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Thermodynamic Properties of Bismuth Trifluoride from Vapour Pressure Measurements

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증기압 측정으로부터 BiF_3의 열역학적 계산

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ABSTRACT

Sublimation vapour pressures and sublimation enthalpy of anhydrous bismuth trifluoride have been measured by the continuous gravimetric Knudsen-effusion method from 639.7 to 782.8 K. Additional effusion measurements have also been made from 750.6 to 863.1 K by the torsion-effusion method. Based on a correlation of $\Delta_{sub}H^{o}_{298.15}$ and $\Delta_{sub}S^{o}_{298.15}$, a recommended P(T) equation has been obtained for $BiF_3(s)$;

$$\log P = -C/T + 5.2375\log T - 3.205\times10^{-3}T + 4.661\times10^{4}/T^{2} + 1.348$$

where P is in Pa, T in Kelvin, $\Delta_{sub}H^{o}_{298.15}$ in kJ mol^{-1} and $C=(\Delta_{sub}H^{o}_{298.15}-13.5149)/1.9146\times10^{-2}$. Condensation coefficients and their temperature dependence have been derived from the effusion measurements.

요 약

BiF_3의 승화압과 엔탈피를 639.7에서 782.8 K까지 Knudsen 유출법을 사용하여 측정하였고, 또한 750.6에서 863.1 K까지 Torsion 유출법에 의해 추가 실험을 하였다. 평형 승화압도 이 안정상태 데이타로부터 구하였다. $\Delta_{sub}H^{o}_{298.15}$와 $\Delta_{sub}S^{o}_{298.15}$의 상관관계를 이용하여, 추천할 수 있는 P(T)식을 $BiF_3(s)$에 대해 아래와 같이 구하였다

$$\log P = -C/T + 5.2375\log T - 3.205\times10^{-3}T + 4.661\times10^{4}/T^{2} + 1.348$$

여기서 P는 파스칼, T는 절대온도, $\Delta_{sub}H^{o}_{298.15}$의 단위는 kJ mol^{-1}이고, $C=(\Delta_{sub}H^{o}_{298.15}-13.5149)/1.9146\times10^{-2}$이다. 응축상수와 그것의 온도의존성도 위의 두 방법에 의한 실험으로부터 유도하였다.

1. Introduction

The need for accurately known thermodynamic data and structural information on metal halides is becoming increasingly important as a result of their increasing uses, especially in the field of materials, semiconductors, heat transfer media, reaction media for both electrochemical and chemical processes and as a fuel carrier in nuclear reactors. The physico-chemical properties of an increasing number of metal halides are being examined in order to assess their suitability for these applications.

Two sets of vapour pressure are reported in the literature of BiF_3. Cubicciotti[1] measured the vapour pressure using the transpiration method in the temperature ranges 756~853 K. The vapour pressure may be represented by the equation; $\log P(\mathrm{Pa}) = -9753/T + 9.60$. Standard sublimation enthalpy calculated from this equation is 186.73 kJ mol^{-1}. Also, Maria and coworkers[2)] determined the vapour pressure values on the temperature ranges 569~838 K ultilizing the Knudsen effusion-microcalorimetric technique. The data relative to the sublimation process are $\log P(\mathrm{Pa}) = -(9797 \pm 0.07)/T + (13.915 \pm 0.09)$ and sublimation enthalpy (201.154± 0.975) kJ mol^{-1}. The present study has been undertaken to re-examine the sublimation vapour pressures and enthalpy for BiF_3 using the continuous gravimetric Knudsen and torsion effusion techniques.

2. Experimental and Results

Samples of anhydrous BiF_3 by Johnson Matthey Ltd. of Puratronic grade (10 p.p.m. total metal impurities) were vaporized in this study. Effusion cells, based essentially on a design by Blairs et al.[3)] and fabricated with type-304 stainless steel, were filled inside a nitrogen dry box (moisture level ≤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.

Effusion orifice parameters, orifice Clausing Factors[3)] W_B and recoil force factors[1)] f used in the gravimetric and torsion effusion measurements were reported in the previous papers[6,7)]. And the base of both methods and experimental apparatus was also described.

