Sublimation Pressure and Standard Enthalpy of Bismuth Triiodide by Torsion-Effusion Method

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Torsion-Effusion 법에 의한 Bismuth Triiodide 의 승화압과 표준 엔탈피

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ABSTRACT

Steady-state sublimation vapour pressures of anhydrous bismuth triiodide have been measured by the torsion-effusion method from 488.8 to 570.5 K and equilibrium sublimation pressures were obtained from the steady-state data. The standard sublimation enthalpy changes derived by both second(modified sigma function) and third(average enthalpy method) law methods were 159.316 ± 0.055, 137.67 ± 1.43 kJ $\cdot$ mol^{-1} respectively The standard sublimation entropy change derived by modified sigma function was 232.88 ± 0.10 J $\cdot$ K^{-1} $\cdot$ mol^{-1}. The reliable standard sublimation enthalpy change based on a correlation of $\Delta_{cr}^{g} H_{m}^{o}$ (298.15 K) and $\Delta_{cr}^{g} S_{m}^{o}$ (298.15 K), a recommended p(T) equation has been obtained for BiI$_3$(cr) . lg(p/Pa) = $-(C \cdot K/T) + 5\,071\lg(T/K) - 2.838 \times 10^{-3}(T/K) - 7.758 \times 10^3(K/T)^2 + 1.4519$ where C = {$\Delta_{cr}^{g} H_{m}^{-}$ (298.15K)$/0\,019146$ kJ $\cdot$ mol^{-1}} $-456\,27$.

요 약

BiI$_3$의 steady 상태 승화증기압을 488.8에서 570.5 K 까지 torsion-effusion 방법을 사용하여 측정하였고, 평형 승화압도 이 steady 상태 데이타로 부터 구하였다. Second(modified sigma function)과 third(엔탈피 평균 방법) 법으로 부터 엔탈피 변화는 각각 159.316±0.055과 137.67±1.43 kJ $\cdot$ mol^{-1}이었고, modified sigma function 에 의한 표준 승화 엔트로피 변화는 232.88±0.10 J $\cdot$ K^{-1} $\cdot$ mol^{-1}이었다. $\Delta_{cr}^{g} H_{m}^{o}$(298.15 K) 와 $\Delta_{cr}^{g} S_{m}^{o}$(298.15 K)의 상관 제수로 부터 얻어진 믿을만한 표준 승화 엔탈피 변화는 136 6 kJ $\cdot$ mol^{-1}이며, BiI$_3$(cr)에 대하여 추천되는 p(T)식은 lg(p/Pa) = $-(C \cdot K/T) + 5\,071 \lg(T/K) - 2.838 \times 10^{-3}(T/K) - 7.758 \times 10^3(K/T)^2 + 1\,4519$로 얻어지고, 여기서 C = {$\Delta_{cr}^{g}$ H$_{m}^{o}$(298.15 K)$/0.019146$ kJ $\cdot$ mol^{-1}} -456.27이다.

1. INTRODUCTION

The need for accurately known thermodynamic data on metal halides is becoming increasingly important as a result of their increasing uses, especially in the field of materials. Areas of application include their use as solid electrolytes, 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.

Sublimation pressures of metal halides may be determined using the continuous gravimetric Knudesen- and torsion-effusion methods, in which the rates at which a halide evaporates in vacua through effusion orifices of different sizes are measured. One of the most convenient ways of determining these rates is by measurement of the contraction of a suitably sensitive spring from which an effusion cell containing the sample is suspended. Such a technique has been described previously[1]. In the torsion-effusion method of measurement, the recoil force of vapour molecules effusing from the effusion cell orifices is measured from the resulting twist of a suitably sensitive torsion wire. If these effusion rates are to be correctly related to equilibrium or saturated vapour pressures, then the influence of the effusion orifice and its departure from an ideal orifice must be considered. In order to obtain sublimation pressure data of significance, measurements should be made using effusion cells of varying orifice area to vaporisation area ratio, and Clausing or recoil force factors must be used to correct for the finite length of effusion orifices.

