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Vapor Pressures and Sublimation Enthalpies of Gadolinium Trichloride, Tribromide, and Triiodide and Terbium Trichloride, Tribromide, and Triiodide

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The equilibrium vapor pressures over $GdCl_3$, $GdBr_3$, α-GdI_3, $TbCl_3$, $TbBr_3$, and α-TbI_3 were measured by the torsion-effusion method. The obtained data are well represented in the covered temperature ranges by the following selected equations:

$GdCl_3$(l) $\log(p/\text{kPa}) = 9.50 \pm 0.30 - (13\,113 \pm 300)(K/T)$ (from 930 to 1213 K)

$GdBr_3$(s) $\log(p/\text{kPa}) = 11.46 \pm 0.20 - (14\,355 \pm 200)(K/T)$ (from 895 to 1057 K)

$GdBr_3$(l) $\log(p/\text{kPa}) = 9.75 \pm 0.30 - (12\,671 \pm 400)(K/T)$ (from 1060 to 1179 K)

α-GdI_3(s) $\log(p/\text{kPa}) = 10.99 \pm 0.20 - (13\,651 \pm 200)(K/T)$ (from 890 to 1012 K)

$TbCl_3$(l) $\log(p/\text{kPa}) = 9.13 \pm 0.20 - (12\,210 \pm 200)(K/T)$ (from 921 to 1117 K)

$TbBr_3$(s) $\log(p/\text{kPa}) = 11.09 \pm 0.20 - (14\,013 \pm 200)(K/T)$ (from 904 to 1108 K)

α-TbI_3(s) $\log(p/\text{kPa}) = 11.33 \pm 0.30 - (13\,850 \pm 400)(K/T)$ (from 861 to 1078 K)

Considering the vapor consists only of the monomeric form, by the second- and third-law treatment of the experimental data, the following standard sublimation enthalpies of the compounds were derived: $\Delta_{\text{sub}}H°(298\text{ K}) = (311 \pm 4, 292 \pm 2, 279 \pm 2, 296 \pm 4, 288 \pm 4, \text{and } 279 \pm 2)\ \text{kJ·mol}^{-1}$ for $GdCl_3$, $GdBr_3$, α-GdI_3, $TbCl_3$, $TbBr_3$, and α-TbI_3, respectively.

Introduction

This work is a continuation of our systematic study carried out in order to determine the sublimation enthalpies of rare-earth trihalides from measurements of their vapor pressures. The standard sublimation enthalpies determined in previous works[1−7] present an evident trend for the light lanthanides going from trichlorides to triiodides (La,[1] Ce,[2] Pr,[3] Nd,[4] and Sm[5]) while they are comparable for the corresponding trihalides of heavy lanthanides (Dy[6] and Ho[7]). In the present paper the results obtained from the study of gadolinium trihalides ($GdCl_3$, $GdBr_3$, and α-GdI_3) and of terbium trihalides ($TbCl_3$, $TbBr_3$, and α-TbI_3) are reported.

The vapor pressures for $GdCl_3$ and $TbCl_3$ were measured by Moriarty[8] and by Myers and Hannay[9] both by using the Knudsen effusion method and, at the highest temperatures, by Dudchik et al.[10] by using the boiling point method. Some Knudsen vapor pressure values for $GdCl_3$ were also measured by Evseeva and Zenkevich.[11] The sublimation enthalpy for this compound was mass-spectrometrically obtained by Ciach et al.[12] from the slope of a log I^+T versus $1/T$ equation. Moreover, in the mass-spectrometric investigations of the vapor above $TbCl_3$,[13,14] partial pressure values of the monomeric ($TbCl_3$), dimeric (Tb_2Cl_6), and trimeric (Tb_3Cl_9) forms were measured and the corresponding partial sublimation enthalpies were derived. As concerns $GdBr_3$ and $TbBr_3$, the vapor pressures of both compounds were mass-spectrometrically measured by Gietmann et al.[15] and, at the highest temperatures, by Makhmadmurodov et al.[16] using the boiling point method. Also Weigel and Trinkl,[17] by using a particular static method, measured the vapor pressures over molten $GdBr_3$. Apparently, the only vapor pressures of gadolinium triiodide and terbium triiodide reported in the literature are those measured by the Knudsen method by Hirayama et al.[18,19]

Experimental Section

The samples of gadolinium and terbium trihalides used in this study were supplied by Aldrich and were 99.9% pure as certified by the supplier. To minimize oxidation and hydrolysis of the samples, the manipulations and loading of the torsion cells were carried out in a drybox. A drop of naphthalene was placed over the effusion holes of the cells to protect the sample during the transfer in the torsion assembly. The torsion apparatus employed in the present work for the measurements of vapor pressures was practically the same as that described in detail and used in our previous work.[20] Several conventional torsion cells with different materials and areas of their effusion holes (cell type A, stainless steel with both holes 0.5 mm in diameter,

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and cell type B, graphite with both holes 1.0 mm in diameter) were used. The molten compounds present creeping-out effects. To minimize this effect and possible interaction with the cell material and to increase the surface of the sample, the samples were put in a small molybdenum nest of close texture inserted in the lodgings of the cell. As in the previous works,[4,5] a particular stainless steel cell, cell C, having two effusion holes with different areas (0.6 and 1.9 mm in diameter, respectively) was also employed in the present work. By using this cell, the vapor pressures of a compound can be measured over a large temperature range in a single experiment. In fact, by filling both lodgings of this cell with the sample, in the first step of the experiment, the torsion of the tungsten wire to which the cell is suspended is due to the effusion of the vapor through both holes (cell C_1). As the sample in the lodging with a large effusion hole vaporizes in a greater amount than that in the other one, when the sample in this lodging is completely vaporized, the torsion of the assembly decreases because it is due to the effusion of the vapor from the sample in the lodging with the smaller hole. This permits us to increase the temperature interval and to obtain vapor pressure values at the highest temperatures under the same experimental conditions of the first step of the measurement. Under these conditions the cell behaves as a new cell (cell C_2). The two cell constants of this “double cell” (cell C_1 and C_2) necessary to convert the torsion angles to pressure values, as well as those of the other cells A and cells B, were determined by vaporizing a pure standard (lead) having a well-known vapor pressure.[21] These constants were checked during the experiments, and their values were found to be reproducible within about 15%. This uncertainty produces a displacement in the final log p values of about ±0.1. The displacement due to errors in the torsion angle measurements is negligible. The uncertainties associated with the temperature values, measured by a calibrated Pt−Pt/Rh (10% Rh) thermocouple inserted in a second cell placed just beneath the torsion one, are also negligible and in the entire temperature range should not exceed ±1 K. To minimize systematic errors and as a check on equilibrium inside the cell, in the pressure measurement the temperatures were increased and decreased at random, although in the tables, for each run, the results are reported as increasing temperatures.