2.1. Gravimetric Knudsen Effusion

Gravimetric Knudsen effusion system 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 g^{-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 vs. 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.

Steady-state Knudsen effusion vapour pressures for solid BiF_3 in the range 639.7 to 782.8 K are reported in Table 1 and are plotted in Fig. 1 for five different effective orifice areas.

2.2. Torsion Effusion

Moment arms of the torsion effusion cells were measured by cathetometer as (0.843± 0.001) cm. A null point torsion effusion apparatus employing a geared stepper motor and electronic driver was also used to measure vapour pressures. Each stepper motor pulse corresponded to a torsion angle of 0.05° and a deflection of (2.88± 0.09) mm was 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 (± 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[8)] 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 was sublimed clearly from the orifices.

Steady-state torsion effusion vapour pressures, measured in the range from 750.6 to 853.9 K are reported in Table 2 and are plotted in Fig. 2 for four different orifice areas. P(T) equations derived by least squares treatment of the steady-state vapour pressures for each orifice size are summarized in Table 3.

3. Discussion

Steady-state vapour pressures from both effusion techniques were found to be dependent on effective orifice area aW_B. Isothermal plots of inverse steady-state vapour pressure versus effective orifice were linear and were extrapolated to obtain inverse values

Table 1. Steady-State Vapour pressure P_K(Pa) and Third-Law Standard Molar Enthalpy $\Delta_{sub}H^{o}_{298.15}$ for BiF_3(s) Determined by Knudsen Effusion Method. W=Steady-State Effusion Rate (mg h^{-1}). (p^{o}=101325 Pa)

Orifice No.	T (K)	W (mg h^{-1})	P_K (Pa)	$\Delta_{sub}H^{o}_{298.15}$ (kJ mol^{-1})
1	727.1	0.38789	1.986077	206.75
	740.9	0.98218	5.034546	204.72
	744.6	1.12537	5.770165	204.85
	750.8	1.30090	6.673144	205.53
	756.3	1.54867	7.947186	205.86
2	697.9	0.45059	0.723620	204.75
	702.9	0.58012	0.934790	204.64
	707.4	0.73345	1.185462	204.49
	712.1	0.79890	1.295350	205.26
	716.6	1.06781	1.736550	204.74
	721.8	1.46963	2.398256	204.20
	727.5	1.82581	2.990607	204.38
	735.5	2.47785	4.079891	204.61
	741.7	2.85146	4.713639	205.33
	753.5	4.21052	7.012703	205.92
	758.9	4.97595	8.315849	206.23
	762.7	7.60108	12.732978	204.49
	770.5	9.03042	15.200508	205.31
	777.9	12.67227	21.426556	204.91
3	678.7	0.48253	0.330853	203.81
	686.1	0.63727	0.439191	204.30
	692.0	0.88029	0.609163	204.10
	702.9	0.97998	0.683210	206.47
	706.6	1.29154	0.902726	205.89
	719.0	1.47715	1.040954	208.43
	725.6	2.47540	1.752056	207.11
	728.4	2.59424	1.839582	207.58
	733.6	3.50388	2.493035	207.12
	734.6	5.17743	3.686030	204.99
	740.0	5.57624	3.983885	205.94
	742.9	6.25934	4.480058	205.95
	748.5	7.87253	5.655081	205.98
	752.1	8.51496	6.130295	206.39
	758.0	9.94658	7.187622	206.91
	763.7	11.74270	8.515606	207.28
	768.4	14.47802	10.559272	207.13
	773.4	17.69713	12.910604	207.07
	777.9	23.00292	16.827441	206.47
	782.8	26.47201	19.423641	206.77
4	697.4	1.24074	0.368996	208.53
	702.6	1.59061	0.474721	208.54
	720.8	3.23944	0.978653	209.32
	726.3	3.76600	1.141839	209.89
	738.5	6.73064	2.056924	209.61
	743.9	8.34514	2.559109	209.69
	748.0	9.70393	2.983594	209.83
	752.9	11.21188	3.457969	210.20
	758.0	15.38311	4.759635	209.52
	762.6	16.89314	5.241822	210.10
	766.6	21.71819	6.755617	209.50
	771.1	25.69587	8.014967	209.54
5	639.7	0.44294	0.062608	201.46
	644.8	0.61952	0.087899	201.16
	650.9	0.83190	0.118564	201.39
	661.5	1.20558	0.173146	202.43
	667.1	1.60641	0.231648	202.45
	670.6	2.11399	0.305602	201.93
	676.0	2.75463	0.399754	201.98
	681.4	3.47139	0.505692	202.19
	692.6	3.86998	0.568140	204.67
	700.9	4.48111	0.661626	206.13
	704.5	8.18894	1.212007	203.58
	707.6	8.80454	1.305826	203.98
	711.4	10.30583	1.532367	204.07
	717.4	14.86780	2.219537	203.49
	722.5	20.30099	3.040790	202.95
	727.3	24.71903	3.714281	203.02

