BiCl₃ 승화에 대한 연구

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Sublimation Study of BiCl₃

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요 약. BiCl₃의 승화압과 엔탈피를 370.6에서 488.8 K까지 Knudsen 유출법을 사용하여 측정하였고, 또한 438.2에서 495.7 K까지 Torsion 유출법에 의해 추가 실험을 하였다. 평형 승화압도 이 안정상태 데이타로부터 구하였다. $\Delta_{sub}H^0_{298.15}$와 $\Delta_{sub}S^0_{298.15}$의 상관관계를 이용하여, 추천할 수 있는 p(T) 식을 BiCl₃(s)에 대해 아래와 같이 구하였다. BiCl₃(s); $\log(p/\text{Pa}) = -C/(\text{T/K}) - 2.838\log(\text{T/K}) - 8.097\times10^{-2}(\text{K/T})^2 + 22.588$, 여기서 p는 파스칼, T는 절대온도, $\Delta_{sub}H^0_{298.15}$의 단위는 kJ mol⁻¹이고, $C = (\Delta_{sub}H^0_{298.15} + 5.9988)/1.9146\times10^{-2}$이다. 응축상수와 그것의 온도 의존성도 위의 두 방법에 의한 실험으로부터 유도하였다.

ABSTRACT. Steady-state sublimation vapour pressures of anhydrous bismuth trichloride have been measured by the continuous gravimetric Knudsen effusion method from 370.6 to 488.8 K. Additional effusion measurements have also been made from 438.2 to 495.7 K by the torsion effusion method. Based on a correlation of $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$, a recommended p(T) equation has been obtained for BiCl₃(s); $\log(p/\text{Pa}) = -C/(\text{T/K}) - 2.838\log(\text{T/K}) - 8.097\times10^{-2}(\text{K/T})^2 + 22.588$, where p is in Pa, T in Kelvin and $\Delta_{sub}H^0_{298.15}$ in kJ mol⁻¹ and $C = (\Delta_{sub}H^0_{298.15} + 5.9988)/1.9146\times10^{-2}$. Condensation coefficients and their temperature dependence have been derived from the effusion measurements.

INTRODUCTION

Vapour pressures of BiCl₃(*l*) have been measured by several investigators[1~5] using mainly static methods. Johnson *et al.*[6] determined vapour pressures by an inverted capillary technique from 721 to 1175 K. Other investigators[7,8] have used the effusion technique to obtain data for solid in the interval 371 to 475 K and those obtained by Yanai *et al.*[9] with the static method from 425 to 503 K. Sublimation pressures are generally in good agreement with these three sets of data. Standard sublimation enthalpies (298.15 K) derived from these studies are in the range of 93.7 ± 2.0 to 135.6 ± 7.3 kJ mol⁻¹. The present study has been under-

taken to obtain new sublimation pressures of BiCl₃ (*cr*) using the continuous gravimetric Knudsen and torsion-effusion techniques.

EXPERIMENTAL AND RESULTS

Anhydrous BiCl₃ of Puratronic grade (10 ppm total metal impurities, Johnson Matthey Ltd.) was used in this study. Effusion cells, based essentially on a design by Blairs *et al.*[10] and fabricated from type-304 stainless steel, were filled inside a nitrogen dry box (moisture level ≤20 vpm). 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^{-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 laboratary 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 thermocouples. All temperatures reported are in terms of IPTS-68(International Practical Temperature Scale of 1968).