Vapour and sublimation pressures of BiI_3 were repoted by continuous gravimetric Knudsen-effusion method in the temperature ranges $430.0-558.9$ K[1]. The present additional effusion measurements has also been undertaken to obtain sublimation vapour pressures for BiI_3 using the torsion-effusion method in
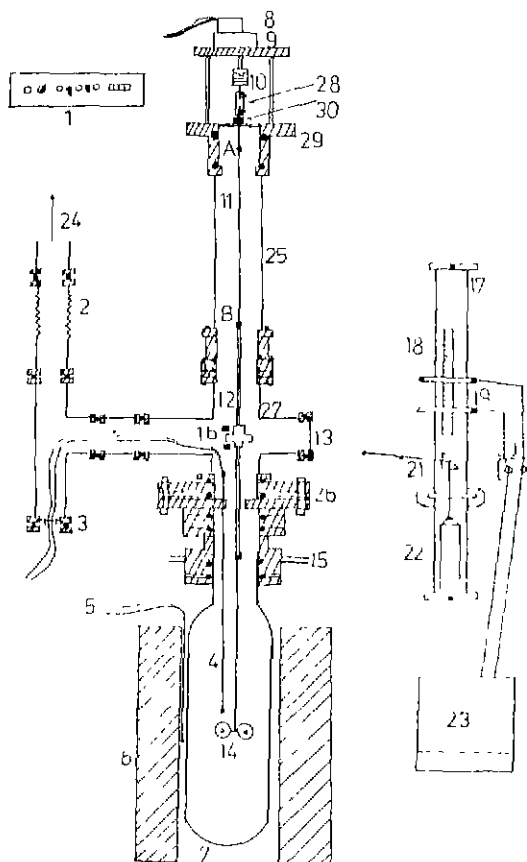
1	Stepper motor IC driver	16.	Alcomax damping magnet
2.	Bellows	17.	Optical bench
3	Instrumentation feedthrough	18.	Graduated scale
4.	Measuring thermocouple	19.	Laser switch
5	Control thermocouple	20.	Game port interface
6	Furnace	21	90° prism
7.	Pyrex tube	22.	Laser
8	Stepper motor	23	Apple IIe computer
9.	Gear reduction unit	24.	to vacuum pumps
10.	Oldham coupling	25.	Stainless steel envelope
11.	Tungsten wire	26.	Compression Coupling
12.	Torsion pendulum assembly	27.	Six-way cross
13.	Viewport	28.	Cylindrical sleeve
14.	Cell holder	29.	Flanged union
15.	Cooling water	30.	Rotary shaft seal

Fig.1. Torsion effusion apparatus

the temperature ranges of 488.8 to 570.5 K, described the method and compared with the previous continuous gravimetric Knudsen-effusion technique at substantially y lower temperatures than previous investigations[2-5].

2. EXPERIMENTAL AND RESULTS

The torsion-effusion apparatus used in this study is shown schematically in Fig.1. The apparatus was fabricated chiefly from proprietary stainless steel, ultra high vacuum fittings(Vacuum Generators Ltd., FC series). The upper section of the vacuum envelope consisted of a type-304 stainless steel tube, and carried an o-ring sealed flanged union which was machined flat to provide a seating surface for the brass torsion head. The lower part of the stainless steel tube vacuum envelope attaches to a six-way cross via an o-ring sealed union allowing other lengths of stainless steel tubing to be substituted, so that the length of the torsion wire could be varied.

A stepper motor (North American Philips Airpax, type-K82801-p2) and gear reduction unit were mounted on the torsion head via four support rods. The lower section of the vacuum envelope comprised a closed-ended pyrex tube, 55cm long and 6cm in diameter attached to the lower port of the six-way cross via o-ring sealed compression and piston seals. A zero-length, optically flat view port was sealed via an annealed copper gasket to the front port of the six-way cross. Flange mounted and copper gasket sealed suspension arrest and magnetic damping components attach to lateral ports of the six-way cross. The rear port of the six-way cross connects to the vacuum pumps and instrumentation feedthrough.

The torsion pendulum assembly, shown in Fig.2 was suspended from a fine tungsten wire of length 42.5 cm and diameter 0.005 cm, using proprietary minature pin chucks A and B. Each end of the tungsten wire was sealed into a short length of hypodermic needle (length 15 mm, inside diameter 0.5 mm and outside diameter 2.4 mm) using an epoxy resin, to facilitate gripping of

the wire by the pin chucks. Pin chuck A was attached to a rotary shaft seal and pin chuck B to an aluminium rod. The aluminium rod has length 38.1 cm and diameter 3.2 mm and carries a concentric, horizontal, collared duralumin disk, 2.86 cm in diameter and 0.24 cm thick, at a point 9.5 cm from the upper end. The collar has flats machined on it and the disk was positioned in the gap between the poles of a horse shoe -shaped Alcomax magnet. Eddy currents induced in the disk damp extraneous oscillations.

