Vapor Pressures and Standard Sublimation Enthalpies for Thulium Trichloride, Tribromide, and Triiodide

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The total vapor pressures of thulium trihalides $TmCl_3$, $TmBr_3$, and TmI_3 were measured by the torsion method, and their temperature dependence can be expressed by the following equations over the given temperature ranges: $TmCl_3(cr)$, $\log(p/kPa) = (11.60 \pm 0.20) - (14810 \pm 200)(T/K)$ from (945 to 1093) K; $TmBr_3(cr)$, $\log(p/kPa) = (11.67 \pm 0.20) - (14330 \pm 200)(T/K)$ from (921 to 1155) K; $TmI_3(cr)$, $\log(p/kPa) = (11.54 \pm 0.20) - (13790 \pm 200)(T/K)$ from (887 to 1051) K. Treating the results by second- and third-law methods, the standard sublimation enthalpies were determined to be $\Delta_{sub}H°(298\ K) = \{(296 \pm 4)\ kJ\cdot mol^{-1}$ and $(285 \pm 5)\ kJ\cdot mol^{-1}\}$ for $TmCl_3$ and $TmBr_3$, respectively. For TmI_3, the proposed enthalpy, $\Delta_{sub}H°(298\ K) = (277 \pm 4)\ kJ\cdot mol^{-1}$, was only derived by the second-law method. From this standard enthalpy, a set of free-energy functions and standard entropy, $S°(298\ K) = 227\ J\cdot K^{-1}\cdot mol^{-1}$ for solid TmI_3 was evaluated by third-law treatment of the data.

Introduction

The thermodynamic properties and in particular their vapor pressures for the great many rare-earth halides are in general quite scarce, and trihalides of thulium are not an exception. Apparently in fact the only vapor-pressure values of $TmCl_3$ were those measured by a static method (boiling point),[1] by the mass-loss Knudsen effusion method[2] above the molten compound, and by Knudsen effusion mass spectrometry (KEMS)[3] above the solid phase. In this last work, the authors report that not only monomer but more complex molecules are also present in the vapor. Concerning the other compounds, the only reliable vapor-pressure values for $TmBr_3$ are those measured by Gietmann et al.[4] by KEMS while for TmI_3 there are measurements obtained by the mass-loss Knudsen effusion method.[5] The mass spectrum of the vapor over TmI_3 was determined at 913 K,[6] and this was very similar to those of other triiodides of the rare-earth elements.[7]

This work is part of a continuing systematic study[8−16] carried out in order to obtain accurate measurements of the vapor pressures of rare-earth trihalides and to derive their standard sublimation enthalpies. In particular, the aim of the present paper was to determine the standard sublimation enthalpies of thulium trichloride, tribromide, and triiodide measuring their vapor pressures.

Experimental Section

Chemicals. The samples of thulium trihalides used in this work have a nominal purity of about 99.8%, as certified by the supplier (Aldrich). To minimize the effect of their oxidation, the samples were loaded into the cells in a drybox and rapidly introduced into the assemblies for their vapor pressures' measurement and the systems were quickly evacuated.

Apparatus and Procedures. The vapor pressures of thulium trihalides were measured by using the torsion−effusion method.[17] Some pressure values were also obtained by the mass-loss Knudsen effusion method.[18] Both the torsion assembly and the Knudsen one were described in detail in our previous work.[19] Pyrophyllite torsion and Knudsen cells having different nominal area of their effusion holes were employed in this study (see Table 1). A pyrophyllite torsion cell (cell C), similar to that described in previous works,[11] was used in this work. The lodgings of this cell have the effusion holes with different area (0.4 mm and 1.8 mm in diameter), and this allowed in a single experiment the measurement of the vapor pressures of a compound in a large temperature range. In fact, by filling both lodgings of this cell with the sample, the torsion of the assembly is due to the effusion of the vapor from both lodgings (cell C1). When the sample in the lodging with the large effusion hole is completely vaporized, the torsion angles decrease because the torsion is due only to the vapor effusing from the lodging with the smaller hole; the cell now behaves as a new cell (cell C2). In this way, the vapor pressure of a compound can be measured in two different temperature ranges of the same experimental condition. The instrumental constant values necessary to convert the experimental data (torsion angles in the torsion measurements or weight losses in the Knudsen measurements) into pressure data are reported in the same Table 1. These values were evaluated by vaporizing in separate experiments pure standard elements (cadmium or lead) that have reliable vapor-pressure values.[20] The constants so obtained are well reproducible (within about 20% of their average values) both for the Knudsen cells and for the torsion ones. This produces in the derived log p value a shift of about ±0.1. In the torsion experiments, the torsion angle was measured with an uncertainty of ±0.1°, and therefore, as the first points influence heavily the slope of the final log p vs $1/T$ equation, the measurements were actually started when the measured torsion angles were grater than about 2° with negligible error in their measurements. The Knudsen pressures were measured at temperatures lower than