of the equilibrium 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: $\log P_K(Pa) = -(10121 \pm 75)/T + (14.244 \pm 0.097)$ and $\log P_T(Pa) = -(9625 \pm 80)/T + (13.816 \pm 0.099)$. These equilibrium P(T) equations are shown with experimental points on Figs. 1 and 2 and with literature vapour pressures[1,2] for comparison in Fig. 3. Extrapolated Knudsen effusion equilibrium vapour pressures are in good agreement with those reported in references 1 and 2.

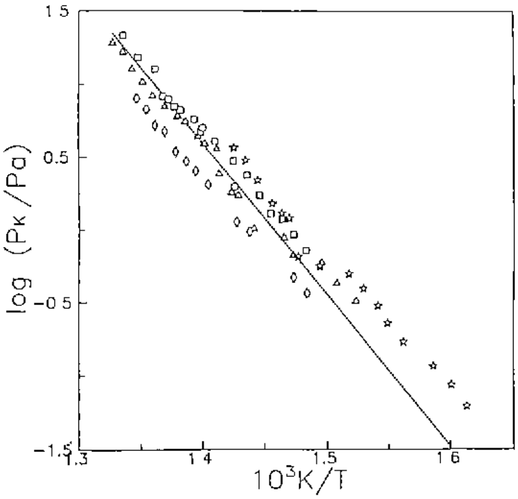

Fig. 1. Steady-state vapour pressures for BiF_3(s) measured by Knudsen effusion method.
○, orifice 1; □, orifice 2; △, orifice 3; ◆, orifice 4; ★, orifice 5; —, equilibrium line.

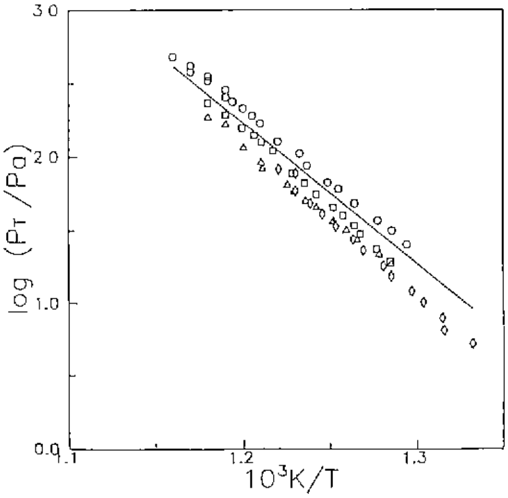

Fig. 2. Steady-state vapour pressures for BiF_3(s) measured by torsion effusion method.
○, orifice 1; □, orifice 2; △, orifice 3; ◆, orifice 4; —, equilibrium line.

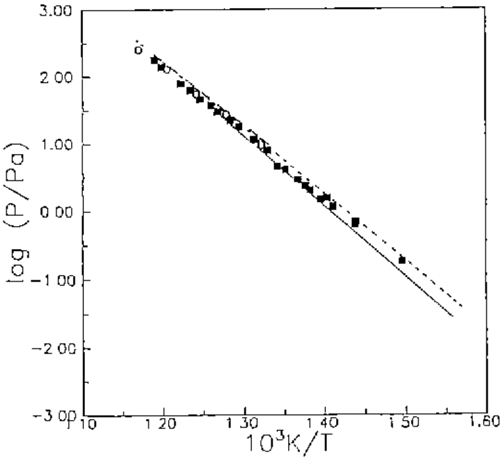

Fig. 3. Comparison of BiF_3 vapour pressures.
○, Cubicciotti[1]; ■, Maria and co-workers[2]; —, Knudsen effusion equilibrium line; ---, torsion effusion equilibrium line; ···, recommended P (T)