Orifice areas, a and lengths L were measured using a Leitz Wetzlar metallograph at known magnification. Orifice Clausing Factors[11] W_B and recoil force factors[12] 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 *Table* 1 and 2. The smallest effusion orifice No. 1, used in the gravimetric effusion measurements had complex geometry and its effective orifice area aWB was determined using 99.999 mass per cent cadmium and 99.9 mass per cent benzoic acid as sublimation vapour pressure standards. Orifices 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 0.05o and a deflection of (2.88 ± 0.09) mm as measured using an optical lever and a He-Ne laser beam. 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[13] was used. Orifices of matched pairs of torsion cells were sealed with drops of naphthalene inside the dry box. On solidification,

Table 1. Knudsen-effusion orifice parameters. a, r, L and W_B are the orifice areas, radius, lengths and Clausing factors[11] 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$^2 = (1.2373 \times 10^{-5} \pm 2.194 \times 10^{-7})(T/K) + (1.1506 \times 10^{-2} \pm 1.064 \times 10^{-4})$.

Table 2. Torsion-effusion orifice parameters. a_1, a_2, r_1, r_2, L_1 and L_2 are the areas, radii and lengths of the effusin orifices. f_1 and f_2 are the corresponding recoil force factors.[12]

Cell No.	a_1 (mm^2)	a_2	r_1 (cm)	r_2	L_1 (mm)	L_2	f_1	f_2
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 3. Steady-state sublimation vapour pressure p/Pa and third-law standard molar sublimation enthalpy $\Delta_{sub}H^0_{298.15}$ for BiCl$_3$(s) determined by Knudsen-effusion method. W=steady-state effusion rate (mg h^{-1}). (p° =101325 Pa)

Orifice No.	T (K)	W (mg h^{-1})	p (Pa)	$\Delta_{sub}H^0_{298.15}$ (kJ mol$_{-1}$)
1	410.9	0.2636	1.151465	114.68
	415.9	0.4309	1.886765	114.34
	421.2	0.6258	2.746867	114.46
	425.7	1.0086	4.435982	113.94
	431.4	1.2855	5.667560	114.56
	439.3	2.1452	9.489059	114.69
	444.5	3.1214	13.836301	114.62
	450.1	4.3288	19.230497	114.80
	454.1	5.5164	24.543846	114.86
	456.8	6.4986	28.942604	114.88
	462.7	10.0487	44.851295	114.63
	468.4	15.5669	69.622362	114.28
	475.8	19.9292	89.361978	115.04
	483.0	30.0386	135.015710	115.05
	488.8	40.8727	184.054690	115.11
2	397.2	0.2350	0.264232	115.82
	401.4	0.3260	0.368450	115.90
	405.1	0.4985	0.565887	115.50
	413.7	0.8132	0.932577	116.17
	418.5	1.3499	1.556859	115.72
	422.1	1.8713	2.167155	115.53
	425.8	2.4511	2.850419	115.52
	426.9	3.0148	3.510764	115.10
	431.6	3.9960	4.677868	115.29
	432.5	4.5101	5.284965	115.08
	436.4	6.4832	7.630159	114.75
	442.6	9.5744	11.345292	114.87
	448.3	16.0944	19.191473	114.36
	453.4	20.4947	24.572964	114.69
	459.4	27.3192	32.961727	115.02
	464.1	38.9903	47.279655	114.78
	469.3	57.2309	69.770324	114.49
3	392.0	0.2587	0.125016	116.76
	396.1	0.3948	0.191771	116.56
	402.0	0.6278	0.307175	116.68
	406.0	0.8557	0.420712	116.76
	411.3	1.4078	0.696476	116.52
	416.4	2.3347	1.162024	116.16
	419.8	2.8128	1.405498	116.42
	422.3	3.4291	1.716445	116.40
	425.4	5.1036	2.566154	115.80
	427.2	5.8508	2.948277	115.77
	430.5	6.8410	3.460275	116.08

