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The Sublimation Pressure and Standard Enthalpy of Sublimation of Bismuth Triiodide

Jun - Hak Kim

School of Materials Science and Engineering, University of New South Wales

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BiI_3에 대한 승화압과 승화 표준 엔탈피

김 준 학

호주 NSW 대학교 재료과학공학과

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요 약

BiI_3의 steady 상태 승화증기압을 430.0 에서 558.9 K 까지 Continuous Gravimetric Knudsen - Effusion 방법을 사용하여 측정하였고, 평형 승화압도 이 steady 상태 데이타로 부터 구하였다. 응축상수와 그것의 온도 의존도를 Effusion 측정으로 부터 유도하였다. BiI_3의 응축상수는 0.159 부터 0.048(475에서 500K)이었고, 응축에 대한 활성엔탈피와 엔트로피는 −93.38 kJmol^{-1}과 −212.70 JK^{-1}mol^{-1} 이었다. Second(modified sigma function)과 third(엔탈피 평균 방법)법으로 부터 엔탈피 변화는 각각 138.261±0.023과 138.74±0.002 kJmol^{-1} 이었고, modified sigma function에 의한 표준 승화 엔트로피 변화는 191.98±0.047 JK^{-1}mol^{-1}이었다. $\Delta^g_{cr}H^\circ_m$(298.15 K)와 $\Delta^g_{cr}S^\circ_m$(298.15 K)의 상관 계수로 부터 얻어진 믿을만한 표준 승화 엔탈피 변화는 136 8 kJmol^{-1}이며, BiI_3(cr)에 대하여 추천되는 p(T) 식은 $\lg(p/Pa) = -C/(T/K) + 5.0711\lg(T/K) - 2.838\times10^{-3}(T/K) - 7.758\times10^{3}(K/T)^2 + 1.4519$로 얻어지고, 여기서 p는 파스칼, T는 절대온도, $\Delta^g_{cr}H^\circ_m$ (298.15K) kJmol^{-1}이며, $C = (\Delta^g_{cr}H^\circ_m(298.15K) - 8.7358)/1.9146\times10^{-2}$이다.

ABSTRACT

Steady - state sublimation vapour pressures of anhydrous bismuth triiodide have been measured by the continuous gravimetric Knudsen - effusion method from 430.0 to 558.9 K and equilibrium sublimation pressures were obtained from the steady - state data. Condensation coefficients and their temperature dependence have been derived from the effusion measurement. Condensation coefficients ranged from 0.159 to 0.048(475 to 500 K), the activation enthalpy and entropy for condensation have been obtained as −93.38 kJmol^{-1} and −212.70 JK^{-1}mol^{-1}. The standard sublimation enthalpy changes derived by both second(modified sigma function) and third(average enthalpy method) law methods were 138.261±0.023, 138.74±0.002 kJmol^{-1} respectively. The standard sublimation entropy change derived by modified sigma function was 191.98±0.047 JK^{-1}mol^{-1}. The reliable standard sublimation enthalpy change based on a correlation of $\Delta^g_{cr}H^\circ_m$(298.15K) and $\Delta^g_{cr}S^\circ_m$(298.15K), a recommended p(T) equation has been obtained for BiI_3(cr) ; $\lg(p/Pa) = -C/(T/K) + 5.0711\lg(T/K) - 2.$

$838\times10^{-3}(T/K)-7.758\times10^{3}(K/T)^{2}+1.4519$ where p is in Pa, T in Kelvin, $\Delta^{g}_{cr}H^{\circ}_{m}(298.15K)$ in kJmol^{-1} and $C=(\Delta^{g}_{cr}H^{\circ}_{m}(298.15\ K)-8\ 7358)/1.9146\times10^{-2}$.