From literature value for BiF_3(s) vapour pressures, equations of form $\log P(Pa) = -A/T + B$ were derived and the coefficients A and B are given in Table 4. Second-law values of $\Delta_{sub}H^{o}_{298}$ and $\Delta_{sub}S^{o}_{298}$ also given in Table 6 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 BiF_3(s) and BiF_3(g). Polynomial expressions[1] C^{o}_{p} ($J\,mol^{-1}\,K^{-1}$) $= 38.97 + 123.17 \times 10^{-3}T + 8.95 \times 10^{5}T^{-2}$ and C^{o}_{p}($J\,mol^{-1}\,K^{-1}$) $= 82.51 + 0.46 \times 10^{-3}T - 8.90 \times 10^{5}T^{-2}$, for BiF_3(s) and BiF_3(g) respectively were employed in this research.

All the structural and spectroscopic quantities used in the thermodynamic calculations are presented in Table 5. Thermodynamic functions $\Delta(G^{o}_{T} - H^{o}_{298.15})/T$ for BiF_3(g) were computed for a rigid-rotator harmonic-oscillator ideal gas monomer and pyramidal C_{3v} symmetry.

Thermodynamic functions $\Delta[(G^{o}_{T} - H^{o}_{298.15})/T]$ and $S^{o}_{298.15}$ for BiF_3(s) were derived from $\Delta_{sub}S^{o}_{298.15} = (194.97 \pm 3.35)$ $J\,mol^{-1}\,K^{-1}$[1], and $S^{o}_{298.15} = 317.65\ J\,mol^{-1}\,K^{-1}$ for BiF_3(g) computed as outlined above and C^{o}_{p} ($J\,mol^{-1}\,K^{-1}$) $= 38.97 + 123.17 \times 10^{-3}T + 8.95 \times 10^{5}T^{-2}$ for BiF_3(s)[1]. Thermodynamic functions for BiF_3(s) at selected temperatures are presented in Table 5.

Third-law $\Delta_{sub}H^{o}_{298.15}$ at each effusion temperature are also reported in Tables 1 and 2 and shown in Fig. 4 for both effusion techniques. Individual $\Delta_{sub}H^{o}_{298}$ values obtained using effusion methods are independent of temperature and effective orifice area.

The average third-law $\Delta_{sub}H^{o}_{298.15}$, (206.38 ± 0.014) $kJ\,mol^{-1}$, shown in Fig. 4 together with its standard

Table 2. Steady-State Vapour Pressure P_T(Pa) and Third-Law Standard Molar Sublimation Enthalpy $\Delta_{sub}H^{\circ}_{298.15}$ for BiF_3(s) Determined by Torsion Effusion Method

Cell No.	T (K)	PT (Pa)	$\Delta_{sub}H^{\circ}_{298.15}$ (kJ mol^{-1})
1	772.8	25.547808	202.54
	778.0	31.741234	202.40
	782.9	37.181644	202.56
	791.2	48.435085	202.79
	796.9	60.625656	202.68
	800.8	67.373726	202.88
	808.7	87.806023	202.95
	811.6	105.806931	202.36
	820.1	128.469254	202.97
	826.8	170.815033	202.55
	830.0	192.919205	202.42
	833.5	216.516373	202.39
	837.6	239.540009	202.60
	839.8	259.387939	202.54
	843.2	286.717682	202.59
	848.3	329.199188	202.73
	851.2	358.017639	202.76
	853.9	381.401154	202.89
2	778.5	19.535908	205.66
	783.3	23.887911	205.54
	789.0	30.084953	205.42
	791.2	34.172871	205.11
	795.3	40.104599	205.03
	798.8	45.376152	205.03
	805.0	55.784843	205.13
	809.6	66.588478	205.01
	814.4	77.783432	205.09
	822.0	110.581863	204.44
	826.4	127.038094	204.48
	829.3	141.520020	204.40
	833.8	158.098022	204.66
3	778.2	19.103920	205.74
	782.3	22.163235	205.79
	790.3	27.769369	206.24
	794.2	32.283962	206.18
	798.8	37.233524	206.36
	805.0	46.258907	206.37
	809.1	51.132515	206.67
	813.8	58.916679	206.82
	816.2	65.829697	206.64
	826.0	84.734634	207.17
4	750.6	5.295873	206.93
	760.2	6.600476	208.01
	760.7	7.975427	206.95
	767.2	10.276388	206.97
	771.2	12.268122	206.84
	778.1	15.529016	207.06
	780.9	18.241421	206.70
	788.0	23.319967	206.83
	791.6	27.540911	206.62
	797.8	33.852264	206.76
	802.8	41.055187	206.66
	807.4	48.496510	206.63