Table 3. Continued

Orifice No.	T (K)	W (mg h^{-1})	p (Pa)	$\Delta_{sub}H^0_{298.15}$ (kJ mol$_{-1}$)
	433.5	9.2567	4.697747	115.75
	439.0	13.0642	6.670958	115.91
	444.1	19.5070	10.016922	115.72
	450.0	27.6925	14.310582	115.86
	455.3	43.1985	22.452765	115.50
	459.6	52.1742	27.241157	115.81
4	380.2	0.3007	0.061302	115.58
	386.7	0.4861	0.099925	115.94
	393.6	0.7677	0.159187	116.45
	396.4	1.2431	0.258645	115.66
	404.0	1.7301	0.363330	116.68
	408.7	3.0113	0.635988	116.12
	410.4	3.6000	0.761804	115.96
	412.7	4.2840	0.909099	116.01
	415.4	4.9920	1.062593	116.19
	417.7	6.0415	1.289467	116.15
	424.7	9.7871	2.105920	116.32
	429.3	14.6763	3.174459	116.08
	434.8	19.1207	4.161111	116.53
	440.4	24.5100	5.367612	117.07
	447.8	40.2386	8.883189	117.10
	453.3	61.8589	13.737682	116.85
5	370.6	0.2745	0.027371	115.20
	377.2	0.4474	0.044996	115.63
	381.2	0.7283	0.073634	115.28
	386.7	1.0355	0.105431	115.78
	390.5	1.5917	0.162827	115.47
	394.5	2.3213	0.238660	115.39
	396.1	2.9860	0.307601	115.00
	399.9	3.8065	0.393954	115.26
	403.8	4.8449	0.503799	115.53
	406.8	5.7411	0.599111	115.77
	408.3	7.2155	0.754351	115.41
	411.0	9.8260	1.030515	115.08
	415.3	13.0777	1.378553	115.26
	422.0	21.1563	2.247588	115.37
	426.7	28.0788	2.999113	115.59
	432.3	38.5224	4.140739	115.91
	437.6	57.1095	6.174718	115.83

naphthalene sealed the orifices and protected the halide from hydrolysis during transfer to the torsion effusion apparatus. On evacuation, naphthalene was sublimed and cleared the orifices.

Prior to measurements on BiCl$_3$, 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.[14] Steady state Knudsen effusion sublimation vapour pressures for solid BiCl₃ in the range of 370.6 to 488.0 K are reported in *Table* 3 and are plotted in *Fig.* 1 for five different effective orifice areas. Steady state torsion effusion sublimation vapour pressures, measured in the range from 438.2 to 504.7 K are reported in *Table* 4 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* 5.

DISCUSSION

Steady-state sublimation vapour pressures from both effusion techniques were found to depend on effective 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 $p(T)$ equations were obtained from the Knudsen and torsion-effusion measurements:
$\log(p/\text{Pa}) = -(6175 \pm 73)(\text{K}/\text{T}) + (14.927 \pm 0.123)$
and $\log(p/\text{Pa}) = -(8162 \pm 149)(\text{K}/\text{T}) + (19.666 \pm 0.326)$, respectively. These equilibrium $p(T)$ equations are shown with experimental points on *Fig.* 1 and 2 are shown with literature vapour and sublimation pressures[1~9] for comparison in *Fig.* 3. 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 BiCl₃(s), sublimation vapour pressures, equations of form $\log(p/\text{Pa}) = -A/(\text{T}/\text{K}) + B$ were derived and gave the coefficients A and B summarized in *Table* 6. Second-law $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$ also given in *Table* 6 were calculated by assuming the coefficients A and B applying at the mean temperatures of the various ranges together with the following $C^0_P(\text{T})$ for BiCl₃

Table 4. Steady-state sublimation vapour pressure p/Pa and third-law standard molar sublimation enthalpy $\Delta_{sub}H^0_{298.15}$ for BiCl₃(s) determined by torsion-effusion method