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Table 1. Instrumental Constants of Torsion and Knudsen Effusion Cells

cell	method	nominal effusion	diameter of hole (mm)	$-\log[K_\alpha/(\text{kPa}\cdot\text{degree}^{-1})]$	$-\log(K_k/(\text{kPa}\cdot\text{s}\cdot\text{mg}^{-1}\cdot\text{K}^{-1/2}))$
B	torsion	1.0	1.0	3.30 ± 0.05 (4)[a]	
C (as C1)	torsion	0.4	1.8	3.56 ± 0.09 (3)[b]	
				3.53 ± 0.10 (1)[a]	
C (as C2)	torsion	0.4		2.20 ± 0.11 (3)[b]	
				2.23 ± 0.10 (1)[a]	
Ak	Knudsen	0.6			−0.10 ± 0.06 (4)[a]
Bk	Knudsen	1.2			0.51 ± 0.04 (2)[b]
					0.53 ± 0.10 (1)[a]

[a,b] K values obtained using Pb and Cd as standards, respectively. In parentheses are reported the number of the experimental runs.

Table 2. Torsion $TmCl_3$ Partial Pressures

run 1, cell C1		run 2, cell C1		run 3, cell C1		run 4, cell C1		run 5, cell C1		run 6, cell C1		run 7, cell B		run 8, cell B	
T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$
K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa
971	3.59	959	3.68	945	4.02	1020	3.07	1030	2.77	1011	3.06	1018	3.01	1018	3.07
980	3.45	968	3.55	960	3.77	1027	2.97	1034	2.72	1021	2.93	1027	2.89	1028	2.89
990	3.26	978	3.38	973	3.55	1038	2.83	1046	2.56	1033	2.77	1036	2.77	1034	2.83
1001	3.13	988	3.25	986	3.35	1047	2.72	1060	2.38	1043	2.64	1047	2.64	1043	2.72
1013	2.99	997	3.11	1003	3.07	1052	2.64	1071	2.24	1053	2.51	1055	2.54	1051	2.60
1023	2.81	1006	2.97	1018	2.85	1062	2.51	1080	2.11	1063	2.36	1065	2.41	1059	2.49
1034	2.65	1015	2.82	1034	2.60	1076	2.32	1087	2.02	1075	2.21	1077	2.23	1068	2.39
1043	2.50	1024	2.68	1050	2.41	1089	2.15	1093	1.94	1086	2.05	1085	2.12	1077	2.26
1052	2.40	1034	2.55	1061	2.31							1093	2.02	1088	2.12
1062	2.29	1042	2.45	1063	2.28										
1069	2.19	1049	2.37												

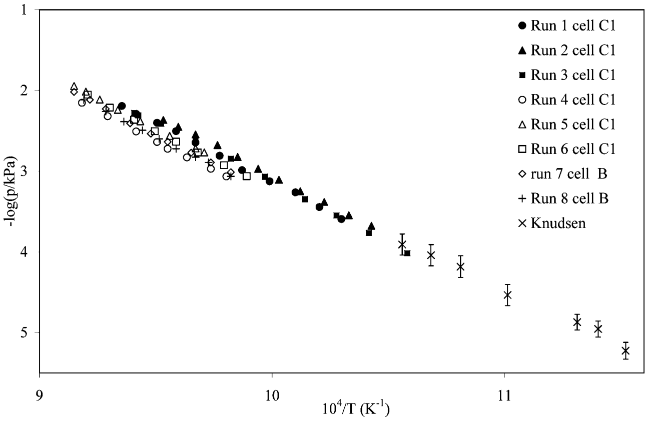

Figure 1. Experimental $TmCl_3(g)$ partial pressures.

those of the torsion experiments. The uncertainty in the temperature measurements of the samples in both assemblies should not exceed ±1 K.

Experimental Results. The vapor pressures of thulium trihalides were measured above the solid phase. Only for $TmCl_3$ was the pressure also measured above the molten compound by using mainly the cell C as C2, but the obtained results were not reproducible, and going on the vaporization of the sample, the pressure data lies on log p vs $1/T$ lines having decidedly low slopes compared to those obtained above the solid phase corrected for the heat of fusion. This behavior can be explained considering that, although the sample was placed in the cell on small quartz wool flocks, the molten compound wetted the inner walls of the pyrophyllite cell and crept up to the effusion holes so that their area might be partially reduced. Considering this possibility, all points taken at temperatures over the melting point (1092 K)[21] were not taken into account. From the partial pressure data reported in the literature[3] for $TmCl_3(g)$ and $Tm_2Cl_6(g)$ (the other more complex molecules are decidedly negligible), the experimental total torsion vapor-pressure values were opportunely reduced in order to obtain the $TmCl_3(g)$ partial pressures. The values so obtained are those reported in Table 2 and in Figure 1.

For $TmBr_3$, the amount of dimer is reported to be negligible (∼1%),[4] while for TmI_3, no relevant pressures of the dimer form are reported in the literature;[6] therefore, the measured total vapor pressures of these compounds, reported in Tables 3 and 4 and in Figures 2 and 3, were considered partial pressures of their monomeric forms.