Table 3. Coefficients with Standard Deviations of the Equation $\log P(Pa) = -A/T + B$ Derived from BiF_3 Steady-State Knudsen and Torsion Effusion Vapour Pressure Measurements Determined in the Temperature Range T_1 to T_2

Method	Orifice No.	T_1	T_2	Number of Points	A	B
		(K)				
Knudsen	1	727.1	756.3	5	11301± 1528	15.891± 2.054
	2	697.9	777.9	14	9684± 219	13.752± 0.298
	3	678.7	782.8	20	9243± 286	13.057± 0.568
	4	697.4	771.1	12	9683± 171	13.433± 0.340
	5	639.7	727.3	16	8911± 318	12.735± 0.464
Torsion	1	772.8	853.9	18	9765± 120	14.038± 0.149
	2	778.5	833.8	13	10740± 116	15.095± 0.144
	3	778.2	826.0	10	8784± 98	12.569± 0.123
	4	750.6	807.4	12	10540± 219	14.743± 0.281

Table 4. Summary of BiF_3(s) Vapour Pressures

T (K)	A	B	2nd law		3rd law
			$\Delta_{sub}H^\circ_{298.15}$ (kJ mol^{-1})	$\Delta_{sub}S^\circ_{298.15}$ (J mol^{-1} K^{-1})	$\Delta_{sub}H^\circ_{298.15}$ (kJ mol^{-1})
756.4-853.1[1)]	9657	13.731	193.194	194.452	205.28
	± 155	± 0.193	± 2.968	± 3.695	± 0.411
669 -838[2),(c)]	9845	13.979	193.957	195.133	204.89
	± 104	± 0.137	± 0.858	± 2.67	± 0.649
639.7-782.8[(a)]	10121	14.244	200.598	202.178	206.38
	± 75	± 0.097	± 1.436	± 0.019	± 0.014
750.6-837.6[(b)]	9625	13.816	192.870	196.476	206.28
	± 80	± 0.099	± 1.532	± 0.019	± 0.035

[a]Gravimetric Knudsen-effusion method, [b]Torsion-effusion method, [c]Knudsen effusion-Microcalorimetric method.

Table 5. Standard Molar Thermodynamic Functions for BiF_3(s) and BiF_3(g) at Selected Temperatures. υ/cm^{-1}, 505, 203, 425, 175; Geometric Constants:[1)] r(Bi-F)=0.236 nm; r(Bi-Bi)=0.285 nm; ∠F-Bi-F=100° (R=8.31451 J mol^{-1} K^{-1}; p°=101325 Pa: T′=298.15 K)

T (K)	C°_p (J mol^{-1} K^{-1})	$(H^\circ_T-H^\circ_{298.15})$ (kJ mol^{-1})	$\Delta(S^\circ_T-S^\circ_{298.15})$ (J mol^{-1} K^{-1})	$-\Delta[(G^\circ_T-H^\circ_{298.15})/T$ (J mol^{-1} K^{-1})
		solid[a]		
298.15	85.817	0	0	122.591
300	85.865	0.772	0.531	120.548
400	93.829	9.112	26.234	126.045
500	104.131	18.999	48.253	132.846
600	115.354	29.968	68.221	140.865
700	127.011	42.084	86.874	149.345
		gas		
298.15	73.644	0	0	322.548
300	73.740	0.136	0.456	322.550
400	77.440	7.714	22.232	325.494
500	79.316	15.560	39.730	331.159
600	80.427	23.552	54.298	337.594
700	81.120	31.631	66.752	344.112
800	81.580	39.768	77.616	350.454
900	81.901	47.943	87.244	356.522