The Alcomax magnet could be located in either an active position for damping or withdrawn to an inactive position using a rotary shaft seal when measuring the suspension's torsion constant. Front
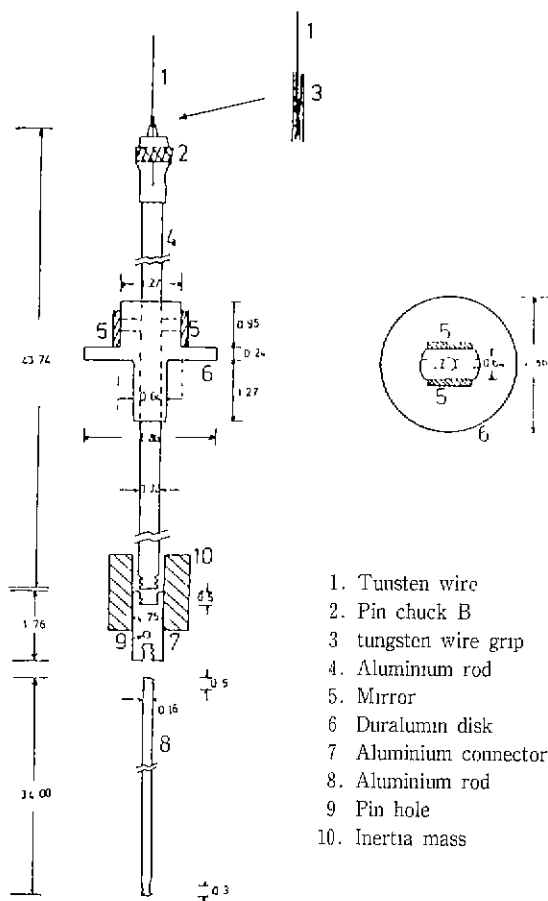

1. Tungsten wire
2. Pin chuck B
3. tungsten wire grip
4. Aluminium rod
5. Mirror
6. Duralumin disk
7. Aluminium connector
8. Aluminium rod
9. Pin hole
10. Inertia mass

Fig.2. Torsion pendulum assembly (dimensions in cm).

-surfaced plane mirrors, 1 cm in diameter and 2 mm in thickness(Spindle Hoyer, Crown glass, flatness 1/4λ) were bonded to the collar flats using an epoxy resin. One mirror was positioned nominally parallel to the system view port. The lower end of the aluminium rod was screwed into an aluminum connector. A second aluminium rod threaded at both ends, having length and diameter of 24 cm and 0.16 cm respectively was also attached to the aluminium connector. The torsion cell holder was attached to the lower end of the second aluminium rod

Effusion cells, based essentially on a design by Blairs et al.[6] and fabricated from type-304 stainless steel, were filled inside a nitrogen dry box(mole fraction of $H_2O \leq 2 \times 10^{-5}$). 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.

Dynamic vacua better than 1.33×10^{-4} 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 IPTS-68.

Orifice areas, a and lengths L were measured using a Leitz Wetzlar metallograph at known magnification. Orifice recoil force factors[7] 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 torsion-effusion measurements are reported in Table 1

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

Table 1. 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[7].

Cell	a_1 (mm²)	a_2 (mm²)	r_1 (mm)	r_2 (mm)	L_1 (mm)	L_2 (mm)	f_1	f_2
1	0.1717	0.1751	0.2336	0.2359	0.3450	0.2813	0.6564	0.7018
2	0.2301	0.2400	0.2706	0.2762	0.2771	0.3616	0.7288	0.6832
3	0.4038	0.1036	0.3585	0.3584	0.3535	0.3267	0.7357	0.7520
4	0.7928	0.7807	0.5023	0.4985	0.3388	0.3226	0.8066	0.8133

Table 2. Steady-State Sublimation Vapour Pressures and Third-Law Standard Molar Sublimation Enthalpies $\Delta_{cr}^g H_m^o$(298.15 K) for BiI_3(cr) Determined by the Torsion-Effusion Method

T (K)	P (Pa)	$\Delta_{cr}^g H_m^o$ (298.15 K) (kJ·mol⁻¹)	T (K)	P (Pa)	$\Delta_{cr}^g H_m^o$ (298 15 K) (kJ·mol⁻¹)
Orifice no 1
505.9	6.138275	135.72	543.9	49.344494	136.60
511.8	9.121808	135.65	550.6	68.664703	136.79
524.5	15.473855	136.72	555.3	87.826599	136.84
529.1	20.089701	136.79	562.4	131.774048	136.71
533.4	25.639906	136.83	568.1	179.356720	136.63
539.4	41.064339	136.30	570.5	198.609268	136.75
Orifice no 2
512.4	10.239496	135.32	543.6	51.583893	136.33
515.9	11.816971	135.62	550.2	72.949234	136.41
522.4	15.950344	136.06	556.7	102.429092	136.49
530.1	23.332393	136.39	559.5	127.925270	136.15
537.0	35.203094	136.36	562.3	150.401474	136.08
538.2	39.473164	136.17	566.2	172.451721	136.37
Orifice no 3
516.9	5.008388	139.30	544.9	33.182999	138.61
523.7	8.960714	138.86	549.8	45.379208	138.44
527.0	10.872197	138.89	553.7	57.714291	138.33
533.9	16.222116	138.96	555.8	65.708794	138.27
539.6	24.088722	138.70	560.0	72.296577	138.26
Orifice no.4
488.8	1.451175	136.90	526.0	8.832179	139.53
496.1	1.952460	137.72	530.9	11.836615	139.55
501.0	2.359196	138.31	536.6	15.905175	139.73
507.7	3.152207	138.96	541.9	21.431627	139.78
514.0	4.421371	139.24	549.0	31.510596	139.86
519.7	6.098821	139.41	554.6	41.234280	140.08

sublimation vapour pressures. Each stepper motor pulse corresponded to a torsion angle of 0.00028π and a deflection of (2.88 ± 0.09) mm as measured using an optical lever and a (He-Ne) laser. The torsion constant $k = (2.1504\pm0.1486)\times10^{-7}$ N·m·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

