L_2	f_1	f_2
	(mm^2)		(cm)		(mm)			
1	0.1717	0.1751	2.3364	2.3586	0.3450	0.2813	0.6564	0.7018
2	0.2301	0.2400	2.7062	2.7623	0.2771	0.3616	0.7288	0.6832
3	0.4038	0.4036	3.5848	3.5840	0.3535	0.3267	0.7357	0.7520
4	0.7928	0.7807	5.0233	4.9851	0.3388	0.3226	0.8066	0.8133

TABLE III Continued

Orifice No.	T (K)	W (mg h^{-1})	p (Pa)	$\Delta_{sub}H^0_{298}$ (kJ mol^{-1})
4	380.7	0.2867	0.049036	123.14
	385.9	0.4205	0.072394	123.51
	392.5	0.7851	0.136295	123.50
	398.3	1.0348	0.180918	124.29
	403.6	1.3840	0.243540	124.90
	α 406.6	2.2798	0.402607	124.07
	408.8	3.3020	0.584659	123.45
	411.0	3.7674	0.668812	123.62
	414.4	4.7882	0.853463	123.76
	415.8	5.2094	0.930057	123.86
	421.0	7.0846	1.272455	124.24
	424.6	10.0997	1.821557	123.99
	427.2	11.0378	1.996636	124.38
	431.0	17.8002	3.233761	123.71
	435.3	23.6655	3.233761	123.85
	437.1	26.8465	4.320350	123.85
	438.1	29.6257	4.910626	123.77
	β 440.2	34.5232	5.424927	123.76
	442.3	32.6841	6.336455	124.31
	442.8	37.9667	6.380876	124.07
	448.3	61.3009	7.031411	123.75
5	369.3	0.2249	0.018759	122.54
	374.1	0.3345	0.028091	122.81
	380.8	0.5033	0.042636	123.61
	385.5	0.8308	0.070808	123.48
	389.4	1.4878	0.127416	122.76
	393.5	2.3685	0.204396	123.06
	α 402.3	3.2571	0.283430	124.00
	404.0	4.6475	0.405220	123.28
	408.0	5.3484	0.468561	123.96
	412.5	7.2513	0.638667	124.20
	417.8	10.4346	0.924791	124.45
	422.2	13.3458	1.188875	124.82
	428.7	21.7060	1.947853	124.88
	431.9	40.9320	3.147389	124.06
	434.3	45.5110	4.110342	123.74
	436.6	50.1301	4.539112	124.02
	β 439.3	69.1332	6.277843	123.54
	441.5	73.0016	6.645569	123.94
	444.3	87.5251	8.001591	124.01
	446.1	95.0657	8.697811	124.17

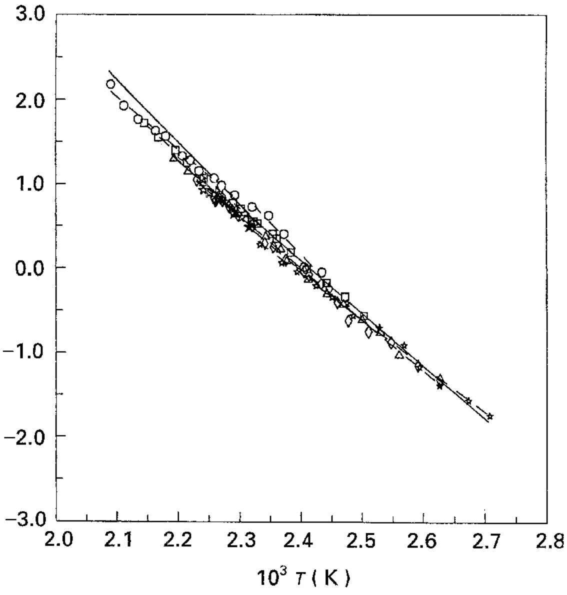

Figure 1 Steady-state sublimation vapour pressures for $BiBr_3$(s) measured by Knudsen–effusion method. ○, orifice 1; □, orifice 2; △, orifice 3; ◇, orifice 4; ☆, orifice 5; — equilibrium line. $T_t^{-1} = 2.320$.

