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Vaporization Study of $YbCl_3$, $YbBr_3$, YbI_2, $LuCl_3$, $LuBr_3$, and LuI_3 and a New Assessment of Sublimation Enthalpies of Rare Earth Trichlorides

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The vapor pressures of $YbCl_3$, $YbBr_3$, YbI_2, $LuCl_3$, $LuBr_3$, and LuI_3 were measured by torsion and Knudsen effusion methods. Their temperature dependences may be reported as follows: $YbCl_3$(s): $\log(p/\text{kPa}) = (11.30 \pm 0.20) - (14420 \pm 200)/(T/\text{K})$ from (944 to 1096) K; $YbBr_3$(s): $\log(p/\text{kPa}) = (11.51 \pm 0.20) - (14070 \pm 300)/(T/\text{K})$ from (891 to 1032) K; YbI_2(s): $\log(p/\text{kPa}) = (9.37 \pm 0.30) - (13580 \pm 300)/(T/\text{K})$ from (968 to 1049) K; YbI_2(l): $\log(p/\text{kPa}) = (9.04 \pm 0.25) - (13220 \pm 300)/(T/\text{K})$ from (1068 to 1192) K; $LuCl_3$(s): $\log(p/\text{kPa}) = (11.68 \pm 0.15) - (14940 \pm 150)/(T/\text{K})$ from (942 to 1075) K; $LuBr_3$(s): $\log(p/\text{kPa}) = (11.34 \pm 0.20) - (14040 \pm 300)/(T/\text{K})$ from (903 to 1038) K; LuI_3(s): $\log(p/\text{kPa}) = (11.99 \pm 0.40) - (14270 \pm 300)/(T/\text{K})$ from (862 to 1004) K. Treating the vapor pressures of $YbCl_3$ and $LuCl_3$ by second- and third-law, the following standard sublimation enthalpies, $\Delta_{\text{sub}}H°(298\ \text{K}) = (288 \pm 6)$ and (295 ± 5) kJ·mol^{-1}, respectively, were derived. Comparison of these enthalpies with those of other rare earth trichlorides, recalculated by using a new set of thermodynamic functions, was made. From the $YbBr_3$, $LuBr_3$, and LuI_3 vapor pressures, the second-law sublimation enthalpies, extrapolated at 298 K by estimated enthalpic increments, $\Delta_{\text{sub}}H°(298\ \text{K}) = (285 \pm 9)$, (285 ± 9), and (288 ± 9) kJ·mol^{-1}, respectively, were evaluated. For YbI_2, $\Delta_{\text{sub}}H°(298\ \text{K}) = (302 \pm 6)$ kJ·mol^{-1} was obtained by use of thermal functions estimated by analogy with the published data on EuI_2.

Introduction

The present work is the last of our systematic study[1−10] on the vaporization thermodynamics of rare earth trihalides carried out in order to determine their sublimation enthalpies from vapor pressure measurements. In this paper, the sublimations of ytterbium trihalides ($YbCl_3$ and $YbBr_3$), ytterbium diiodide, and lutetium trihalides ($LuCl_3$, $LuBr_3$, and LuI_3) were studied.

As for the great many of rare earth trihalides, at present the thermodynamic properties, in particular vapor pressures and sublimation enthalpies, of these compounds are scarce. Apparently the oldest vapor pressure data above $YbCl_3$ and $LuCl_3$ are some values measured by Moriarty[11] by using the Knudsen method. Using this method, new vapor pressure values of $YbCl_3$ were measured from (933 to 1063) K by Evseeva and Zenkevich.[12] In a mass spectrometric study[13] of this compound, it was observed that the dimer form (Yb_2Cl_6) is also present in very small amounts in the vapor phase (less than 1 % of monomer) and that the heating procedure of the sample conditions its vaporization process; in particular a rapid heating leads to a partial thermal decomposition of $YbCl_3$ in $YbCl_2$. The rate of decomposition is decidedly negligible when the sample is heated by a gradual increase in temperature. Two second-law sublimation enthalpy values of this compound were derived from the slopes of log p versus $1/T$ equations reported in both works.[12,13] A sublimation enthalpy value was also obtained in a mass spectrometric study.[14] Recently Kudin and Vorob'ev[15] analyzed the vapor pressures found in the literature over rare earth trichlorides, $YbCl_3$ and $LuCl_3$ included, and using thermodynamic functions computed by Gorokhov and Osina for the gaseous phases and by Bergman for the condensed states (both functions reported by Kudin et al.[16]) proposed a new set of second- and third-law standard sublimation enthalpies for these compounds. As concerns $LuCl_3$, in a mass spectrometer study of the vapor of this compound carried out by Hastie et al.,[17] its sublimation enthalpy, $\Delta_{\text{sub}}H°(945\ \text{K}) = (263 \pm 8)$ kJ·mol^{-1}, was measured from the slope of log $[I(LuCl_2^+)]T$ versus $1/T$ line ($LuCl_2^+$ is the more abundant ion species present in the spectrum having $LuCl_3$ as molecular precursor). The authors report that this enthalpy value agrees with that estimated by Polyachenok and Novikov,[18] but we are not able to check this agreement. Two log p versus $1/T$ lines obtained by boiling point method above the molten compound were reported by Nieselson et al.[19] and by Dudchik et al.[20] At last, a mass spectrometric analysis of the vapor above $LuCl_3$ carried out by Pogrebnoi et al.[21] shows different species $(LuCl_3)_n$ where $n = 1−6$, but the monomer and dimer are decidedly the most abundant, the partial pressure of Lu_2Cl_6 being about 20 % of the total vapor pressure at 1000 K. Temperature dependence of the partial pressures of the observed species and the corresponding partial sublimation enthalpies were reported in the work. Apparently the vapor pressures of other halides are not known; the only data found in the literature are two log p versus $1/T$ equations for $YbBr_3$ and $LuBr_3$, both in liquid phase, obtained at high temperatures by boiling point method.[22]

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Table 1. Torsion Vapor Pressures of $YbCl_3$

run 1 cell B		run 5 cell B		run 6 cell A		run 7 cell A	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
953	3.80	958	3.80	972	3.60	974	3.50
961	3.66	966	3.72	982	3.42	994	3.20
966	3.60	976	3.55	990	3.33	1015	2.91
974	3.46	986	3.39	1001	3.14	1035	2.66
982	3.36	996	3.20	1010	3.01	1050	2.47
990	3.22	1005	3.07	1020	2.87	1054	2.40
999	3.12	1015	2.93	1029	2.77	1063	2.30
1007	3.00	1023	2.82	1038	2.65	1072	2.16
1016	2.85	1036	2.68	1046	2.54	1081	2.05
		1044	2.57	1055	2.42	1090	1.92
		1063	2.33	1063	2.31		
		1071	2.23	1072	2.20		
				1082	2.06		

run 9 cell A		run 10 cell B		run 13 cell B		run 14 cell B	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
980	3.42	952	3.90	950	3.90	944	3.80
1000	3.10	962	3.72	962	3.72	958	3.55
1020	2.81	970	3.60	970	3.60	975	3.30
1036	2.63	975	3.50	981	3.42	993	3.06
1052	2.42	983	3.36	990	3.27	1005	2.87
1062	2.29	992	3.25	999	3.16	1017	2.72
1071	2.17	1000	3.12	1008	3.04	1030	2.54
1081	2.04	1010	3.00	1017	2.91	1044	2.34
1088	1.92	1019	2.88	1026	2.79	1055	2.17
		1029	2.77	1036	2.65		
		1038	2.66	1044	2.52		
		1048	2.52	1053	2.42		
		1057	2.39	1062	2.30		
		1064	2.31	1071	2.16		
		1072	2.19	1079	2.08		
		1079	2.08	1088	1.94		
		1087	2.00				
		1096	1.87				

In this work the vapor pressures of $YbCl_3$, $YbBr_3$, YbI_2, $LuCl_3$, $LuBr_3$, and LuI_3 were measured by torsion and Knudsen effusion methods. From these, the standard sublimation enthalpies of these compounds were derived. The obtained results for $YbCl_3$ and $LuCl_3$were compared with those found in the literature and with those of other lanthanide trichlorides. In particular, the vapor pressures of these compounds measured by us in previous works[1−10] were treated by second- and third-law methods using the new enthalpic increments $[(H°(T) - H°(298\ \mathrm{K})]$ and free energy functions (fef), $[G°(T) - H°(298\ \mathrm{K})]/T$, [16] in order to obtain a new assessment of their standard sublimation enthalpies.

Experimental Section

Apparatus and Procedure. Both torsion and Knudsen assemblies used in the present study were substantially the ones used in the previous worksand described in detail in another paper.[23] Pyrophyllite Knudsen and torsion effusion cells were found to be non-reactive containers. Two torsion cells, different for the nominal area of their effusion holes (0.8 mm and 1.2 mm in diameter for cells A and B, respectively), were employed. For both cells, the corresponding cell constants necessary to convert the experimental torsion data in pressure values were evaluated vaporizing very pure lead having well-known vapor pressure[24] and comparable with those of the studied compounds in the covered experimental temperature ranges. The cell-constant values, checked in some runs carried out during the study of a compound, were found to be reproducible within about 10 %. This uncertainty produces negligible displacements in the final log p values. The temperatures, measured by a calibrated Pt−Pt/Rh (10 % Rh) inserted in a twin cell, were measured with an uncertainty estimate of about 2 K. To check the existence of thermodynamic equilibrium condition in the torsion effusion cell, some second-law sublimation enthalpy values of lead were determined from the slopes of some log α versus $1/T$ lines obtained during its vaporization (α is the torsion data). The enthalpy values agree well, within about 3 %, with the selected one.[24] The absolute lead vapor pressures were also treated by the third-law in order to derived the standard sublimation enthalpy of this compound. The enthalpy values so obtained at different temperatures do not present an evident temperature trend, and this was taken as a check that errors in temperature measurements were not large (within ± 2 K as estimated). In any case to minimize systematic errors, in each run the temperatures were increased and decreased at random, although in the corresponding tables the results are reported as increasing temperatures. Some vapor pressure values of the studied compounds were measured by the Knudsen method.[25] In this study, a pyrophyllite Knudsen effusion cell, having the effusion hole of 1 mm in diameter, was employed. The cell constant necessary to convert the mass loss rate into vapor pressure value was determined by vaporizing pure lead, and its value was checked in same runs inserted in the vaporization runs of the studied compounds.