Fig.3. Steady-state sublimation vapour pressures for BiI$_3$(cr) measured by torsion-effusion method. $\bigcirc$, orifice 1 ; $\square$, orifice 2 ; $\triangle$, orifice 3 ; $\diamondsuit$, orifice 4 . —— equilibrium line.

Table 3. Coefficients with Standard Deviations of the Equation lg(p/Pa) $= -(A \cdot K/T) + B$ Derived from BiI$_3$ Steady-State Torsion-Effusion Sublimation Vapour Pressure Measurements Determined in the Temperature Range T$_1$ to T$_2$

Orifice No	T$_1$ (K)	T$_2$ (K)	Number of Points	A	B
1	505 0	570 5	12	6806±133	14 209±0 246
2	512 4	566 2	12	6805±128	14.245±0 237
3	516 9	560 0	10	8047±90	16 292±0 167
4	488 8	554 6	12	6177±166	12.715±0 319

precision timer for this purpose(±0.0001 s) The design of the torsion-effusion apparatus precluded direct mounting of loaded effusion cells form 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 sublimed from and cleared the orifices.

Anhydrous BiI$_3$ of Puratronic grade (10^{-5} total mass metallic fraction of impurities, Johnson Matthey Ltd.) was used in this study Prior to measurements on BiI$_3$, the sublimation vapour pressure of 99 999 mass percent cadmium was measured by this effusion method in the interval 529 6 to 592.1 K. Cadmium sublimation vapour pressures showed good agreement with the equation recommended by Iwu and Blairs[9].

The basis of the torsion method and the experimental apparatus have been described above. After selection of a new effusion temperature the deflected beam was returned to the null position using the stepper motor and the extra pulses noted. By this method, the sublimation vapour pressures were calculated from the deflection angles of the cell by use of this equation,

$$P = 2k\theta/(a_1f_1L_1 + a_2f_2L_2) \cdots\cdots(1)$$

where k is the torsion constant of the tungsten fiber.

Steady-state torsion effusion sublimation vapour pressures, measured in the range from 488.8 to 583. 1 K are reported in Table 2 and are plotted in Fig.3 for four different orifice areas. p(T) equations derived by least-squares treatment of the steasy-state sublimation vapour pressures for each orifice size are summarized in Table 3.

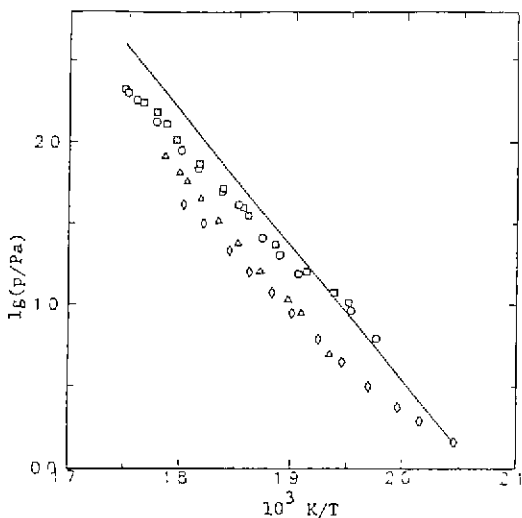## 3. DISCUSSION

Steady-state sublimation vapour pressures from

this effusion technique were found to depend on effective orifice area. 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 torsion-effusion measurement : $\lg(p/Pa) = -(8255\pm35)(K/T) + (17.044\pm0.065)$. This equilibrium p(T) equation is shown with experimental points on Fig.3 and with literature vapour and sublimation pressures[1-5] for comparison in Fig.4.

Extrapolated equilibrium sublimation vapour pressures are in good agreement with the privious Knudsen-*effusion measurents and are slightly higher than those* in references 2-5

Linear least-square treatments of $BiI_3(cr)$ sublimation pressures were represented by

$$\lg(p/Pa) = -(A \cdot K/T) - B \quad \cdots\cdots(2)$$

and gave the coefficients A and B summarized in Table 4. Second-law $\Delta_{cr}^g H_m^0(298.15\,K)$ and $\Delta_{cr}^g S_m^0$ (298.15 K) also given in Table 4 were calculated by assuming the coefficients A and B apply at the mean temperatures of the various ranges together with the following $C_{p,m}^0$ (T) for $BiI_3(cr)$ and $BiI_3(g)$. Polynomial expressions[10] $C_{p,m}^0$ $(J \cdot K^{-1} \cdot mol^{-1}) = 39.96 + 110.4\times10^{-3}$ (T/K) $+2.97\times10^5$ (K/T)^2, and $C_{p,m}^0$ $(J \cdot K^{-1} \cdot mol^{-1}) = 83.16 - 3.35\times10^{-3}(T/K) - 0.94\times10^5$ (K/T)^2, for BiI_3 (cr) and BiI_3 (g) respectively were employed in this study.