TABLE IV Steady-state sublimation vapour pressure p and third-law standard molar sublimation enthalpy $\Delta_{sub}H^0_{298}$ for β-$BiBr_3$(s) determined by torsion–effusion method

Orifice No.	T (K)	p (Pa)	$\Delta_{sub}H^0_{298}$ (kJ mol^{-1})
1	456.0	12.307729	125.47
	460.0	15.935419	125.51
	464.0	19.341408	125.81
	468.5	25.445980	125.89
	472.6	35.027832	125.69
	478.6	51.128258	125.69
2	454.6	9.736707	125.98
	456.6	10.451722	126.24
	460.5	12.534099	126.56
	463.7	14.667056	126.80
	467.7	19.415428	126.75
	473.0	28.793184	126.56
	477.8	37.923790	126.18
3	435.4	0.750316	130.21
	439.4	1.114255	129.91
	442.7	1.464470	129.82
	447.9	2.104296	129.93
	453.0	2.943156	130.08
	461.7	6.290706	129.53
4	438.8	0.465042	132.81
	443.7	0.667557	132.86
	450.1	1.124978	132.71
	454.8	1.626818	132.67
	459.0	2.127853	132.83
	463.4	2.887190	132.86

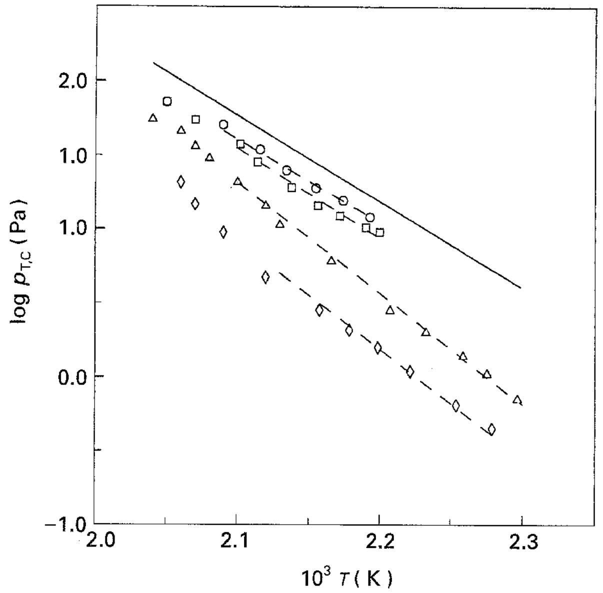

Figure 2 Steady-state sublimation vapour pressures for $BiBr_3$(s) measured by torsion-effusion method. ○, orifice 1; □, orifice 2; △, orifice 3; ◇, orifice 4; — equilibrium line.

sublimation vapour pressures, measured in the range 435.4–478.6 K are reported in Table IV and are plotted in Fig. 2 for four different orifice areas. $p(T)$ equations derived by least-squares treatment of the steady-state sublimation vapour pressures for each orifice size are summarized in Table V.

3. Discussion

Steady-state sublimation vapour pressures from both effusion techniques were found to depend on effective

TABLE V Coefficients with standard deviations of the equation log p(Pa) = $-A/T + B$ derived from $BiBr_3$(s) steady-state Knudsen- and torsion–effusion sublimation vapour pressure measurements determined in the temperature range T_1 to T_2.

Method	Orifice No.		Δ (K)		Number of points	A	B
Knudsen	1	α	399.9	431.0	5	7233 ± 1065	19.379 ± 2.116
		β	436.3	478.8	11	6198 ± 192	17.322 ± 0.382
	2	α	399.5	430.5	9	6197 ± 129	14.970 ± 0.310
		β	434.4	466.2	8	6464 ± 100	15.582 ± 0.191
	3	α	390.6	431.0	10	6099 ± 158	17.124 ± 0.313
		β	436.0	455.8	5	6541 ± 244	18.004 ± 0.484
	4	α	380.7	431.0	14	5927 ± 168	16.783 ± 0.335
		β	435.3	448.3	7	6001 ± 488	16.930 ± 0.969
	5	α	369.3	428.7	13	5435 ± 121	15.805 ± 0.241
		β	431.9	446.1	7	5927 ± 406	16.784 ± 0.806
Torsion	1	β	456.0	478.6	6	5972 ± 207	14.175 ± 0.443
	2	β	454.6	477.8	7	5974 ± 399	14.091 ± 0.859
	3	β	435.4	461.7	6	6842 ± 211	15.602 ± 0.472
	4	β	438.8	463.4	6	6601 ± 12	14.711 ± 0.203