The Knudsen vapor pressures reported in Table 5 and drawn in Figures 1−3 were obtained vaporizing the samples for several hours at temperatures within the low range besides the torsion one. The associated errors were quoted from the uncertainty for the evaporated amounts of sample and the times to thermostatate the cell. The total Knudsen pressures measured above $TmCl_3(cr)$ were obtained employing a molecular weight of the vapor that takes into account the presence of about 7% of dimer.[3] These values were reduced by using the same procedure employed for the torsion data in order to obtain the $TmCl_3(g)$ partial pressure values reported in Table 5 and in Figure 1. The mass-loss Knudsen effusion data agree satisfactorily with those obtained in the torsion−effusion experiments. The temperature dependence of the only torsion partial pressures, linearized by a least-squares treatment, was approximated for each run by a log p vs $1/T$ equation. Considering the small number of the Knudsen pressure values, these were not sufficient to obtain a reliable log p vs $1/T$ equation but were taken only as a check of the reliability of the torsion data. All the torsion pressure equations obtained for each run are reported in Table 6. By weighing slopes and intercepts of these equations proportional to the number of experimental points, the following equations were selected

$$TmCl_3(cr)\ \log(p/\text{kPa}) = (11.60 \pm 0.20) - (14810 \pm 200)(T/\text{K}) \quad (\text{from 945 to 1093 K}) \quad (1)$$

$$TmBr_3(cr)\ \log(p/\text{kPa}) = (11.67 \pm 0.20) - (14330 \pm 200)(T/\text{K}) \quad (\text{from 921 to 1155 K}) \quad (2)$$

$$TmI_3(cr)\ \log(p/\text{kPa}) = (11.54 \pm 0.20) - (13790 \pm 200)(T/\text{K}) \quad (\text{from 887 to 1051 K}) \quad (3)$$

The errors associated with slopes and intercepts of these

Table 3. Torsion Total Vapor Pressures for $TmBr_3$

run 1, cell B		run 2, cell B		run 3, cell C1		run 3, cell C2		run 4, cell C1		run 4, cell C2		run 5, cell C1		run 5, cell C2	
T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$
K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa
931	3.69	937	3.69	924	3.90	999	2.62	927	3.87	1006	2.57	921	3.94	1013	2.39
952	3.39	947	3.51	938	3.66	1009	2.49	938	3.56	1015	2.46	942	3.64	1022	2.27
964	3.18	956	3.34	949	3.46	1020	2.34	947	3.39	1026	2.32	953	3.44	1048	1.89
974	3.01	965	3.18	961	3.30	1028	2.25	958	3.23	1039	2.16	968	3.20	1073	1.56
984	2.88	976	3.04	971	3.14	1038	2.11	967	3.11	1050	2.02	988	2.87	1089	1.39
1004	2.59	987	2.89	980	3.01	1046	2.02	978	2.96	1061	1.84	1004	2.64	1105	1.19
1013	2.49	995	2.79	990	2.84	1056	1.87	988	2.82	1070	1.70	1015	2.50	1123	1.01
1025	2.33	1007	2.61	1000	2.70	1066	1.70	1001	2.65	1080	1.58	1024	2.36	1136	0.87
1035	2.18	1019	2.45			1076	1.60	1009	2.53	1092	1.46	1033	2.26	1143	0.78
1043	2.07	1027	2.34			1088	1.47	1020	2.33	1103	1.33	1042	2.18	1155	0.67
		1037	2.24			1096	1.37	1030	2.25	1116	1.17	1063	1.88		
						1107	1.21			1127	1.03				
						1118	1.10								
						1127	0.98								
						1135	0.89								

Table 4. Torsion Total Vapor Pressures for TmI_3

run 1, cell C1		run 1, cell C2		run 2, cell B		run 3, cell B		run 4, cell C1		run 4, cell C2		run 5, cell B		run 6, cell B		run 7, cell B	
T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$	T	$-\log(p)$
K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa	K	kPa
887	3.88	959	2.74	906	3.64	907	3.68	902	3.68	966	2.64	909	3.80	888	4.11	905	3.77
897	3.80	968	2.56	914	3.51	916	3.54	911	3.54	978	2.47	916	3.68	899	3.93	914	3.63
905	3.63	976	2.44	921	3.43	925	3.38	920	3.34	987	2.34	925	3.54	906	3.80	923	3.47
912	3.50	983	2.36	928	3.30	932	3.27	930	3.18	991	2.30	933	3.41	912	3.68	932	3.33
920	3.35	991	2.26	936	3.18	939	3.15	939	3.04	999	2.20	940	3.28	922	3.50	941	3.18
930	3.20	999	2.15	946	3.02	948	3.02	946	2.95	1008	2.06	949	3.14	931	3.38	951	3.01
938	3.08	1006	2.03	955	2.88	953	2.94	954	2.83	1017	1.94	956	3.03	938	3.26	960	2.89
948	2.94	1014	1.95	963	2.76	961	2.84	961	2.72	1025	1.84	964	2.91	947	3.12	966	2.80
956	2.80	1024	1.82	971	2.63	969	2.73	970	2.60	1034	1.71	971	2.80	955	2.98	976	2.67
966	2.68	1032	1.70	980	2.51	975	2.60	976	2.53	1043	1.59	980	2.69	963	2.87	984	2.56
973	2.59	1043	1.55	988	2.41	981	2.55			1051	1.48	989	2.55	973	2.73	993	2.45
		1051	1.43											981	2.62	1002	2.31
														989	2.51		