Chemicals. All compounds used in this work were supplied by Aldrich Chemicals and were 99.9 % pure as certified by the supplier. To minimize oxidation and/or hydrolysis of the samples, the cells were loaded in a drybox,

Table 2. Torsion Vapor Pressures of $YbBr_3$

run 2 cell A		run 3 cell A		run 5 cell B		run 6 cell B	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
928	3.72	913	3.96	909	3.96	897	4.10
938	3.55	923	3.80	916	3.80	906	3.90
947	3.42	936	3.60	924	3.66	915	3.80
956	3.27	946	3.46	933	3.50	923	3.66
965	3.12	955	3.28	942	3.36	934	3.46
973	3.01	965	3.16	952	3.20	943	3.33
983	2.86	974	3.03	964	3.03	953	3.16
992	2.72	984	2.87	973	2.90	965	3.00
1000	2.62	994	2.72	982	2.77	974	2.86
1009	2.50	1002	2.60	990	2.66	993	2.59
1018	2.40	1012	2.47			1003	2.44
1026	2.30	1021	2.36			1013	2.33
		1032	2.24			1022	2.19

run 8 cell A		run 9 cell B		run 11 cell B	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
923	3.66	897	4.20	891	4.33
932	3.50	905	4.03	905	4.20
940	3.37	916	3.80	912	4.10
948	3.25	926	3.66	920	3.90
958	3.10	937	3.46	929	3.80
969	2.95	945	3.33	936	3.66
978	2.80	954	3.20	945	3.48
985	2.70	963	3.07	956	3.30
995	2.56	972	2.93	965	3.14
1008	2.38	980	2.80	975	3.01
1021	2.20	988	2.69	979	2.95
		997	2.57	991	2.79
		1006	2.46		

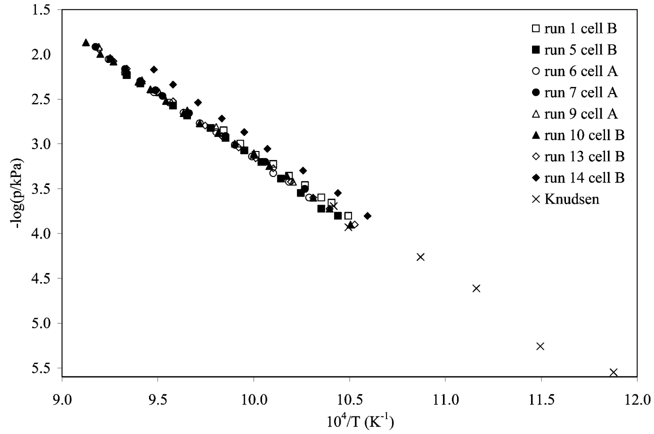

Figure 1. Torsion vapor pressures of $YbCl_3$.

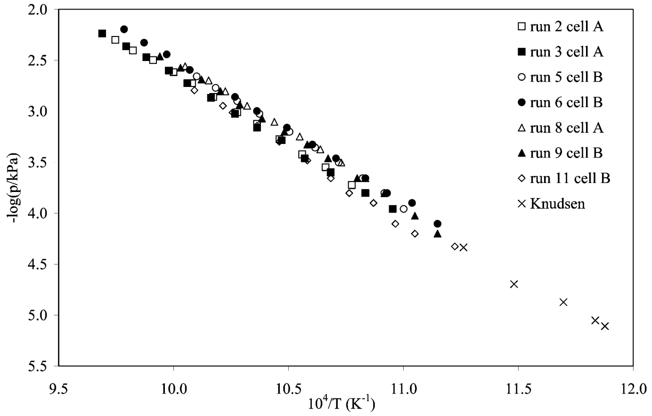

Figure 2. Torsion vapor pressures of $YbBr_3$.

rapidly introduced into the torsion or Knudsen apparatus previously filled with nitrogen, and then quickly evacuated.

(A) Ytterbium Trichloride and Tribromide. To minimize the thermal decomposition of $YbCl_3$,[13] the samples of this compound were heated by a gradual small increase in temperature, practically with a heating rate of about 2 $K\cdot min^{-1}$. The measured total vapor pressures above $YbCl_3$ and $YbBr_3$, all in solid phase, are reported in Tables 1 and 2 and in Figures 1 and 2. For each run, slope and intercept of the log p versus $1/T$ equation representative of the experimental data in the covered temperature range were evaluated by the linear least squares and are summarized in Table 3. Apparently, no evident dependence on the effusion hole area of the used cells was observed. The Knudsen vapor pressures and the corresponding experimental data from which they were derived are reported in Table 4 and shown in Figures 1 and 2. Considering that these were measured at the lowest temperatures of the torsion experiments, their values influence heavily the slopes of the log p versus $1/T$ equations so that these were not employed in the evaluation of the final equations but were only considered as a check of the reliability of the absolute torsion pressure measurements.

Weighing slope and intercept of each equation reported in Table 3 proportionally to the experimental points, the following final equations representative of the total vapor pressures for solid $YbCl_3$ and $YbBr_3$, valid in the covered temperature ranges, were derived:

$$\mathrm{YbCl_3(s)}\quad \log(p/\mathrm{kPa}) = (11.30 \pm 0.20) - (14420 \pm 200)/(T/\mathrm{K}) \text{ from } (944 \text{ to } 1096)\ \mathrm{K} \quad (1)$$

$$\mathrm{YbBr_3(s)}\quad \log(p/\mathrm{kPa}) = (11.51 \pm 0.20) - (14070 \pm 300)/(T/\mathrm{K}) \text{ from } (891 \text{ to } 1032)\ \mathrm{K} \quad (2)$$

The associated errors were estimated.

Table 3. Temperature Dependence of the Vapor Pressures of $YbCl_3$, $YbBr_3$, and YbI_2

				ΔT	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
compound	run	cell	no. of points	K	A^a	B^a
$YbCl_3$(s)	1	B	9	953−1016	11.24 ± 0.20	14328 ± 201
$YbCl_3$(s)	5	B	12	958−1071	11.31 ± 0.20	14486 ± 206
$YbCl_3$(s)	6	A	13	972−1082	11.31 ± 0.10	14481 ± 108
$YbCl_3$(s)	7	A	10	974−1090	11.16 ± 0.14	14287 ± 148
$YbCl_3$(s)	9	A	9	980−1088	11.34 ± 0.19	14461 ± 200
$YbCl_3$(s)	10	B	18	952−1096	11.18 ± 0.12	14324 ± 125
$YbCl_3$(s)	13	B	16	950−1088	11.45 ± 0.08	14597 ± 82
$YbCl_3$(s)	14	B	9	944−1055	11.40 ± 0.15	14343 ± 152
$YbBr_3$(s)	2	A	12	928−1026	11.30 ± 0.13	13932 ± 130
$YbBr_3$(s)	3	A	13	913−1032	11.22 ± 0.10	13866 ± 99
$YbBr_3$(s)	5	B	10	909−990	11.70 ± 0.20	14201 ± 193
$YbBr_3$(s)	6	B	13	897−1022	11.38 ± 0.10	13873 ± 97
$YbBr_3$(s)	8	A	11	923−1021	11.44 ± 0.06	13927 ± 54
$YbBr_3$(s)	9	B	13	897−1006	11.74 ± 0.15	14263 ± 147
$YbBr_3$(s)	11	B	12	891−991	11.81 ± 0.38	14455 ± 355
YbI_2(s)	1	B	10	1003−1049	9.67 ± 0.43	13945 ± 436
YbI_2(l)	1	B	13	1068−1189	9.14 ± 0.09	13315 ± 105
YbI_2(l)	2	A	8	1081−1124	8.70 ± 0.10	12881 ± 113
YbI_2(s)	5	B	8	976−1043	9.54 ± 0.33	13751 ± 337
YbI_2(l)	5	B	10	1103−1192	8.92 ± 0.17	13080 ± 190
YbI_2(s)	7	B	7	989−1043	9.82 ± 0.47	14056 ± 482
YbI_2(l)	7	B	12	1073−1179	9.19 ± 0.10	13418 ± 126
YbI_2(s)	8	B	7	997−1049	9.05 ± 0.38	13232 ± 391
YbI_2(s)	10	B	8	968−1040	9.26 ± 0.74	13462 ± 739
YbI_2(s)	12	B	9	975−1043	9.07 ± 0.35	13282 ± 353
YbI_2(s)	13	B	9	982−1046	9.22 ± 0.39	13357 ± 391

[a] The quoted errors are standard deviations.