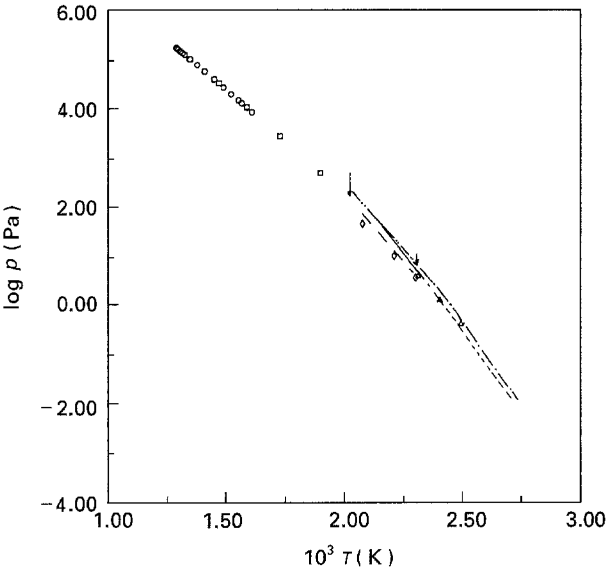

Figure 3 Comparison of $BiBr_3$ vapour pressures. ○, Evnevich [1]; □, Cubicciotti and Keneshea [2]; △ Imparatori *et al.* [3]; —, Knudsen–effusion equilibrium line; – – –, torsion–effusion equilibrium line; -----, recommended $p(T)$; T_t, transition temperature 431 K. $T_m^{-1} = 2.037$, $T_t^{-1} = 2.320$.

orifice area aW_B. Isothermal plots of inverse steady-state sublimation vapour pressure versus effective orifice were linear and were extrapolated to obtain inverse values of the equilibrium sublimation vapour pressures for zero effective orifice area. From the equilibrium sublimation pressures, the following $p(T)$ equations were obtained from the Knudsen and torsion–effusion measurements respectively: $\log p(\mathrm{Pa}) = -(6677 \pm 67)/T + (16.140 \pm 0.160)$ for α-$BiBr_3$ and $\log p(\mathrm{Pa}) = -(6401 \pm 19)/T + (15.447 \pm 0.043)$ for β-$BiBr_3$ from Knudsen–effusion method and $\log p(\mathrm{Pa}) = (5924 \pm 12)/T + (14.209 \pm 0.025)$ for β-$BiBr_3$ from torsion–effusion. These equilibrium $p(T)$ equations are shown with experimental points in Figs 1 and 2 and with literature vapour and sublimation pressures [1–4] for comparison in Fig. 3. Extrapolated Knudsen–effusion equilibrium sublimation vapour pressures are in good agreement with those reported in [3] but are slightly higher than those in [1–2].

From literature values for $BiBr_3$(cr) sublimation vapour pressures, equations of form $\log[p(\mathrm{Pa})] = -A/[T(K)] + B$ were derived and gave the coefficients

TABLE VI Summary of $BiBr_3$(s) sublimation vapour pressures

T_1–T_2 (K)	A	B	Second-law		Third-law
			$\Delta_{sub}H^0_{298}$ (kJ mol^{-1})	$\Delta_{sub}S^0_{298}$ (J K^{-1}mol^{-1})	$\Delta_{sub}H^0_{298}$ (kJ mol^{-1})
400.0–431.0^{a,b,c}	5490 ± 15	13.300 ± 0.200	107.80 ± 2.87	166.712 ± 3.83	123.10 ± 0.994
433.0–478.0^{a,b,c}	5100 ± 15	12.300 ± 0.200	98.254 ± 2.87	139.948 ± 10.684	125.50 ± 1.343
369.3–431.0^{a,d}	6677 ± 67	16.140 ± 0.160	130.570 ± 1.28	221.153 ± 3.063	122.81 ± 0.175
431.9–466.2^{b,d}	6401 ± 19	15.447 ± 0.043	122.505 ± 0.364	201.459 ± 0.823	122.86 ± 0.085
435.8–478.6^{b,d}	5924 ± 12	14.209 ± 0.025	113.627 ± 0.23	178.318 ± 0.479	124.47 ± 0.093