Orifice No.	T (K)	p (Pa)	$\Delta_{sub}H^0_{298.15}$ (kJ mol₋₁)
1	451.2	9.276664	117.88
	458.3	15.303702	117.77
	462.9	22.384922	117.46
	469.5	35.496754	117.28
	476.6	59.379063	116.94
	483.0	93.614105	116.63
	488.5	136.032410	116.39
	491.6	171.381790	116.15
	493.5	196.861649	116.02
	495.7	234.270493	115.80
2	448.4	6.218703	118.66
	450.9	7.734438	118.51
	457.2	12.863936	118.16
	462.4	18.871973	117.98
	467.7	27.781336	117.79
	473.2	40.393478	117.66
	480.3	65.141151	117.45
	487.4	104.996758	117.18
	490.3	139.532883	116.70
	492.1	158.867096	116.56
	493.2	174.890564	116.42
	494.7	188.392822	116.46
3	444.2	3.701813	119.50
	447.4	4.841487	119.35
	452.8	7.600168	119.05
	459.3	12.071970	118.92
	465.5	19.718790	118.58
	468.3	23.620070	118.58
	470.9	28.090359	118.53
	476.0	37.580940	118.60
	484.9	60.204601	118.84
	489.3	75.844254	118.95
	493.2	90.485588	119.13
4	438.2	1.106805	122.35
	445.4	1.599897	122.92
	452.6	2.534091	123.13
	458.0	3.786317	123.03
	464.2	6.181988	122.75
	469.0	8.976612	122.52
	473.3	12.735343	122.22
	477.9	16.943575	122.23
	485.4	28.512163	121.98
	489.1	35.190163	122.02
	491.4	41.351807	121.91

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Table 5. Coefficients with standard deviations of the equation $\log(p/\text{Pa}) = -A(\text{K}/\text{T}) + B$ derived from BiCl₃ steady-state Knudsen and torsion-effusion sublimation vapour pressure measurements determinedin the temperature range of T_1 to T_2

Method	Orifice No.	T_1 (K)	T_2 (K)	Number of points	A	B
Knudsen	1	410.9	488.8	15	5607± 66	13.754± 0.148
	2	397.2	469.3	17	6314± 74	15.307± 0.172
	3	392.0	459.6	17	6314± 56	15.210± 0.133
	4	380.2	453.3	16	5578± 83	13.443± 0.199
	5	370.6	437.6	17	5800± 70	14.075± 0.178
Torsion	1	451.2	495.7	10	7030± 53	16.533± 0.246
	2	448.4	494.7	12	7040± 64	16.498± 0.134
	3	444.2	493.2	11	6226± 148	14.629± 0.317
	4	438.2	491.4	11	6612± 135	15.059± 0.290

Fig. 1. Steady state sublimation vapour pressures for BiCl₃(s) measured by Knudsen-effusion method. ○, orifice 1; □, orifice 2; △, orifice 3; ◇, orifice 4; ☆, orifice 5; − equilibrium line.

Fig. 2. Steady state sublimation vapour pressures for BiCl₃(s) measured by torsion-effusion method. ○, orifice 1; □, orifice 2; △, orifice 3; ◇, orifice 4; − equilibrium line.

(s) and BiCl₃(g). Polynomial expressions[15] $C_P^0(s) = 10^5$ J K^{-1} mol^{-1}, and $C_P^0(g) = 83.05 - 3.10 \times 10^5 (\text{K}/\text{T})^2$ J K^{-1} mol^{-1},[16] for BiCl₃(cr) and BiCl₃(g), respectively were employed in this research.

Third-law $\Delta_{sub}H^0_{298.15}$ at each effusion temperature are also reported in *Table* 3 and 4. The thermodynamic functions $\Delta[(G_T^0 - H^0_{298.15})/\text{T}]$ for BiCl₃ (g) were computed for rigid-rotator harmonic-oscillator ideal gas monomer and pyramidal C_{3v} symmetry. The molecular constants[17,18] and the calculated thermodynamic functions[19] are presented in

Table 7. The thermodynamic functions $\Delta[(G_T^0 - H^0_{298.15})/\text{T}]$ were derived from $S^0_{298.15} = (171.51 \pm 8.34)$ J K^{-1} mol^{-1},-20 and $S^0_{298.15} = 357.31 \pm 4.18$ J K^{-1} mol^{-1} computed as outlined above for BiCl₃(g). Thermodynamic functions for BiCl(cr) at selected temperatures are presented in *Table* 8.