1. INTRODUCTION

Vapour and sublimation pressures of BiI_3 have been measured by several investigators[1-4]. Cubicciotti and Keneshea[1] determined vapour pressures of liquid BiI_3 by the transportation method from 683 to 738 K. Other investigators[2-4] have used the membrane manometer technique to obtain vapour and sublimation pressures for BiI_3 in the interval 618 to 811 K. Apart from values obtained by Karpenko and Zabrodskya[2] for BiI_3 (cr), vapour and sublimation pressures are generally in good agreement. Standard sublimation enthalpies at 298 15 K derived from these studies range from(126. 0±1.1) to (150.6±7.1) kJ · mol^{-1}. The present study has been undertaken to obtain new sublimation vapour pressures for BiI_3 using the continuous gravimetric Knudsen - effusion technique at substantially lower temperatures than previous investigations. This Knudsen effusion method is applicable in the pressure range 10^{-3} to 10^{2} Pa. In this technique the sample is enclosed in a chemically inert, non - volatile cell which carries a small effusion orifice.

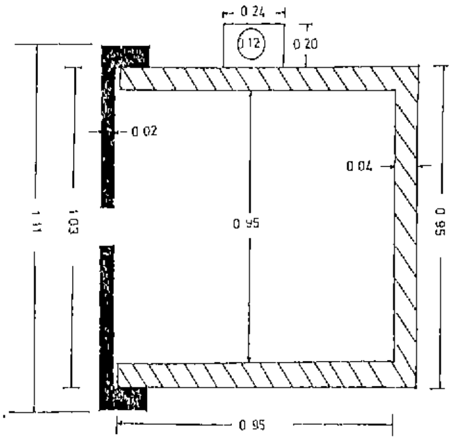
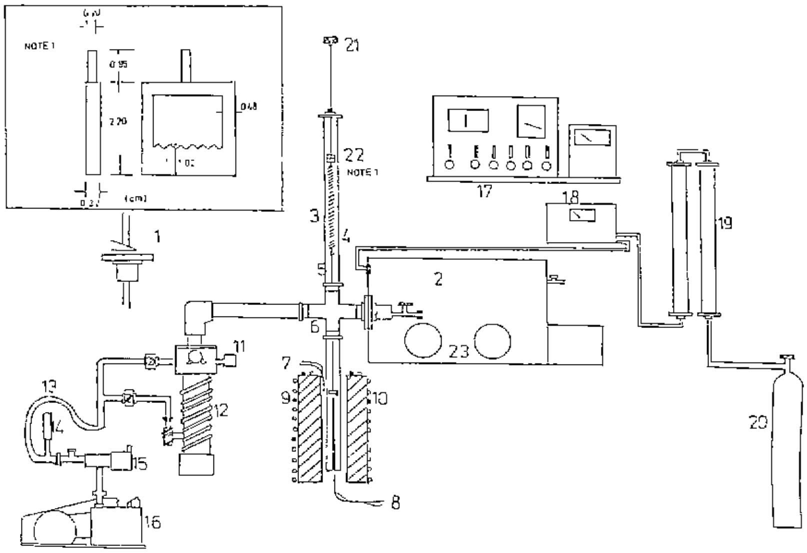


Fig.1 Gravimetric effusion cell(dimensions in mm).

2. EXPERIMENTAL AND RESULTS

Anhydrous BiI_3 of Puratronic grade (10p.p.m. total metal impurities, Johnson Matthey Ltd) was used in this study. Effusion cells(Fig.1), based essentially on a design by Blairs et al[5]. and fabricated from 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. 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 · g^{-1}) inside the effusion apparatus (Fig 2). 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 Actual cell temperatures were determined in separate dummy runs in which fine calibrated NiCr/NiAl thermocouple-s were inserted into the effusion cell bodies via the orifices and measured concurrently with the measurement thermocouples. All temperatures reported are in terms of IPTS−68.

Orifice areas, a and lengths L were measured using a Leitz Wetzlar metallograph at known magnification. Orifice Clausing Factors[6] W_B derived from their length to radius ratios L/r are reported in Table 1. The smallest effusion orifice No. 1, used in the



1. Cathetometer
2. Glove box
3. Ni−Span−C 902 alloy spring
4. Pyrex envelope
5. Tungsten wire
6. Yorkshire fitting
7. Control thermocouple
8. Measuring thermocouple
9. Effusion cell
10. Furnace
11. Penning gauge head
12. Diffusion pump
13. Flexible coupling
14. Thermistor gauge head
15. Magnetic valve
16. Rotary pump
17. Instrument panel
18. Moisture monitor
19. Drying tower
20. N_2 cylinder
21. Rotary shaft
22. Spring balance suspension
23. Glove port

Fig.2. Gravimetric Knudsen effusion apparatus.