Third-law $\Delta_{cr}^g H_m^0(298\,15\,K)$ values at each effusion temperature are also calculated from torsion-effusion sublimation vapour pressure and thermodynamic functions, $\Phi_m^0 + \Delta_0^{298\,15K} H_m^0/T$ for $BiI_3(cr)$ and $BiI_3(g)$.

$$\Phi_m^0 + \Delta_0^{298\,15K}\,H_m^0/T$$
$$= -[G_m^0(T) - H_m^0(298\,15\,K)]/T \quad \cdots\cdots(3)$$

Fig.4. Comparison of BiI_3 vapour pressures. ○, Cubicciotti and Keneshea ; [2] ◇, Karpenko and Zabrodskya ; [3] □, Kulieva et al. ; [4] △, Ryazantsev et al. ; [5] ——, Knudsen-effusion equilibrium line , [1] ----, torsion-effusion equilibrium line ; ·····, recommended p(T) ; T_m, melting temperature 681 K

Table 4. Summary of $BiI_3(cr)$ Sublimation Vapour Pressures.

T_1 (K) T_2 (K)	A	B	2nd-law $\Delta_{cr}^g H_m^0$ $(kJ \cdot mol^{-1})$	2nd-law $\Delta_{cr}^g S_m^0$ (R)	Third-law $\Delta_{cr}^g H_m^0$ $(kJ \cdot mol^{-1})$
623 2-679.3[a,d]	5532 ±388	12 206 ±0.593	126.51 ±2 00	168.686 ±4.6	122 31 ±0.47
641.3-677.4[a,e]	5715 ±292	12.306 ±0 425	127.75 ±3 00	168 101 ±2.510	124.52 ±0 30
619 0-680.0[a,f]	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 54
488.8-570.5[c]	8255 ±35	17.044 ±0.065	159.36 ±0 67	228.032 ±7 161	137.67 ±1 43

a   Manometer Membrane method.
b : Gravimetric Knudsen-effusion method. from reference 1.
c   Torsion-effusion method.
d   From reference 3.
e   From reference 4
f   From reference 5

Thus, $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K})$

$$= -RT1g(p/Pa) - T\Delta_{cr}^{g}(\Phi_{m}^{o} + \Delta_{0}^{298.15K} H_{m}^{o}/T) \cdots\cdots (4)$$

Thermodynamic function, $(\Phi_{m}^{o} + \Delta_{0}^{298.15K} H_{m}^{o}/T)$ for $BiI_{3}(g)$ were computed for a rigid-rotator harmonic-oscillator ideal gas monomer and pyramidal C_{3v} symmetry using the modified Beyer's computer program[12] to be suitable for the experimental condition of this study. The molecular constants[10-11] and the calculated thermodynamic functions are presented in Table 5.

Thermodynamic function, $(\Phi_{m}^{o} + \Delta_{0}^{298.15K} H_{m}^{o}/T)$ and $S_{m}^{o}(298.15 \text{ K})$ for $BiI_{3}(cr)$ were derived from $\Delta_{cl}^{T} S_{m}^{o}$ $(298.15 \text{ K}) = (183.7 \pm 1.3)$ J·K^{-1}·mol$^{-1,12}$ and S_{11}^{o}

Table 5. Standard Molar Thermodynamic Functions for $BiI_{3}(cr)$ and $BiI_{3}(g)$ at Selected Temperatures. ν/cm^{-1}, 45, 63, 131, 129, Geometric Constants.[10-11] $r(Bi-I) = 0.280$ nm ; $r(Bi-Bi) = 0.285$ nm, $(1-Bi-1) = 100°$ $(R = 8.31451$ J·K^{-1}·mol^{-1} ; $p^{o} = 101325$ Pa ; $T' = 298.15$ K).