Results

Gadolinium Trihalides. The total vapor pressures measured in various runs above liquid $GdCl_3$, $GdBr_3$ in both the solid and liquid phases (melting point at 1058 K[22]), and solid GdI_3 , in both in the α and β phases (transition at 1013 K [23]), are reported in Table 1 and Figure 1. In Figure 2 are reported the experimental torsion angles obtained by using cell C in the study of $GdBr_3$ (runs A1 and A2). Among all the vapor pressure data for $GdBr_3$ measured by this cell in the first step of each experiment (when both lodgings were full of sample, cell C_1), the only values measured at temperatures lower than the melting point (mp = 1058 K[22]) above the solid compound were reported and taken into account in the evaluation of the sublimation enthalpy. Among all the vapor pressures measured in the second step of the experiments, using cell C as C_2 (when the only lodging with the smaller hole was still full of sample), only those measured at temperatures higher than the melting point above the molten compound were taken into account. Equally, for α-GdI_3 in the experiments carried out with cell C as C_1 and C_2, only vapor pressures measured at temperatures lower and higher than the crystal transition (1013 K) above the α and β solid phases, respectively, were reported in Table 1 and Figure 1. For each run, the slope and intercept of the log p versus $1/T$ equation representative of the experimental data was obtained by the least-squares method. In Table 2 are reported the so obtained values with the corresponding standard deviations together with the covered temperature ranges. The slight inconsistencies among log p versus $1/T$ equations could be due to unavailable small errors in the experimental torsion and temperature measurements, to errors associated with the cell constants of the different used cells, and to the expected failure of the least-squares treatment when applied both to a too small number of data points and over a small temperature range. Apparently no evident dependence of the pressure values on the area of the effusion holes of the used cells, and in particular of cell C, was observed. By weighting the slopes and intercepts reported in Table 2 proportionally to the corresponding numbers of experimental points, the following log p versus $1/T$ equations representative of the vapor pressures of gadolinium trihalides were selected:

$GdCl_3(l)$

$$\log(p/\mathrm{kPa}) = 9.50 \pm 0.30 - (13\,113 \pm 300)(K/T) \quad \text{(from 930 to 1213 K)} \tag{1}$$

$GdBr_3(s)$

$$\log(p/\mathrm{kPa}) = 11.46 \pm 0.20 - (14\,355 \pm 200)(K/T) \quad \text{(from 895 to 1057 K)} \tag{2}$$

$GdBr_3(l)$

$$\log(p/\mathrm{kPa}) = 9.75 \pm 0.30 - (12\,671 \pm 400)(K/T) \quad \text{(from 1060 to 1179 K)} \tag{3}$$

α-$GdI_3(s)$

$$\log(p/\mathrm{kPa}) = 11.99 \pm 0.20 - (13651 \pm 200)(K/T) \quad \text{(from 890 to 1012 K)} \tag{4}$$

where the associated errors were estimated. As concerns GdI_3, because the number of experimental points obtained by cell C used as C_2 above the β phase is small, the errors associated with slopes and intercepts of the corresponding log p versus $1/T$ equations are decidedly larger than those calculated as standard deviations, so that a final equation representative of the vapor pressure of β-GdI_3 was not selected as reliable. The vapor pressure values measured by cell C_2 above β-GdI_3 were only taken as a check that not large errors should have been made in the pressure measured above α-GdI_3 by using cell B and cell C as C_1. As concerns $GdBr_3$, from the log p versus $1/T$ equations obtained above solid and liquid phases (run A, D, and G in Table 4) and from the selected ones (eqs 2 and 3), rough values of the enthalpy of fusion and of the melting point of this compound were calculated and reported in Table 3 together with the corresponding calorimetric values obtained by Dworkin and Bredig.[22] Considering the procedure for melting point calculation, the errors associated with their values are difficult to evaluate because they are connected with the uncertainties of the slope and intercept of the log p versus $1/T$ equation and mainly with those of the cell constants of the used cell C. In any case, they are decidedly very large but the obtained data are important because they show that not large errors should have been made in the absolute temperature measurements.

Terbium Trihalides. The experimental total vapor pressures over liquid $TbCl_3$, solid $TbBr_3$, and solid α-TbI_3 are reported in Table 4 and in Figure 3. By treating the

Table 1. Total Vapor Pressures Measured by the Torsion Method above GdX_3 (X = Cl, Br, I)

$GdCl_3$

run A (cell B)		run B1 (cell C_1)		run B2 (cell C_2)		run D1 (cell C_1)		run D2 (cell C_2)		run E (cell A)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
958	4.20	930	4.48	1044	3.00	996	3.65	1099	2.47	1093	2.52
965	4.11	952	4.17	1061	2.87	1011	3.48	1107	2.38	1107	2.38
973	4.01	957	4.08	1076	2.66	1023	3.32	1116	2.29	1120	2.22
983	3.85	970	3.89	1086	2.57	1042	3.10	1120	2.23	1134	2.06
994	3.71	983	3.75	1091	2.47	1052	2.99	1126	2.18	1151	1.90
1004	3.60	1002	3.49	1103	2.36	1062	2.86	1135	2.10	1165	1.74
1015	3.45	1022	3.25	1113	2.24	1071	2.76	1144	2.00	1177	1.62
1024	3.31	1046	3.00	1117	2.22	1082	2.63	1154	1.88	1190	1.50
		1054	2.85	1126	2.12	1090	2.56			1203	1.39
				1138	2.01					1213	1.30
				1147	1.89						
				1156	1.80						
				1170	1.66						
				1187	1.49						

$GdBr_3$

run A1 (cell C_1)		run A2 (cell C_2)		run B (cell B)		run C (cell B)		run D1 (cell C_1)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
895	4.48	1060	2.19	910	4.38	951	3.60	951	3.85
917	4.11	1073	2.07	928	4.11	959	3.49	968	3.55
926	3.95	1085	1.93	945	3.81	965	3.41	979	3.37
937	3.78	1096	1.80	957	3.65	969	3.33	990	3.21
947	3.63	1105	1.69	968	3.49	973	3.26	1002	3.04
957	3.48	1114	1.62	979	3.33	979	3.17	1014	2.87
967	3.33	1123	1.55	984	3.25	983	3.10	1026	2.70
980	3.12	1140	1.37	989	3.15	988	3.03	1041	2.50
987	3.00	1148	1.29	999	2.99	993	2.96	1049	2.38
990	2.97	1155	1.21	1008	2.85	1000	2.86	1057	2.28
997	2.84			1015	2.77	1004	2.80		
1001	2.81			1018	2.72	1011	2.70		
1011	2.66			1023	2.66	1014	2.66		
1014	2.61			1029	2.56	1019	2.60		
1020	2.54			1032	2.53	1025	2.52		
1029	2.43			1035	2.47	1030	2.44		
						1041	2.29		
						1045	2.24		
						1049	2.18		

run D2 (cell C_2)		run E (cell B)		run F (cell B)		run G1 (cell C_1)		run G2 (cell C_2)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
1074	2.13	914	4.20	920	4.11	919	4.05	1067	2.03
1091	1.94	929	3.98	934	3.87	932	3.86	1078	1.92
1099	1.86	941	3.77	945	3.69	953	3.49	1087	1.84
1108	1.75	956	3.55	956	3.52	962	3.35	1098	1.72
1119	1.64	971	3.31	964	3.40	969	3.24	1108	1.63
1130	1.52	981	3.15	974	3.26	977	3.12	1119	1.52
1140	1.42	994	2.96	986	3.05	990	2.94	1128	1.43
1150	1.31	1003	2.83	996	2.91	999	2.81	1138	1.33
1159	1.23	1012	2.71	1006	2.79	1008	2.70	1150	1.21
1168	1.15	1023	2.56	1015	2.66	1018	2.56	1161	1.10
1179	1.04	1032	2.43	1025	2.52	1026	2.46	1169	1.04
		1043	2.29	1034	2.40	1036	2.33		
		1051	2.18	1043	2.29				
		1057	2.11	1051	2.18				
				1057	2.08				

