Vapor Pressure and Sublimation Enthalpies of Holmium Trichloride, Tribromide, and Triiodide

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The total vapor pressure of $HoCl_3$, $HoBr_3$, and HoI_3 was measured by the torsion and Knudsen effusion methods. By a least-squares treatment of the obtained data, the following equations were selected as representative for the temperature dependence of their vapor pressures in the covered temperature ranges: $HoCl_3$(s), $\log(p/\text{kPa}) = 10.91 \pm 0.10 - (14216 \pm 150)(K/T)$ (from 883 to 994 K); $HoCl_3$(l), $\log(p/\text{kPa}) = 9.16 \pm 0.10 - (12466 \pm 150)(K/T)$ (from 1002 to 1164 K); $HoBr_3$(s) $\log(p/\text{kPa}) = 10.95 \pm 0.10 - (14168 \pm 150)(K/T)$ (from 904 to 1105 K); HoI_3(s), $\log(p/\text{kPa}) = 12.24 \pm 0.10 - (14656 \pm 150)(K/T)$ (from 872 to 1066 K). When the data are treated by the second- and third-law methods, the standard sublimation enthalpies for $HoCl_3$ and $HoBr_3$, $\Delta_{\text{sub}}H°(298\ \text{K}) = 296 \pm 10$ and $290 \pm 5\ \text{kJ·mol}^{-1}$, respectively, were derived. For HoI_3 the proposed enthalpy, $\Delta_{\text{sub}}H°(298\ \text{K}) = 296 \pm 8\ \text{kJ·mol}^{-1}$, was only derived by the second-law method. From this standard enthalpy, a set of free energy functions for solid HoI_3 was evaluated by a third-law treatment of the data.

Introduction

Studies on the vaporization of holmium trihalides, and in particular measurements of their total saturated vapor pressures, are scanty. The only vapor pressure data available for $HoCl_3$ are four values measured by Moriarty[1] using the Knudsen method and two log p vs $1/T$ equations obtained mass spectrometrically by Kudin et al.[2] above solid and liquid phases. A $p-T$ equation for the liquid phase was determined by the boiling point method by Dudchik et al.[3] at high temperatures.

For $HoBr_3$ the pressure data are those selected by Knacke and Kubaschewski[4] and those measured at high temperatures by the boiling point method by Makhmadmurodov et al.[5,6] Recently, pressure determinations for $HoBr_3$ and HoI_3 have been carried out mass spectrometrically by Gietmann et al.[7,8] The authors report also some pressure values obtained by the Knudsen method. In their work the pressures of the dimer species, Ho_2Br_6 and Ho_2I_6, and an interesting investigation on the binary system $HoBr_3-HoI_3$ were also reported.

The vapor pressures above HoI_3 were measured by the Knudsen method by Hirayama et al.[9] and mass spectrometrically by Kaposi et al.[10]

By continuation of our research program on the study of the vaporization of lanthanide trihalides (Brunetti et al.[11,12] and Villani et al.[13,14]), the total vapor pressures of holmium trichloride, tribromide, and triiodide were measured. The obtained data were treated by the second- and third-law methods to derive the corresponding standard sublimation enthalpies of these compounds.

Experimental Details and Results

The vapor pressures of holmium trihalides were measured by the torsion method.[15] Some pressure values were also obtained by the Knudsen method.[16]

The holmium trihalide samples have a nominal purity of about 99.8%, as certified by Aldrich, supplier of these compounds. Because these compounds are very hygroscopic, their loading in the cells was carried out in a nitrogen-filled drybox and quickly introduced in the torsion or Knudsen assembly under vacuum. The used torsion assembly was described in detail in a previous work.[17] In this study three conventional graphite torsion cells having effusion orifices at 0.6, 1.0, and 1.8 mm diameter (cells A, B, and C, respectively) were used. In the vaporizations of $HoCl_3$, to increase the surface of the sample when it was molten and to minimize creeping-out effects, the sample was put on small quartz wool flocks. The temperature were measured by a calibrated chromel−alumel thermocouple inserted in a second cell equal to the torsion cell and placed beneath it. To measure the correct temperature of the sample, a particular procedure described in the previous work[17] was used. As usual, the cell constant values necessary to convert the experimental torsion angles into pressure data were obtained by vaporizing very pure standards having well-known vapor pressures. In this work pure lead and silver were used as standards.[18]

All experimental results obtained above $HoCl_3$, $HoBr_3$, and HoI_3 are reported in Tables 1−3 and Figures 1−3. For $HoCl_3$ the data are referred to the solid and liquid phases, while for $HoBr_3$ and HoI_3 the data are only referred to the solid phase.

Some vapor pressure values of these compounds were measured by the Knudsen method using an effusion assembly, the essential part of which consists of a stainless steel block in which a graphite conventional Knudsen cell (with the effusion hole of 0.8 mm in diameter) was inserted. The assembly was heated in an isothermal zone of a furnace, and the temperature of the cell was measured by two calibrated chromel−alumel thermocouples inserted into the top and the bottom of the block. The differences between the two temperature values were comparable to the uncertainty associated with their fluctuations (about ±1 K) observed during the time of the isothermal vaporiza-

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Table 1. Total Vapor Pressures Measured by the Torsion Method above Solid and Liquid $HoCl_3$

run A1 (cell A)		run A2 (cell A)		run B1 (cell B)		run B2 (cell B)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
883	5.29	888	5.19	929	4.34	928	4.34
894	5.11	907	4.89	942	4.19	932	4.27
908	4.89	923	4.49	950	4.01	942	4.12
914	4.69	933	4.34	962	3.85	947	4.04
925	4.59	949	4.11	966	3.74	955	3.92
933	4.44	959	4.01	971	3.71	964	3.78
940	4.33	968	3.87	974	3.63	967	3.72
945	4.25	976	3.74	980	3.58	973	3.64
951	4.11	986	3.59	982	3.53	977	3.59
962	3.97	990	3.51	987	3.47	983	3.50
973	3.80					987	3.44
983	3.65			1011	3.13		
994	3.47			1020	3.02	1002	3.22
				1028	2.93	1011	3.07
				1038	2.82	1017	3.02
				1047	2.72	1020	2.96
				1055	2.62	1027	2.88
				1063	2.51	1034	2.80
				1072	2.42	1043	2.71
				1082	2.31	1050	2.64
				1089	2.24	1057	2.56
				1094	2.19	1066	2.47
				1100	2.13	1074	2.37
						1083	2.26
						1089	2.20
						1097	2.10