[a] Gravimetric Knudsen–effusion method
[b] Torsion–effusion method
[c] From reference [3]
[d] This study

TABLE VII Standard molar thermodynamic functions for $BiBr_3$(cr) and $BiBr_3$(g) at selected temperatures. $\nu(cm^{-1}) = 196.2$, 103.7; 169.0, 90.4, geometric constants r(Bi–I) = 0.263 nm; r(Bi–Bi) = 0.266 nm; (I – Bi – I) = 100° ($R = 8.31451\ J\ K^{-1}\ mol^{-1}$; $p^0 = 101325$ Pa; $T' = 298.15\ K$).

T (K)	C_p (R)	$\Delta(H^0_T - H^0_{298})$ (R K)	$\Delta(S^0_T - S^0_{298})$ (R)	$\Delta[(G^0_T - H^0_{298})/T]$ (R)
Solid[a]				
298.15	14.752	0	0	24.410
400	12.100	1367	3.965	27.806
420	11.579	1604	4.542	28.209
431	11.293	1730	4.838	28.404
431	12.271	2103	5.703	29.272
450	11.363	2328	6.213	29.566
470	10.411	2545	6.686	29.808
gas				
298.15	9.890	0	0	46.205
300	9.773	18	0.006	46.205
400	9.871	1001	2.406	46.590
500	9.917	1990	5.095	47.317
600	9.942	2984	6.906	48.138
700	9.958	3979	8.440	48.961
800	9.967	4975	9.770	49.756
900	9.975	5972	10.944	50.514

[a] Derived using heat capacity and standard entropy from reference [2, 12] fefs were obtained from reference [16]

A and B summarized in Table VI. Second-law $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$ also given in Table VI were calculated by assuming the coefficients A and B apply at the mean temperatures of the various ranges together with the following $C_p(T)$ for α-$BiBr_3$(s), β-$BiBr_3$(s) and $BiBr_3$(g). Polynomial expressions $C_p(T) = 187.2 - 21.65 \times 10^{-2}\ T$ [9], $273.3 - 39.7 \times 10^{-2}\ T$ [10] and $83.31 - 0.15 \times 10^{-3}\ T - 1.83 \times 10^5\ T^{-2}$ [9] $J\ K^{-1}\ mol^{-1}$ for α-$BiBr_3$(s), β-$BiBr_3$(s) and $BiBr_3$(g) respectively were employed in this study. The coefficients A obtained from $p(T)$ for Knudsen- and torsion–effusion measurements were used to derive values for the enthalpy change associated with the solid state transition at 431 K, $\Delta_{trans}H^0_{431} = 5.29 \pm 0.92$ (Knudsen) and 9.14 ± 1.05 kJ mol^{-1} (Knudsen + torsion). These values may be compared with those determined by Yosin *et al.* [11], 4 kJ mol^{-1} and by Imperatori *et al.* [3] 7 ± 4 kJ mol^{-1}, respectively.

Third-law $\Delta_{sub}H^0_{298}$ at each effusion temperature are also reported in Tables III and IV. Thermodynamic functions $\Delta[(G^0_T - H^0_{298})/T]$ for $BiBr_3$(g) were computed for a rigid-rotator harmonic-oscillator ideal gas monomer and pyramidal C_{3v} symmetry. The molecular constants [9, 12] and the calculated thermodynamic functions [13] are presented in Table VII. Thermodynamic functions $\Delta[(G^0_T - H^0_{298})/T]$ and S^0_{298} for $BiBr_3$(s) were derived from $\Delta_{sub}S^0_{298} = (181.2 \pm 0.3)\ J\ K^{-1}\ mol^{-1}$ [1] and S^0_{298} (298.15 K) = 384.1 $J\ K^{-1}\ mol^{-1}$ for $BiBr_3$(g) computed as outlined above and $C_p = 187.2 - 21.65 \times 10^{-2}\ T$ and $C_p = 273.3 - 39.7 \times 10^{-2} T$ for α-$BiBr_3$(s) and β-$BiBr_3$(s). Thermodynamic functions for $BiBr_3$(cr) at selected temperatures are presented in Table VIII.