GdI_3

run A (cell B)		run B1 (cell C_1)		run B2 (cell C_2)		run C (cell B)		run D (cell B)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
913	3.95	914	4.05	1023	2.17	905	4.07	891	4.25
925	3.75	924	3.91	1033	2.06	918	3.87	911	3.95
934	3.57	928	3.84	1045	1.90	928	3.71	919	3.81
942	3.46	936	3.70	1055	1.77	939	3.53	928	3.68
952	3.31	943	3.61	1064	1.66	947	3.41	937	3.55
962	3.15	951	3.48	1074	1.52	957	3.24	944	3.45
974	2.99	959	3.35	1083	1.40	966	3.10	955	3.28
983	2.87	966	3.24	1094	1.27	975	2.97	962	3.15
992	2.76	978	3.08	1102	1.17	984	2.84	970	3.04
		988	2.94			993	2.72	979	2.90
		997	2.86			1002	2.60	987	2.79
		1006	2.72			1011	2.48	995	2.67
								1003	2.57
								1012	2.45

run E1 (cell C_1)		run E2 (cell C_2)		run F1 (cell C_1)		run F2 (cell C_2)		run G (cell B)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
890	4.35	1019	2.47	901	4.08	1021	2.41	901	4.25
901	4.17	1026	2.39	914	3.86	1033	2.27	912	4.05
916	3.95	1040	2.22	922	3.75	1042	2.16	920	3.95
927	3.76	1052	2.06	929	3.63	1054	2.01	927	3.82
937	3.60	1066	1.87	938	3.49	1066	1.84	933	3.72
948	3.43	1082	1.67	946	3.40	1076	1.68	942	3.57
957	3.34			955	3.22	1086	1.55	954	3.38
967	3.14			964	3.10	1097	1.43	966	3.20
978	2.97			973	2.97			975	3.05
990	2.81			985	2.80			983	2.94
1002	2.66			993	2.69			992	2.85
1011	2.55			1002	2.60				

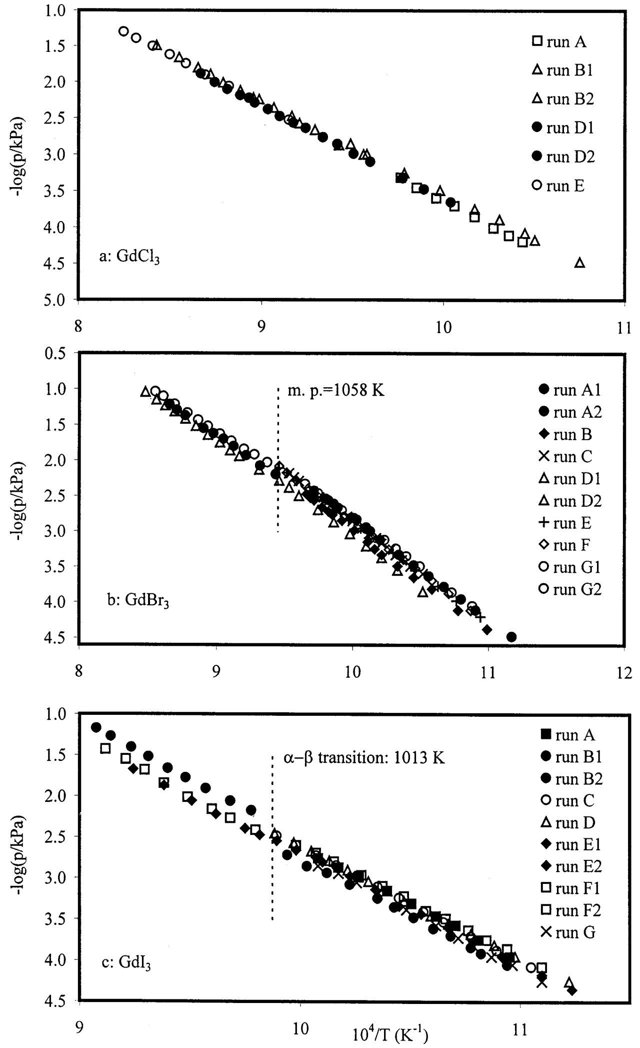

Figure 1. Experimental vapor pressure of $GdCl_3$ (a), $GdBr_3$ (b), and α-GdI_3 (c) measured by the torsion method.

experimental data as for gadolinium trihalides, the log *p* versus 1/*T* equations representative of the vapor pressures of these compounds measured in each run were calculated and reported in Table 5. From these the following final equations were derived:

$TbCl_3(l)$

$$\log(p/\text{kPa}) = 9.13 \pm 0.20 - (12210 \pm 200)(K/T) \quad \text{(from 921 to 1117 K)} \quad (5)$$

$TbBr_3(s)$

$$\log(p/\text{kPa}) = 11.09 \pm 0.20 - (14013 \pm 200)(K/T) \quad \text{(from 904 to 1108 K)} \quad (6)$$

α-$TbI_3(s)$

$$\log(p/\text{kPa}) = 11.33 \pm 0.30 - (13850 \pm 400)(K/T) \quad \text{(from 861 to 1078 K)} \quad (7)$$

where all the quoted errors were estimated.

Discussion

The pressure dependences of the vapor pressures of gadolinium and terbium trihalides measured in the present work are well represented by the selected log *p* versus 1/*T* equations (eqs 1−7). These equations are reported in Table 6 and in Figures 4 and 5 together with those found in the literature. In general our pressure data, within the errors limits, are not in conflict with the reference data. Only for α-GdI_3, although the absolute pressure values are comparable, is the slope of our final equation lower than that reported by Hirayama et al.[19]

Table 2. Temperature Dependence of the Total Vapor Pressure of GdX_3 (X = Cl, Br, I)