Table 4. Experimental Data and Vapor Pressures Obtained by Knudsen Method

	T (±2)	time (±5)^a	mass loss (±0.2)	pressure in kPa	
compd	K	min	mg	Knudsen	Torsion^b
$YbCl_3$	842	13956	3.0	$2.83 \cdot 10^{-6}$	$1.48 \cdot 10^{-6}$ (1)
$YbCl_3$	870	8430	3.5	$5.51 \cdot 10^{-6}$	$5.26 \cdot 10^{-6}$
$YbCl_3$	896	4994	9.1	$2.44 \cdot 10^{-5}$	$1.59 \cdot 10^{-5}$
$YbCl_3$	920	3090	12.4	$5.47 \cdot 10^{-5}$	$4.19 \cdot 10^{-5}$
$YbCl_3$	953	5070	43.2	$1.18 \cdot 10^{-4}$	$1.46 \cdot 10^{-4}$
$YbCl_3$	960	1934	28.2	$2.02 \cdot 10^{-4}$	$1.88 \cdot 10^{-4}$
$YbBr_3$	842	10972	8.0	$7.79 \cdot 10^{-6}$	$6.26 \cdot 10^{-6}$ (2)
$YbBr_3$	845	16386	13.6	$8.86 \cdot 10^{-6}$	$7.18 \cdot 10^{-6}$
$YbBr_3$	855	10832	13.5	$1.34 \cdot 10^{-5}$	$1.12 \cdot 10^{-5}$
$YbBr_3$	871	6122	11.3	$2.01 \cdot 10^{-5}$	$2.25 \cdot 10^{-5}$
$YbBr_3$	888	2902	12.2	$4.61 \cdot 10^{-5}$	$4.60 \cdot 10^{-5}$
YbI_2	903	10700	3.0	$3.05 \cdot 10^{-6}$	$2.16 \cdot 10^{-6}$ (3)
YbI_2	918	8850	3.3	$4.09 \cdot 10^{-6}$	$3.81 \cdot 10^{-6}$
YbI_2	943	11076	8.6	$8.67 \cdot 10^{-6}$	$9.43 \cdot 10^{-5}$
YbI_2	948	6092	9.6	$1.75 \cdot 10^{-5}$	$1.12 \cdot 10^{-5}$
YbI_2	960	4814	6.6	$1.55 \cdot 10^{-5}$	$1.70 \cdot 10^{-5}$
$LuCl_3$	891	9100	6.0	$8.07 \cdot 10^{-6}$	$8.04 \cdot 10^{-6}$ (5)
$LuCl_3$	903	3166	2.4	$9.28 \cdot 10^{-6}$	$1.34 \cdot 10^{-5}$
$LuCl_3$	923	2630	7.2	$3.41 \cdot 10^{-5}$	$3.07 \cdot 10^{-5}$
$LuCl_3$	943	2518	9.9	$4.92 \cdot 10^{-5}$	$6.76 \cdot 10^{-5}$
$LuBr_3$	846	7932	4.9	$6.65 \cdot 10^{-6}$	$5.62 \cdot 10^{-6}$ (6)
$LuBr_3$	861	11100	16.4	$1.59 \cdot 10^{-5}$	$1.09 \cdot 10^{-5}$
$LuBr_3$	880	7984	14.3	$1.95 \cdot 10^{-5}$	$2.46 \cdot 10^{-5}$
$LuBr_3$	886	5570	21.1	$4.14 \cdot 10^{-5}$	$3.16 \cdot 10^{-5}$
$LuBr_3$	899	2280	9.6	$4.66 \cdot 10^{-5}$	$5.35 \cdot 10^{-5}$

[a] Uncertainty is linked with the time for heating and cooling the Knudsen cell. [b] Vapor pressures calculated by the selected torsion equations (in parentheses the equation from which they were calculated).

(B) Ytterbium Diiodide. Taking in account the melting point of this compound (1046 to 1053 K) and the sensitivity of the used instrument, the vapor pressures above the solid phase were measured in small temperature ranges. The temperature ranges covered above the liquid phase are larger. To minimize a possible creeping-out of the molten compound through the effusion holes, this was put in the cell in a small amount and on a small quartz wool flock. The experimental data are reported in Table 5 and in Figure 3 while the slopes and the intercepts of the derived log p versus $1/T$ equations are given in Table 3. In several experiments, only the vapor pressures measured above the solid phase were taken in account because those measured above the molten compound were found not to be well-reproducible, increasing and decreasing the temperature (probable small creeping-out). The temperature dependence of the vapor pressure above solid and liquid phases can be expressed by the following equations:

$$YbI_2(\mathrm{s}) \quad \log(p/\mathrm{kPa}) = (9.37 \pm 0.30) - (13580 \pm 300)/(T/\mathrm{K}) \text{ from } (968 \text{ to } 1049)\ \mathrm{K} \quad (3)$$

$$YbI_2(\mathrm{l}) \quad \log(p/\mathrm{kPa}) = (9.04 \pm 0.25) - (13220 \pm 300)/(T/\mathrm{K}) \text{ from } (1068 \text{ to } 1192)\ \mathrm{K} \quad (4)$$

where the associated errors were estimated.

(C) Lutetium Trihalides. The torsion total vapor pressures of $LuCl_3$, $LuBr_3$, and LuI_3, all measured above solid phase, are reported in Tables 6, 7, and 8 and in Figures 4, 5, and 6; the corresponding Knudsen data are in Table 3 and in the same figures. The Knudsen vapor pressures of $LuCl_3$ were calculated taking in account the presence in the vapor of 20 % of dimer form. Treating the data as for ytterbium trihalides, the log p versus $1/T$ equation for each run was derived, and the corresponding slopes and intercepts are summarized in Table 9 from which the following final equations were selected:

$$LuCl_3(\mathrm{s}) \quad \log(p/\mathrm{kPa}) = (11.68 \pm 0.15) - (14940 \pm 150)/(T/\mathrm{K}) \text{ from } (942 \text{ to } 1075)\ \mathrm{K} \quad (5)$$

$$LuBr_3(\mathrm{s}) \quad \log(p/\mathrm{kPa}) = (11.34 \pm 0.20) - (14040 \pm 300)/(T/\mathrm{K}) \text{ from } (903 \text{ to } 1038)\ \mathrm{K} \quad (6)$$

$$LuI_3(\mathrm{s}) \quad \log(p/\mathrm{kPa}) = (11.99 \pm 0.40) - (14270 \pm 300)/(T/\mathrm{K}) \text{ from } (862 \text{ to } 1004)\ \mathrm{K} \quad (7)$$

For these equations, the associated errors were also estimated.

Discussion

(A) $YbCl_3$ and $LuCl_3$. The selected equations (eqs 1 and 4) representative of the vapor pressure of these compounds were compared with those found in the literature in Table 10 and in Figures 7 and 8. The absolute total vapor pressures above $YbCl_3$ agree with the Knudsen data found by Evseeva and Zenkevich[12] but are higher than those proposed by Kudin et al.[13,15] The disagreement with the Kudin et al. results can be due, as the authors hypothesized, to a decreased thermodynamic activity of $YbCl_3$ tied to the procedure followed for the production of the samples (in situ by thermal decomposition of $YbCl_2$). As concerns $LuCl_3$, even though our absolute vapor total pressure data are in substantial agreement with those proposed by Pogrebnoi et al.[21] and by Kudin and Vorob'ev,[15] the derived log p versus $1/T$ equation presents a higher slope. While for $YbCl_3$ the monomer is practically the only gaseous species present in the vapor. For $LuCl_3$ the contribution of the dimer form to the total vapor pressure is relevant, as found in the mass spectrometric study.[21] Even though the slopes of the log p versus $1/T$ lines for monomer and dimer species reported in the Pogrebnoi's work[21] are slightly different, we have considered the dimer amount present in the vapor, in the covered experimental temperature ranges, constant and equal to 20 % of the total vapor pressure. On this basis from the slopes of eqs 1 and 5, the

Table 5. Torsion Vapor Pressures of YbI_2

run 1 cell B		run 2 cell A		run 5 cell B		run 7 cell B	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
1003	4.20	1081	3.22	976	4.55	989	4.42
1008	4.20	1088	3.14	987	4.42	998	4.25
1013	4.10	1098	3.03	996	4.25	1008	4.12
1019	4.03	1106	2.94	1006	4.12	1017	4.02
1023	3.96	1116	2.85	1015	4.02	1025	3.88
1029	3.90	1124	2.77	1026	3.88	1034	3.77
1035	3.80	1132	2.68	1035	3.77	1043	3.68
1039	3.76	1140	2.60	1043	3.63	1073	3.30
1043	3.69			1103	2.92	1082	3.20
1049	3.63			1112	2.84	1092	3.09
1068	3.33			1122	2.73	1101	3.00
1078	3.20			1132	2.65	1111	2.90
1087	3.12			1143	2.53	1119	2.80
1098	3.00			1152	2.45	1128	2.70
1108	2.86			1162	2.32	1138	2.60
1117	2.77			1173	2.22	1148	2.51
1127	2.67			1183	2.12	1158	2.40
1137	2.56			1192	2.05	1168	2.29
1148	2.47					1179	2.17
1158	2.36						
1168	2.24						
1179	2.16						
1189	2.06						

run 8 cell B		run 10 cell B		run 12 cell B		run 13 cell B	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
997	4.20	968	4.72	975	4.55	982	4.42
1006	4.10	978	4.42	982	4.42	989	4.25
1014	4.03	989	4.32	991	4.32	996	4.18
1022	3.90	999	4.25	999	4.25	1005	4.07
1030	3.80	1011	4.07	1008	4.12	1013	3.94
1039	3.69	1020	3.94	1017	4.02	1021	3.85
1049	3.55	1030	3.82	1025	3.88	1030	3.74
		1040	3.68	1035	3.74	1038	3.66
				1043	3.64	1046	3.55