run B3 (cell B)		run C1 (cell C)		run C2 (cell C)		run C3 (cell C)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
935	4.19	1008	3.24	1013	3.23	1014	3.19
947	3.94	1021	3.07	1023	3.06	1025	3.05
957	3.81	1032	2.97	1031	3.01	1034	2.91
963	3.73	1041	2.83	1039	2.86	1046	2.80
967	3.66	1048	2.75	1048	2.81	1058	2.69
969	3.64	1055	2.69	1056	2.69	1070	2.51
974	3.56	1065	2.60	1063	2.63	1083	2.37
976	3.53	1076	2.50	1074	2.51	1091	2.31
		1088	2.32	1085	2.41	1102	2.19
1007	3.17	1101	2.21	1096	2.28	1110	2.13
1019	3.02	1112	2.09	1108	2.15	1116	2.05
1035	2.82	1124	1.97	1117	2.07	1123	1.97
1042	2.74	1138	1.83	1130	1.92	1131	1.91
1054	2.60	1151	1.71				
1065	2.49	1164	1.60				
1075	2.38						
1085	2.29						
1095	2.17						
1104	2.07						

tions. At each experimental temperature the sample mass loss rate was evaluated by measuring the amount of sample vaporized over a known time period. The Knudsen constant necessary to convert the mass loss rates into vapor pressure data was determined by vaporizing highly pure lead. The vapor pressures and the experimental data from which they were derived are reported in Table 4. The vaporization runs were carried out at the lowest temperatures of the torsion experiments. The pressures obtained in this way agree satisfactorily with the values obtained from the torsion experiments (see Figures 1−3 and Table 4).

When the experimental torsion data are treated by linear least squares, for each run a log p vs $1/T$ equation was determined. The equations so determined are reported in Table 5. The few Knudsen pressures allow a check of the reliability of the torsion pressure values and were not employed in the calculation of the log p vs $1/T$ equations because, determined at low temperatures, their values influence heavily the final slopes. When the slope and intercept of each equation reported in Table 5 are weighed proportionally to the number of the experimental points, the following equations were selected:

$$HoCl_3(s) \quad \log(p/\mathrm{kPa}) = 10.91 \pm 0.10 - (14216 \pm 150)\,(K/T) \quad (\text{from 883 to 994 K}) \qquad (1)$$

$$HoCl_3(l) \quad \log(p/\mathrm{kPa}) = 9.16 \pm 0.10 - (12466 \pm 150)\,(K/T) \quad (\text{from 1002 to 1164 K}) \qquad (2)$$

$$HoBr_3(s) \quad \log(p/\mathrm{kPa}) = 10.95 \pm 0.10 - (14168 \pm 150)\,(K/T) \quad (\text{from 904 to 1105 K}) \qquad (3)$$

$$HoI_3(s) \quad \log(p/\mathrm{kPa}) = 12.24 \pm 0.10 - (14656 \pm 150)\,(K/T) \quad (\text{from 872 to 1066 K}) \qquad (4)$$

The errors associated with the slopes and intercepts were estimated and considered to be practically equal for all of the equations. These equations are compared with those found in the literature in Table 6 and in Figures 4−6.

Table 2. Total Vapor Pressures Measured by the Torsion Method above Solid $\mathrm{HoBr_3}$

run A1 (cell A)		run B1 (cell B)		run B2 (cell B)		run B3 (cell B)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
904	4.72	923	4.31	936	4.11	932	4.19
917	4.54	930	4.21	947	3.99	946	3.99
924	4.42	944	4.01	955	3.85	957	3.85
934	4.32	949	3.91	961	3.71	966	3.68
941	4.12	960	3.71	968	3.61	973	3.59
953	3.94	970	3.57	976	3.47	983	3.41
965	3.72	983	3.39	983	3.37	991	3.29
972	3.68	995	3.22	987	3.31	1004	3.12
979	3.54	1009	3.03	993	3.23	1013	2.97
988	3.44			999	3.16		
994	3.34			1005	3.07		
1002	3.21			1024	2.82		
1011	3.07			1041	2.63		

run B4 (cell B)		run C1 (cell C)		run C2 (cell C)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
926	4.29	967	3.85	963	3.87
940	4.04	980	3.50	973	3.72
952	3.89	991	3.45	982	3.49
960	3.81	1001	3.28	991	3.39
974	3.55	1007	3.19	1001	3.27
982	3.43	1015	3.10	1015	3.09
993	3.26	1021	3.03	1033	2.84
1004	3.11	1034	2.82	1048	2.65
1013	2.99	1050	2.67	1066	2.39
1024	2.84	1063	2.51	1088	2.15
1030	2.75	1074	2.32	1092	2.11
1037	2.69	1091	2.14	1098	2.01
				1105	1.94

Table 3. Total Vapor Pressures Measured by the Torsion Method above Solid $\mathrm{HoI_3}$

run A1 (cell A)		run B1 (cell B)		run B2 (cell B)		run B3 (cell B)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
872	4.65	967	2.79	939	3.35	911	3.77
883	4.47	982	2.55	945	3.26	923	3.56
891	4.35	992	2.40	953	3.12	934	3.39
898	4.17	1002	2.27	960	3.00	946	3.19
914	3.87	1012	2.12	967	2.90	957	2.99
923	3.75	1020	2.00	973	2.78	968	2.83
932	3.57	1023	1.96	984	2.61	978	2.64
943	3.38	1034	1.79	993	2.48	988	2.51
949	3.28	1040	1.77	1005	2.32	998	2.35
960	3.12			1016	2.15	1008	2.21
968	3.01			1024	2.04	1018	2.06
974	2.92					1026	1.96
983	2.80					1036	1.80

run B4 (cell B)		run B5 (cell B)		run C1 (cell C)		run C2 (cell C)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
905	3.92	931	3.65	971	2.91	1004	2.43
912	3.77	940	3.48	980	2.77	1012	2.32
917	3.69	948	3.37	989	2.61	1018	2.25
928	3.51	956	3.24	1000	2.44	1027	2.09
936	3.35	961	3.14	1008	2.33	1035	2.00
944	3.22	967	3.05	1016	2.22	1045	1.85
952	3.10	973	2.97	1023	2.13	1053	1.75
960	2.97	979	2.89	1032	2.01	1059	1.67
970	2.82	984	2.79	1039	1.91	1065	1.60
982	2.62	991	2.70	1046	1.81		
990	2.50	997	2.61	1052	1.74		
999	2.39			1061	1.64		
1010	2.21			1066	1.58		
1020	2.07						
1030	1.91						
1040	1.79						
1049	1.68						