			no. of	ΔT	$\log(p/\text{kPa}) = A - B/(T/\text{K})$	
compd	cell	run	points	K	A^a	B^a
$GdCl_3(l)$	B	A	8	958−1024	9.41 ± 0.19	13 041 ± 187
$GdCl_3(l)$	C_1	B1	9	930−1054	9.09 ± 0.15	12 608 ± 151
$GdCl_3(l)$	C_2	B2	14	1044−1187	9.69 ± 0.15	13 293 ± 170
$GdCl_3(l)$	C_1	D1	9	996−1090	9.12 ± 0.08	12 728 ± 87
$GdCl_3(l)$	C_2	D2	8	1099−1154	9.59 ± 0.26	13 251 ± 287
$GdCl_3(l)$	A	E	10	1093−1213	9.93 ± 0.09	13 612 ± 105
$GdBr_3(s)$	C_1	A1	16	895−1029	11.42 ± 0.08	14 238 ± 79
$GdBr_3(l)$	C_2	A2	10	1060−1155	9.71 ± 0.14	12 626 ± 158
$GdBr_3(s)$	B	B	16	910−1035	11.50 ± 0.14	14 480 ± 139
$GdBr_3(s)$	B	C	19	951−1049	11.62 ± 0.07	14 484 ± 66
$GdBr_3(s)$	C_1	D1	10	951−1057	11.63 ± 0.10	14 698 ± 101
$GdBr_3(l)$	C_2	D2	11	1074−1179	10.13 ± 0.06	13 166 ± 62
$GdBr_3(s)$	B	E	14	914−1057	11.41 ± 0.05	14 287 ± 52
$GdBr_3(s)$	B	F	15	920−1057	11.41 ± 0.05	14 272 ± 50
$GdBr_3(s)$	C_1	G1	12	919−1036	11.23 ± 0.10	14 035 ± 98
$GdBr_3(l)$	C_2	G2	11	1067−1169	9.41 ± 0.11	12 215 ± 118
α-$GdI_3(s)$	B	A	9	913−992	11.02 ± 0.21	13 654 ± 201
α-$GdI_3(s)$	C_1	B1	12	914−1006	10.66 ± 0.14	13 443 ± 138
β-$GdI_3(s)$	C_2	B2	9	1023−1102	11.94 ± 0.15	14 454 ± 164
α-$GdI_3(s)$	B	C	12	905−1011	11.27 ± 0.06	13 892 ± 62
α-$GdI_3(s)$	B	D	14	891−1012	10.98 ± 0.11	13 598 ± 109
α-$GdI_3(s)$	C_1	E1	12	890−1011	10.90 ± 0.13	13 590 ± 125
β-$GdI_3(s)$	C_2	E2	6	1019−1082	11.37 ± 0.20	14 116 ± 205
α-$GdI_3(s)$	C_1	F1	12	901−1002	10.79 ± 0.12	13 392 ± 118
β-$GdI_3(s)$	C_2	F2	8	1021−1097	12.08 ± 0.32	14 824 ± 343
α-$GdI_3(s)$	B	G	11	901−992	11.32 ± 0.15	14 028 ± 138

[a] The quoted errors are standard deviations.

Table 3. Melting Point and Enthalpy of Fusion for $GdBr_3$

	$\Delta_{fus}H°$	T_{fus}
source	$kJ \cdot mol^{-1}$	K
runs A_1 and A_2	31 ± 4	943
runs D_1 and D_2	29 ± 3	1022
runs G_1 and G_2	35 ± 4	999
eqs 2 and 3	32 ± 11	982
Dworkin and Bredig [22]	38	1058

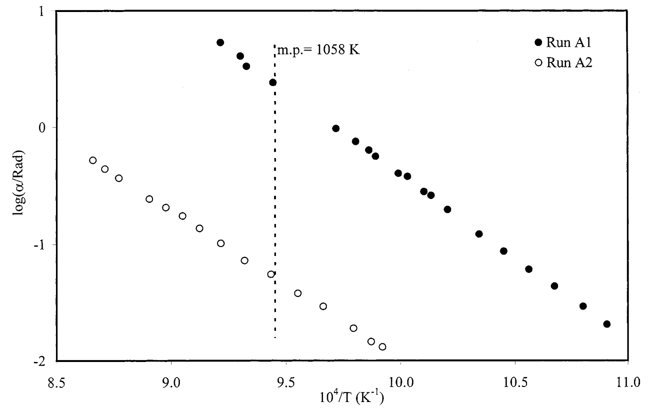

Figure 2. Experimental torsion angles measured over $GdBr_3$ by cell C in the A1 and A2 runs.

As in the covered temperature ranges the amount of the dimer form in the gaseous phase above all the studied compounds was considered negligible compared to that of the monomer form, the measured total vapor pressures were considered partial pressures of the corresponding monomers. In this way, the second-law sublimation or vaporization enthalpies of the studied trihalides in monomeric form were calculated, at the middle experimental

Table 4. Total Vapor Pressures Measured by the Torsion Method above TbX_3 (X = Cl, Br, I)

$TbCl_3$

run A (cell B)		run B (cell B)		run C (cell A)		run E (cell B)		run F (cell A)		run H (cell A)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
942	3.68	946	3.78	979	3.35	921	4.17	979	3.48	976	3.48
957	3.48	957	3.61	994	3.15	931	4.00	995	3.30	992	3.30
971	3.30	967	3.48	998	3.10	937	3.87	1009	3.13	1006	3.13
988	3.08	980	3.30	1010	2.94	943	3.77	1017	3.04	1017	3.00
999	2.97	990	3.18	1017	2.88	950	3.69	1028	2.91	1027	2.91
1011	2.83	999	3.04	1026	2.75	953	3.66	1035	2.83	1037	2.80
1021	2.72	1010	2.91	1034	2.67	961	3.54	1043	2.72	1048	2.68
1033	2.59	1020	2.80	1043	2.58	965	3.52	1054	2.61	1058	2.58
1045	2.45	1029	2.68	1054	2.45	971	3.43	1067	2.43	1071	2.43
1053	2.35	1038	2.59	1056	2.43	975	3.39			1082	2.27
1064	2.24	1047	2.48	1059	2.41	984	3.27			1093	2.15
1071	2.17	1057	2.38	1072	2.28	994	3.13			1105	2.04
1081	2.07	1065	2.29	1073	2.28	1006	2.98			1117	1.93
1092	1.95	1075	2.21	1091	2.07	1017	2.87				
1102	1.85					1024	2.78				
						1037	2.60				

$TbBr_3$

run A (cell A)		run B (cell A)		run C (cell B)		run D (cell B)		run E (cell A)		run F1 (cell C_1)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
957	3.48	922	4.08	904	4.32	915	4.32	920	4.08	915	4.38
970	3.30	940	3.68	915	4.12	922	4.21	940	3.78	925	4.14
993	2.97	958	3.48	920	4.07	930	4.07	958	3.54	933	4.02
1004	2.83	974	3.24	924	3.98	937	3.91	976	3.30	940	3.92
1015	2.70	992	2.97	930	3.88	943	3.85	989	3.08	950	3.78
1025	2.58	1004	2.80	935	3.82	950	3.74	1004	2.89	957	3.64
1035	2.48	1015	2.65	940	3.74	956	3.64	1014	2.78	964	3.54
1047	2.24	1025	2.53	944	3.68	962	3.56	1024	2.62	971	3.45
1059	2.07	1035	2.38	948	3.62	969	3.44	1032	2.53	977	3.37
1068	1.96	1042	2.27	954	3.53	975	3.37	1045	2.33	983	3.27
1076	1.85	1051	2.17	960	3.44			1054	2.19		
1088	1.76	1059	2.08					1064	2.04		
1099	1.64	1068	1.94					1071	1.95		
1108	1.54	1076	1.85					1078	1.85		
		1085	1.74								

run F2 (cell C_2		run G (cell A)		run H (cell B)		run I (cell B)		run L (cell B)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
962	3.43	928	4.02	912	4.42	908	4.33	921	4.12
973	3.27	937	3.86	920	4.32	917	4.09	934	3.92
983	3.13	944	3.73	934	4.07	931	3.92	939	3.82
993	3.00	957	3.56	941	3.94	947	3.67	945	3.73
1002	2.88	960	3.50	948	3.85	962	3.46	955	3.57
1012	2.76	977	3.24	955	3.72	978	3.21	964	3.41
1020	2.65	988	3.06	962	3.62	991	3.00	973	3.30
1030	2.53	1000	2.90	968	3.53	1003	2.86	981	3.18
1039	2.40	1007	2.81	974	3.45	1014	2.68	990	3.04
1049	2.24			980	3.37	1019	2.59	999	2.94
1058	2.15								
1067	2.00								
1076	1.89								
1088	1.80								