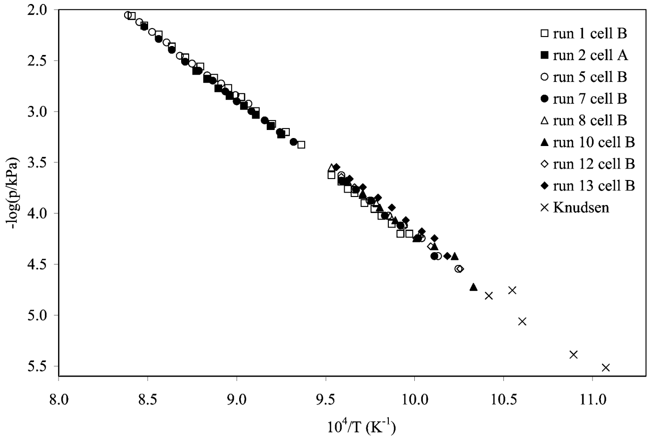

Figure 3. Torsion vapor pressures of YbI_2.

second-law sublimation enthalpies at the corresponding middle temperatures ($\Delta_{sub}H°(1020\ K) = (276 \pm 4)\ kJ\cdot mol^{-1}$ and $\Delta_{sub}H°(1009\ K) = (288 \pm 5)\ kJ\cdot mol^{-1}$ for $YbCl_3$ and $LuCl_3$, respectively) were calculated. These enthalpies were corrected at 298 K by the differences of enthalpic increments for solid and gaseous compounds proposed by Kudin and Vorob'ev,[15] $\Delta_{sub}H°(298\ K) = (290 \pm 5)$ and $(304 \pm 6)\ kJ\cdot mol^{-1}$ for $YbCl_3$ and $LuCl_3$ respectively, where the errors were in increments of $1\ kJ\cdot mol^{-1}$ in order to take into account the probable uncertainty associated with the enthalpic increments.

Four standard sublimation enthalpy values of these compounds were also obtained by the third-law method at (950, 1000, 1050, and 1100) K using the total vapor pressures calculated at these temperatures from eqs 1 and 5; those above $LuCl_3$ were reduced 20 % in order to obtain the $LuCl_3(g)$ partial pressures. The free energy functions necessary for these calculations were those computed by Kudin et al.[16] The third-law enthalpy values so obtained and reported in Table 11 do not present an evident temperature trend, and their average values are as follows: $\Delta_{sub}H°(298\ K) = (284 \pm 1)$ and $(293 \pm 2)\ kJ\cdot mol^{-1}$ for $YbCl_3$ and $LuCl_3$, respectively, where the errors were estimated only on the basis of the dispersion of the results reported in same Table 11. Both values are slightly lower than the corresponding second-law results.

For a consistent comparison of these results with the standard sublimation enthalpies of other rare earth trichlorides previously studied by us,[1−10] the vapor pressures of these compounds were treated by the second- (2-L) and third-law (3-L) method employing the new sets of enthalpic increments and fef.[16] The standard sublimation enthalpy values so obtained are summarized in Table 12. To check eventual temperature trends, the 3-L $\Delta_{sub}H°(298\ K)$ were recalculated at 50 K intervals in the respective experimental temperature ranges covered in the original work and reported in Table 11. The recent enthalpy values recommended by Kudin and Vorob'ev[15] are also reported in Table 12. From a concise critical analysis of the data, new $\Delta_{sub}H°(298\ K)$ values for all studied compounds were selected. The associated errors were estimated. In particular as follows:

(i) $LaCl_3$. No evident temperature trend of 3-L $\Delta_{sub}H°(298\ K)$ was observed above both solid and liquid phases.

Table 6. Torsion Vapor Pressures of $LuCl_3$

run 1 cell B		run 2 cell B		run 4 cell B		run 6 cell A		run 7 cell B		run 9 cell A	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
942	4.20	945	4.10	945	4.10	969	3.72	946	4.10	953	4.10
955	3.90	959	3.90	963	3.85	984	3.46	958	3.96	969	3.72
968	3.80	976	3.66	976	3.66	1001	3.22	970	3.80	982	3.50
978	3.60	991	3.39	998	3.33	1005	3.20	981	3.60	998	3.26
991	3.42	1004	3.21	1005	3.20	1017	3.00	992	3.42	1013	3.04
1002	3.25	1016	3.03	1018	3.01	1024	2.91	1004	3.24	1031	2.79
1012	3.10	1029	2.84	1024	2.91	1033	2.75	1017	3.04	1046	2.58
1024	2.91	1042	2.66	1033	2.78	1048	2.55	1030	2.84	1062	2.41
1032	2.79	1051	2.53	1047	2.57	1060	2.40	1042	2.67	1075	2.27
1042	2.65	1060	2.43	1053	2.50	1071	2.27	1059	2.45		
1050	2.53							1071	2.31		
1058	2.44										
1066	2.35										
1075	2.26										

Table 7. Torsion Vapor Pressures of $LuBr_3$

run 2 cell B		run 3 cell B		run 5 cell B		run 6 cell B		run 7 cell B	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
908	4.10	910	4.20	917	4.03	910	4.20	909	4.03
919	3.90	920	3.96	926	3.90	921	4.03	918	3.85
929	3.69	930	3.80	935	3.72	930	3.90	929	3.69
939	3.55	938	3.60	956	3.37	940	3.72	937	3.55
950	3.39	948	3.46	966	3.21	950	3.55	948	3.36
960	3.22	958	3.31	975	3.09	960	3.37	957	3.25
969	3.10	968	3.18	986	2.92	969	3.21	966	3.10
979	2.96	978	3.04	996	2.80	979	3.04	976	2.96
989	2.82	988	2.89	1006	2.68	989	2.91	984	2.84
997	2.71	998	2.75	1018	2.52	998	2.79	995	2.71
1006	2.60	1008	2.62	1028	2.41	1007	2.66	1004	2.59
		1018	2.49			1017	2.53	1013	2.48
		1027	2.40			1027	2.42		

run 9 cell A		run 10 cell A		run 12 cell B		run 13 cell B	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
921	3.96	924	3.85	910	4.03	903	4.20
931	3.80	936	3.63	918	3.90	914	4.03
938	3.66	946	3.50	927	3.72	926	3.72
948	3.50	956	3.36	938	3.55	938	3.55
958	3.33	965	3.17	948	3.42	947	3.42
967	3.18	973	3.04	956	3.30	957	3.25
978	3.03	981	2.93	966	3.14	967	3.10
987	2.88	989	2.80	976	2.98	977	2.97
997	2.75	999	2.68	986	2.85	986	2.84
1007	2.62	1009	2.55	995	2.75	996	2.71
1016	2.50	1018	2.45	1004	2.62	1006	2.59
1026	2.39	1027	2.30	1013	2.51	1017	2.47
		1038	2.14	1023	2.39		

The recalculated 2-L and 3-L enthalpy values are slightly higher than those proposed in our previous work.[1] As in the previous study, the new 2-L enthalpies are higher than the new 3-L ones. Both values are slightly higher than that recommended by Kudin and Vorob'ev.[15] On this basis, we propose the final value of (342 ± 5) kJ·mol^{-1} for $\Delta_{sub}H°(298\ K)$ for this compound.

(ii) $CeCl_3$. The 3-L enthalpy values of this compound do not present a trend in a large temperature range. The new thermodynamic data agree with those calculated in our previous work[2] and that recommended by Kudin and Vorob'ev.[15] The proposed final value is $\Delta_{sub}H°(298\ K) = (334 \pm 4)$ kJ·mol^{-1}.

(iii) $PrCl_3$. For this compound a small temperature trend of 3-L $\Delta_{sub}H°(298\ K)$ calculated above the solid phase was observed. The new results confirm that the two average 3-L enthalpy values obtained above solid and liquid phases are about 10 kJ·mol^{-1} lower that the corresponding 2-L ones (see Table 12). Giving more weight to the 3-L results and also taking into account Kudin's value, we propose $\Delta_{sub}H°(298\ K) = (330 \pm 5)$ kJ·mol^{-1} for this compound.