Third-law $\Delta_{sub}H^0_{298}$ values obtained in this work are shown in Fig. 4 for both effusion techniques. Individual $\Delta_{sub}H^0_{298}$ values obtained from torsion–effusion measurements show some temperature and effective orifice dependence whereas those obtained from gravimetric Knudsen measurements are independent of these parameters. The average third-law $\Delta_{sub}H^0_{298} = (122.81 \pm 0.175)$ kJ mol^{-1} shown in Fig. 4 together with its standard deviation, is based only on the Knudsen–effusion data (α-$BiBr_3$) and is comparable with $\Delta_{sub}H^0_{298} = (117.89 \pm 6.18)$ kJ mol^{-1} derived later from an enthalpy–entropy correlation. Average third-law $\Delta_{sub}H^0_{298}$ values derived from literature sublimation vapour pressures are also included in Table VI.

TABLE VIII $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$ for $BiBr_3$(s) derived from the modified sigma function method [14]

$\Delta_{sub}H^0_{298}$ ($J\ mol^{-1}$)	$\Delta_{sub}S^0_{298}$ ($J\ K^{-1}\ mol^{-1}$)
114966 ± 338[a]	182.289 ± 0.556[a]
117381 ± 952[b]	185.564 ± 1.368[b]
98147 ± 968[c]	143.308 ± 11.325[c]
124418 ± 309[d]	206.282 ± 0.066[d]
119862 ± 19[e]	192.702 ± 0.040[e]

[a] From reference [2]
[b] From reference [1]
[c] From reference [3]
[d] This study, Knudsen–effusion
[e] This study, torsion–effusion

Ambiguity of temperature to which the coefficients A and B summarized in Table VI apply may be avoided by use of the modified sigma function method [14]. $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$ values were derived from the least squares slopes and intercepts of modified sigma function plots of the various literature $BiBr_3$ vapour pressure data sets [1–3] as well as the present measurements. For these calculations, in addition to the free energy functions of gaseous and solid $BiBr_3$ reported in Table VII, a value of $C_p = 166.26 - 44.03 \times 10^{-3}\ T\ J\ K^{-1}\ mol^{-1}$ [9], and a molar enthalpy of fusion of 20.84 kJ mol^{-1}, was used to obtain thermal functions for liquid $BiBr_3$. The resulting $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$ are summarized in Table VIII and have been plotted as $\Delta_{sub}H^0_{298}$ versus

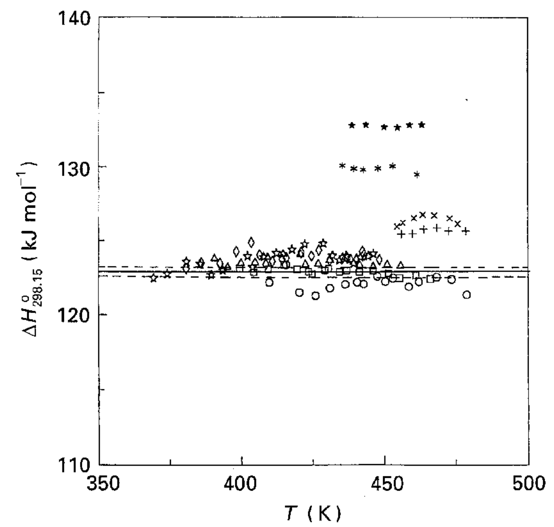

Figure 4 Enthalpy of sublimation at 298.15 K of $BiBr_3$(s) determined in this research. Knudsen–effusion: ○, orifice 1; □, orifice 2; △, orifice 3; ◇ orifice 4; ☆, orifice 5. Torsion–effusion: *, orifice 1; +, orifice 2; ×, orifice 3; ★, orifice 4. (——) is at 122.81 kJ mol^{-1}.