TbI_3

run A1 (cell C_1)		run A2 (cell C_2)		run B (cell B)		run C (cell A)		run D (cell A)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
871	4.55	971	2.98	861	4.72	972	2.72	955	3.02
883	4.37	979	2.85	879	4.48	983	2.62	971	2.78
892	4.21	986	2.77	897	4.18	990	2.54	988	2.54
902	4.04	994	2.64	913	3.91	998	2.42	1004	2.32
912	3.88	1001	2.55	929	3.64	1005	2.32	1016	2.15
922	3.73	1008	2.47	940	3.47	1012	2.24	1027	2.01
930	3.62	1015	2.36	948	3.37	1019	2.12	1037	1.88
939	3.47	1022	2.26	959	3.16	1028	2.02	1043	1.79
948	3.33	1029	2.17	967	3.04	1036	1.89	1049	1.69
958	3.18	1037	2.05	973	2.94	1043	1.79	1059	1.58
966	3.05	1044	1.94	983	2.82	1049	1.71	1066	1.50
973	2.93	1050	1.87	993	2.66	1057	1.61	1072	1.41
980	2.83	1058	1.76	1003	2.54	1064	1.51	1078	1.34
986	2.74	1064	1.68						
995	2.62	1070	1.58						
		1077	1.49						

Table 4. (Continued)

TbI$_3$ (Continued)

run E (cell B)		run F (cell B)		run G (cell A)		run H (cell B		run I (cell B)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
895	4.15	884	4.42	942	3.17	884	4.30	885	4.30
909	3.94	891	4.32	952	3.00	900	4.00	907	3.90
926	3.68	897	4.24	964	2.87	911	3.82	917	3.76
938	3.50	903	4.12	975	2.73	921	3.70	927	3.60
947	3.39	909	4.02	987	2.54	928	3.60	937	3.46
958	3.20	915	3.94	995	2.41	936	3.47	945	3.32
971	3.00	920	3.85	1003	2.30	944	3.35	953	3.22
980	2.86	927	3.74	1012	2.17	951	3.26	961	3.11
988	2.75	931	3.68	1020	2.04	959	3.13	967	3.01
998	2.60	935	3.62	1029	1.93	966	3.02	976	2.87
1006	2.51	940	3.55	1039	1.79	972	2.92	987	2.72
		947	3.44	1049	1.65	977	2.85	998	2.56
		953	3.35	1059	1.51	985	2.73	1009	2.42
		963	3.18	1066	1.42	992	2.63	1018	2.30
		973	3.02			998	2.55	1029	2.16
		981	2.91			1004	2.47		
		988	2.81			1008	2.41		
		994	2.74			1013	2.35		
		1002	2.62			1017	2.28		
		1009	2.55			1021	2.21		
						1026	2.18		
						1033	2.09		

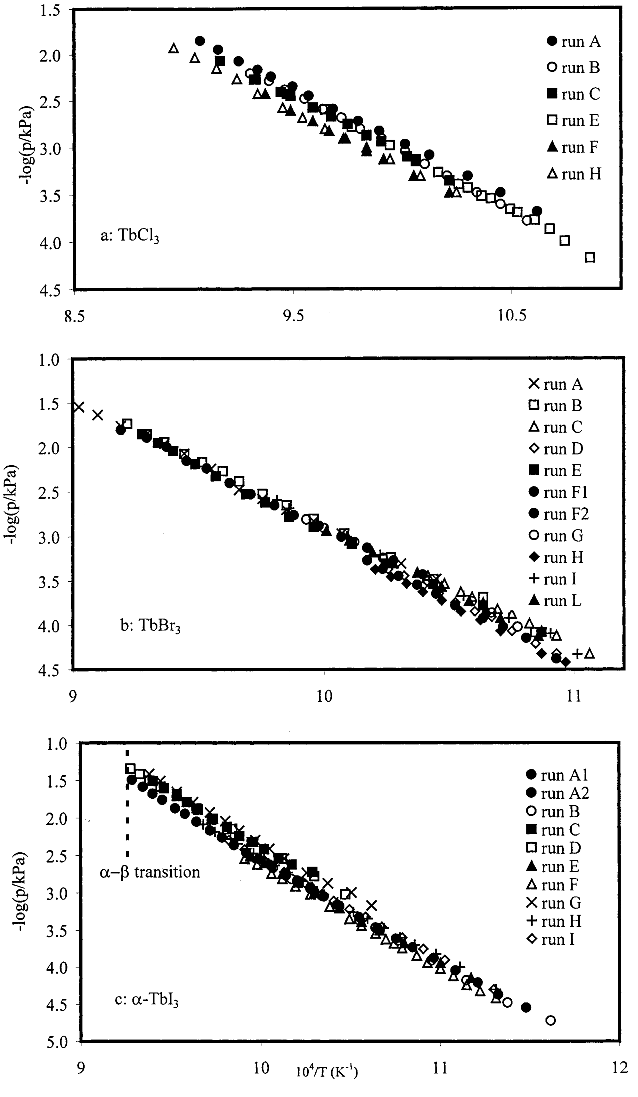

Figure 3. Experimental vapor pressure of TbCl$_3$ (a), TbBr$_3$ (b), and α-TbI$_3$ (c) measured by the torsion method.

temperatures, from the slopes of the selected equations (eqs 1−7). The enthalpies so obtained are reported in Table 7.

Table 5. Temperature Dependence of the Total Vapor Pressure of TbX$_3$ (X = Cl, Br, I)