Table 1. 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[6]
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] $aW_B/mm^2 = (1.2373\times10^{-5}\pm2.194\times10^{-7})\ (T/K) + (1.1506\times10^{-2}\pm1.064\times10^{-4})$

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.

Prior to measurements on BiI_3 and to correct for systematic errors on bismuth triiodide the sublimation vapour pressure of 99.999 mass per cent cadmium was measured in the interval 529.6 to 529 1K. Cadmium sublimation vapour pressures showed good agreement with the equation recommended by Iwu and Blairs[7]. Steady - state Knudsen - effusion sublimation vapour pressures for solid BiI_3 in the range 430.0 to 558.9K are reported in Table 2 and are plotted in Fig.3 for five different effective orifice areas p(T) equation derived by least - squares treatment of the steady - state sublimation vapour pressures for each orifice size are summarized in Table 3.

3. DISCUSSION

Steady - state sublimation vapour pressures were found to depend on effective orifice area aW_B.

Table 2. Steady-State Sublimation Vapour Pressure p/Pa and Third-law Standard Molar Sublimation Enthalpy $\Delta^{g}_{cr}H^{o}_{m}$(298.15 K) for BiI_3(cr) Determined by Knudsen-Effusion Method. W=Steady-State Effusion Rate ($mg \cdot h^{-1}$). (p^{o}=101325Pa)

Orifice No.	T/K	W/$mg \cdot h^{-1}$	P/Pa	$\Delta^{g}_{cr}H^{o}_{m}$(298.15K)/$kJ \cdot mol^{-1}$
1	478.8	0.31546	1.035421	138.11
	486.3	0.46084	1.516329	138.73
	489.9	0.64473	2.123865	138.39
	495.8	0.95552	3.153434	138.41
	501.0	1.31617	4.350575	138.53
	506.4	2.09020	6.920137	138.06
	511.4	2.70391	8.964662	138.29
	513.4	3.24584	10.767727	138.07
	518.8	4.18692	13.910268	138.39
	522.3	5.95132	19.791211	137.80
	527.0	7.68325	25.582574	137.91
	531.9	10.22821	34.099473	137.90
	537.1	13.32696	44.488484	138.04
	543.2	16.68402	55.778342	138.57
	548.3	24.00153	80.341200	138.21
	553.0	36.01466	120.683980	137.50
	558.9	48.77019	163.647270	137.55
2	451.0	0.12062	0.105471	138.67
	458.2	0.22433	0.197677	138.49
	463.6	0.38452	0.340759	138.02
	472.2	0.76001	0.679544	137.87
	480.5	1.09853	0.990598	138.80
	484.0	1.47171	1.331630	138.59
	489.3	1.94030	1.764908	138.96
	491.6	2.28410	2.082522	138.95
	495.8	3.12501	2.860858	138.82
	498.1	3.93003	3.606023	138.51
	502.8	4.93315	4.546859	138.83
	507.9	5.94861	5.509467	139.42
	512.1	8.74422	8.131037	138.91
	514.1	9.91072	9.233373	138.92
	519.0	14.26897	13.354074	138.63
	524.2	19.34304	18.189689	138.65
	530.1	26.75200	25.293798	138.76
	536.0	38.16704	36.279973	138.69
	542.4	61.55183	58.843156	138.14
3	446.6	0.22504	0.084726	138.14
	450.8	0.31352	0.118590	138.19
	456.5	0.40306	0.153387	138.96
	463.3	0.77322	0.296362	138.48
	470.5	1.08756	0.419965	139.27
	471.9	1.38417	0.535249	138.72
	477.8	1.85696	0.722434	139.27
	479.2	2.45730	0.957321	138.55
	484.9	3.38858	1.327677	138.86
	489.4	4.36240	1.716952	139.11
	494.3	5.34687	2.114466	139.63
	495.6	6.46247	2.558883	139.21
	498.4	7.96175	3.161326	139.14
	501.3	10.87959	4.331750	138.61
	506.4	13.68402	5.475336	139.05
	511.6	20.78758	8.358792	138.67
	517.8	26.93872	10.895276	139.19
	524.0	34.75352	14.135876	139.70
	529.2	48.28282	19.733055	139.61
	535.0	69.57991	28.586087	139.48
4	430.0	0.1487	0.023531	137.60
	436.4	0.2148	0.034237	138.27
	441.5	0.3077	0.049329	138.55
	446.6	0.4324	0.069701	138.87
	450.6	0.7731	0.125176	137.93
	456.3	1.0414	0.169653	138.51
	461.5	1.4339	0.234847	138.84
	469.3	2.3750	0.392208	139.17
	474.5	3.1567	0.524077	139.57
	477.6	3.9314	0.654773	139.60
	479.8	4.9261	0.822292	139.34
	484.5	6.7136	1.125881	139.41
	488.1	8.6514	1.456160	139.42
	489.5	10.8226	1.823997	138.88
	494.4	15.8050	2.676620	138.70
	500.1	22.7758	3.878734	138.76
	506.7	29.9984	5.140950	139.38
	511.8	45.6067	7.853927	138.98
	515.7	58.3924	10.092209	138.95
5	430.3	26.45	0.020732	138.12
	435.3	0.3749	0.029558	138.47
	441.1	0.6481	0.051436	138.28
	443.3	0.8574	0.095578	137.93
	446.4	1.1974	0.145708	137.62
	452.5	1.8133	0.215089	137.93
	457.0	2.6639	0.215089	137.81
	462.0	3.3586	0.272604	138.40
	465.1	4.1299	0.336319	138.53
	466.8	4.9390	0.402927	138.34
	472.5	6.3524	0.521264	139.00
	476.0	8.3738	0.689570	138.91
	478.0	8.8167	0.727580	139.30
	481.0	12.3159	1.019423	138.83
	483.8	14.5242	1.205567	138.95
	489.0	20.8539	1.739843	138.93
	494.2	30.3403	2.544324	138.85
	500.6	37.4295	3.158500	139.75