TABLE IX Equilibrium sublimation vapour pressures and condensation coefficients for $BiBr_3$(s) at selected temperatures derived from plots of inverse steady-state sublimation vapour pressure and effective orifice area

		Knudsen method			Torsion method		
		T (K)	P (Pa)	$\alpha_o \times 10^2$	T (K)	P (Pa)	$\alpha_o \times 10^2$
$BiBr_3$	α	405	0.455	3.321			
		410	0.723	2.361			
		415	1.133	1.823			
		420	1.757	1.469			
		425	2.693	1.221			
		430	4.101	1.038			
	β	435	5.369	2.649	455	15.374	
		440	7.911	2.368	460	21.350	
		445	11.556	2.140	465	29.314	
		450	16.739	1.950	470	40.147	
					475	54.636	
					480	73.857	

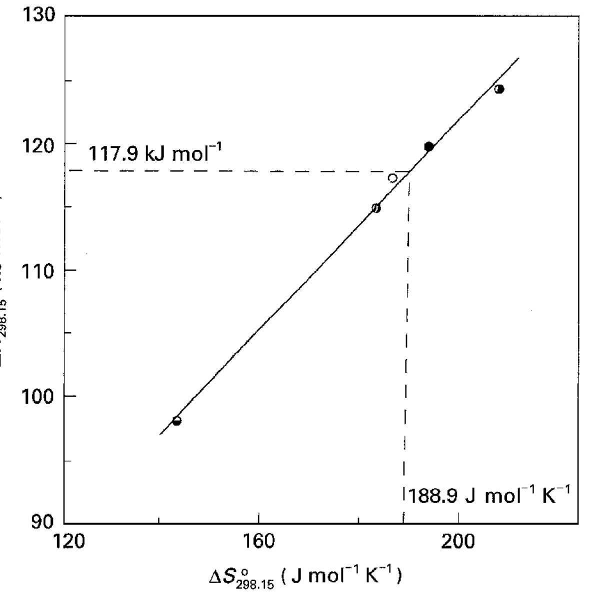

Figure 5 Correlation of molar enthalpy and entropy of sublimation at 298.15 K for $BiBr_3$(s). ○, Evnevich [1]; ⦶, Cubicciotti and Keneshea [2]; ◒, Imperatori *et al.* [3]; ◑, this study, Knudsen–effusion; ●, this study, torsion–effusion.

$\Delta_{sub}S^0_{298}$ in Fig. 5. The values are linearly correlated by the least-squares equation $\Delta_{sub}H^0_{298} = (37.5658 \pm 3.0477) + (0.4252 \pm 0.0166) \times \Delta_{sub}S^0_{298}$, (correlation coefficient = 0.998) where $\Delta_{sub}H^0_{298}$ is in kJ mol^{-1} and $\Delta_{sub}S^0_{298}$ is in J K^{-1}mol^{-1}.

Previous studies have indicated that values of $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$ generated from sets of $\log p$ versus T are frequently linearly correlated. McCreary and Thorn [15] suggest an explanation for this type of correlation in that the error or errors inadvertently encountered in vapour pressure determinations, are in the sense of $\Delta_{sub}H^0_T$ versus $\Delta_{sub}S^0_T$ systematic rather than random. Thus one can define a procedure whereby the apparent precision of the third-law procedure is retained but inconsistencies are removed by using information available in the analysis of $\log p$ versus T^{-1}. For $BiBr_3$, Pankratz [16] reports an assessed $\Delta_{sub}S^0_{298}$ of 188.9 J K^{-1}mol^{-1}. The corresponding $\Delta_{sub}H^0_{298}$ from the linear correlation of $\Delta_{sub}H^0_{298}$ and $\Delta_{sub}S^0_{298}$ is 117.89 ± 6.18 kJ mol^{-1} as shown in Fig. 5.