compd	cell	run	no. of points	ΔT K	$\log(p/\text{kPa}) = A - B/(T/\text{K})$ A^a	B^a
TbCl$_3$(l)	B	A	15	942−1102	8.87 ± 0.04	11 828 ± 45
TbCl$_3$(l)	B	B	14	946−1075	9.41 ± 0.10	12 460 ± 97
TbCl$_3$(l)	A	C	14	979−1091	8.96 ± 0.10	12 036 ± 104
TbCl$_3$(l)	B	E	16	921−1037	9.37 ± 0.16	12 427 ± 154
TbCl$_3$(l)	A	F	9	979−1067	9.20 ± 0.20	12 440 ± 201
TbCl$_3$(l)	A	H	13	976−1117	8.93 ± 0.16	12 145 ± 165
TbBr$_3$(s)	A	A	14	957−1108	11.02 ± 0.20	13 898 ± 202
TbBr$_3$(s)	A	B	15	922−1085	11.26 ± 0.12	14 117 ± 126
TbBr$_3$(s)	B	C	11	904−960	10.62 ± 0.18	13 496 ± 168
TbBr$_3$(s)	B	D	10	915−975	11.25 ± 0.26	14 241 ± 246
TbBr$_3$(s)	A	E	14	920−1078	11.10 ± 0.22	14 022 ± 217
TbBr$_3$(s)	C$_1$	F1	10	915−983	11.20 ± 0.28	14 217 ± 262
TbBr$_3$(s)	C$_2$	F2	14	962−1088	10.91 ± 0.16	13 807 ± 165
TbBr$_3$(s)	A	G	9	928−1007	11.35 ± 0.13	14 255 ± 128
TbBr$_3$(s)	B	H	10	912−980	11.04 ± 0.18	14 107 ± 171
TbBr$_3$(s)	B	I	10	908−1019	11.11 ± 0.21	13 989 ± 203
TbBr$_3$(s)	B	L	10	921−999	11.24 ± 0.16	14 146 ± 151
α-TbI$_3$(s)	C$_1$	A1	15	871−995	11.02 ± 0.11	13 591 ± 106
α-TbI$_3$(s)	C$_2$	A2	16	971−1077	12.07 ± 0.12	14 630 ± 126
α-TbI$_3$(s)	B	B	13	861−1003	11.04 ± 0.17	13 630 ± 157
α-TbI$_3$(s)	A	C	13	972−1064	11.70 ± 0.26	14 075 ± 266
α-TbI$_3$(s)	A	D	13	955−1078	11.70 ± 0.08	14 068 ± 79
α-TbI$_3$(s)	B	E	11	895−1006	10.93 ± 0.17	13 520 ± 160
α-TbI$_3$(s)	B	F	20	884−1009	11.01 ± 0.08	13 671 ± 77
α-TbI$_3$(s)	A	G	14	942−1066	11.96 ± 0.18	14 280 ± 183
α-TbI$_3$(s)	B	H	22	884−1033	11.10 ± 0.09	13 627 ± 86
α-TbI$_3$(s)	B	I	15	885−1029	10.95 ± 0.07	13 492 ± 62

[a] The quoted errors are standard deviations.

Gadolinium Trihalides. The standard sublimation enthalpies of these compounds were obtained from their corresponding second-law values by the enthalpic increments, $H°(T) - H°(298\ \text{K})$, for the condensed and gaseous compounds selected by Pankratz.[23] The $\Delta_{\text{sub}}H°(298\ \text{K})$ values so obtained are reported in Table 7. As concerns GdBr$_3$, considering the few experimental runs carried out above the molten compound, the final second-law standard sublimation enthalpy value, $\Delta_{\text{sub}}H°(298\ \text{K}) = 293\ \text{kJ·mol}^{-1}$ with an estimated error of $\pm 4\ \text{kJ·mol}^{-1}$, was evaluated giving a twin weight to the enthalpic value determined above the solid phase. The third-law standard sublimation enthalpies for gadolinium trihalides were also determined at some temperatures using the vapor pressure values

Table 6. Comparison of the Temperature Dependence of the Total Vapor Pressures of GdX_3 and TbX_3 (X = Cl, Br, I)

				ΔT	$\log(p/\mathrm{kPa}) = A - BK/T - C\log(T/\mathrm{K})$		
compd	ref	method	no. of points	K	*A*	*B*	*C*
$GdCl_3$(l)[a]	10	boiling point	18	1369−1603	30.04	15 715	6
$GdCl_3$(l)	11	Knudsen	18	933−1073	8.23 ± 0.30	11 600 ± 300	
$GdCl_3$(l)	9	Knudsen	17	973−1044	10.10 [b]	13 788[b]	
$GdCl_3$(l)	this work	torsion	58	930−1213	9.50 ± 0.30	13 113 ± 300	
$GdBr_3$(s)	15	mass-spectr	45	854−1020	11.093 ± 0.050	13 664 ± 57	
$GdBr_3$(l)	16	boiling point		1220−1532	25.93 ± 45	13 603 ± 97	5
$GdBr_3$(l)	17	static	41	1205−1621	7.97	10 384	
$GdBr_3$(s)	this work	torsion	102	895−1057	11.46 ± 0.20	14 355 ± 200	
$GdBr_3$(l)	this work	torsion	32	1060−1179	9.75 ± 0.30	12 671 ± 400	
GdI_3(s)	19	Knudsen		917−1025	13.56 ± 0.28	16 009 ± 273	
α-GdI_3(s)	this work	torsion	82	890−1012	10.99 ± 0.20	13 651 ± 200	
$TbCl_3$(l)[c]	10	boiling point	17	1326−1653	29.79	14 995	6
$TbCl_3$(l)	9	Knudsen	19	936−1044	9.37 [b]	12 777[b]	
$TbCl_3$(l)	13	mass-spectr	60	890−1060	8.03 ± 0.65	11 678 ± 261	
$TbCl_3$(l)	14	mass-spectr	32	919−1054	8.32 ± 0.63	12 150 ± 031	
$TbCl_3$(l)	this work	torsion	81	921−1117	9.13 ± 0.20	12 210 ± 200	
$TbBr_3$(s)	15	mass-spectr	46	836−1021	12.168 ± 0.165	14 607 ± 165	
$TbBr_3$(l)	16	boiling point		1219−1536	26.76 ± 0.11	13 349 ± 72	5
$TbBr_3$(s)	this work	torsion	127	904−1108	11.09 ± 0.20	14 013 ± 200	
TbI_3(s)	19	Knudsen		889−995	11.71 ± 0.25	14 021 ± 231	
α-TbI_3(s)	this work	torsion	152	861−1078	11.33 ± 0.30	13 850 ± 400	

[a] Four Knudsen vapor pressure values were also reported by Moriarty[8] and drawn in Figure 3. [b] Equation obtained by us by treating with the least-squares method the experimental data reported in the Myers's paper.[9] [c] Four Knudsen vapor pressure values were also reported by Moriarty[8] and drawn in Figure 4.

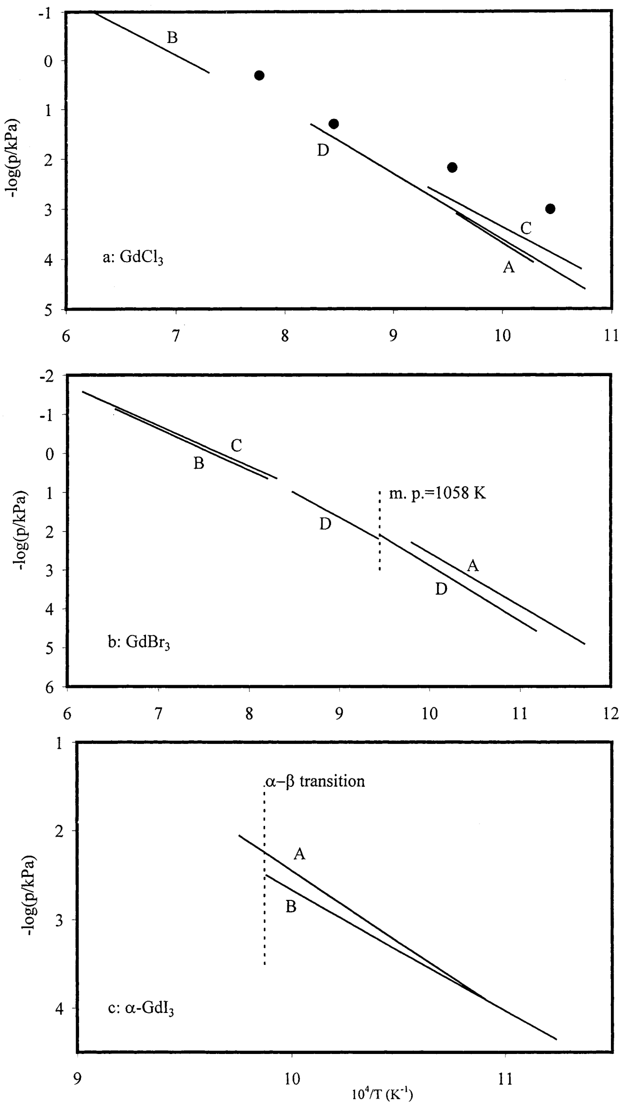

Figure 4. Comparison of vapor pressures for (a) $GdCl_3$: (●) Moriarty;[8] (A) Myers;[9] (B) Dudchik;[10] (C) Evseeva;[11] (D) this work. (b) $GdBr_3$: (A) Gietmann;[15] (B) Makhmadmurodov;[16] (C) Weigel;[17] (D) this work. (c) GdI_3: (A) Hirayama;[18] (B) this work.