[a]Derived using C°_p and $\Delta_{sub}S^\circ_{298}$ for BiF_3(s) from reference 1 and S°_{298}(g) calculated in this work[12)].

deviation, is based only on the Knudsen-effusion data and is comparable with $\Delta_{sub}H^\circ_{298.15}=201.3$ kJ mol^{-1} derived later from an enthalpy-entropy correlation. Average third-law $\Delta_{sub}H^\circ_{298.15}$ values derived from literature vapour pressures are also included in Table 4.

Uncertainty of temperature to which the coefficients A and B summarized in Table 4 are valid may be avoided by use of the modified sigma function method[10)]. $\Delta_{sub}H^\circ_{298.15}$ and $\Delta_{sub}S^\circ_{298.15}$ values were derived from the least squares slopes and intercepts of modified sigma function plots of the literature BiF_3 vapour pressure data sets[1,2)] as well as the present measurements. For these calculations, in addition to the free energy functions of gaseous and solid BiF_3 reported in Table 5, a value of $C^\circ_p=44.0$ J mol^{-1} K^{-1}[1)], and a molar enthalpy of fusion of (909.18± 12.55) kJ mol^{-1}[1)], were used

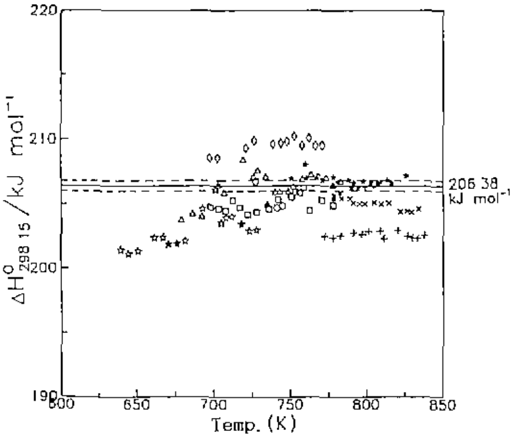

Fig. 4. Enthalpy of sublimation at 298.15 K of $BiF_3(s)$ determined in this research.
Knudsen effusion: ○, orifice 1; □, orifice 2; △, orifice 3; ◆, orifice 4; ★, orifice 5.
Torsion effusion: *, orifice 1; +, orifice 2; ×, orifice 3; ★, orifice 4.

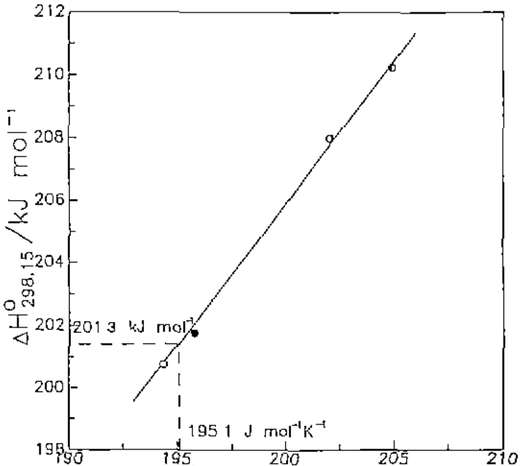

Fig. 5. Correlation of molar enthalpy and entropy of sublimation at 298.15 K for $BiF_3(s)$.
○, Cubicciotti[1]; ●, Maria and co-workers[2]; ◑, This study, Knudsen effusion; ◐, This study, torsion effusion.

to obtain thermal functions for liquid BiF_3. The resulting $\Delta_{sub}H^o_{298.15}$ and $\Delta_{sub}S^o_{298.15}$ are summarized in Table 6 and have been plotted as $\Delta_{sub}H^o_{298.15}$ vs. $\Delta_{sub}S^o_{298.15}$ in Fig. 5. The values are linearly correlated by the least-squares equation $\Delta_{sub}H^o_{298.15} = (20.1648 \pm 6.3924) + (0.9282 \pm 0.0320)\Delta_{sub}S^o_{298.15}$, (correlation coefficient $= 0.999$) *where* $\Delta_{sub}H^o_{298.15}$ *is in kJ mol*$^{-1}$ *and* $\Delta_{sub}S^o_{298.15}$ is in J mol^{-1} K^{-1}.