T (K)	$C_{p,m}^{o}$ (R)	$\Delta_{T'}^{1} H_{m}^{o}$ (R·K)	$\Delta_{T'}^{T} S_{m}^{o}$ (R)	$\Phi_{m}^{o} - \Delta_{0}^{1'} H_{m}^{o}/T$ (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	1507	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 $\Delta_{cl}^{g} S_{m}^{o}(298.15 \text{ K})$ for BiI_{3} cr) from reference 10 and $S_{m}^{o}(BiI_{3}, g, 298.15 \text{ K})$ calculated in this work [13]

$(298.15 \text{ K}) = 417.5$ J·K^{-1}·mol^{-1} for $BiI_{3}(g)$ computed as outlined above and $C_{p,m}^{o}(\text{J·K}^{-1}\cdot\text{mol}^{-1}) = 39.96 + 110.4 \times 10^{-3}(T/K) + 2.97 \times 10^{5}(K/T)^{2}$ for $BiI_{3}(cr)$[10]. Thermodynamic functions for BiI_{3} (cr) at selected temperatures are presented in Table 5. Third-law $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K})$ values obtained in this work are shown in Fig.5. Individual $\Delta_{cr}^{g} H_{m}^{o}(298.15K)$ values obtained from torsion-effusion measurement show some temperature and effective orifice dependence. The average third-law $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K}) = (138.74 \pm 0.54)$ kJ·mol^{-1} shown on Fig.5 together with its standard deviation is based only on the previous Knudsen-effusion results and is comparable with the average value of (137.67 ± 0.37) kJ·mol^{-1} in this study and (136.60 ± 29.39) kJ·mol^{-1} derived later from an enthalpy-entropy correlation. Average third-law $\Delta_{cr}^{g} H_{m}^{o}(298.15 \text{ K})$ values derived from literature sublimation vapour pressures are also included in Table 4.

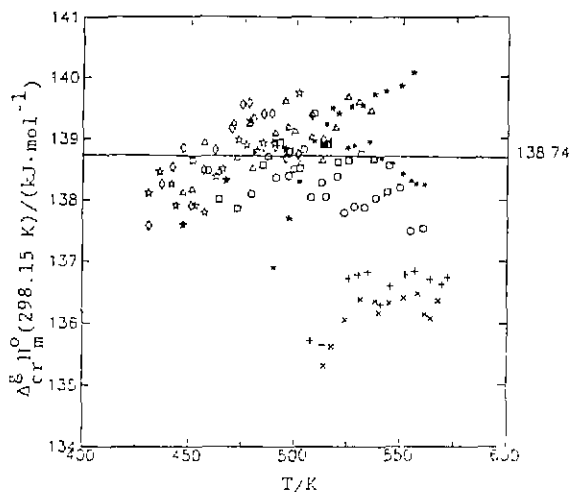Ambiguity of temperature to which the coefficients

Fig.5. Enthalpy of sublimation at 298.15 K of $BiI_{3}(cr)$ determined by the previous and present effusion techniques. Knudsen-effusion $\bigcirc$, orifice 1 ; $\square$, orifice 2 ; $\triangle$, orifice 3 ; $\diamondsuit$, orifice 4, $\star$, orifice 5 Torsion-effusion $\cdot$, +, orifice 1, $\times$, orifice 2 ; $*$, orifice 3 ; $\bigstar$, orifice 4

A and B summarized in Table 4 apply may be avoided by use of the modified sigma function method[13], where

$$\Sigma' = -R\lg(p/Pa) - \Delta_{cl}^{g}\{H_{m}^{o}(T) - H_{m}^{o}(298\ 15\ K)\}$$
$$(K/T) + \Delta_{cl}^{g}\{S_{m}^{o}(T) - S_{m}^{o}(298.15\ K)\ \cdots\cdots(5)$$

whence $\Sigma' = \Delta_{cl}^{g}H_{tn}^{o}(298.15\ K)(K/T) - \Delta_{cr}^{g}S_{m}^{o}$
$(298\ 15\ K) \cdots\cdots (6)$

$\Delta_{cl}^{g}H_{m}^{o}(298.15\ K)$ and $\Delta_{cl}^{g}S_{m}^{o}(298.15\ K)$ values were derived from the least squares slopes and intercepts of modified sigma function plots of the various literature BiI_3 vapour pressure data sets[1-5] as well as the present measurements For these calculations, in addition to the tree energy functions of gaseous and solid BiI_3 reported in Table 5, a value of $C_{px,m}' = 150$ $62\ J \cdot K^{-1} \cdot mol^{-1}$, [10] and a molar enthalpy of fusion of $(39\ 12\pm0.03)\ kJ \cdot mol^{-1}$ [10], were used to obtain thermal functions for liquid BiI_3. The resulting $\Delta_{cl}^{g}H_{m}^{o}(298.15\ K)$ and $\Delta_{cr}^{g}S_{m}^{o}(298.15\ K)$ are summarized in Table 6 and have been plotted as $\Delta_{cl}^{g}H_{m}^{o}(298.15\ K)$ vs. $\Delta_{cl}^{g}S_{m}^{o}(298.15\ K)$ in Fig.6. The values are linearly correlated by the least-squares equation $\Delta_{cr}^{g}H_{m}^{o}(298\ 15\ K) = (39.5716\pm15.16125) + (0.5285\pm0.0775)$ $\Delta_{cl}^{g}S_{m}^{o}(298.15\ K)$, (correlation coefficient = 0.96),