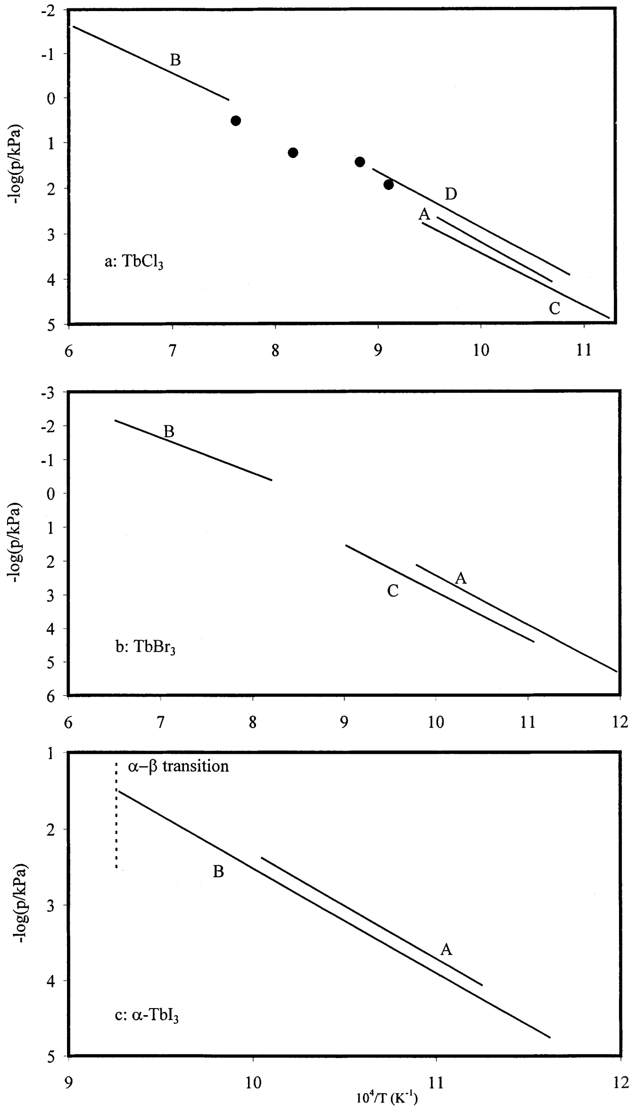

Figure 5. Comparison of vapor pressures for (a) $TbCl_3$: (●) Moriarty;[8] (A) Myers;[9] (B) Dudchik;[10] (C) Khasanshin;[13] (D) this work. (b) $TbBr_3$: (A) Gietmann;[15] (B) Makhmadmurodov;[16] (C) this work. (c) TbI_3: (A) Hirayama;[19] (B) this work.

Table 7. Second- and Third-Law Sublimation Enthalpies in kJ·mol^{-1} for GdX_3 and TbX_3 (X = Cl, Br, I)

	T	second-law		third-law
compd	K	$\Delta_{sub,vap}H°(T)$	$\Delta_{sub}H°(298\ K)$	$\Delta_{sub}H°(298\ K)$
$GdCl_3$(l)	1071	251 ± 6	317 ± 6	309 ± 1
$GdBr_3$(s)	976	275 ± 4	289 ± 4	292 ± 1
$GdBr_3$(l)	1119	242 ± 8	301 ± 8	295 ± 1
α-GdI_3(s)	951	261 ± 4	276 ± 4	280 ± 1
$TbCl_3$(l)	1019	234 ± 4	292 ± 4	300 ± 2
$TbBr_3$(s)	1006	268 ± 4	285 ± 4	292 ± 2,[a] 287 ± 2[b]
α-TbI_3(s)	970	265 ± 4	282 ± 4	277 ± 2

[a] Values obtained using for $TbBr_3$(g) the free energy function reported by Pankratz.[23] [b] Values obtained using for $TbBr_3$(g) the free energy function reported by Gietmann.[15]

calculated by the selected eqs 1−4 and the corresponding free energy functions (fef), $[G°(T) - H°(298\ K)]/T$, reported in Pankratz's Tables.[23] The results are reported in Table 8. The third-law $\Delta_{sub}H°(298\ K)$ values so obtained do not present evident temperature trends and are decidedly in good agreement with the corresponding second-law enthalpies (see Table 7). The difference of about 2 kJ·mol^{-1} between the third-law $\Delta_{sub}H°(298\ K)$ values for $GdBr_3$ determined by using the vapor pressures measured above molten and solid compounds (see Table 8) can be mainly due to a very small shift of the pressure data connected mainly with errors in the cell constants of cell C. Incidentally, this shift can also be the cause of the lower values of the melting point determined from the intersection of the log versus $1/T$ straight lines (see Table 3) than the selected one.[22] In any case, the vapor pressures measured above the solid compound were considered more reliable in view of the agreement of the pressure values determined by using several cells B and of the higher number of experimental points compared to those measured above the liquid phase.

On this basis we propose the following standard sublimation enthalpies, $\Delta_{sub}H°(298\ K)$ = (311 ± 4), (292 ± 2), and (279 ± 2) kJ·mol^{-1} for $GdCl_3$, $GdBr_3$, and GdI_3, respectively. Our $\Delta_{sub}H°(298\ K)$ value for $GdCl_3$ agrees with that mass-spectrometrically determined, from the slope of a log(I^+T) versus $1/T$ equation, by Ciach et al.[12] [(298 ± 17) kJ·mol^{-1}] and that obtained by Myers and Hannay [9] [(311 ± 12) kJ·mol^{-1}] from Knudsen measurements. Decidedly lower is the Knudsen enthalpy value reported by Evseeva and Zenkevich[11] [$\Delta_{sub}H°(1003\ K)$ = (222 ± 11) kJ·mol^{-1}]. As concerns $GdBr_3$, our selected enthalpy value is slightly higher than that selected by Gietmann,[15] $\Delta_{sub}H°(298\ K)$ = (280.2 ± 12.5) kJ·mol^{-1}. Our sublimation enthalpy found for α-GdI_3 is lower than those reported by Hirayama et al. [(295 ± 2) kJ·mol^{-1} (ref 18) and 321 ± 5 kJ·mol^{-1} (ref 19)].