Discussion

The total vapor pressures measured above holmium trihalides were considered to be equal to the partial pressures of the monomeric gaseous species because the contribution of the dimer species was considered negligible, being about 1% of the total pressures as observed in the mass spectrometric studies on $\mathrm{HoBr3}$[8] and $\mathrm{HoI_3}$.[10] In any case, we believe that also the vaporization behavior of

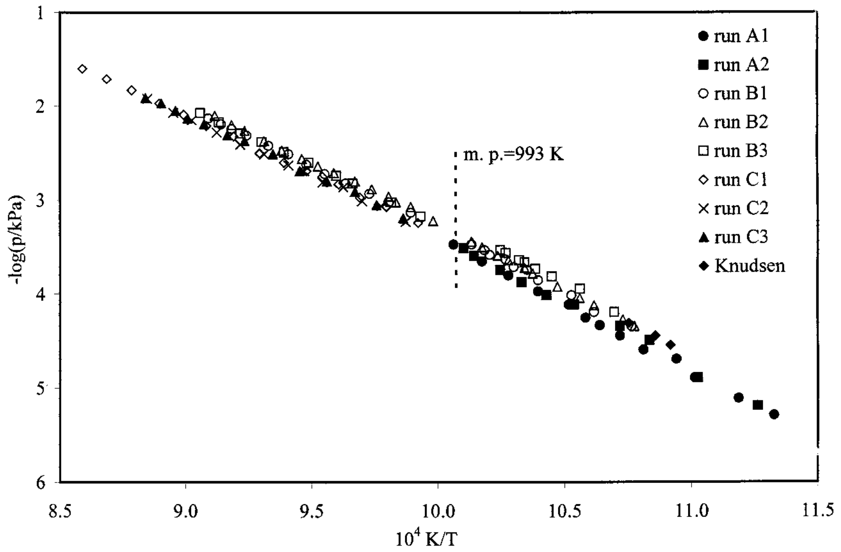

Figure 1. Total vapor pressures for $HoCl_3$.

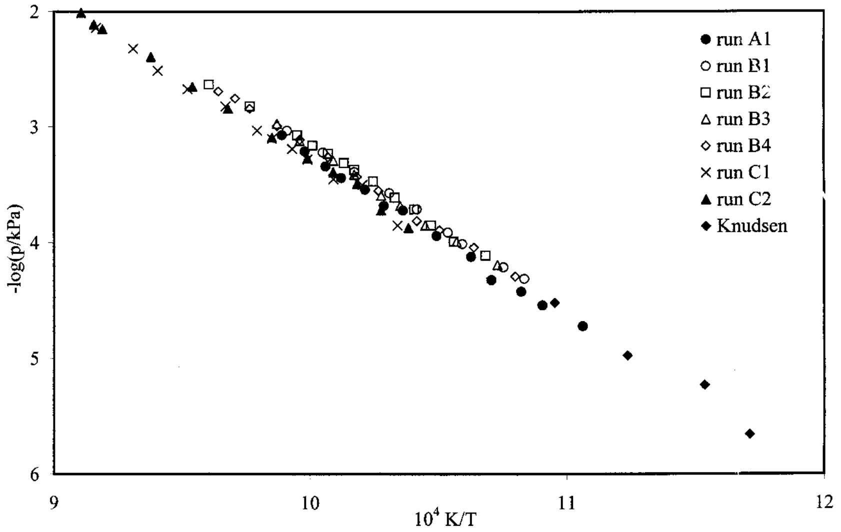

Figure 2. Total vapor pressures for $HoBr_3$.

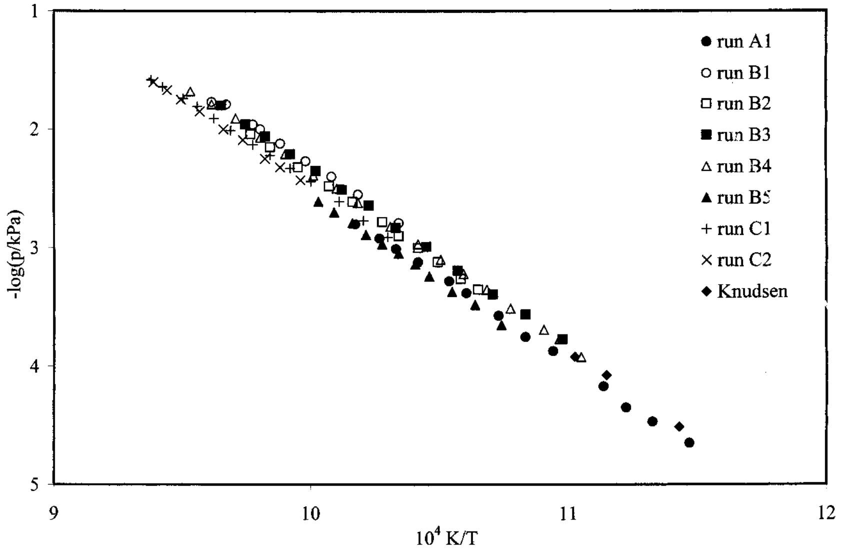

Figure 3. Total vapor pressures for HoI_3.

$HoCl_3$ is quite similar to that of the other holmium trihalides and that the contribution of dimer to the total vapor pressure is negligible. The Knudsen pressure values obtained by assuming the molecular weight of the vapor to be equal to that of the monomer are in good agreement with the torsion effusion pressure values (see Table 4).