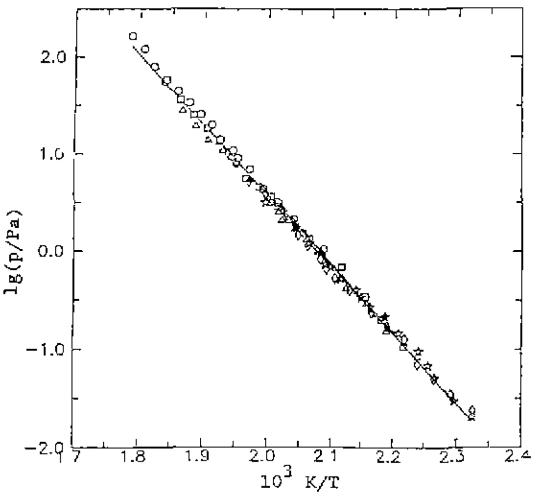


Fig.3. Steady - state sublimation vapour pressures for BiI_3(cr), measured by Knudsen - effusion method.
○, orifice 1 ; □, orifice 2 ; Δ, orivice 3 ; ◇, orifice 4 ; ☆, orivice 5 , ——equilibrium line

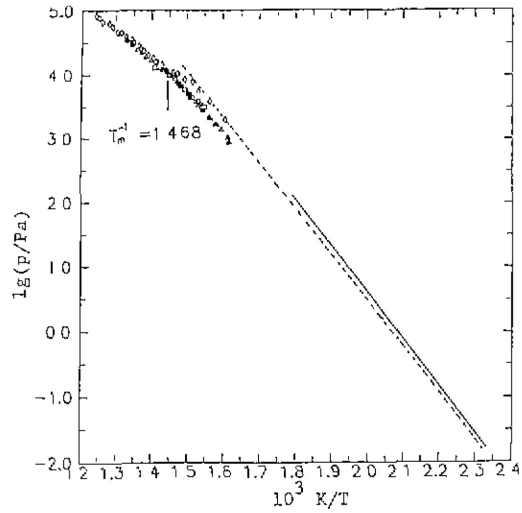


Fig.4. Comparison of BiI_3 vapour pressures ○, Cubicciotti and Keneshea ,[1] □, Karpenko and Zabrodskya ;[2] Δ, Kulieva et al. ;[3] ◇, Ryazantsev et al. ,[4] —, Knudsen - effusion equilibrium line ; - ---, recommended p(T) , T_m, melting temperature 681K.