Terbium Trihalides. From the second-law sublimation enthalpies for these compounds reported in Table 7, the corresponding standard values were obtained using the enthalpic increments selected by Pankratz.[23] The enthalpic increment for $TbBr_3$(s) was evaluated by the expression of the temperature dependence of the heat capacity, $c_p = (94.6 + (1.84 \times 10^{-2})T/K)$ J·mol^{-1}, proposed by Myers and Graves.[24] The so obtained second-law $\Delta_{sub}H°(298\ K)$ values of terbium trihalides are also reported in Table 7. The third-law values of these enthalpies were also calculated by using the vapor pressures derived from eqs 5−7 at some temperatures and the corresponding fef selected by Pankratz.[23] In absence in Pankratz's Tables of thermodynamic data for $TbBr_3$(s), the fef of this compound were evaluated using the standard entropy reported by Gietmann et al.,[15] $S°(298\ K)$ = 194 J·mol^{-1}·K^{-1}, and the heat capacity above-mentioned. The third-law sublimation enthalpies so obtained for all compounds present decidedly negligible temperature trends (see Table 8), and their average values may be considered in agreement with the corresponding second-law ones. On this basis we propose as standard sublimation enthalpy for $TbCl_3$ the value $\Delta_{sub}H°(298\ K)$ = 296 kJ·mol^{-1}, the average of the second- and third-law results, with an estimated error of ±4 kJ·mol^{-1}. This value agrees within the errors with those determined by Myers and Hannay,[9] (303 ± 13) kJ·mol^{-1}, and by Kudin et al.,[14] (290 ± 6) kJ·mol^{-1}. The mass-spectrometric value obtained by Khasanshin et al.[13] [(280

Table 8. Third-Law Sublimation Enthalpies for GdX_3 and TbX_3 (X = Cl, Br, I)

	T	p	$-R\ \ln(p/atm)$	$-\Delta$(fef)	$\Delta H°(298\ K)$
compd	K	kPa	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}
$GdCl_3$(l)	900	8.45×10^{-6}	135.5	208.7	309.8
$GdCl_3$(l)	1000	2.42×10^{-4}	107.6	202.1	309.7
$GdCl_3$(l)	1100	3.77×10^{-3}	84.8	196.2	309.1
$GdCl_3$(l)	1200	3.71×10^{-2}	65.8	190.8	307.9
$GdBr_3$(s)	900	3.27×10^{-5}	124.2	200.2	292.0
$GdBr_3$(s)	1000	1.29×10^{-3}	93.7	198.7	292.4
$GdBr_3$(s)	1058	7.87×10^{-3}	78.7	197.8	292.5
$GdBr_3$(l)	1058	5.94×10^{-3}	81.0	197.8	295.0
$GdBr_3$(l)	1100	1.70×10^{-2}	72.2	195.8	294.9
$GdBr_3$(l)	1200	1.55×10^{-1}	53.9	191.3	294.2
α-GdI_3(s)	900	6.57×10^{-5}	118.4	192.2	279.6
α-GdI_3(s)	950	4.13×10^{-4}	103.2	191.4	279.8
α-GdI_3(s)	1000	2.16×10^{-3}	89.4	190.6	280.0
α-GdI_3(s)	1013[c]	3.23×10^{-3}	86.1	190.4	280.1
$TbCl_3$(l)	900	3.62×10^{-5}	123.4	208.5	298.7
$TbCl_3$(l)	1000	8.23×10^{-4}	97.4	202.5	299.9
$TbCl_3$(l)	1100	1.06×10^{-2}	76.2	197.1	300.6
$TbBr_3$(s)	900	3.32×10^{-5}	124.1	199.1,[a] 194.1[b]	290.9,[a] 286.4[b]
$TbBr_3$(s)	1000	1.20×10^{-3}	94.3	197.5,[a] 192.8[b]	291.8,[a] 287.2[b]
$TbBr_3$(s)	1100	2.25×10^{-2}	69.9	195.9,[a] 191.2[b]	292.4,[a] 287.3[b]
α-TbI_3(s)	800	1.05×10^{-6}	152.8	193.5	277.1
α-TbI_3(s)	900	8.78×10^{-5}	116.0	191.8	277.0
α-TbI_3(s)	1000	3.04×10^{-3}	86.6	190.1	276.7
α-TbI_3(s)	1080[d]	3.22×10^{-2}	66.9	188.7	276.1

[a] Values obtained using the free energy function for $TbBr_3$(g) reported by Pankratz.[23] [b] Values obtained using the free energy function for $TbBr_3$(g) reported by Gietmann.[15] [c] Solid α−β transition for GdI_3(s) [d] Solid α−β transition for TbI_3(s)

± 5) kJ·mol^{-1}] is slightly more low. Two third-law $\Delta_{sub}H°$-(298 K) values were calculated for $TbBr_3$: one, (287 ± 2) kJ·mol^{-1}, using for the gaseous compound the fef proposed by Gietmann et al.[15] and another one, (292 ± 2) kJ·mol^{-1}, using the fef selected by Pankratz[23] (see Table 8). The first value is in better agreement with the second-law one [(285 ± 4) kJ·mol^{-1}], so that we propose as sublimation enthalpy for $TbBr_3$ the average value of 288 kJ·mol^{-1} with an overestimated error of ±4 kJ·mol^{-1}. This enthalpic value is practically coincident with that proposed by Gietmann[15] [(288.9 ± 6.3) kJ·mol^{-1}] obtained as the average of the corresponding second- and third-law values [(294.3 ± 7.8) and (279.1 ± 10.5) kJ·mol^{-1}, respectively]. As concerns the results obtained from second- and third-law treatment of the vapor pressures for α-TbI_3, they are in satisfactory agreement, so that we propose as final standard sublimation enthalpy the average of their values, $\Delta_{sub}H°(298\ K) = 279$ kJ·mol^{-1}, with an estimated error limit of ±2 kJ·mol^{-1}. This value, equal to that found in the present work for α-GdI_3, agrees with the value [(284 ± 5) kJ·mol^{-1}] reported by Hirayama et al.[19]

Conclusion

In the present work, the total vapor pressures of gadolinium and terbium trihalides were measured by the torsion-effusion method. As the contribution of partial pressures of the dimer forms should be negligible, in any case of the same order of magnitude of the uncertainties associated with the measured pressure values, the experimental pressure data were treated as partial pressures of the monomeric forms. The selected eqs 1−7 represent the best fit of the temperature dependence of these pressures. By second- and third-law treatment of the vapor pressure data represented by these equations, the standard sublimation enthalpies of these halides were calculated. The selected final values, $\Delta_{sub}H°(298\ K) = (311 \pm 4), (292 \pm 2)$, and (279 ± 2) kJ·mol^{-1} for $GdCl_3$, $GdBr_3$, and α-GdI_3, respectively, present, as observed for the previously studied trihalides of the first lanthanides, a decreasing trend going from trichlorides to triiodides. This trend is also present, but smoother, in the sublimation enthalpies for terbium trihalides, $\Delta_{sub}H°(298\ K) = (296 \pm 4), (288 \pm 4)$, and (279 ± 2) kJ·mol^{-1} for $TbCl_3$, $TbBr_3$, and α-TbI_3, respectively.

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