Table 4. Total Vapor Pressures of Solid $HoCl_3$, $HoBr_3$, and HoI_3 Measured by the Knudsen Method

compound	T/K	Δt (±2)/ min	Δm (±0.1)/ mg	$p \times 10^5$/ kPa	$p \times 10^5$/ kPa
$HoCl_3$	916	810	12.5	2.87	2.46[a]
$HoCl_3$	921	862	16.8	3.63	2.99[a]
$HoCl_3$	930	740	19.5	4.93	4.22[a]
$HoBr_3$	854	4230	6.2	0.22	0.23[b]
$HoBr_3$	867	1210	4.8	0.59	0.41[b]
$HoBr_3$	890	1150	8.1	1.06	1.07[b]
$HoBr_3$	913	250	5.0	3.04	2.71[b]
HoI_3	875	655	15.6	3.06	3.06[c]
HoI_3	897	430	27.9	8.43	7.87[c]
HoI_3	907	282	26.2	12.1	11.9[c]

[a–c] Pressures calculated by eqs 1, 3, and 4, respectively.

Table 5. Experimental Dependence of Vapor Pressure for Holmium Trihalides

				$\log(p/\text{kPa}) = A - B(K/T)$	
compound	run	ΔT/K	no. of points	A[a]	B[a]
$HoCl_3$(s)	A1	883−994	13	10.99 ± 0.22	14390 ± 203
$HoCl_3$(s)	A2	888−990	10	10.84 ± 0.38	14215 ± 358
$HoCl_3$(s)	B1	929−987	10	10.96 ± 0.38	14231 ± 368
$HoCl_3$(l)	B1	1011−1100	12	9.38 ± 0.07	12656 ± 77
$HoCl_3$(s)	B2	928−987	11	10.77 ± 0.06	14025 ± 58
$HoCl_3$(l)	B2	1002−1097	14	9.25 ± 0.13	12475 ± 141
$HoCl_3$(s)	B3	935−976	8	11.00 ± 0.41	14178 ± 390
$HoCl_3$(l)	B3	1007−1104	10	9.19 ± 0.10	12438 ± 101
$HoCl_3$(l)	C1	1008−1164	15	9.02 ± 0.09	12353 ± 102
$HoCl_3$(l)	C2	1013−1130	13	9.05 ± 0.17	12416 ± 178
$HoCl_3$(l)	C3	1014−1131	13	9.10 ± 0.13	12448 ± 140
$HoBr_3$(s)	A1	904−1011	13	10.97 ± 0.24	14217 ± 232
$HoBr_3$(s)	B1	923−1009	9	10.92 ± 0.19	14071 ± 184
$HoBr_3$(s)	B2	936−1041	13	10.98 ± 0.24	14129 ± 236
$HoBr_3$(s)	B3	932−1013	9	11.16 ± 0.25	14335 ± 244
$HoBr_3$(s)	B4	926−1037	12	10.85 ± 0.16	14022 ± 161
$HoBr_3$(s)	C1	967−1091	12	10.90 ± 0.22	14216 ± 221
$HoBr_3$(s)	C2	963−1105	13	10.91 ± 0.16	14197 ± 166
HoI_3(s)	A1	872−983	13	12.08 ± 0.16	14599 ± 153
HoI_3(s)	B1	967−1040	9	12.06 ± 0.27	14354 ± 267
HoI_3(s)	B2	939−1024	11	12.47 ± 0.10	14856 ± 100
HoI_3(s)	B3	911−1036	13	12.56 ± 0.08	14888 ± 76
HoI_3(s)	B4	905−1049	17	12.39 ± 0.06	14750 ± 55
HoI_3(s)	B5	931−997	11	11.98 ± 0.12	14541 ± 112
HoI_3(s)	C1	971−1066	13	12.02 ± 0.11	14478 ± 115
HoI_3(s)	C2	1004−1065	9	12.20 ± 0.17	14687 ± 175

[a] The quoted errors are standard deviations.

Unfortunately, this agreement cannot be taken as a proof that the dimer species in the vapor is negligible. A possible presence in the vapor of a very large amount of dimer, for example, 20%, changes the log p by ~0.04 unit, a variation comparable to the uncertainty associated with the torsion pressure value.

On this basis, the second-law sublimation enthalpies of the monomeric species of holmium trihalides were obtained from the slopes of the corresponding selected log p vs $1/T$ in eqs 1−4.

When the pressure data were treated by the third-law method, the standard sublimation enthalpies for $HoCl_3$ and $HoBr_3$ were also calculated. Because, apparently, no free energy functions (fef), $[G°(T) - H°(298\text{ K})]/T$, for solid HoI_3 were found in current databases, the third-law method was employed in order to evaluate the values of these thermodynamic functions.

The following results were obtained.

A. $HoCl_3$. Some values of the melting point and of the enthalpy of fusion for $HoCl_3$ were calculated by the slopes and the intercepts of two log p vs $1/T$ equations (obtained in runs in which the vapor pressure of this compound was measured above both solid and liquid phases) and of the selected eqs 1 and 2. From the values so obtained (see Table 7), approximate values of the enthalpy of fusion, $\Delta_{fus}H = 31\text{ kJ}\cdot\text{mol}^{-1}$, and of the melting point, $T_{fus} = 1000$ K, were derived. Considering the large uncertainties associated with the used procedure, the very good agreement of the obtained values with the data selected in the literature ($\Delta_{fus}H = 30.6\text{ kJ}\cdot\text{mol}^{-1}$ and $T_{fus} = 993$ K) indicates that no large errors in the temperature measurements were made. The vaporization enthalpy values for lead, obtained from the slopes of some log α vs $1/T$ equations (with α being the experimental torsion angles) determined in the calibration runs, agree within about 3% with that selected in the literature.[18]

The second-law sublimation enthalpy, $\Delta_{sub}H°(939\text{ K}) = 272.1 \pm 3.0\text{ kJ}\cdot\text{mol}^{-1}$, and vaporization enthalpy, $\Delta_{sub}H°(1083\text{ K}) = 238.5 \pm 3.0\text{ kJ}\cdot\text{mol}^{-1}$, at the average temperatures of the covered ranges, were derived from eqs 1 and 2, respectively. These values were reduced to 298 K, $\Delta_{sub}H°(298\text{ K}) = 286 \pm 3\text{ kJ}\cdot\text{mol}^{-1}$ and $290 \pm 3\text{ kJ}\cdot\text{mol}^{-1}$, respectively, by using the enthalpic increments and the enthalpy of fusion reported by Pankratz.[19]

By giving more weight to the result obtained for the sublimation enthalpy of solid $HoCl_3$, the average value, $\Delta_{sub}H°(298\text{ K}) = 287\text{ kJ}\cdot\text{mol}^{-1}$, was selected as the second-law standard sublimation enthalpy of $HoCl_3$ with an overestimated associated error of $\pm 6\text{ kJ}\cdot\text{mol}^{-1}$, which also takes into account the uncertainties of the used enthalpic increments.