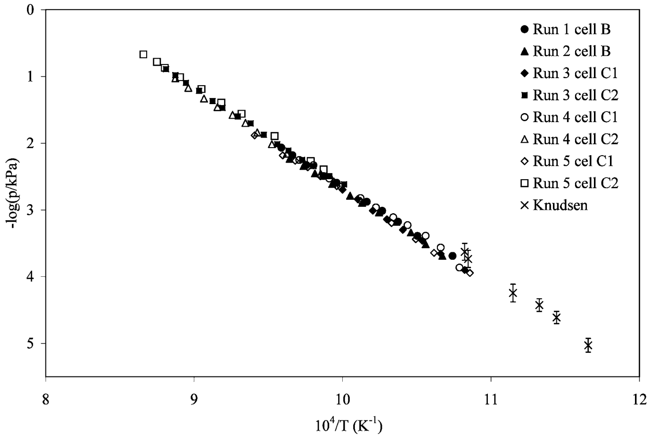

Figure 2. Experimental vapor pressure above $TmBr_3$.

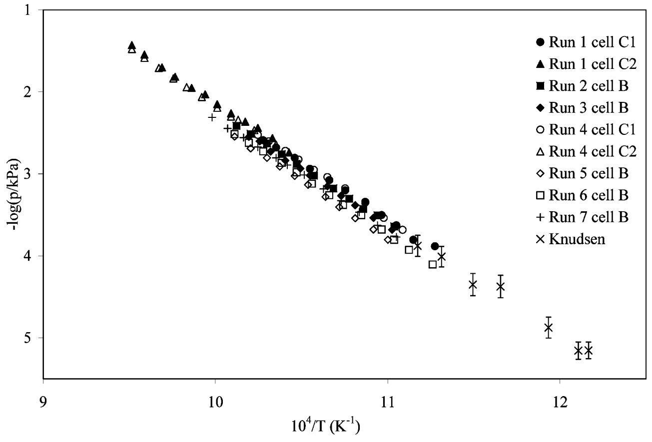

Figure 3. Experimental vapor pressure above TmI_3.

equations were estimated to be practically equal for all the studied compounds.

The Knudsen total vapor pressures of all thulium halides (calculated taken in to account the presence of 7% of dimer for $TmCl_3$ and negligible amount for $TmBr_3$ and TmI_3), agree sufficiently well with the torsion results, but this agreement, considering the experimental errors associated both with the torsion and the Knudsen measurements, was not taken as a check of the composition of the vapor. In fact, a change of the vapor molecular weight of the vapor (present in the Knudsen equation)[18] for the presence of about 10% of dimer, influences the final Knudsen log p value for about ±0.02, a value comparable with the errors connected with the experimental measurements.

The selected eqs 1−3 are compared with the few data reported in the literature in Figures 4−6. As concerns $TmCl_3$, our pressures are lower by about a factor of 2 than those measured by Kudin et al.[3] For $TmBr_3$, the vapor pressures measured by KEMS[4] at the lowest temperatures [$\log(p/\mathrm{kPa}) = (11.256 \pm 0.277) - (13954 \pm 280)(T/\mathrm{K})$] are in excellent agreement with our values, though the slope of their log p vs $1/T$ equation is slightly lower. Also for TmI_3, our vapor-pressure values agree enough with those measured by the Knudsen method,[5] but the slope of our data is decidedly lower.

Discussion and Conclusion

From the slopes of the selected log p vs $1/T$ eqs 1−3, the second-law enthalpies associated to the sublimation pro-

Table 5. Knudsen Partial Vapor Pressures for $TmCl_3(g)$ and Total Vapor Pressures for $TmX_3(g)$ (X = Br, I)