Previous studies have indicated that values of $\Delta_{sub}H^o_{298.15}$ and $\Delta_{sub}S^o_{298.15}$ generated from sets of log P(Pa) versus T^{-1} are frequently linearly correlated. McCreary and Thorn[11] suggest an explanation for this type of correlation in that the error or errors inadvertently encountered in vapour pressure determinations, are systematic in the plot of $\Delta_{sub}H^o_T$ versus $\Delta_{sub}S^o_T$ 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(Pa) versus T^{-1}. *For* BiF_3, *Pankratz*[12] *reports an assessed* $\Delta_{sub}S^o_{298.15}$ of 195.1 J mol^{-1} K^{-1}. The corresponding $\Delta_{sub}H^o_{298.15}$ from the linear correlation of $\Delta_{sub}H^o_{298.15}$ and $\Delta_{sub}S^o_{298.15}$ is 201.3 kJ mol^{-1} as shown in Fig. 5. The third-law $\Delta_{sub}H^o_{298.15}$ 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 vapour pressure of BiF_3 is: $\log P = -C/T + 5.2375 \log T - 3.205 \times 10^{-3}T + 4.661 \times 10^4/T^2 + 1.348$ with, $C = (\Delta_{sub}H^o_{298.15} - 13.5149)/1.9146 \times 10^{-2}$. In this equation p is in Pa, T in Kelvin and $\Delta_{sub}H^o_{298.15}$ in kJ mol^{-1}. This equation was used to compute the recommended line *for* $BiF_3(s)$ *shown on Fig. 3.*

Table 6. $\Delta_{sub}H^o_{298.15}$ and $\Delta_{sub}S^o_{298.15}$ for $BiF_3(s)$ Derived from The Modified Sigma Function Method[11]

$\Delta_{sub}H^o_{298.15}$ (kJ mol^{-1})	$\Delta_{sub}S^o_{298.15}$ (J mol^{-1} K^{-1})
200750 ± 2994^a	194.398 ± 3.730^a
201728 ± 2087^b	195.867 ± 2.762^b
208000 ± 121^c	202.110 ± 0.156^c
210218 ± 219^d	204.903 ± 0.272^d

[a]from reference 1; [b]from reference 2; [c]This study, Knudsen effusion; [d]This study, torsion effusion.

Condensation coefficients α_c were obtained from the slopes and intercepts of isothermal linear plots of inverse steady-state vapour pressure and effective orifice area. From the slopes and intercepts of semi-logarithmic plots of log α_c vs. T^{-1} (Fig. 6), an apparent activation sublimation enthalpy $\Delta_{cond}H^*_{780} = -129.52$ kJ mol^{-1}

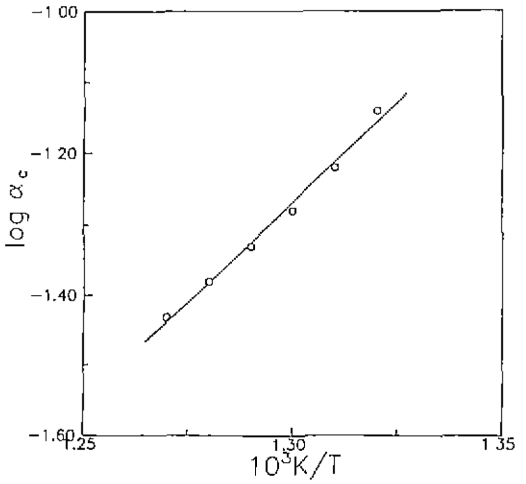

Fig. 6. log α_c versus 1/T (Gravimetric Knudsen method).