This standard sublimation enthalpy was also calculated by the third-law treatment of the vapor pressure data by using the fef values reported in Pankratz's tables.[19] The enthalpies calculated at 900 and 1100 K (two approximate extreme temperatures of the experimental ranges) and reported in Table 8 present a small temperature trend. The average value, $\Delta_{sub}H°(298\text{ K}) = 314\text{ kJ}\cdot\text{mol}^{-1}$ with an estimated error of about $\pm 4\text{ kJ}\cdot\text{mol}^{-1}$, was selected as the third-law standard sublimation enthalpy of $HoCl_3$. This value is higher than that obtained by the second-law method [$\Delta_{sub}H°(298\text{ K}) = 287 \pm 6\text{ kJ}\cdot\text{mol}^{-1}$] but still comparable with that derived as the difference of the standard enthalpies of formation for solid and gaseous $HoCl_3$ reported by Pankratz[19] [$\Delta_{sub}H°(298\text{ K}) = 323\text{ kJ}\cdot\text{mol}^{-1}$].

A critical analysis of the error sources associated with the procedure for the calculation of the enthalpies leads to the following considerations: the error associated with the second-law sublimation enthalpy value should be minor considering the good agreement of the experimental vapor pressure data among themselves and of the derived slopes of the log p vs $1/T$ equations (see Table 5). Concerning the errors in the third-law evaluation of the data, large uncertainties in temperature measurements excluded, two are the principal error sources, one associated with the absolute vapor pressures and the other associated with the used fef values. Considering that the pressure in the third-law enthalpy calculation is evaluated as a logarithm, this error source can be considered negligible. In any case, in the present study, the absence of any evident spread of the vapor pressure values in different experimental runs and the substantial agreement of the Knudsen vapor pressures with those determined by the torsion method lead us to believe that the absolute vapor pressure values are sufficiently correct. Concerning the uncertainties connected to the use of wrong fef values, it is difficult to quantify them, but the small temperature trend in the third-law $\Delta_{sub}H°(298\text{ K})$ values (see Table 8) leads us to conclude that the used fef should be a real error source.

Table 6. Comparison of the Temperature Dependence of the Total Vapor Pressures of HoX_3 (X = Cl, Br, and I)

						$\log(p/\text{kPa}) = A - B(K/T) - C\log(T/K)$		
compound	ref	method	no. of points	T or T limit/K	$p \times 10^3$/kPa	A	B	C
$HoCl_3$(l)	1	Knudsen	4	1043, 1143, 1198, 1123	3.64, 33.8, 143.9, 278.6			
$HoCl_3$(l)	3	boiling point		from 1273 to 1643		29.86	14946	6
$HoCl_3$(s)	2	mass-spectr.		from 887 to 993		12.08	15422	
$HoCl_3$(l)	2	mass-spectr		from 993 to 1051		8.95	12317	
$HoCl_3$(s)	this work	torsion	52	from 883 to 994		10.91 ± 0.10	14216 ± 150	
$HoCl_3$(l)	this work	torsion	77	from 1002 to 1164		9.16 ± 0.10	12466 ± 150	
$HoBr_3$(l)	5, 6	boiling point		from 1208 to 1523		26.13 ± 0.13	13418 ± 86	5
$HoBr_3$(s)	4	selected		from 900 to 1000		11.59	14479	
$HoBr_3$(s)	8	Knudsen	2	971 and 1003	0.77 and 2.27			
$HoBr_3$(s)	8	mass-spectr.	55	from 803 to 987		11.491±0.242	14275 ± 210	
$HoBr_3$(s)	this work	torsion	81	from 904 to 1105		10.95 ± 0.10	14168 ± 150	
HoI_3(s)	9	Knudsen		from 924 to 1029		13.19 ± 0.31	15586 ± 304	
HoI_3(s)	10	mass-spectr.	7	from 935 to 1055		10.60 ± 0.13[a]	12990 ± 133[a]	
HoI_3(s)	8	Knudsen	2	935 and 975	1.35 and 3.31			
HoI_3(s)	8	mass-spectr.		from 773 to 898		11.990 ± 0.051	14106 ± 72	
HoI_3(s)	this work	torsion	96	from 872 to 1066		12.24 ± 0.10	14656 ± 150	

[a] Value obtained by treating by the least-squares method seven partial pressure values of HoI_3 and Ho_2I_6 reported in Kaposi's work.[10]

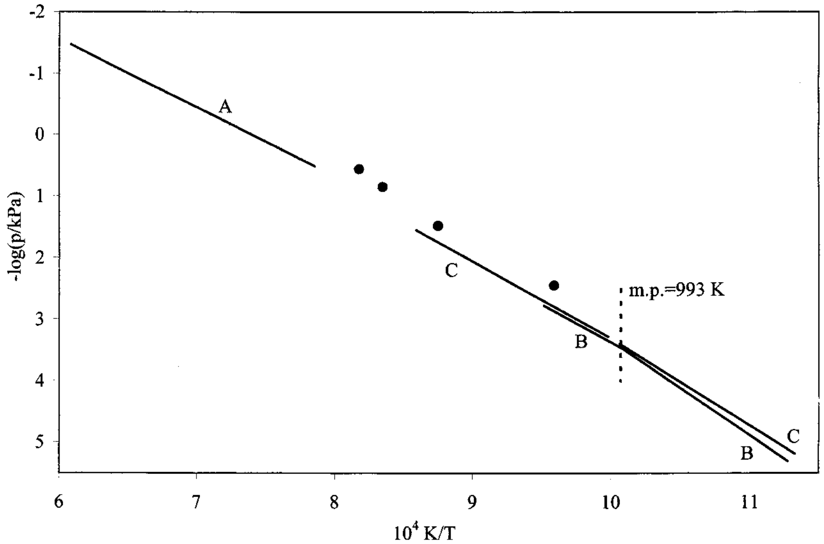

Figure 4. Comparison of vapor pressures for $HoCl_3$: A, Dudchik et al.;[3] B, Kudin et al.;[2] C, this work; ●, Moriarty.[1]