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) equation was obtained from the Knudsen - effusion measurement : $\lg(p/Pa) = -(7195\pm1)(K/T) + (14.988\pm0.001)$. This equilibrium p(T) equation is shown with experimental points on Fig.3 and with literature vapour and sublimation pressures[1-4] for comparison in Fig.4. Extrapolated Knudsen - effusion equilibrium sublimation vapour pressures are in good agreement with those reported in reference 2 but are slightly higher than those in references 3−4. From literature values for

Table 3. Summary of BiI_3(cr) Sublimation Vapour Pressures.

$\frac{T_1-T_2}{K}$	A	B	Second-law $\frac{\Delta^g_{cr}H^o_m}{kJ\cdot mol^{-1}}$	Second-law $\frac{\Delta^g_{cr}S^o_m}{R}$	Third-law $\frac{\Delta^g_{cr}S^o_m}{kJ\cdot mol^{-1}}$
623 2−679.3[a,c]	5532 ±388	12.206 ±0.593	126.51 ±2.00	168.686 ±4.6	122.31 ±0 47
641.3−677 4[a,d]	5715 ±292	12.306 ±0.425	127 75 ±3 00	168.101 ±2.510	124.52 ±0.30
619.0−680.0[a,e]	6322 ±78	13 210 ±0 120	124.91 ±3 00	163.787 ±5 021	124 98 ±0 61
430.0−558.9[b]	7195 ±1	14 988 ±0.001	138.28 ±0 02	190.236 ±0.383	138 74 ±0.02

a Manometer Membrane method. b . Gravimetric Knudsen - effusion method.
c From reference 2. d From reference 3. e From reference 4

$BiI_3(cr)$ sublimation vapour pressures, equations of form $\lg(p/Pa)=-A/(T/K)+B$ were derived and gave the coefficients A and B summarized in Table 3. Second-law $\Delta^g_{cr}H^o_m(298.15\ K)$ and $\Delta^g_{cr}S^o_m(298.15\ K)$ also given in Table 3 were calculated by assuming the coefficients A and B apply at the mean temperatures of the various ranges together with the following $C^o_{p,m}(T)$ for $BiI_3(cr)$ and $BiI_3(g)$.

Polynomial expressions[8) $C^o_{p,m}\ (J\cdot K^{-1}\cdot mol^{-1})=39.96+110.4\times10^{-3}(T/K)+2.97\times10^5(K/T)^2$, and $C^o_{p,m}\ (J\cdot K^{-1}\cdot mol^{-1})=83.16-3.35\times10^{-3}(T/K)-0.94\times10^5(K/T)^2$, for $BiI_3(cr)$ and $BiI_3(g)$ respectively were employed in this research.

Third-law $\Delta^g_{cr}H^o_m(298.15\ K)$ at each effusion temperature are also reported in Table 2. Thermodynamic functions $\Phi^o_m(T, 298.15\ K)$ for $BiI_3(g)$ were computed for a rigid-rotator harmonic-oscillator ideal gas monomer and pyramidal C_{3v} symmetry. The molecular constants[8-9) and the calculated thermodynamic functions[13) are presented in Table 4. Thermodynamic functions $\Phi^o_m(T, 298.15\ K)$ and $S^o_m(198.15\ K)$ for $BiI_3(cr)$ were derived from $\Delta^g_{cr}S^o_m(298.15K)=(183.7\pm1.3)\ J\cdot K^{-1}\cdot mol^{-1}$[1,8) and $S^o_m(298.15K)=417.5\ J\cdot K^{-1}\cdot mol^{-1}$ for $BiI_3(g)$ computed as outlined above and $C^o_{p,m}(J\cdot K^{-1}\cdot mol^{-1})=39.96+110.4\times10^{-3}\ (T/K)+2.97\times10^5\ (K/T)^2$ for $BiI_3(cr)$[8). Thermodynamic functions for $BiI_3(cr)$ at selected temperatures are presented in Table 4.