(iv) $NdCl_3$. The two recalculated 2-L enthalpy values above solid and liquid phases are different by about 15 kJ·mol^{-1} and equal to those reported in the previous work.[4] The corresponding two 3-L enthalpies recalculated from the vapor pressures measured above solid and liquid phases are in good agreement. Above the molten compound, the 3-L values present a very small temperature trend (see Table 11) but decidedly smaller than found in the previous work (320 and 317 kJ·mol^{-1} at 1100 and 1200 K, respectively). The final 3-L enthalpy values are lower but not in conflict with the 2-L value obtained from vapor pressures measured above solid phase. Giving more weight to the 3-L results, we propose the value (326 ± 8) kJ·mol^{-1} as the standard sublimation enthalpy of this compound, a value

Table 8. Torsion Vapor Pressures of LuI_3

run 1 cell B		run 3 cell B		run 4 cell A		run 6 cell A		run 7 cell A	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
895	3.92	896	3.82	899	3.82	904	3.82	901	3.92
911	3.62	906	3.65	909	3.68	911	3.71	912	3.68
916	3.52	917	3.46	921	3.48	920	3.57	920	3.54
923	3.43	928	3.29	931	3.29	928	3.44	929	3.41
933	3.24	938	3.12	943	3.12	937	3.29	938	3.27
942	3.12	948	2.98	951	2.97	945	3.16	948	3.11
952	2.95	958	2.84	960	2.82	953	3.03	958	2.94
958	2.85	968	2.65	970	2.67	963	2.85	967	2.79
967	2.71	976	2.53	977	2.54	972	2.72	975	2.67
977	2.54	986	2.40	986	2.43	978	2.61	975	2.67
985	2.44	995	2.30	996	2.30	985	2.50	983	2.53
993	2.33					994	2.39	993	2.41

run 10 cell B		run 11 cell A		run 13 cell B		run 14 cell A		run 14 cell A	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
883	4.12	892	4.12	862	4.52	909	3.78	897	3.92
893	3.98	900	3.98	875	4.22	918	3.62	906	3.78
905	3.74	909	3.82	888	4.05	927	3.46	916	3.62
913	3.62	919	3.68	894	3.92	936	3.29	928	3.41
924	3.44	926	3.57	898	3.82	945	3.14	935	3.27
932	3.30	938	3.38	904	3.74	954	3.00	943	3.16
940	3.16	945	3.24	915	3.57	962	2.87	951	3.05
950	2.99	955	3.08	926	3.35	972	2.74	959	2.91
961	2.83	964	2.91	938	3.14	979	2.64	969	2.79
972	2.65	974	2.76	949	3.03	987	2.52	977	2.67
979	2.53	983	2.62	959	2.84	995	2.44		
985	2.44	994	2.47	968	2.70				
991	2.37			976	2.59				
1004	2.20			985	2.49				
				994	2.38				
				1004	2.25				

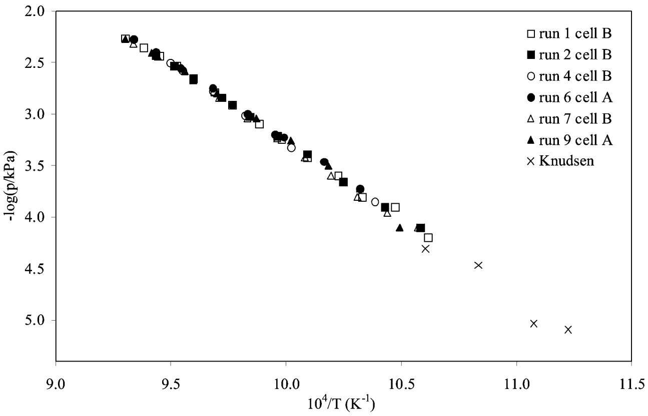

Figure 4. Torsion vapor pressures of $LuCl_3$.

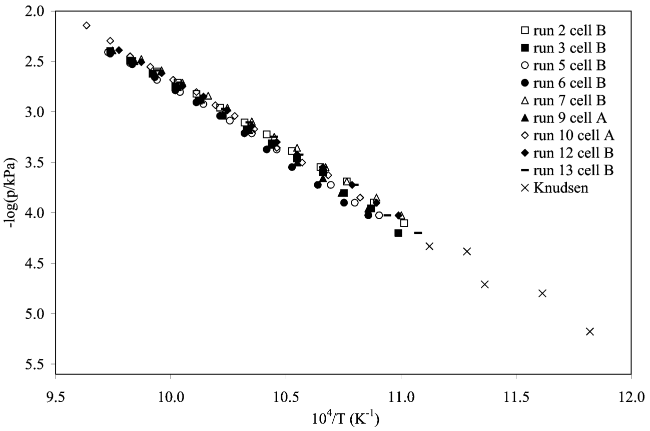

Figure 5. Torsion vapor pressures of $LuBr_3$.

higher than that recommended by Kudin and Vorob'ev[15] [(310 ± 8) kJ·mol^{-1}].

(v) $SmCl_3$. the 2-L $\Delta_{sub}H°$(298 K) value obtained in the previous work[5] above the molten compound [(266 ± 2) kJ·mol^{-1}] was lower, also taking in account the heat of fusion, than the corresponding one obtained above the solid phase [(296 ± 6) kJ·mol^{-1}]. This disagreement was justified as due to the large difference of the slopes of log p versus 1/T lines above the two phases in consequence of probable errors in vapor pressure measurements. Using the new enthalpic increments, this disagreement is practically annulled so that we believe that large errors in the vapor pressures measured in the previous work were not made. At 1000 K the Pankratz's[26] enthalpic increment for liquid (125 kJ·mol^{-1})[26] and that estimated by Myers and Graves[27] for vapor (81 kJ·mol^{-1}), both used in the previous work,[5] are decidedly different than the new values (135 and 62 kJ·mol^{-1}, respectively) used in the present work. The average of the 2-L and 3-L results, (312 ± 5) kJ·mol^{-1} (obtained giving more weight to 3-L results), is not in conflict with the value recommended by Kudin and Vorob'ev[15] [(306 ± 4) kJ·mol^{-1}].

(vi) $GdCl_3$. The trend of 3-L enthalpies recalculated in a large temperature range is decidedly negligible. Their average value [(311 ± 2) kJ·mol^{-1}] is slightly lower than that obtained by 2-L [(323 ± 6) kJ·mol^{-1}]. For this compound the new final value, $\Delta_{sub}H°$(298 K) = (315 ± 5) kJ·mol^{-1}, obtained by giving more weight to the 3-L result, is proposed. This value is slightly higher than that recommended by Kudin and Vorob'ev[15] [(299 ± 5) kJ·mol^{-1}].

(vii) $TbCl_3$. The new 3-L enthalpy, (279 ± 2) kJ·mol^{-1}, is lower than both the 2-L value, (291 ± 4) kJ·mol^{-1}, and that recommended by Kudin and Vorob'ev,[15] (294 ± 8) kJ·mol^{-1}. This disagreement is probably due to the new

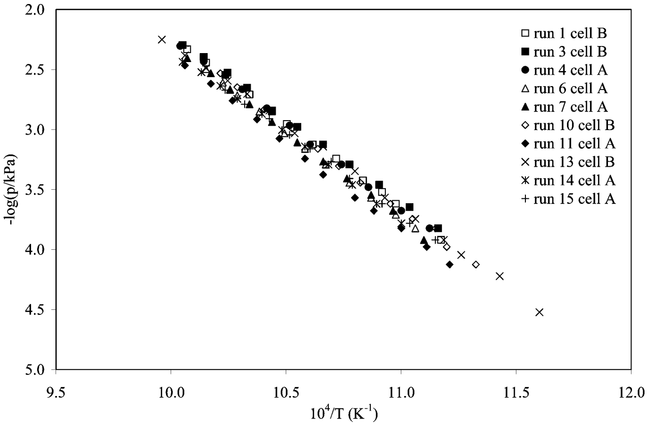

Figure 6. Torsion vapor pressures of LuI_3.

Table 9. Temperature Dependence of the Vapor Pressure for $LuCl_3$, $LuBr_3$ and LuI_3

			no. of	ΔT	$\log(p/\text{kPa}) = A - B/(T/\text{K})$	
compd	run	cell	points	K	A^a	B^a
$LuCl_3$	1	B	14	942−1075	11.62 ± 0.19	14881 ± 194
$LuCl_3$	2	B	10	945−1060	11.59 ± 0.13	14847 ± 129
$LuCl_3$	4	B	10	945−1053	11.76 ± 0.19	15028 ± 191
$LuCl_3$	6	A	10	969−1071	11.59 ± 0.19	14834 ± 194
$LuCl_3$	7	B	11	946−1071	11.73 ± 0.19	15027 ± 193
$LuCl_3$	9	A	9	953−1075	11.80 ± 0.43	15070 ± 431
$LuBr_3$	2	B	11	908−1006	11.21 ± 0.19	13877 ± 178
$LuBr_3$	3	B	13	910−1027	11.38 ± 0.27	14105 ± 261
$LuBr_3$	5	B	11	917−1028	11.16 ± 0.20	13915 ± 198
$LuBr_3$	6	B	13	910−1027	11.89 ± 0.18	14656 ± 174
$LuBr_3$	7	B	12	909−1013	11.04 ± 0.14	13669 ± 133
$LuBr_3$	9	A	12	921−1026	11.58 ± 0.17	14294 ± 169
$LuBr_3$	10	A	13	924−1038	11.56 ± 0.16	14235 ± 156
$LuBr_3$	12	B	13	910−1023	10.85 ± 0.11	13527 ± 109
$LuBr_3$	13	B	12	903−1017	11.34 ± 0.29	13991 ± 276
LuI_3	1	B	12	895−993	12.14 ± 0.11	14367 ± 99
LuI_3	3	B	11	896−995	11.70 ± 0.13	13909 ± 124
LuI_3	4	A	11	899−996	12.15 ± 0.16	14376 ± 149
LuI_3	6	A	12	904−994	12.30 ± 0.15	14592 ± 139
LuI_3	7	A	12	901−993	12.29 ± 0.14	14585 ± 129
LuI_3	10	B	14	883−1004	12.17 ± 0.10	14408 ± 91
LuI_3	11	A	12	892−994	12.14 ± 0.16	14521 ± 150
LuI_3	13	B	16	862−1004	11.57 ± 0.14	13842 ± 134
LuI_3	14	A	11	909−995	11.95 ± 0.20	14279 ± 192
LuI_3	15	A	10	897−977	11.53 ± 0.18	13860 ± 169

[a] The quoted errors are standard deviations.

fef values for the liquid phase. Infact the fef value at 1000 K (−236 J·K^{-1}·mol^{-1}) is too high as compared to ones for other rare earth trichlorides (ranging, at the same temperature, from −186 J·K^{-1}·mol^{-1} for $SmCl_3$ to −230 J·K^{-1}·mol^{-1} for $DyCl_3$). while the fef for the gaseous phase at same temperature (−418 J·K^{-1}·mol^{-1}) is included in the range of the other trichlorides (−394 J·K^{-1}·mol^{-1} for $LuCl_3$ and −420 J·K^{-1}·mol^{-1} for $NdCl_3$, $DyCl_3$, and $HoCl_3$). Notwithstanding this, it is interesting to note that the 3-L results present a decidedly negligible temperature trend (see Table 11). On this basis, we propose the value of 286 kJ·mol^{-1} as the standard sublimation enthalpy for $TbCl_3$, obtained as an average of 2-L and 3-L results, with an estimated error of 6 kJ·mol^{-1}.