compound	cell	$T \pm 1$	$(\Delta t \pm 0.02) \times 10^{-4}$	$\Delta m \pm 0.2$	$-\log(p)$[a]
		K	s	mg	kPa
$TmCl_3$	B_k	868	40.59	4.5	5.22 ± 0.10
	B_k	877	29.11	5.9	4.95 ± 0.10
	B_k	884	29.57	7.3	4.86 ± 0.10
	A_k	908	73.37	9.6	4.53 ± 0.13
	A_k	925	23.74	6.9	4.18 ± 0.14
	A_k	936	24.95	10.0	4.03 ± 0.13
	A_k	947	21.04	11.4	3.90 ± 0.13
$TmBr_3$	B_k	858	32.89	6.8	5.03 ± 0.10
	B_k	874	33.57	18.1	4.61 ± 0.09
	B_k	883	15.67	12.9	4.43 ± 0.09
	A_k	897	10.38	3.2	4.25 ± 0.13
	A_k	922	5.49	5.4	3.73 ± 0.13
	A_k	927	7.15	9.0	3.63 ± 0.13
TmI_3	B_k	822	28.59	5.3	5.15 ± 0.10
	B_k	826	22.65	4.1	5.16 ± 0.11
	B_k	838	5.95	2.1	4.88 ± 0.13
	A_k	858	22.14	6.0	4.37 ± 0.14
	A_k	870	23.27	6.6	4.35 ± 0.14
	A_k	884	42.34	26.1	4.01 ± 0.13
	A_k	895	18.45	15.3	3.88 ± 0.13

[a] The errors were estimated taking into account only the uncertainties in sublimation weight and the time necessary for the initial thermostatation of cell.

Table 6. Temperature Dependence of the Partial Pressures for $TmCl_3(g)$ and Total Vapor Pressure of $TmX_3(g)$ (X=Br, I)

compound	run	cell	no. of points	ΔT	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
				K	A[a]	B[a]
$TmCl_3$	1	C1	11	971−1069	11.67 ± 0.18	14814 ± 187
$TmCl_3$	2	C1	11	959−1049	11.90 ± 0.15	14950 ± 147
$TmCl_3$	3	C1	10	945−1063	11.78 ± 0.19	14918 ± 194
$TmCl_3$	4	C1	8	1020−1089	11.36 ± 0.18	14728 ± 188
$TmCl_3$	5	C1	8	1030−1093	11.58 ± 0.16	14793 ± 174
$TmCl_3$	6	C1	8	1011−1086	11.47 ± 0.16	14702 ± 168
$TmCl_3$	7	B	9	1018−1093	11.50 ± 0.21	14785 ± 222
$TmCl_3$	8	B	9	1018−1088	11.43 ± 0.18	14743 ± 191
$TmBr_3$	1	B	10	931−1043	11.38 ± 0.13	14035 ± 126
$TmBr_3$	2	B	11	937−1037	11.28 ± 0.21	13991 ± 210
$TmBr_3$	3	C1	8	924−1000	11.81 ± 0.16	14510 ± 157
$TmBr_3$	3	C2	15	999−1135	11.91 ± 0.11	14544 ± 114
$TmBr_3$	4	C1	11	927−1030	11.69 ± 0.40	14331 ± 389
$TmBr_3$	4	C2	12	1006−1127	11.89 ± 0.16	14566 ± 167
$TmBr_3$	5	C1	11	921−1063	11.64 ± 0.17	14363 ± 171
$TmBr_3$	5	C2	10	1013−1155	11.64 ± 0.13	14196 ± 143
TmI_3	1	C1	11	887−973	11.31 ± 0.26	13505 ± 243
TmI_3	1	C2	12	959−1051	11.77 ± 0.18	13891 ± 185
TmI_3	2	B	11	906−988	11.41 ± 0.13	13643 ± 125
TmI_3	3	B	11	907−981	11.43 ± 0.15	13707 ± 142
TmI_3	4	C1	10	902−976	11.60 ± 0.25	13770 ± 237
TmI_3	4	C2	11	966−1051	11.70 ± 0.13	13867 ± 131
TmI_3	5	B	11	909−989	11.74 ± 0.10	14128 ± 93
TmI_3	6	B	13	888−989	11.64 ± 0.11	13982 ± 106
TmI_3	7	B	12	905−1002	11.28 ± 0.10	13611 ± 92

[a] The quoted errors are standard deviations.