Table 4. Standard Molar Thermodynamic Functions for $BiI_3(cr)$ and $BiI_3(g)$ at Selected Temperatures.
ν/cm^{-1}, 45, 63, 131, 129 ; Geometric Constants :[8,9) $r(Bi-I)=0.280$ nm ; $r(Bi-Bi)=0.285$ nm ; $(I-Bi-I)=100^\circ$ ($R=8.31451\ J\cdot K^{-1}\cdot mol^{-1}$; $p^\circ=101325$ Pa ; $T^\circ=298.15$ K).

$\frac{T}{K}$	$\frac{C^o_{p,m}}{R}$	$\frac{\Delta^T_{T^\circ} H^o_m}{R\cdot K}$	$\frac{\Delta^T_{T^\circ} S^o_m}{R}$	$\frac{\Phi^o_m}{R}$
		solid[a]		
298 15	9 167	0	0	28.120
400	10.340	992	2.854	28.493
450	10.958	1524	4.107	28 839
500	11 588	2088	5.294	29.238
550	12.227	2683	6 429	29 669
600	12 872	3311	7.520	30 122
650	13.521	3971	8.576	30.587
		gas		
298.15	9 888	0	0	50.213
400	9.938	1010	2.914	50 602
450	9.951	1057	4.085	50 949
500	9.960	2005	5.134	50.976
550	9.966	2503	6.084	51.745
600	9.972	3002	6.951	52.161
650	9 976	3500	7 749	52.577

a Derived using $C^o_{p,m}$ and $\Delta^g_{cr}S^o_m(298.15K)$ for $BiI_3(cr)$ from reference 8 and $S^o_m(BiI_3, g, 298.15K)$ calculated in this work[11).

Individual third-law $\Delta^g_{cr}H^o_m(298.15\ K)$ values shown in Fig.5 are independent of the temperatures and orifice areas. The average third-law $\Delta^g_{cr}H^o_m(298.15\ K)=(138.74\pm0.002)\ kJ\cdot mol^{-1}$ shown on Fig.5 together with its standard deviation is comparable with $\Delta^g_{cr}H^o_m(298.15K)=136.75\ kJ\cdot mol^{-1}$ derived later from an enthalpy-entropy correlation. Average third-law $\Delta^g_{cr}H^o_m(298.15\ K)$ values derived from literature sublimation vapour pressures are also included in Table 3.

Ambiguity of temperature to which the coefficients A and B summarized in Table 3 apply may be avoided by use of the modified sigma function method[11). Δ^g_{cr}

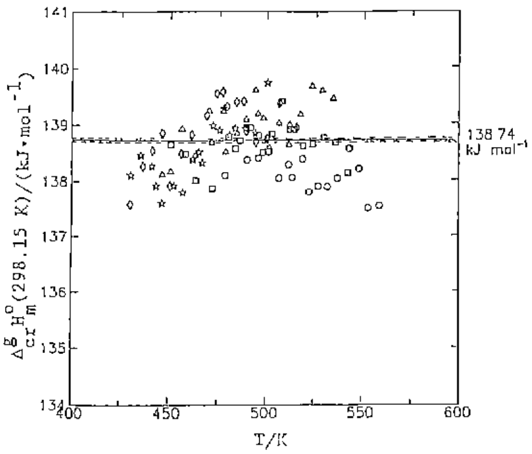


Fig 5. Enthalpy of sublimation at 298.15 K of BiI_3 (cr) determined in this research. Knudsen-effusion : ○, orifice 1 ; □, orifice 2 , Δ, orifice 3 , ◇, orifice 4 ; ☆, orifice 5.