(viii) $DyCl_3$. The absence of trend in the 3-L enthalpy values in a large temperature range and the substantial agreement between 2-L and 3-L results permit us to select the final value of (289 ± 4) kJ·mol^{-1} as the standard sublimation enthalpy of this compound. This value is slightly higher than that selected in our previous work[6] [(283 ± 5) kJ·mol^{-1}] and that proposed by Kudin and Vorob'ev[15] [(283 ± 8) kJ·mol^{-1}].

(ix) $HoCl_3$. The two 2-L enthalpy values obtained above the solid and liquid phases and the corresponding two 3-L values are in agreement—but slightly different (see Table 12). No temperature trend was observed in the 3-L enthalpies. On this basis we propose $\Delta_{\text{sub}}H°(298\ \text{K}) = (295 \pm 5)$ kJ·mol^{-1} as the final value for the average of 2-L and 3-L results.

(x) $ErCl_3$. The differences of fef associated with the sublimation of this compound (−193.8 and −192.2 J·K^{-1}·mol^{-1} at 900 and 1000 K, respectively) used in the present work are much lower than those taken from Pankratz's tables and used at the same temperatures in the previous work[9] (−213.8 and −212.1 J·K^{-1}·mol^{-1}). We believe that the new Δfef, decidedly comparable with those for other trichlorides, are more reliable. The 3-L values present a very small temperature trend, and their average value [(291 ± 1) kJ·mol^{-1}] is lower than that obtained by the 2-L procedure [(304 ± 4) kJ·mol^{-1}]. The final value of (297 ± 5) kJ·mol^{-1}, the average of 2-L and 3-L results, is proposed. The value proposed by Kudin and Vorob'ev[15] [(286 ± 6) kJ·mol^{-1}] is lower.

(xi) $TmCl_3$. In the previous work,[10] two sets of Δfef were used, one of which was from the same source as the present work. The 3-L sublimation enthalpies obtained by using this set do not present an evident temperature trend, and their average value [(294 ± 2) kJ·mol^{-1}] is in comparable agreement with the 2-L sublimation enthalpy [(300 ± 4) kJ·mol^{-1}]. The 3-L values obtained by using the other Δfef set, calculated using fef reported by Rycerz and Gaune-Escard[28] and by Pankratz,[26] are higher and present an evident temperature trend. The proposed value of $\Delta_{\text{sub}}H°(298\ \text{K}) = (296 \pm 4)$ kJ·mol^{-1} is slightly higher than that selected by Kudin and Vorob'ev[15] [(287 ± 7) kJ·mol^{-1}].

(xii) $YbCl_3$. The 3-L enthalpy determined in the present work [(283 ± 1) kJ·mol^{-1}] seems to be too low as compared with the trend of the corresponding 3-L values of the other trichlorides (see Table 12). As for $TbCl_3$, we believe that the new Δfef values of both compounds (−182 and −185 J·K^{-1}·mol^{-1} at 1000 K, for $TbCl_3$ and $YbCl_3$, respectively) are lower than those of the other trichlorides ranging from −190 J·K^{-1}·mol^{-1} ($LuCl_3$ and $DyCl_3$) to −212 J·K^{-1}·mol^{-1} ($LaCl_3$ and $CeCl_3$). On this basis we propose for $YbCl_3$ the enthalpy value of $\Delta_{\text{sub}}H°(298\ \text{K}) = (288 \pm 6)$ kJ·mol^{-1}, obtained giving more weight to the 2-L result.

(xiii) $LuCl_3$. The 3-L enthalpy values present a very negligible temperature trend. Their average value [(293 ± 2) kJ·mol^{-1}] is lower than the 2-L one [(304 ± 6) kJ·mol^{-1}]. Considering that the 2-L value, based on the assumption that the dimmer amount (20 %) is constant in the covered temperature range, is more influenced by this assumption than the 3-L one, we propose the final value of $\Delta_{\text{sub}}H°(298\ \text{K}) = (295 \pm 5)$ kJ·mol^{-1} as the standard sublimation enthalpy of this compound, which was obtained by giving more weight to the 3-L value.

(B) $YbBr_3$ and $LuBr_3$. The vaporization behavior of these compounds are comparable. Our vapor pressures were compared in Figure 9 with those measured by boiling point[22] above molten compounds. From the slopes of eqs 2 and 6, practically equal, the second-law sublimation enthalpy for both compounds equal to $\Delta_{\text{sub}}H°(T) = (296 \pm 6)$ kJ·mol^{-1} was derived. As apparently no thermodynamic data are available in the literature for reducing this enthalpy to 298 K, the difference of the enthalpic increments for solid and gaseous phases, $\Delta[H°(T) - H°(298\ \text{K})] = (16 \pm 3)$ kJ·mol^{-1}, was used, which was estimated from the corresponding increments proposed by Pankratz[26] for

Table 10. Comparison of the Temperature Dependence of the Total Vapor Pressures of $YbCl_3$ and $LuCl_3$

				$\log(p/\text{kPa}) = A - B/T - C \log T$			$\Delta H°(298\ \text{K})/\text{kJ·mol}^{-1}$	
compd	ref	method	$\Delta T/\text{K}$	A	B	C	II law	III law
$YbCl_3$ [a]	Evseeva and Zenkevich[12]	Knudsen effusion		12.12 ± 0.14	14870 ± 140		298 ± 3[b]	
$YbCl_3$	Kudin et al.[13]	Knudsen mass spectr.	from 1000 to 1130	9.92 ± 0.74	14348 ± 650		294 ± 10	292 ± 13
$YbCl_3$	Evdokimov et al.[14]	mass spectr.					284 ± 8	
$YbCl_3$	Kudin and Vorob'ev[15]	Knudsen mass spectr.	from 1008 to 1100	9.42 ± 0.50	13860 ± 530		280 ± 23	311 ± 8
$YbCl_3$	this work	torsion effusion	from 944 to 1096	11.30 ± 0.20	14420 ± 200		290 ± 5	283 ± 1
$LuCl_3$ [c]	Hastie et al.[17]	Knudsen mass spectr.	from 890 to 960				263 ± 8[d]	
$LuCl_3$	Nieselson et al.[19]	boiling point		8.65	11130			
$LuCl_3$	Dudchik et al.[20]	boiling point	from 1273 to 1640	30.07	14718	6	~280	
$LuCl_3$	Pogrebnoi et al.[21]	Knudsen mass spectr.	from 885 to 1100	10.2 ± 0.2	13650 ± 260		285 ± 5	
$LuCl_3$	Kudin and Vorob'ev.[15]	Knudsen mass spectr.	from 885 to 1059	11.16 ± 0.62	13900 ± 570		281 ± 24	290 ± 10
$LuCl_3$	this work	torsion effusion	from 942 to 1075	11.68 ± 0.15	14940 ± 150		304 ± 6	293 ± 2

[a] Four vapor pressures were measured by Moriarty[11] and drawn in Figure 7. [b] By us, calculated by using the enthalpic increments for gaseous and solid $YbCl_3$ reported in ref 16. [c] Three vapor pressures were measured by Moriarty[11] and drawn in Figure 8. [d] As derived from Figure 5 of the work (ref 17).

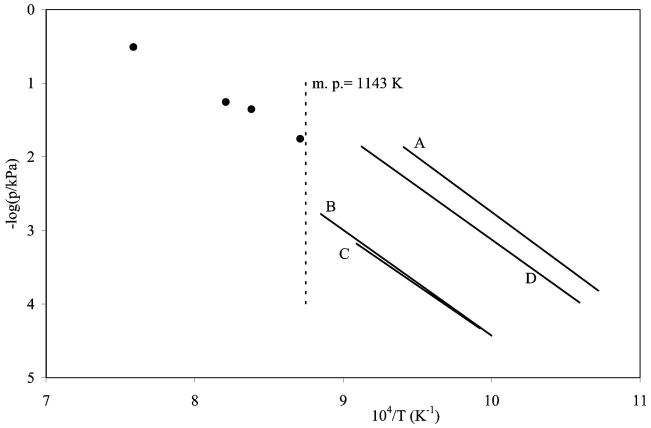

Figure 7. Comparison of $YbCl_3$ vapor pressures: ●, Moriarty;[11] A, Evseeva and Zenkevich;[12] B, Kudin and Vorob'ev;[15] C, Kudin et al.;[13] D, this work.