Results from such calculations are shown in *Fig.* 4 for both effusion techniques. Individual $\Delta_{sub}H^0_{298.15}$ 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 $\Delta_{sub}H^0_{298.15} = (115.50 \pm 0.125)$ kJ mol^{-1} shown on *Fig.* 4 together with its standard deviation, is based only on the Knudsen-effusion data and is comparable with $\Delta_{sub}H^0_{298.15} = 136.60$ kJ mol^{-1} derived later from an enthalpy-entropy correlation. Average third-law $\Delta_{sub}H^0_{298.15}$ values derived from literature sublimation vapour pressures are also included in *Table* 6.

Fig. 3. Comparison of BiCl₃ vapour pressures. ○, Cubicciotti *et al.*;[4] □, Tarasenkov *et al.*;[3] △, Evnevich;[2] ◇, Imperatori *et al.*;[8] ☆, Johnson *et al.*;[6] ×, Yanai *et al.*;[9] *, Maier *et al.*;[1] ★, Darnell *et al.*;[7] ——, Knudsen-effusion equilibrium; ----, torsion effusion equilibrium line; ····, recommended p(T); T$_m$, melting temperature 505 K.

It is appropriate to compare literature sublimation pressure values determined by effusion methods with the present measurements. Imperatori *et al.*[8] using both gravimetric Knudsen and torsion effusion methods have examined BiCl₃, while Darnell and Yosim[9] have examined BiCl₃ by the gravi-

Table 7. Ideal gas standard molar thermodynamic functions for BiCl₃ at selected temperatures.[19] ν/cm^{-1}, 100, 130, 242, 288; geometric constants:[17,18] r(Bi-Cl) $s = 0.248$ nm; r(Bi-Bi) $= 0.266$ nm; Cl-Bi-Cl $= 100°$, R $= 8.31451$ J K^{-1} mol^{-1}; $p° = 101325$ Pa; $T' = 298.5$ K)

T (K)	$C°_p$ (R)	$\Delta(H^0_T - H^0_{298.15})$ (R K)	$\Delta(S^0_T - S^0_{298.15})$ (R)	$\Delta[(G^0_T - H^0_{298.15})/T]$ (R)
Solid[a]				
298.15	12.629	0	0	20.629
300	12.629	23	0.078	20.630
350	12.629	655	2.025	20.783
400	12.629	1286	3.711	21.125
450	12.629	1918	5.199	21.566
500	12.629	2549	6.529	22.060
Gas				
298.15	9.581	0	0	42.982
300	9.586	18	0.059	42.982
400	9.761	986	2.784	43.361
500	9.845	1967	5.032	44.080
600	9.892	2954	6.832	44.890
700	9.920	3945	8.359	45.706
800	9.939	4938	9.685	46.495

[a]Derived using $C°_p$ and $S^0_{298.15}$ for BiCl₃(s) and $S^0_{298.15}$(g) from references 15 and 16.

Table 6. Summary of results with those other investigators

| T_1 T_2 (K) | A | B | Second-law | | Third-law |
			$\Delta_{sub}H^0_{298.15}$ (kJ mol^{-1})	$\Delta_{sub}S^0_{298.15}$ (J K^{-1} mol^{-1})	$\Delta_{sub}H^0_{298.15}$ (kJ mol^{-1})
424.5~503.7[a,d]	4394± 56	11.484± 0.120	88.332± 1.072	135.334± 2.298	113.76± 0.284
371.0~468.0[d,f]	6200± 44	14.949± 0.106	119.421± 0.851	192.436± 2.023	116.17± 0.453
390 ~475[c,d,g]	5700± 11	13.819± 0.255	112.521± 2.144	180.120± 4.882	118.87± 1.272
367.2~485.4[k,h]	392± 34	5.532± 0.082	10.634± 0.651	18.930± 1.570	93.11± 0.728
370.6~488.8[c]	6157± 53	14.927± 0.123	121.240± 1.015	199.349± 2.355	115.50± 0.125
410.7~495.7[d]	8162± 149	19.666± 0.326	160.385± 2.853	291.798± 6.242	111.97± 0.987

[a]Static method (Bourdon-type sickle gauge). [b]Static method (Spiral gauge). [c]Gravimetric Knudsen-effusion method. [d]Torsion-effusion method. [e]From reference 9. [f]From reference 7. [g]From reference 8. [h]From reference 1.