Table 6. $\Delta_{cl}^{g}H_{m}^{o}(298.15\ K)$ and $\Delta_{cr}^{g}S_{m}^{o}(298.15\ K)$ for $BiI_3(cr)$ Derived from the Modified Sigma Function Method[13]

$\Delta_{cl}^{g}H_{m}^{o}(298.15\ K)$ $(R \cdot K)$	$\Delta_{cr}^{g}S_{m}^{o}(298.15\ K)$ (R)
130928 ± 1425[a]	$174\ 068\pm1.969$[a]
125969 ± 1091[b]	$167\ 661\pm1\ 535$[b]
150564 ± 7129[c]	$201.521\pm0\ 620$[c]
148874 ± 4568[d]	$198\ 307\pm6\ 716$[d]
$138261\pm\ 23$[e]	$191\ 980\pm0\ 047$[e]
$159316\pm\ 55$[f]	$232\ 881\pm0.101$[f]

[a] from reference 2. [b] from reference 3. [c] from reference 4 [d] from reference 5. [e] from reference 1. [f] This study, torsion-effusion.

where $\Delta_{cl}^{g}H_{m}^{o}(298.15\ K)$ is in $kJ \cdot mol^{-1}$ and $\Delta_{cl}^{g}S_{m}^{o}$ $(298.15\ K)$ is in $J \cdot K^{-1} \cdot mol^{-1}$.

Previous studies have indicated that values of $\Delta_{cr}^{g}H_{m}^{o}(298\ 15\ K)$ and $\Delta_{cl}^{g}S_{m}^{o}(298.15\ K)$ generated from sets of $\lg(p/Pa)$ versus T^{-1} are frequently linearly correlated The slopes of $\Delta H_{m}^{o}(298.15\ K)$ versus $\Delta S_{m}^{o}(298.15\ K)$ can be a useful indication of systematic errors. McCreary and Thorn[14] 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 $\Delta_{cr}^{g}H_{m}^{o}(T/K)$ versus $\Delta_{cr}^{g}S_{m}^{o}(T/K)$ 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 $\lg(p/Pa)$ versus T^{-1} For BiI_3, Pankratz[15] reports an assessed $\Delta_{cl}^{g}S_{m}^{o}(298.15\ K)$ of $183.6\ J \cdot K^{-1} \cdot mol^{-1}$.
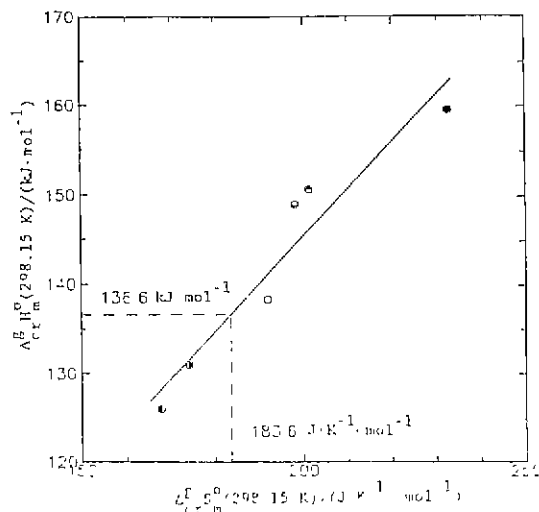

Fig.6. Correlation of molar enthalpy and entropy of sublimation at 298 15 K for $BiI_3(cr)$. (●, Cubicciotti and Keneshea ; [2] ◖, Karpenko and Zabrodskya , [3] ◗, Kulieva et al. ; [4]◓, Ryazantsev et al. ; [5]○, Previous study[1], Knudsen-effusion , ●, This study, torsion-effusion.

The corresponding $\Delta_{cr}^g H_m^o$ (298 15 K) from the linear correlation of $\Delta_{cr}^g H_m^o$(298.15 K) and $\Delta_{cr}^g S_m^o$ (298 15 K) is (136.60 ± 29.39) kJ $\cdot$ mol^{-1} as shown on Fig.5. The present $\Delta_{cr}^g H_m^o$ (298.15 K) 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 which is consistent with the thermal data. The resulting p(T) equation recommended for the sublimation vapour pressure of BiI$_3$ is $\lg(p/Pa) = -(C \cdot K/T) + 5\ 071\ \lg(T/K) - 2\ 838 \times 10^{-3}(T/K)\ 7\ 758 \times 10^3(K/T)^2 - 1\ 4519$ with, $C = (\Delta_{cr}^g H_m^o (298\ 15\ K)/0.019146 - 456\ 27$ In this equation P is in Pa, T in Kelvin and $\Delta_{cr}^g H_m^o(298\ 15\ K)$ in kJ $\cdot$ mol^{-1} This equation was used to compute the recommended line for BiI$_3$(cr) shown on Fig 4

4. CONCLUSION

The present study has provided a consistent set of sublimation vapour pressures for anhydrous bismuth triiodide by the torsion-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 Standard sublimation enthalpy changes, $\Delta_{cr}^g H_m^o$(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, $\Delta_{cr}^g S_m^o$ (298.15 K), have also been derived by the modified function method.