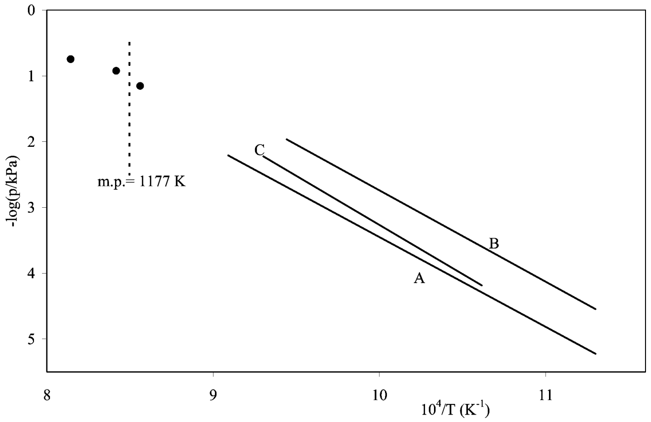

Figure 8. Comparison of $LuCl_3$vapor pressures: ●, Moriarty;[11] A, Pogrebnoi et al.;[21] B, Kudin and Vorob'ev;[15] C, this work.

some other tribromides (see Table 13) in increments ranging from 21 kJ·mol^{-1} ($PrBr_3$) to 14 kJ·mol^{-1} ($GdBr_3$). On this basis, the final value of $\Delta_{\text{sub}}H°(298\ \text{K}) = (285 \pm 9)$ kJ·mol^{-1} was selected as the standard sublimation enthalpy for both $YbBr_3$ and $LuBr_3$. The value is compared with the corresponding enthalpy obtained in our previous works for other rare earth tribromides and reported in Table 13.

(C) YbI_2. It is interesting to note that, in the covered temperature range, the absolute vapor pressures measured above this molten compound (eq 4) were comparable with those measured above the other diiodide, SmI_2(l), studied in a previous work[5] [$\log(p/\text{kPa}) = 8.10 - 12370/T$]. The difference of the slopes and the intersection of eqs 3 and 4 give enthalpy of fusion (7 kJ·mol^{-1}) and the melting point (1022 K) of this compound with large uncertainties. If the $p-T$ equations of only the three experiments in which the pressures were measured above both solid and liquid phases in the same run were used, the derived values of the enthalpy of fusion were higher (12.1, 12.8, and 12.2 kJ·mol^{-1} in runs 1B, 3B, and 7B, respectively), and we believe that the average of those least values (12.5 kJ·mol^{-1}) is more reliable than that obtained from eqs 3 and 4. Unfortunately, a part the value of the melting point ranging from (1053 to 1045) K[30] has no comparison for the enthalpy of fusion of this compound because apparently no data was found in the literature. Because the vapor pressures measured above the solid phase were taken in small temperature ranges, the errors associated with the slopes of the corresponding $p-T$ equations are larger than those obtained from the vapor pressures measured above the liquid phase, so that only eq 4 was taken into account in order to calculate the second-law vaporization enthalpy of YbI_2, $\Delta_{\text{vap}}H°(1130\ \text{K}) = (253 \pm 4)$ kJ·mol^{-1}. The thermal functions for YbI_2 were considered equal to that used for EuI_2 by Hariharan and Eick;[31] in particular $S°(298\ \text{K}) = 174$ J·K^{-1}·mol^{-1} and the heat capacities, in J·K^{-1}·mol^{-1}, of the solid, liquid, and gaseous phases: $C_p(\text{s}) = 78.58 + 0.0146T$, $C_p(\text{l}) = 110$, and $C_p(\text{g}) = 62.3$, respectively. The heat of fusion was that evaluated in the present work, $\Delta_{\text{fus}}H° = 12.5$ kJ·mol^{-1}. Also fef for YbI_2(g), (401.6 and 409.9 J·K^{-1}·mol^{-1} at 1000 and 1200 K, respectively) were those employed for EuI_2(g).[31] From those thermal functions, the second- and third-law standard sublimation enthalpy values for YbI_2 of $\Delta_{\text{sub}}H°(298\ \text{K}) = (297 \pm 6)$ and (304 ± 2) kJ·mol^{-1}, respectively, were calculated. The third-law sublimation enthalpies, evaluated at a 50 K interval of temperature and reported in Table 14, do not present evident temperature dependence. The errors associated with the enthalpy values were estimated considering also the large uncertainties associated with the employed thermal functions. On this basis, we propose as standard sublimation enthalpy of YbI_2 the value $\Delta_{\text{sub}}H°(298\ \text{K}) = (302 \pm 6)$ kJ·mol^{-1}. This value is higher than that found for SmI_2 [(272 ± 10) kJ·mol^{-1}] in the previous work. [5] It is interesting to note that, as also observed in the previous work, the second-law vaporization enthalpy of SmI_2, $\Delta_{\text{vap}}H°(1121\ \text{K}) = (237 \pm 4)$ kJ·mol^{-1}, obtained above molten compound could be considered as a lower limit as compared with the vaporization enthalpy value of the same compound obtained by Hirayama et al.[32] [$\Delta_{\text{vap}}H°(1082\ \text{K}) = (256 \pm 5)$ kJ·mol^{-1}] and the value (268 ± 13) kJ·mol^{-1} mass spectrometrically determined by these authors[32] from the slopes

Table 11. Third-Law $\Delta_{sub}H°$(298 K) Evaluated by Vapor Pressures Calculated by log p vs 1/T Equations Reported in Table 12 and New Δfef[15,16]

			T/K						
compd	ΔT/K		900	950	1000	1050	1100	1150	1200
$LaCl_3$(s)	1006−1122	p/kPa			$1.99\cdot10^{-5}$	$1.28\cdot10^{-4}$	$6.99\cdot10^{-4}$		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$			−211.9	−210.8	−209.6		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$			340.3	339.8	339.2		
$LaCl_3$(l)	1137−1188	p/kPa						$3.06\cdot10^{-3}$	$9.83\cdot10^{-3}$
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$						−207.1	−204.7
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$						337.7	337.8
$CeCl_3$(s)	955−1070	p/kPa		$7.97\cdot10^{-6}$	$5.85\cdot10^{-5}$	$3.55\cdot10^{-4}$	1.83·10−3		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−213.4	−212.4	−211.2	−209.9		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		331.9	331.8	331.4	330.8		
$PrCl_3$(s)	963−1045	p/kPa		$1.10\cdot10^{-5}$	$8.13\cdot10^{-5}$	$4.98\cdot10^{-4}$			
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−213.7	−211.4	−209.4			
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		329.6	328.1	326.6			
$PrCl_3$(l)	1060−1131	p/kPa					$2.28\cdot10^{-3}$	$7.74\cdot10^{-3}$	
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$					−207.4	−204.3	
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$					326.0	325.6	
$NdCl_3$(s)	974−1031	p/kPa		$1.56\cdot10^{-5}$	$1.11\cdot10^{-4}$				
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−212.0	−210.9				
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		325.3	325.0				
$NdCl_3$(l)	1063−1199	p/kPa				$6.05\cdot10^{-4}$	$2.46\cdot10^{-3}$	$8.85\cdot10^{-3}$	$2.86\cdot10^{-2}$
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$				−208.3	−205.7	−202.7	−199.7
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$				323.7	323.5	322.5	321.2
$SmCl_3$(s)	895−941	p/kPa	$8.89\cdot10^{-6}$	$6.66\cdot10^{-5}$					
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$	−213.9	−212.0					
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$	314.1	313.8					
$SmCl_3$(l)	965−1077	p/kPa			$2.24\cdot10^{-4}$	$7.93\cdot10^{-4}$	$2.50\cdot10^{-3}$		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$			−210.1	−206.7	−203.2		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$			318.4	319.7	320.6		
$GdCl_3$(l)	930−1213	p/kPa	$8.51\cdot10^{-6}$	$4.98\cdot10^{-5}$	$2.44\cdot10^{-4}$	$1.03\cdot10^{-3}$	$3.79\cdot10^{-3}$	$1.25\cdot10^{-2}$	$3.74\cdot10^{-2}$
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$	−211.9	−208.3	−204.7	−201.5	−198.3	−195.4	−192.5
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$	312.6	312.6	312.3	312.0	311.3	310.7	309.8
$TbCl_3$(l)	921−1117	p/kPa	$3.66\cdot10^{-5}$	$1.89\cdot10^{-4}$	$8.32\cdot10^{-4}$	$3.17\cdot10^{-3}$	$1.07\cdot10^{-2}$		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$	−187.7	−184.8	−181.8	−179.1	−176.4		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$	279.9	279.7	279.1	278.6	277.8		
$DyCl_3$(l)	924−1214	p/kPa		$1.34\cdot10^{-4}$	$6.12\cdot10^{-4}$	$2.42\cdot10^{-3}$	$8.42\cdot10^{-3}$	$2.63\cdot10^{-2}$	$7.48\cdot10^{-2}$
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−191.6	−189.4	−187.3	−185.1	−183.1	−181.0
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		288.9	289.3	289.5	289.5	289.4	289.1
$HoCl_3$(s)	883−994	p/kPa	$1.30\cdot10^{-5}$	$8.83\cdot10^{-5}$					
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$	−199.9	−199.0					
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$	298.7	299.2					
$HoCl_3$(l)	1002−1164	p/kPa			$4.94\cdot10^{-4}$	$1.94\cdot10^{-3}$	$6.72\cdot10^{-3}$	$2.09\cdot10^{-2}$	$5.91\cdot10^{-2}$
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$			−198.1	−195.8	−193.5	−191.4	−189.3
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$			299.8	300.4	300.9	301.2	301.4
$ErCl_3$(s)	880−1040	p/kPa	$1.57\cdot10^{-5}$	$1.21\cdot10^{-4}$	$7.60\cdot10^{-4}$				
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$	−193.81	−193.01	−192.20				
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$	291.7	291.0	290.3				
$TmCl_3$(s)	945−1093	p/kPa		$1.02\cdot10^{-4}$	$6.17\cdot10^{-4}$	$3.13\cdot10^{-3}$	$1.37\cdot10^{-2}$ [a]		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−195.4	−194.5	−193.7	−193.1		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		294.6	294.3	294.0	293.9		
$YbCl_3$(s)	944−1096	p/kPa		$1.31\cdot10^{-4}$	$7.52\cdot10^{-4}$	$3.66\cdot10^{-3}$	$1.54\cdot10^{-2}$		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−186.23	−185.56	−184.90	−184.24		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		284.0	283.7	283.4	283.1		
$LuCl_3$(s)	942−1075	p/kPa[b]		$7.08\cdot10^{-5}$	$4.33\cdot10^{-4}$	$2.23\cdot10^{-3}$	$9.88\cdot10^{-3}$		
		Δfef/ $J\cdot K^{-1}\cdot mol^{-1}$		−190.9	−190.1	−189.3	−188.5		
		$\Delta_{sub}H°$(298 K)/$kJ\cdot mol^{-1}$		293.3	292.8	292.3	291.8		

[a] At 1093 K, melting point of $TmCl_3$. [b] $LuCl_3$ partial pressures calculated by eq 4 considering the amount of dimmer form Lu_2Cl_6, (20 % of the total ones) equal in all the experimental temperature range.

of some log I^+T versus 1/T equations (I^+ is the ion intensities of the species produced by electron bombardment of the vapor). This induced us to believe that new measurements of the sublimation enthalpy of SmI_2 are necessary.