cesses of thulium halides at the midpoint temperatures

$$TmX_3(cr) \rightarrow TmX_3(g) \qquad (X = Cl, Br, I) \qquad (4)$$

were calculated to be: $\Delta_{sub}H°(1019\ K) = 283 \pm 4\ kJ\cdot mol^{-1}$, $\Delta_{sub}H°(1038\ K) = 274 \pm 4\ kJ\cdot mol^{-1}$, and $\Delta_{sub}H°(969\ K) = 264 \pm 4\ kJ\cdot mol^{-1}$ for $TmCl_3$, $TmBr_3$, and TmI_3, respectively. The differences of the enthalpy increments, $\Delta[H°(T) - H°(298\ K)]$, required for reducing these enthalpies at 298 K were taken from Pankratz[22] for gaseous $TmCl_3$ and TmI_3, from Rycerz and Gaune-Escard[21] for solid $TmCl_3$, and from Gardner and Preston[23] for solid TmI_3, respectively. The differences so determined are (16 and 13) $kJ\cdot mol^{-1}$ for $TmCl_3$ and TmI_3, respectively. The increment for $TmCl_3$ is equal to that used by Kudin et al.[3] for reducing their sublimation enthalpy measured at 985 K, a temperature comparable to our midpoint (1019 K). As, apparently, for solid $TmBr_3$ no thermodynamic data are available in the literature, for this compound, the value of the enthalpy increment, $\Delta[H°(T) - H°(298\ K)] = 16\ kJ\cdot mol^{-1}$ was used for the reduction; the value was estimated considering the corresponding data reported by Pankratz[22] for other homologous rare-earth bromides. Considering the differences of the enthalpy increments for $TmCl_3$, this value can be considered an upper limit. The obtained final values for the second-law sublimation enthalpy were: $\Delta_{sub}H°(298\ K) = (299 \pm 4), (290 \pm 5)$, and $(277 \pm 4)\ kJ\cdot mol^{-1}$ for $TmCl_3$, $TmBr_3$, and TmI_3, respectively, where the error for $TmBr_3$ was raised to $\pm 5\ kJ\cdot mol^{-1}$ considering the uncertainty in the enthalpy increment.

Table 7. fef, in $J\cdot K^{-1}\cdot mol^{-1}$, of Solid and Gaseous TmX_3 (X = Cl, Br, I)

compound	T/K		
	900	1000	1100
$TmCl_3(cr)$[a]	194.97	202.44	208.97 (at 1092 K)
$TmCl_3(g)$[b]	409.09	414.97	420.14 (at 1092 K)
	196.4[c]	194.5[c]	193.1[c] (at 1092 K)
$TmBr_3(cr)$[d]	242	249	256
$TmBr_3(g)$[b]	436.58	442.51	448.12
$TmBr_3(g)$[e]	432.0	437.9	443.5
$TmI_3(cr)$[f]	269	276	283
$TmI_3(g)$[b]	465.55	471.52	477.15

[a] Rycerz and Gaune-Escard.[21] [b] Pankratz.[22] [c] Differences between the free energy functions for gaseous and solid $TmCl_3$ as reported in the literature (ref 3). [d] Evaluated by us (see text). [e] Gietmann et al.[4] [f] Evaluated in the present work (see text).

Table 8. Third-Law Standard Sublimation Enthalpies for $TmCl_3$ and $TmBr_3$

compound	T	p	$-R \ln p$	Δfef		$\Delta H°(298\ K)$	
	K	kPa	$J\cdot mol^{-1}$	$J\cdot K^{-1}\cdot mol^{-1}$		$kJ\cdot mol^{-1}$	
$TmCl_3$	900	$1.40\cdot 10^{-5}$	131.3	214.1[a]	196.4[b]	310.9[a]	294.9[b]
$TmCl_3$	1000	$6.20\cdot 10^{-4}$	99.8	212.5[a]	194.5[b]	312.3[a]	294.3[b]
$TmCl_3$	1092	$1.10\cdot 10^{-2}$	75.9	211.2[a]	193.1[b]	313.5[a]	293.7[b]
$TmBr_3$	900	$5.58\cdot 10^{-5}$	119.8	194.6[c]	190.0[d]	282.9[c]	278.8[d]
$TmBr_3$	1000	$2.18\cdot 10^{-3}$	89.3	193.5[c]	188.9[d]	282.8[c]	278.2[d]
$TmBr_3$	1100	$4.38\cdot 10^{-2}$	64.4	192.1[c]	187.5[d]	282.2[c]	277.1[d]

[a] Calculated using the free energy function reported by Rycerz and Gaune-Escard [21] and Pankratz.[22] [b] Calculated by using differences of the free energy functions reported in the literature (ref 3). [c] Calculated by the fef for $TmBr_3(g)$ reported by Pankratz[22] (see text). [d] Calculated by the fef function for $TmBr_3(g)$ reported by Gietmann et al.[4] (see text).

The standard enthalpy values associated to the sublimation processes (eq 4) were also calculated by the third-law method; for $TmCl_3$, the enthalpies were calculated at (900, 1000, and 1092) K (1092 K is the melting point)[21] by using the partial pressures from eq 1 and two sets of free-energy functions (fef), $[G°(T) - H°(298\ K)]/T$, one taken from the same sources of the enthalpic increments (Rycerz and Gaune-Escard[21] and Pankratz[22]) and another one derived from the results reported in both works in ref 3 (Giricheva et al.[24] for $TmCl_3(g)$ and IVTANTHERMO-96[25] for $TmCl_3(s)$) (see Table 7). The third-law sublimation enthalpy values so obtained are reported in Table 8.