H°_{m}(298.15 K) and $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15 K) values were derived from the least squares slopes and intercepts of modified sigma function plots for the various literature BiI_3 vapour pressure data sets[1-4] as well as the present measurements. For these calculations, in addition to the free energy functions of gaseous and solid BiI_3 reported in Table 4, a value of $C^{\circ}_{p,m}$=150.62 J·K^{-1}·mol^{-1}[1,8], and a molar enthalpy of fusion of (39.12±0.03) kJ·mol^{-1}, was used to obtain thermal functions for liquid BiI_3. The resulting $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15 K) and $\Delta^{g}_{cr}S^{\circ}_{m}$ (298 15K) are summarized in Table 5 and have been plotted as $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15 K) vs $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15 K) in Fig.6. The values are linearly correlated by the least-squares equation $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15 K)=8.3990+0.6991 $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15 K), (correlation coefficient=0.97) where $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15K) is in kJ·mol^{-1} and $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15 K) is in J·K^{-1}·mol^{-1}. Previous studies have indicated that values of $\Delta^{g}_{cr}H^{\circ}_{m}$ and $\Delta^{g}_{cr}S^{\circ}_{m}$(298 15 K) generated from sets of lg(p/Pa) versus T^{-1} are frequently linearly correlated.

McCreary and Thorn[12] 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 $\Delta^{g}_{cr}H^{\circ}_{m}$(T K) versus $\Delta^{g}_{cr}S^{\circ}_{m}$(T K) systematic rather than random. Thus one can define a procedure where by the apparent precision of the third-law procedure is retained but inconsistencies are removed by using information available in the analysis of lg(p/Pa) versus T^{-1}. For BiI_3, Pankratz[13] reports an assessed $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15K) of 183.6 J·K^{-1}·mol^{-1}. The corresponding $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15K) from the linear correlation of $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15 K) and $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15K) is 136.75 kJ·mol^{-1} as shown on Fig. 6

The third-law $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15K) 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 of BiI_3 is $\lg(p/Pa) = -C/(T/K) + 5.071\lg(T/K) - 2.838\times10^{-3}(T/K) - 7.758\times10^{3}(K/T)^{2} + 1.4519$ with, $C = (\Delta^{g}_{cr}H^{\circ}_{m}(298.15\ K) - 8.7358)/1.9146\times10^{-2}$. In this equation p is in Pa, T in Kelvin and $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15 K) in kJ·mol^{-1}. This equation was used to compute the recommended line for BiI_3(cr) shown on Fig.4

Condensation coefficients α_c were obtained from the slopes and intercepts of isothermal linear plots of inverse steady-state sublimation vapour pressure and

Table 5. $\Delta^{g}_{cr}H^{\circ}_{m}$(298 15 K) and $\Delta^{g}_{cr}S^{\circ}_{m}$(298.15 K) for BiI_3(cr) Derived from the Modified Sigma Function Method[13].

$\Delta^{g}_{cr}H^{\circ}_{m}$(298 15K) R·K	$\Delta^{g}_{cr}S^{\circ}_{m}$(298.15 K) R
130928±1425^{a}	174.068±1 969^{a}
125969±1091^{b}	167 661±1.535^{b}
150564±7129^{c}	201.521±10.620^{c}
148874±4568^{d}	198.307±6 716^{d}
138261± 23^{e}	191 980±0.047^{e}

a, from reference 1, b; from reference 2, c; from reference 3, d, from reference 4, e; This study, Knudsen-effusion --

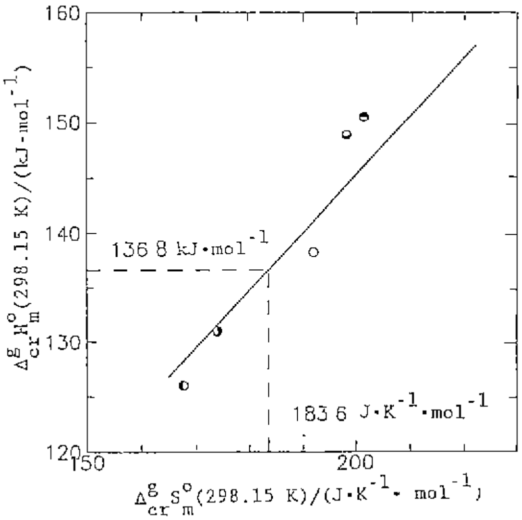


Fig.6. Correlation of molar enthalpy and entropy of sublimation at 298.15 K for BiI_3(cr). ◑, Cubicciotti and Keneshea, [1] ◐, Karpenko and Zabrodskya; [2] ◓, Kulieva et al., [3] ◒, Ryazantsev et al., [4] ○, This study, Knudsen-effusion.