In principle, the difference between the second- and third-law results can be justified by the presence of the vapor of the dimer form in different amounts at different temperatures. In particular, in our case, to obtain a higher second-law enthalpy value, reducing in this way also the difference with the third-law result, at the lowest temperatures the dimer species could be more abundant so that the monomer partial pressures could be lower than the total pressures as used in our calculations. However, this is not thermodynamically true because lower pressures decrease the dimer form and is not realistic because, for an increase of about 10 kJ·mol^{-1} in the second-law enthalpy value, the amount of dimer in the vapor at 900 K should be comparable to that of the monomer while at 1000 K its amount should be negligible. In light of the preceding considerations, we are not able to explain the discrepancy of about 25 kJ·mol^{-1} between the second- and third-law enthalpy values; however, we believe that the more important error source is probably the use of erroneous Δfef values. The comparison with the results reported by Kudin et al.[2] [$\Delta_{\text{sub}}H°(298\text{ K}) = 283 \pm 14$ and 284 ± 12 kJ·mol^{-1} for second- and third-law sublimation enthalpies, respectively] shows an agreement with the second-law enthalpy determined in the present work. If the vaporization and sublimation enthalpies of $HoCl_3$ are calculated from the slopes of the log p vs $1/T$ equations reported by Kudin et a1.[2] (see Table 6), one obtains a vaporization enthalpy [$\Delta_{\text{vap}}H°(1022\text{ K}) = 236$ kJ·mol^{-1}] comparable with our second-law value [$\Delta_{\text{sub}}H°(1083\text{ K}) = 238.5 \pm 3.0$ kJ·mol^{-1}] but a sublimation enthalpy [$\Delta_{\text{sub}}H°(940\text{ K}) = 295$ kJ·mol^{-1}] higher than that determined in the present work at the same temperature [$\Delta_{\text{sub}}H°(939\text{ K}) = 272.1 \pm 3.0$ kJ·mol^{-1}]. The reduction of these values to 298 K was made by Kudin et al.[2] using enthalpy increments computed by a method of statistical thermodynamics in the rigid rotator—harmonic oscillator approximation on the basis of molecular constants taken from a doctoral thesis[20] and not available to us. We note that, surprisingly, the use of these thermodynamic functions causes a decrease of the sublimation enthalpy value when it was reduced to 298 K. Concerning the third-law enthalpy reported by Kudin et al.,[2] the necessary fef values were computed by the same procedure and by the molecular constants used for the calculation of the enthalpic increments. In principle, because our vapor pressure values agree sufficiently well with those measured by Kudin et al.[2] (see Figure 4), the sublimation third-law enthalpy obtainable by using these fef sets should be comparable with the corresponding values calculated by

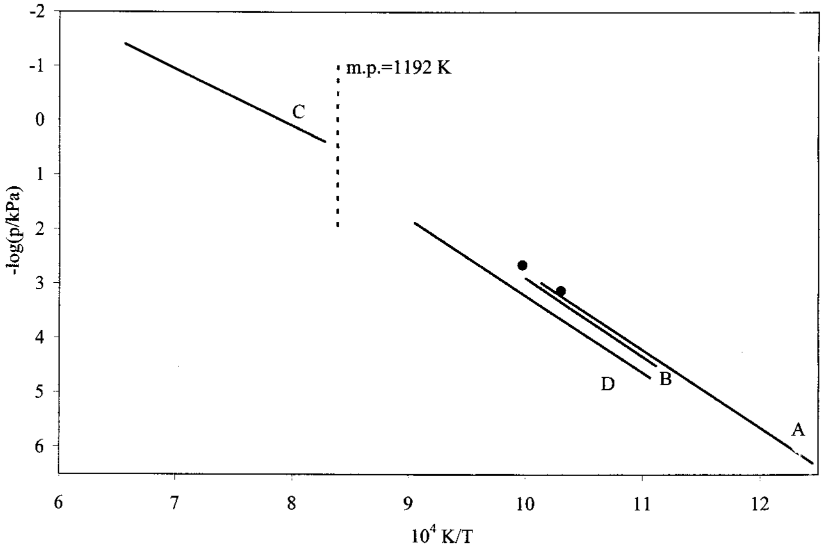

Figure 5. Comparison of vapor pressures for $HoBr_3$: A (mass spectrometric) and ● (Knudsen), Gietmann et al.;[8] B, Knacke and Kubaschewski;[4] C, Makhmadmurodov et al.;[5,6] D, this work.

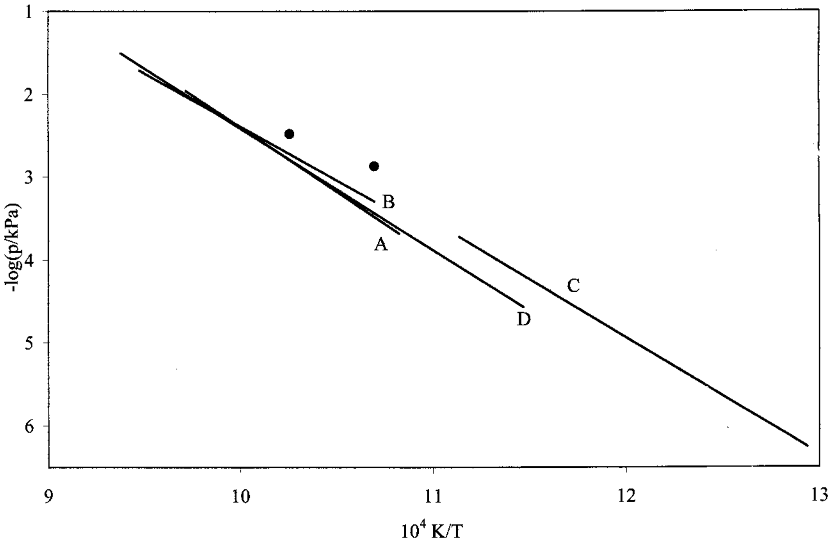

Figure 6. Comparison of vapor pressures for HoI_3: A, Hirayama et al.;[9] B, Kaposi et al.;[10] C (mass spectrometric) and ● (Knudsen), Gietmann et al.;[8] D, this work.