The values of the differences of Δfef are decidedly different. The agreement of the enthalpy increment values obtained from the same sources leads to the conclusion that the disagreement for Δfef is connected with different values of the standard entropies for solid and/or gaseous com-

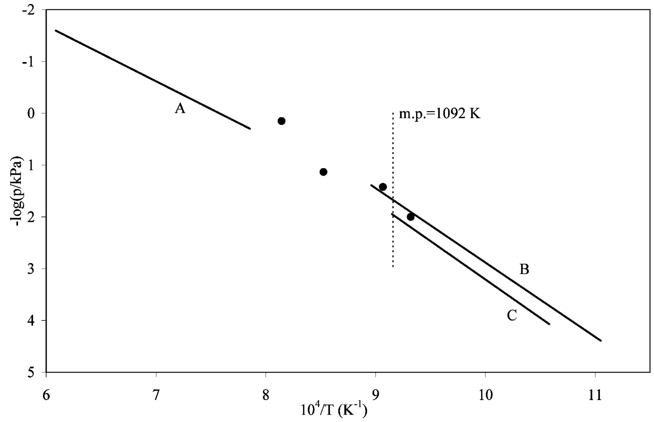

Figure 4. Comparison $TmCl_3$(g) partial pressures: ●, Moriarty;[2] A, Dudchik et al.;[1] B, Kudin et al.;[3] C, this work.

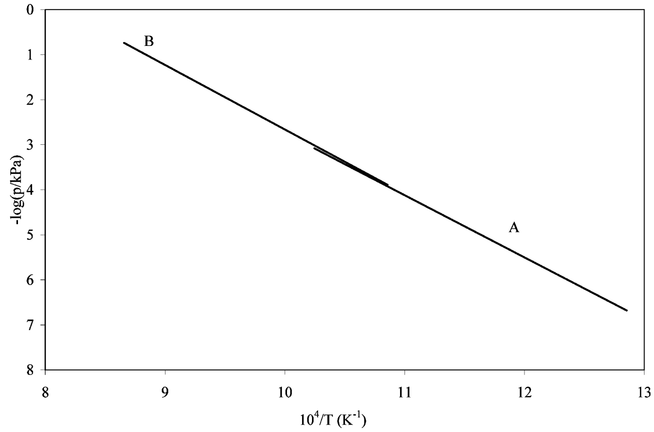

Figure 5. Comparison of total vapor pressures for $TmBr_3$: A, Gietmann et al.;[4] B, this work.

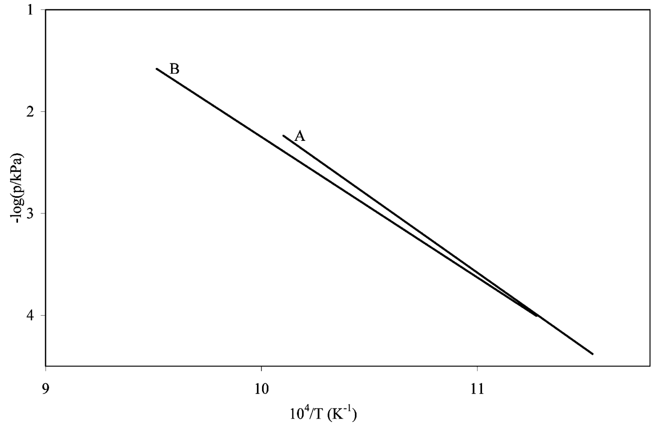

Figure 6. Comparison of total vapor pressures for TmI_3: A, Hirayama et al.;[5] B, this work.

pounds. The third-law sublimation enthalpies obtained using the Kudin's fef do not present an evident trend, and their average value (294 ± 2 kJ·mol^{-1}) is in better agreement with the second-law value (299 ± 4 kJ·mol^{-1}) than the results obtained by using the fef from Rycerz and Gaune-Escard[21] and Pankratz[22] (312 kJ·mol^{-1}, see Table 8). On this basis, we propose the average value $\Delta_{sub}H°(298\ K) = (296 \pm 2)$ kJ·mol^{-1} as a standard sublimation enthalpy of $TmCl_3$. The value is in agreement within the associated error with those reported in the literature (292,[1] 298,[2] and 291 ± 5[3]) kJ·mol^{-1}.

Like $TmCl_3$, also for $TmBr_3$ some standard sublimation enthalpy values were calculated by the third-law treatment of the vapor pressures at (900, 1000, and 1100) K. The fef for solid $TmBr_3$ (reported in Table 6) necessary for this calculation was estimated by us from the corresponding values for other solid tribromides of heavy lanthanides and in particular from $HoBr_3$,[21] from those for $TbBr_3$[15] and $ErBr_3$[16] (both calculated from their $S°(298\ K)$ and the experimental temperature dependence of their heat capacities), and from $DyBr_3$[13] (derived from third-law treatment of the vapor-pressure data). The difference between the lowest fef values ($HoBr_3$) and the highest ones ($DyBr_3$), equal to about 3 kJ·mol^{-1}, is practically constant in the temperature range (900 to 1100) K. For gaseous $TmBr_3$ are used the fef reported by Pankratz[22] and those reported in the Gietmann's work.[4] By use of these fef, two sets of third-law sublimation enthalpies of $TmBr_3$ were calculated and reported in Table 8. The two sets of enthalpies so obtained are different for about 5 kJ·mol^{-1} but both show a negligible temperature trend. The average third-law enthalpy value, $\Delta_{sub}H°(298\ K) = 282.5$ kJ·mol^{-1}, obtained by using the Pankratz's fef for $TmBr_3$(g), is higher than the average enthalpy value (278 kJ·mol^{-1}) obtained by Gietmann's fef but is in better agreement with the second-law result (290 ± 5 kJ·mol^{-1}). On this basis, considering the uncertainties in the fef and enthalpy function for both the solid and gaseous phases, we propose as standard sublimation enthalpy for $TmBr_3$ the value: $\Delta_{sub}H°(298\ K) = 285$ kJ·mol^{-1}, with an estimated error that should not exceed ±5 kJ·mol^{-1},