Table 8. $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$ for $BiCl_3(s)$ derived from the modified sigma function method

$\Delta_{sub}H^0_{298.15}$ (J mol^{-1})	$\Delta_{sub}S^0_{298.15}$ (J K^{-1} mol^{-1})
115387± 7071[a]	183.153± 9.968[a]
114274± 229[b]	182.809± 0.408[b]
91300± 1602[c]	167.685± 2.334[c]
93659± 1974[d]	172.319± 3.834[d]
121635± 0940[e]	198.720± 2.236[e]
135556± 7290[f]	224.958± 16.814[f]
123571± 1640[g]	195.424± 1.875[g]
54484± 4821[h]	96.557± 9.150[h]
121076± 0045[i]	198.829± 0.105[i]
160155± 0043[j]	291.135± 0.094[j]

[a]from reference 3; [b]from reference 4; [c]from reference 2; [d]from reference 9; [e]from reference 7; [f]from reference 8; [g]from reference6; [h]from reference 1; [i]This study, Knudsen effusion; [j]This study, torsion effusion.
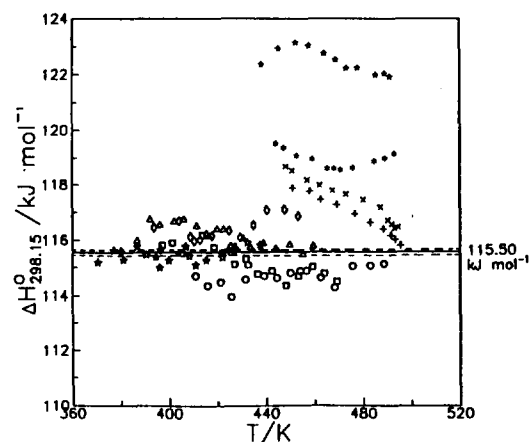

Fig. 4. Enthalpy of sublimation at 298.15 K of $BiCl_3$ determined in this research. Knudsen effusion: ○, orifice 1; □, orifice 2; △, orifice 3; ◇, orifice 4; ☆, orifice 5. Torsion effusion: +, orifice 1; ×, orifice 2; *, orifice 3; ★, orifice 4.

metric Knudsen effusion method. In these two effusion studies, Darnell and Yosim used a single effusion orifice with an effective orifice area $aW_B/cm^2 = 7.75 \times 10^{-3}$. In their torsion effusion measurements Imperatori *et al.* used three effusion orifices with aW_B in the range $1.63 \sim 1.84 \times 10^{-3}$ cm^2. Limited gravimetric Knudsen effusion measurements with $aW_B/cm^2 = 7.87 \times 10^{-3}$ were
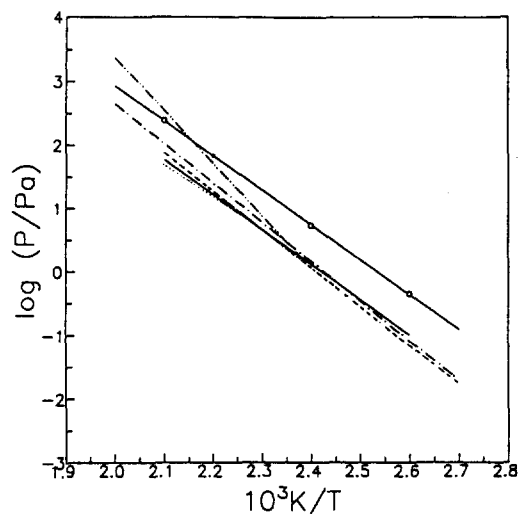