Table 7. Temperature and Enthalpy for Fusion of $HoCl_3$

source	T_{fus}/K	$\Delta_{fus}H$/kJ·mol^{-1}
equations obtained in run B1	999	30.2
equations obtained in run B2	1020	29.7
equations obtained in run B3	962	33.3
selected eqs 1 and 2	1003	33.6

Table 8. Third-Law Standard Sublimation Enthalpies for $HoCl_3$ and $HoBr_3$ ($p° = 1$ atm $= 101.325$ kPa)

compound	T/K	p/kPa	$-\Delta[G°(T) - H°(298\ K)]/T$/ (J·K^{-1}·mol^{-1})	$\Delta_{sub}H°(298\ K)$/ kJ·mol^{-1}
$HoCl_3$(s)	900	$1.30 \times 10^{-5\,a}$	214.4	311.7
$HoCl_3$(l)	1100	$6.80 \times 10^{-3\,b}$	208.2	316.9
$HoBr_3$(s)	900	$1.61 \times 10^{-5\,c}$	195.9	293.4
$HoBr_3$(s)	1100	$1.18 \times 10^{-2\,c}$	192.6	294.7

$^{a-c}$ Pressure values calculated from eqs 1−3, respectively.

Kudin et al.[2] and also with our second-law enthalpy. However, we are doubtful to use “tout court” in our calculation, the Δfef associated with the sublimation of $HoCl_3$ [values derivable from Kudin’s vapor pressure data and the corresponding third-law $\Delta_{sub}H°(298\ K)$ because, unfortunately, the thermodynamic function values are not reported in their work], but the comparison of our third-law enthalpy with that proposed by Kudin et al.[2] consolidates the suspicion that the fef reported by Pankratz[19] for some trichlorides of lanthanides may be not correct, suspicion advanced in our previous study on dysprosium trichloride.[11]

On this basis, our third-law enthalpy could be considered an upper value and, therefore, giving double weight to the second-law enthalpy value, we propose as a standard sublimation enthalpy of $HoCl_3$ the value of $\Delta_{sub}H°(298\ K) = 296$ kJ·mol^{-1}, with an estimated error of ±10 kJ·mol^{-1}.

B. $HoBr_3$. The vapor pressures of holmium tribromide were measured only above the solid phase. From the slope of the selected eq 3, the second-law sublimation enthalpy, $\Delta_{sub}H°(1004\ K) = 271 \pm 3$ kJ·mol^{-1}, was determined and reduced to 298 K, $\Delta_{sub}H°(298\ K) = 288 \pm 3$ kJ·mol^{-1}, by using the enthalpic increments listed for the solid phase in Pankratz’s[19] tables and for the gaseous phase in Gietmann’s work.[8] When the third-law method is applied to two vapor pressures for this compound calculated by eq 3 at two extreme temperatures, 900 and 1100 K, two

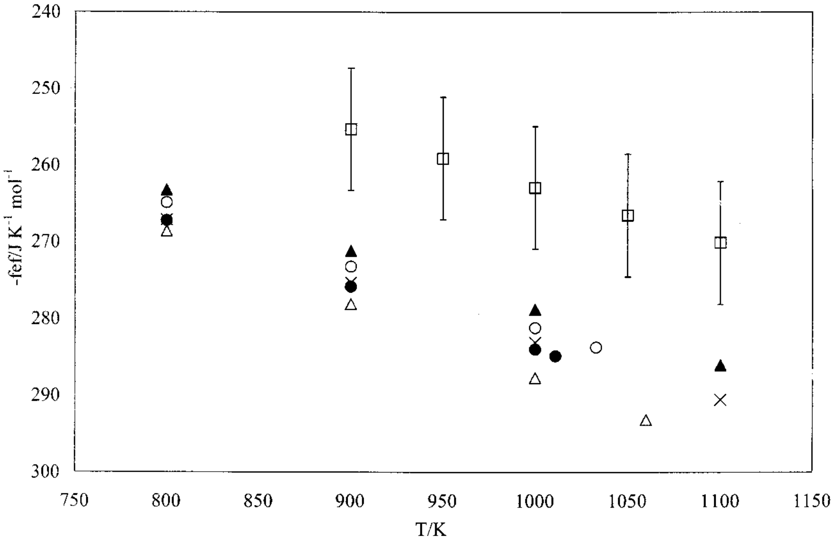

Figure 7. Free energy function for solid lanthanides triiodide: ○, CeI_3; ●, PrI_3; △, NdI_3; ▲, GdI_3; ×, TbI_3; □, HoI_3 (this work).

comparable values of the standard sublimation enthalpy for $HoBr_3$ were obtained (see Table 8). As for the enthalpic increments, the fef values for solid and gaseous $HoBr_3$ were taken from Pankratz[19] and Gietmann et al.,[8] respectively. The average third-law value, $\Delta_{sub}H°(298\ K) = 294\ kJ{\cdot}mol^{-1}$, with an estimated uncertainty of about 4 $kJ{\cdot}mol^{-1}$, is slightly higher than the second-law enthalpy. A comparison with the sublimation enthalpy reported by Gietmann et al.[8] [$\Delta_{sub}H°(298\ K) = 288.2 \pm 8.1$ and $284.7 \pm 10.1\ kJ{\cdot}mol^{-1}$ for second- and third-law values, respectively] shows that the second-law results agree decidedly very well, whereas the third-law enthalpy values are slightly different. Considering that the used fef values are equal, the observed difference in the third-law results could only be due to the different vapor pressure values. Because Gietmann's[8] pressures have been measured by the mass spectrometric technique with inherent associated uncertainties (ionization cross section, multiplier gain, and electron impact fragmentation contribution), we believe that the real vapor pressures might be somewhat lower than those reported in the work. On this basis, we propose as a standard sublimation enthalpy of $HoBr_3$ the value $\Delta_{sub}H°(298\ K) = 290\ kJ{\cdot}mol^{-1}$ with an estimated error that should not exceed $\pm 5\ kJ{\cdot}mol^{-1}$.

This enthalpy value agrees with that derived from the standard enthalpies of formation reported by Pankratz[19] for solid and gaseous $HoBr_3$, $\Delta_{sub}H°(298\ K) = 292\ kJ{\cdot}mol^{-1}$.