Table 6. Equlibrium Sublimation Vapour Pressures and Condensation Coefficients for BiI_3(cr) at Selected Temperatures Derived from Plots of Inverse Steady-State Sublimation Vapour Pressure and Effective Orifice Area. $\lg(p/Pa) = -A(T/K) + B$ and aW_B for This Purpose are Obtained from Table 3.

$\frac{T}{K}$	$\frac{P}{Pa}$	$\alpha_c \times 10^2$	$\frac{T}{K}$	$\frac{P}{Pa}$	$\alpha_c \times 10^2$
475	0 691	15.930	490	2.011	6.630
480	0.994	10.830	495	2.830	5 543
485	1 419	8.218	500	3 956	4.767

effective orifice area. From the slopes and intercepts of semi-logarithmic plots of $\lg\alpha_c$ vs. $1/T$ ($\lg\alpha_c = -\Delta^{cr}_g H_m^*/RT + \Delta^{cr}_g S_m^*/R$), an apparent activation sublimation enthalpy $\Delta_g^{cr}H_m^* = -93.38$ kJ · mol^{-1} and entropy $\Delta_g^{cr}S_m^* = -212$ 70 J · K^{-1} · mol^{-1} for condensation were obtained from the gravimetric effusion measurements. Corresponding values for vaporisation (relative to the solid) were $\Delta^g_{cr}H_m^* = 32.30$ kJ · mol^{-1} and $\Delta^g_{cr}S_m^* = -91.30$ J · K^{-1} · mol^{-1} at 500 K It is to be recognized that values of α_c given in Table 6 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.

4. CONCLUSION

Sublimation vapour pressures above anhydrous bismuth triiodide have measured using the gravimetric Knudsen–effusion method. 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 condensation of bismuth triiodide has been obtained. Standard sublimation enthalpy changes, $\Delta^g_{cr}H^o_m$(298.15 K), have been derived by both second and third law methods, i.e., modified sigma function and averaged enthalpy methods respectively. Standard sublimation entropy changes, $\Delta^g_{cr}S^o_m$(298.15 K), have also been derived by the modified sigma function method.

The role of the correlation between $\Delta^g_{cr}H^o_m$(298.15 K) and $\Delta^g_{cr}S^o_m$(298.15 K) in systematic errors between sets of lgP vs. T^{-1} in vapour and sublimation pressure determinations has also been examined. A linear correlation has been demonstrated where by the separation of systematic errors is indicated. This procedure recognizes and removes systematic errors in standard sublimation enthalpy changes derived from the slopes of lgP vs. T^{-1} and defines a criterion whereby reliable standard sublimation enthalpy changes may be obtained. Using this approach, recommended p(T) equation for the sublimation pressures of anhydrous bismuth triidoide has been derived.

NOMENCLATURE

$\Delta^g_{cr}H^o_m$(298.15 K); standard sublimation enthalpy changes, kJ · mol^{-1}

$\Delta^g_{cr}S^o_m$(298.15 K)· standard sublimation Entropy changes, J · K^{-1} · mol^{-1}

α_c ; condensation coefficient

$C^o_{p,m}$; heat capacity, J · K^{-1}·mol^{-1}

Φ^o_m , free energy function, J · K^{-1}·mol^{-1}

$\Delta_g^{cr}H_m^*$; apparent activation sublimation enthalpy changes for condensation, kJ · mol^{-1}

$\Delta_g^{cr}S_m^*$; apparent activation sublimation entropy changes for condensation, J · K^{-1}·mol^{-1}

ν , fundamental frequency, cm^{-1}

r ; bond distance, nm

R ; gas constant, 8.31451 J · K^{-1}·mol^{-1}

lg ; natural logarithm

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