Fig. 5. Comparison of $BiCl_3$ equilibrium sublimation pressures obtained using by effusion methods. ····· Knudsen-effusion, —— Equilibrium line, Imperatori *et al.*;[8] ----- Knudsen-effusion, Darnell *et al.*;[7] —·—, Knudsen-effusion equilibrium; —··— torsion effusion equilibrium line; -○-○-, recommended p(T); Tm,melting temperature 505 K.

also made for $BiCl_3$. Considering the small number of experimental points and the limited temperature range no separate least-squares analysis was made of their gravimetric Knudsen data. Sublimation pressure equations obtained from effusion studies are shown for comparison in *Fig.* 5. Knudsen effusion measurements, P_{Eq}, obtained in the present work $(aW_B/cm^2 = 0.20 \sim 6.88 \times 10^{-3})$ agree closely with those of Darnell and Yosim $(aW_B/cm^2 = 7.73 \times 10^{-3})$. Knudsen effusion data by Imperatori *et al.* $(aW_B/cm^2 = 7.87 \times 10^{-3})$ are lower than the present values. Torsion effusion values obtained by Imperatori *et al.* $(aW_B/cm^2 = 12.6 \sim 18.4 \times 10^{-3})$ are in close agreement with the present values as shown in *Fig.* 5.

Torsion data obtained by the latter workers for $BiCl_3$ show no consistent trend with effective area (aW_B) and significantly different values between duplicate runs with the same torsion cells. Knudsen data for $BiCl_3$ obtained with a single orifice were lower than their torsion data. Imperatori *et al.* exclude their Knudsen data and weight the slopes and intercepted of the separate least squares
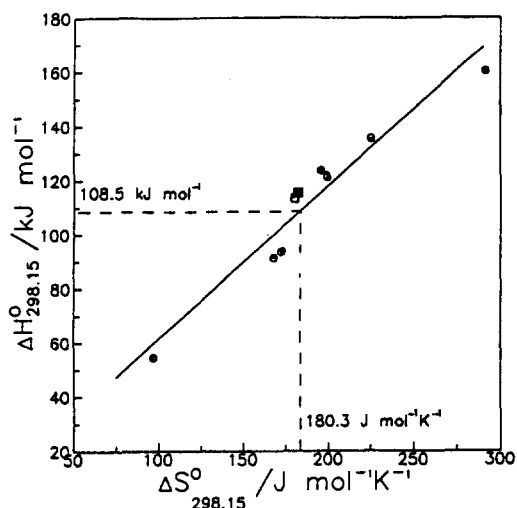
Fig. 6. Enthalpy of sublimation at 298.15 K *vs.* Entropy of sublimation at 298.15 K correlation. □, Cubicciotti *et al.*;[4] ■, Tarasenkov *et al.*;[3] ◓, Evnevich;[3] ◒, Imperatori *et al.*;[8] ◉, Johnson *et al.*;[6] ◎, Yanai *et al.*;[9] ◑, Maier *et al.*;[1] ◔, Darnell *et al.*;[7] ○, This study, Knudsen-effusion; ●, This study, torsion effusion.

equations of log(p/Pa) *vs.* T^{-1} for each torsion cell according to the number of experimental points. While P_{Eq} values from the present torsion measurements fall close to the other effusion data for BiCl₃, the higher slope of the data is noted. Excluding the present torsion effusion values, all other effusion values fall close to the derived recommended p(T) line.