The third-law $\Delta_{sub}H^0_{298}$ obtained from the enthalpy–entropy correlation has been used to derive a sublimation pressure equation which is consistent with the thermal data. The resulting $p(T)$ equation recommended for the sublimation vapour pressure: α-$BiBr_3$; $\log p(\text{Pa}) = -C\alpha/T - 12.294 \log T + 5.79112 \times 10^{-3}\, T + 47.173$ with $C\alpha = (\Delta_{sub}H^0_{298} + 20.6168)/1.9146 \times 10$, and β-$BiBr_3$; $\log p(\text{Pa}) = -C\beta/T - 23.251 \log T + 1.0492 \times 10^{-2}\, T + 77.116$, with $C\beta = (\Delta_{sub}H^0_{298} + 46.2642)/1.9146 \times 10^{-2}$. In these equations T is in Kelvin and $\Delta_{sub}H^0_{298}$ in kJ mol^{-1}. This equation was used to compute the recommended line for $BiBr_3$(s) shown in Fig. 3.

Condensation coefficients α_c were obtained from the slopes and intercepts of isothermal linear plots of inverse steady-state sublimation vapour pressure and effective orifice area. From the slopes and intercepts of semi-logarithmic plots of $\log \alpha_c$ versus T^{-1}, an apparent activation sublimation enthalpy $\Delta_{cond}H^0_{420} = -66.86$ kJ mol^{-1} and entropy $\Delta_{cond}S^0_{420} = -212.70$ J K^{-1}mol^{-1} for condensation were obtained from the gravimetric effusion measurements. Corresponding values for vaporisation (relative to the solid) were $\Delta_{vap}H^0_{420} = 49.62$ kJ mol^{-1} and $\Delta_{vap}S^0_{420} = -55.20$ J K^{-1} mol^{-1}. It is to be recognized that values of α_c given in Table IX were obtained by assignment of the cross-sectional area (71.57 mm^2) of the effusion cell body as the effective area of the vaporising and condensing surface. The actual effective area may well be larger and hence α_c may actually be smaller. Apparent values of α_c and their temperature dependence are characteristic only of effusion systems where steady-state sublimation vapour pressures are independent of sample size. Under these conditions, extrapolation of steady-state pressures to obtain equilibrium values appears quite satisfactory.

References

1. E. V. EVNEVICH and V. A. SUKHODSKII, *Zh. Russ. Fiz. Khim. Obshchestva* **61** (1929) 1503.
2. D. CUBICCIOTTI and F. J. KENESHEA, *J. Phys. Chem.* **62** (1958) 999.
3. D. IMPERATORI, O. FERRO and V. PIACENTE, *J. Chem., Thermodyn.* **14** (1982) 461.
4. S. BLAIRS, A. J. SHELTON and R. UNSWORTH, *J. Sci. Instrum.* **38** (1961) 469.
5. W. C. DEMARCUS, *U.S. At. Energy Comm. K*-1302 (1957).
6. R. D. FREEMAN and J. G. EDWARDS, "The Characterization of High Temperature Vapors", edited by J. L. Margrare (New York, Wiley, 1967) Appendix C.
7. J. R. McCREARY and R. J. THORN, *J. Chem. Phys.* **48** (1967) 3290.
8. G. O. IWU and S. BLAIRS, *J. Chem. Thermodyn.* **2** (1970) 275.
9. D. CUBICCIOTTI and H. EDING, *J. Chem. Eng. Data* **12** (1967) 548.
10. J. H. KIM. PhD Thesis, University of New South Wales, Australia (1990).
11. S. J. YOSIM, L. D. RANSOM and R. A. SALLACH, *J. Phys. Chem.* **66** (1962) 28.
12. T. R. MANLEY and D. A. WILLIAMS, *Spectrochim. Acta* **21** (1965) 1773.
13. R. P. BEYER, U.S. Bureau of Mines, Information Circular 8871 (1982).
14. D. CUBICCIOTTI, *J. Phys. Chem.* **70** (1966) 2410.
15. J. R. McCREARY and R. J. THORN, *High Temp. Sci.* **3** (1971) 300.
16. L. B. PANKRATZ, U.S. Bureau of Mines Bulletin 674 (1984).

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