The role of the correlation between $\Delta_{cr}^g H_m^o$(298.15 K) and $\Delta_{cr}^g S_m^o$(298.15 K) in systematic errors between sets of $\lg(p/Pa)$ 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 $\lg(p/Pa)$ 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 vapour pressures of anhydrous bismuth triiodide has been derived

NOMENCLATURE

$\Delta_{cr}^g H_m^o$ (298.15 K) ; standard sublimation enthalpy changes, kJ $\cdot$ mol^{-1}

$\Delta_{cr}^g S_m^o$(298 15 K) . standard sublimation entropy changes. J $\cdot$ K^{-1} $\cdot$ mol$^-$

$C_{p,m}$. heat capacity, J $\cdot$ K^{-1} $\cdot$ mol^{-1}

$\Phi_m^o + \Delta_0^{298\ 15k} H_m^o/T$, free energy function, J $\cdot$ K^{-1} $\cdot$ mol^{-1}

Φ_m^o . $\Delta_T^o S_m^o - \Delta_T^o H_m^o/T$, J $\cdot$ K^{-1} $\cdot$ mol^{-1}

ν : fundamental frequency, cm^{-1}

r , bond distance, nm

R . gas constant, 8 31451 J $\cdot$ K^{-1} $\cdot$ mol^{-1}

lg , natural logarithm

k   , torsion constant, N $\cdot$ m $\cdot$ rad^{-1}

REFERENCES

1 J H. Kim, "The Sublimation Pressure and Standard Enthalpy of Sublimation of Bismuth Triiodide," *J Kor . Ceram . Soc.*, 27 (7) 943–951 (1990)

2. D. Cubicciotti and Keneshea, F.J , "The Vapor Pressures of BiI$_3$ over Liquid Bi-BiI$_3$ Solutions," *J Phys Chem* , 63, 295–297 (1959).

3 N V. Karpenko and N.G. Zabrodskya, "Thermal Dissociation of Bismuth (III) Iodide," *Vestn, Leningr. Univ., Fiz , Khim.*, 3, 82–86 (1974).

4. S.A Kulieva, S.M Gadzhiev and A.A. Kulieva, "Evaporation of Bismuth Triiodide," *Uch. Zap, Azerb. Univ Ser Khim. Nauk*, No.

1, 23−27, 1972.

5. A.A. Ryazantsev, B.A. Popovkin, A.V. Novosiolova and V.A. Lyakhovitskaya, "Vapor Pressure of Antimony and Bismuth Iodides," *Vestn. Mosk. Univ., Khim.*, **24** (3), 49−53 (1969).

6. S. Blairs, A.J. Shelton and R. Unsworth, "Metal Cell for Use in Vapour Pressure Measurements by the Effusion Method," *J. Sci. Instrum*, **38**, 469−470 (1961).

7. R.D. Freeman and J.G. Edwards, The Characterization of High Temperature Vapors, J. L. Margrave, Ed., Wiley, New York, 1967 ; Appendix C.

8. J.R. McCreacy and R.J. Thorn, "Heat and Entropy of Sublimation of Nickel Dichloride, Dibromide and Diiodide ; Dissociation Energies of Gaseous $NiCl_2$ and $NiBr_2$," *J. Chem. Phys*, **48**, 3290−3297 (1967).

9. G.O. Iwu and S. Blairs, "The Sublimation Pressure and Standard Enthalpy of Sublimation of Cadmium," *J. Chem Thermodyn*, **2**, 275−281 (1970).

10 D. Cubicciotti and H. Eding, "The Thermodynamic Equations above Room Temperature for Antimony and Bismuth Iodides and Their Absolute Entropies," *J. Phys. Chem.* **69**, 3621−3625 (1965).

11. T.R. Manley and D.A Williams, "The Far Infrared Spectra of some Group Vb Trihalides," *Spectrochim. Acta.*, **21**, 1773−1783 (1965).

12. R.P. Beyer, A Computer Program for Calculating Thermodynamic Properties from Spectroscopic Data, *U.S. Bureau of Mines, Inform. Circular* 8871, 1982. 11.

13. D. Cubicciotti, "A New Σ-Plot Treatment of Equilibrium Data and Its Application to the Vaporization of Bismuth Chloride," *J. Phys. Chem..* **78**, 2410−2413 (1966).

14. J.R. McCreacy and R.J. Thorn, "Correlation of Enthalpy and Entropy in Analyses of Systematic Errors : Sublimation of Magnesium," *High Temp, Sci.*, **3**, 300−329 (1971).

15. L.B. Pankratz, Thermodynamic Properties of Halides, *U.S. Bureau of Mines, Bulletin* **674**, 1984.