Ambiguity of temperature to which the coefficients A and B summarized in *Table* 6 apply may be avoided by use of the modified sigma function method.[21] $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$ values were derived from the least squares slopes and intercepts of modified sigma function plots of the various literature BiCl₃ vapour pressure data sets[1~9] as well as the present measurements. For these calculations, in addition to the free energy functions of gaseous and solid BiCl₃ reported in *Table* 7, a value of $C^0_P = 143.51$ J K^{-1} mol^{-1},[22] and a molar enthalpy of fusion of 23.77 kJ mol^{-1},[22] were used to obtain thermal functions for liquid BiCl₃. The resulting $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$ are summarized in *Table* 8 and have been plotted as $\Delta_{sub}H^0_{298.15}$ *vs.* $\Delta_{sub}S^0_{298.15}$ in *Fig.* 6. The values are linearly corre-

lated by the least-squares equation $\Delta_{sub}H^0_{298.15} =$ (15.0849± 14.5562)+(0.5184± 0.0710) $\Delta_{sub}S^0_{298.15}$, with correlation coefficient 0.81 where $\Delta_{sub}H^0_{298.15}$ is in kJ mol^{-1} and $\Delta_{sub}S^0_{298.15}$ is in J K^{-1} mol^{-1}. Previous studies have indicated that values of $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$ generated from sets of log(p/Pa) versus T^{-1} are frequently linearly correlated. McCreary and Thorn[23] 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/Pa) versus T^{-1}. For BiCl₃, Pankratz[24] reports an assessed $\Delta_{sub}S^0_{298.15}$ of 180.3 J K^{-1} mol^{-1}. The corresponding $\Delta_{sub}H^0_{298.15}$ from the linear correlation of $\Delta_{sub}H^0_{298.15}$ and $\Delta_{sub}S^0_{298.15}$ is (108.55± 7.36) kJ mol^{-1} as shown in *Fig.* 6.

The third-law $\Delta_{sub}H^0_{298.15}$ 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 sublimation pressure of BiCl₃ is: log(pPa)$= -C/$(T/K) -2.838 log (T/K)-8.097×10^3(KT)^2+22.588 with $C = (\Delta_{sub}H^0_{298.15} + 5.9958)/1.9146 \times 10^{-2}$. In these equations p is in Pa, T in Kelvin and $\Delta_{sub}H^0_{298.15}$ in kJ mol^{-1}. This equation was used to compute the recommended line for BiCl₃(s) shown on *Fig.* 3.

Condensation coefficients α_c were obtained from the slopes and intercepts of isothermal linear plots of inverse steady state sublimation pressure and effective orifice area. From the slopes and intercepts of semi-logarithmic plots of log α_c *vs.* T^{-1}, an apparent activation sublimation enthalpy $\Delta_{cond}H^*_{450}$ $= -41.28$ kJ mol^{-1} and entropy $\Delta_{cond}S^*_{450} = -121.30$ J K^{-1} mol^{-1} for condensation were obtained from the gravimetric effusion measurements. Corresponding values for vaporisation (relative to the solid) were $\Delta_{vap}H^*_{450} = 75.57$ kJ mol^{-1} and $\Delta_{vap}S^*_{450} = 14.90$ J K^{-1} mol^{-1} at 450 K. It is to be recognized that values of α_c given in *Table* 9 were obtained by assignment of the cross-sectional area (71.57 mm²) of the effusion cell body as the effective area of

Table 9. Equilibrium sublimation vapour pressures condensation coefficients for $BiCl_3$ at selected temperatures derived from plots of inverse steady state sublimation vapour pressures and effective orifice area. $lg(p/Pa) = -A(T/K) + B$ and aW_B for this purpose are obtained from *Table* 5 and 6, respectively

Knudsen method			Torsion method		
T (K)	p (Pa)	$\alpha_c \times 10^2$	T (K)	p (Pa)	$\alpha_c \times 10^2$
415	1.444	0.879	445	21.230	0.152
420	2.178	0.807	450	34.169	0.138
425	3.253	0.746	455	53.542	0.125
430	4.812	0.692	460	84.276	0.114
435	7.053	0.646	465	121.088	0.103
440	10.245	0.604	470	205.681	0.093

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.

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