Table 7. Equlibrium Vapour Pressures and Condensation Coefficients for $BiF_3(s)$ at Selected Temperatures Derived From Plots of Inverse Steady-State Vapour Pressure and Effective Orifice Area. $\log P(Pa) = -A/T + B$ and aW_B for This Purpose Are Obtained from Tables 3 and 4 Respectively

Knudsen-method			Torsion-method		
T (K)	P_K (Pa)	$\alpha_c \times 10^2$	T (K)	P_T (Pa)	$\alpha_c \times 10^2$
760	8.434	7.227	795	51.028	2.429
765	10.314	6.080	800	60.661	2.500
770	12.577	5.252	805	71.943	2.570
775	15.295	4.627	810	85.068	2.645
780	18.550	4.137	815	100.505	2.722
785	22.439	3.744	820	118.398	2.801

and entropy $\Delta_{cond}S^*_{780} = -192.50\ J\ mol^{-1}\ K^{-1}$ for condensation were obtained from the gravimetric effusion measurements. Corresponding values for vaporisation (relative to the solid) were $\Delta_{vap}H^*_{780} = 58.13\ kJ\ mol^{-1}$ and $\Delta_{vap}S^*_{780} = -84.40\ J\ mol^{-1}\ K^{-1}$ at 780 K. It is to be recognized that values of α_c given in Table 7 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 vapour pressures are independent of sample size. Under these conditions, extrapolation of steady-state pressures to obtain equilibrium values appears quite satisfactory.

4. Conclusion

Sublimation pressures above anhydrous bismuth trifluoride have measured using the gravimetric Knudsen and torsion effusion methods. Steady state effusion pressures were found to depend on the effective orifice area of the effusion cells. Equilibrium sublimation pressures obtained from the steady state data have been assessed in the context of literature values.

Condensation coefficients and their temperature dependence have been derived from the steady state sublimation pressures and hence activation enthalpy and entropy changes for the vaporisation and condensation of bismuth trifluoride have been obtained. Standard sublimation enthalpy changes, $\Delta_{sub}H^o_{298.15}$, have been derived by both Second and Third Law methods, i.e., modified Sigma function and averaged enthalpy methods respectively. Standard sublimation entropy changes, $\Delta_{sub}S^o_{298.15}$, have also been derived by the modified function method.

The role of the correlation between $\Delta_{sub}H^o_{298.15}$, and $\Delta_{sub}S^o_{298.15}$, systematic errors between sets of log P vs. T^{-1} in vapour and sublimation pressure determinations has also been examined. A linear correlation has been demonstrated whereby the separation of systematic errors is indicated. This procedure recognizes and removes systematic errors in standard sublimation enthalpy changes derived from the slopes of log P vs. T^{-1} and defines a criterion whereby reliable standard sublimation enthalpy changes may be obtained. Using this approach, recommended P(T) equations for the sublimation pressures of anhydrous bismuth trifluoride have been derived.

NOMENCLATURE

$\Delta_{sub}H^o_{298.15}$: standard sublimation enthalpy changes, $kJ\ mol^{-1}$

$\Delta_{sub}S^o_{298.15}$: standard sublimation entropy changes, $J\ mol^{-1}\ K^{-1}$

$\Delta_{cond}H^*_T$: apparent activation enthalpy changes for condensation, kJ mol^{-1}

$\Delta_{cond}S^*_T$: apparent activation entropy changes for condensation, J $mol^{-1} K^{-1}$

$\Delta_{vap}H^*_T$: apparent activation enthalpy changes for vaporisation, kJ mol^{-1}

$\Delta_{vap}S^*_T$: apparent activation entropy changes for vaporisation, J $mol^{-1} K^{-1}$

$\Delta[(G^\circ_T - H^\circ_{298.15})/T]$: free energy functions, J $mol^{-1} K^{-1}$

W_D : Clausing factors

f : recoil force factors

k : torsion constant, N m^{-1} rad^{-1}

C°_p : heat capacity, J $mol^{-1} K^{-1}$

υ : fundamental frequency, cm^{-1}

r : bond distance, nm

R : gas constant, J $mol^{-1} K^{-1}$

log : natural logarithm

α_c : condensation coefficients

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