C. HoI_3. As for the other compounds, also for HoI_3 the second-law sublimation enthalpy was calculated from the slope of the selected eq 4, $\Delta_{sub}H°(969\ K) = 281 \pm 3\ kJ{\cdot}mol^{-1}$, where the error was evaluated from the estimated uncertainty of the slope. The comparison with the sublimation enthalpies reported in the literature shows that our value is lower than that obtained from Knudsen vapor pressures by Hirayama et al.[9] [$\Delta_{sub}H°(976\ K) = 298\ kJ{\cdot}mol^{-1}$] but higher than those reported by Gietmann et al.[8] [$\Delta_{sub}H°(836\ K) = 270.0 \pm 1.4\ kJ{\cdot}mol^{-1}$] and by Kaposi et al.[10] [$\Delta_{sub}H°(1000\ K) = 265 \pm 1.2\ kJ{\cdot}mol^{-1}$] both mass spectrometrically obtained. Incidentally, the enthalpy reported in Kaposi's[10] work was calculated from the slope of the ln $I^{+}T$ vs $1/T$ plot (I^{+} is the ion intensity), but its value is lowered at 250 $kJ{\cdot}mol^{-1}$ when it is recalculated from the seven absolute HoI_3 partial pressures reported in the same work.

The discrepancies between these second-law enthalpy values are difficult to explain. We can perform only a critical analysis of our results: (i) the slopes of all $p-T$ equations are in acceptable agreement among themselves (see Table 5); (ii) the vaporization enthalpy values for lead obtained in various calibration runs (see the comment for the $HoCl_3$ results) were decidedly in agreement among themselves and with the literature value; (iii) considering the large temperature ranges covered, uncertainties on the slopes of the $p-T$ equations should be small; (iv) errors for the presence in the vapor of the dimer form in different amounts at different temperatures are negligible as observed in the mass spectrometric works by Kaposi et al.[10] and Gietmann et al.[8] On this basis, we believe the errors associated with the slope of the final equation for HoI_3 (± 150) and with the derived sublimation enthalpy ($\pm 3\ kJ{\cdot}mol^{-1}$) should be a realistic estimate of the uncertainty connected to our measurements.

Table 9. Free Energy Function for Solid HoI_3 Calculated by the Third-Law Method, $\Delta_{sub}H°(298\ K) = 296\ kJ{\cdot}mol^{-1}$ ($p° = 1\ atm = 101.325\ kPa$)

T/K	p^{a}/kPa	$-\Delta$fef/ $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$-$fef of $HoI_3(g)^{b}$/ $J{\cdot}K^{-1}{\cdot}mol^{-1}$	$-$fef of $HoI_3(s)$/ $J{\cdot}K^{-1}{\cdot}mol^{-1}$
900	8.92×10^{-5}	212.9	468.2	255.3
950	6.42×10^{-4}	212.0	471.1	259.1
1000	3.79×10^{-3}	211.2	474.1	262.9
1050	1.89×10^{-2}	210.5	477.0	266.5
1100	8.15×10^{-2}	209.8	479.9	270.1

[a] Calculated by eq 4. [b] Selected by Pankratz.[19]

When the difference of the enthalpic increments for solid and gaseous HoI_3, $\Delta[(H°(969\ K) - H°(298\ K)] = 15\ kJ{\cdot}mol^{-1}$ [estimated as the average of the value used at 1000 K by Kaposi et al.[10] (16.9 $kJ{\cdot}mol^{-1}$), at 980 K by Myers and Graves[21] (15.1 $kJ{\cdot}mol^{-1}$), and at a lower temperature, 836 K, by Gietmann et al.[8] (10.8 $kJ{\cdot}mol^{-1}$)], is employed, the standard sublimation enthalpy, $\Delta_{sub}H°(298\ K) = 296\ kJ{\cdot}mol^{-1}$, was derived, with an error that should not exceed $\pm 8\ kJ{\cdot}mol^{-1}$.

Because, apparently, no fef data for solid HoI_3 were available in the literature, using the second-law standard sublimation enthalpy and the vapor pressures calculated by eq 4 at 50 K intervals from 900 and 1100 K, the Δfef values associated with the sublimation of HoI_3 at these temperatures were derived by third-law treatment of the data and reported in Table 9. From the fef values for the gaseous phase reported in Pankratz's [19] tables, the corresponding fef values for solid HoI_3 were derived. These values are higher by about 20 J K^{-1} mol^{-1} than those reported by Pankratz[19] for other triiodides (see Figure 7). Considering the only error associated with $\Delta_{sub}H°(298\ K)$, these fef values are at least uncertain for this error (±8 J K^{-1} mol^{-1}), but this does not justify the gap with the fef of other triiodides. Comparable fef values should be obtained if the standard sublimation enthalpy is higher or if the fef values for gaseous HoI_3 are lower than those used or, of course, for both reasons. For the foregoing considerations, we believe that the sublimation enthalpy should not be much different than that selected in the present work so that we believe that the fef values for $HoI_3(g)$ reported by Pankratz[19] could be considered an upper limit.

Conclusion

The total vapor pressures for $HoCl_3$, $HoBr_3$, and HoI_3 determined by the torsion-effusion method are well represented by eqs 1−4. The $\Delta_{sub}H°(298\ K)$ of these compounds, equal to $\Delta_{sub}H°(298\ K) = 296 \pm 10$ and 290 ± 5 kJ·mol^{-1} for $HoCl_3$ and $HoBr_3$, respectively, as derived by the second- and third-law treatment of their vapor pressures and 296 ± 8 kJ·mol^{-1} for HoI_3 obtained by only the second-law method, are decidedly comparable within their uncertainties. This was previously observed in this laboratory[11] for dysprosium trihalides [$\Delta_{sub}H°(298\ K) = 283 \pm 5$, 289 ± 6, and 282 ± 4 kJ·mol^{-1} for $DyCl_3$, $DyBr_3$, and DyI_3, respectively] in contrast with the general decreasing trend of the standard sublimation enthalpies for trihalides of the first lanthanides (La, Ce, Pr, Nd, and Gd), on going from trichloride to triiodide. The critical analysis of our results, discussed in this and in the previous work,[11] induces us to believe that the proposed standard sublimation enthalpies are sufficiently reliable and that probably the decreasing trend could not be present for trihalides of the heavy lanthanides.

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