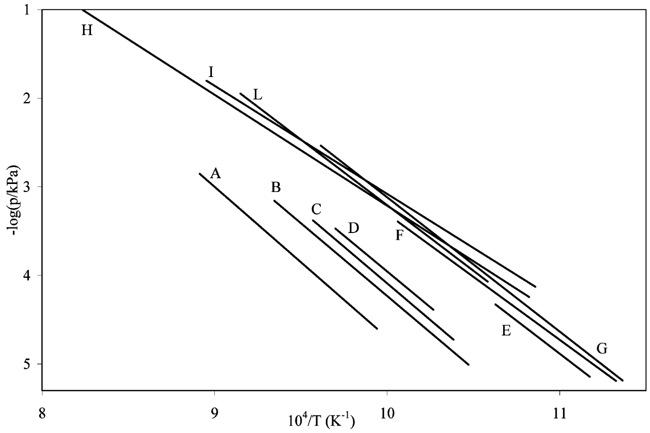

Figure 7. Pressures of solid trichlorides for A, La;[8] B, Ce;[9] C, Pr;[10] D, Nd;[11] E, Sm;[12] F, Ho;[14] G, Er;[16] H, Dy;[13] I, Tb;[16] L, Tm (this work). The pressure values for $ErCl_3$ (G) and $TmCl_3$ (L) are practically equal.

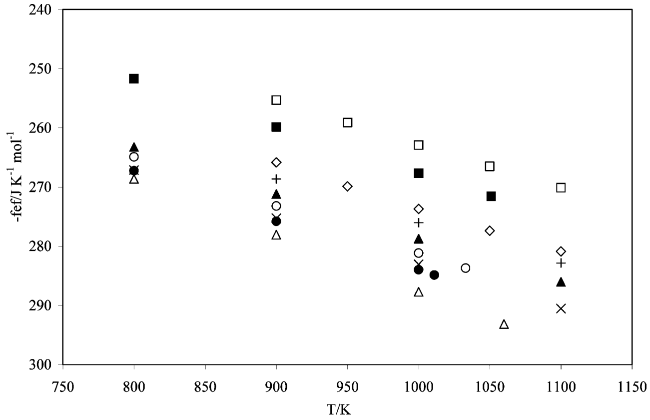

Figure 8. Comparison of the free energy function $[(G°(T) - H°(298\ K)]/T$ for solid lanthanides triiodide reported by Pankratz:[22] ■, LaI_3; ○, CeI_3; ●, PrI_3; △, NdI_3; ▲, GdI_3; ×, TbI_3; □, HoI_3;[14] ◇, ErI_3;[16] +, TmI_3 (this work).

a value slightly higher than the final value (280 ± 6) kJ·mol^{-1} proposed by Gietmann et al.[4]

Concerning TmI_3, by use of the second-law standard sublimation enthalpy $\Delta_{sub}H°(298\ K) = (277\pm4)\ kJ\cdot mol^{-1}$ and the vapor pressures calculated from the eq 3 at (900, 1000, and 1100) K, Δfef associated to the sublimation process of this compound were calculated at these temperatures, $\Delta fef = -197, -195$, and $-194\ J\cdot K^{-1}\cdot mol^{-1}$, respectively. From the fef for $TmI_3(g)$ reported by Pankratz, the corresponding fef for $TmI_3(cr)$ was derived, (269, 276, and 283) $J\cdot K^{-1}\cdot mol^{-1}$ at (900, 1000, and 1100) K, respectively. The analysis of the error sources to evaluate the uncertainty associated with these values leads to a high value (about $\pm10\ J\cdot K^{-1}\cdot mol^{-1}$), but it is interesting to note that the fef for $TmI_3(cr)$ so determined is comparable with those for the triiodides of other lanthanides (see Figure 8) and in particular with those found employing the same procedure for ErI_3.[16]

From these fef and the heat capacities calorimetrically measured by Gardner and Preston,[23] the standard entropy for $TmI_3(cr)$ $S°(298\ K) = 227\ J\ K^{-1}\cdot mol^{-1}$ was derived; the value was included in the range $214\ J\ K^{-1}\cdot mol^{-1}$ (LaI_3) to $230\ J\ K^{-1}\cdot mol^{-1}$ (NdI_3) of other triiodides.[22]

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