Our final selected enthalpy value of YbI_2 is comparable with the third-law one, $\Delta_{sub}H°(298\ K) = (309 \pm 13)\ kJ\cdot mol^{-1}$, reported by Hariharan and Eick[31] for EuI_2.

(D) LuI_3. From eq 7, the second-law enthalpy of this compound, $\Delta_{sub}H°(933\ K) = (273 \pm 6)\ kJ\cdot mol^{-1}$, was derived. This value was reduced at 298 K by a $\Delta[H°(T) - H°(298\ K)]$ value equal to $(15 \pm 3)\ kJ\cdot mol^{-1}$ estimated from the corresponding values of other triiodides (see Table 15). The obtained value, $\Delta_{sub}H°(298\ K) = 288\ kJ\cdot mol^{-1}$, with an error that should not exceed 9 $kJ\cdot mol^{-1}$ is proposed as the standard sublimation enthalpy for LuI_3. No comparison can be made with the literature, but the value is comparable with those for other studied earth triiodides (see Table 15).

Conclusions

In the present work the total vapor pressure of $YbCl_3$, $YbBr_3$, YbI_2, $LuCl_3$, $LuBr_3$, and LuI_3 were measured by torsion and Knudsen effusion methods. The sublimation enthalpies of $YbCl_3$ and $LuCl_3$ were determined from second- and third-law treatment of the vapor pressure data

Table 12. Temperature Dependence of Vapor Pressure Equations and Recalculated Second- and Third-Law Standard Sublimation Enthalpies (kJ·mol^{-1}) of Rare Earth Trichlorides by Using New Sets of [($H°$ (T)−$H°$ (298 K)] and [($G°$ (T)−$H°$ (298 K)]/T (See Text)

			log(p/kPa) = $A - B/T$		second-law		third-law		selected	
compd	ref	ΔT/K	A	B	published	recalculated	published	recalculated[a]	our	Kudin
$LaCl_3$(s)	1	1006−1122	12.31 ± 0.10	17012 ± 100	346 ± 2	351 ± 2	333 ± 1.5	340 ± 1	342 ± 5	338 ± 5
$LaCl_3$(l)	1	1137−1188	9.65 ± 0.23	13989 ± 272		354 ± 5	−	338 ± 1		
$CeCl_3$(s)	2	955−1070	12.21 ± 0.20	16443 ± 150	336 ± 3	337 ± 3	327	331 ± 1	334 ± 4	327 ± 6
$PrCl_3$(s)	3	963−1045	12.45 ± 0.20	16540 ± 200	338 ± 4	339 ± 4	323	328 ± 3	330 ± 5	323 ± 8
$PrCl_3$(l)	3	1060−1131	9.56 ± 0.10	13422 ± 150	336 ± 3	337 ± 3		326 ± 1		
$NdCl_3$(s)	4	974−1031	12.20 ± 0.30	16156 ± 400	332 ± 8	332 ± 8	322 ± 2	325 ± 1	326 ± 8	310 ± 8
$NdCl_3$(l)	4	1063−1199	10.18 ± 0.20	14068 ± 300	348 ± 6	347 ± 6	320 ± 3	323 ± 2		
$SmCl_3$(s)	5	895−941	11.56 ± 0.30	14950 ± 300	296 ± 6	301 ± 6		314 ± 1	312 ± 5	306 ± 6
$SmCl_3$(l)	5	953−1077	7.88 ± 0.10	11530 ± 100	266 ± 2	295 ± 2	314	319 ± 2		
$GdCl_3$(l)	8	930−1213	9.50 ± 0.30	13113 ± 300	317 ± 6	323 ± 6	309 ± 1	311 ± 2	315 ± 5	299 ± 5
$TbCl_3$(l)	8	921−1117	9.13 ± 0.20	12210 ± 200	292 ± 4	291 ± 4	300 ± 2	279 ± 1	286 ± 6	294 ± 8
$DyCl_3$(l)	6	924−1214	9.31 ± 0.30	12523 ± 300	287 ± 6	289 ± 6	281 ± 1	289 ± 1	289 ± 4	283 ± 8
$HoCl_3$(s)	7	883−994	10.91 ± 0.10	14216 ± 150	286 ± 3	287 ± 3	314 ± 4	299 ± 1	295 ± 5	300 ± 8
$HoCl_3$(l)	7	1002−1164	9.16 ± 0.10	12466 ± 150	290 ± 3	291 ± 3		300 ± 1		
$ErCl_3$(s)	9	880−1040	12.04 ± 0.15	15159 ± 200	306 ± 4	305 ± 4	310 ± 1	291 ± 1	297 ± 5	286 ± 6
$TmCl_3$(s)	10	945−1093	11.60 ± 0.20	14810 ± 200	299 ± 4	300 ± 4	294 ± 2	294 ± 2	296 ± 4	287 ± 7
$YbCl_3$(s)	this work	944−1096	11.30 ± 0.20	14420 ± 200		290 ± 5		283 ± 1	288 ± 6	280 ± 10
$LuCl_3$(s)	this work	942−1075	11.68 ± 0.15	14940 ± 150		304 ± 6		293 ± 2	295 ± 5	290 ± 10

[a] The associated errors were estimated only on the ground of the temperature trends of third-law results reported in Table 11.

Table 13. Temperature Dependence of Vapor Pressure Reported in Previous Works and Second- and Third-Law Standard Sublimation Enthalpies (kJ·mol^{-1}) of Solid Rare Earth Tribromide

		ΔT	log(p/kPa) = $A - B/T$		Δ$H°$(T)	Δ[$H°$(T) −	Δ$_{sub}H°$(298 K)		
compd	ref	K	A	B	II law	$H°$(298 K)]	II law	III law	selected
$LaBr_3$	1	955−1045	11.71 ± 0.20	15392 ± 150	295 ± 4	20[a]	315 ± 4	302 ±	304 ± 5
$CeBr_3$	2	887−1003	12.12 ± 0.20	15332 ± 150	294 ± 3	16[a]	310 ± 8	280 ± 2	300 ± 10
$PrBr_3$	3	890−961	12.06 ± 0.30	15060 ± 200	288 ± 4	21[a]	309 ± 4	291	300 ± 10
$NdBr_3$	4	866−954	12.10 ± 0.30	15132 ± 300	290 ± 6	17[a]	307 ± 8	293 ± 4	298 ± 8
$SmBr_3$	5	844−925	11.87 ± 0.30	14470 ± 250	277 ± 5	15[a]	292 ± 10		292 ± 10
$GdBr_3$	8	895−1057	11.46 ± 0.20	14355 ± 200	275 ± 4	14[a]	289 ± 4	292 ± 1	292 ± 2
$TbBr_3$	8	904−1108	11.09 ± 0.20	14013 ± 200	268 ± 4	17[a]	285 ± 4	292 ± 2[c]; 287 ± 2[d]	288 ± 4
$DyBr_3$	6	878−1151	11.47 ± 0.30	14344 ± 300	272 ± 6	17[a]	289 ± 6		289 ± 6
$HoBr_3$	7	904−1105	10.95 ± 0.10	14168 ± 150	271 ± 3	17[a]	288 ± 3	294 ± 4	290 ± 5
$ErBr_3$	9	919−1058	11.09 ± 0.15	14256 ± 200	273 ± 4	16[a]	289 ± 4	296 ± 2	293 ± 4
$TmBr_3$	10	921−1155	11.67 ± 0.20	14330 ± 200	274 ± 4	16[b]	290 ± 5	282.5[c]; 278[d]	285 ± 5
$YbBr_3$	this work	891−1032	11.51 ± 0.20	14070 ± 300	269 ± 6	16 ± 3[b]	285 ± 9		285 ± 9
$LuBr_3$	this work	903−1038	11.34 ± 0.20	14040 ± 300	269 ± 6	16 ± 3[b]	285 ± 9		285 ± 9

[b] By Pankratz.[26] [b] Estimated value. [c] Obtained using Δfef reported by Pankratz.[26] [d] Obtained using Δfef reported by Gietmann.[30]

Table 14. Third-Law Standard Sublimation Enthalpy of YbI_2

T	p	Δ$_{vap}G°$(T)	−Δfef	Δ$_{sub}H°$(298 K)
K	kPa	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
1050	$2.73 \cdot 10^{-4}$	112	183	304
1100	$1.06 \cdot 10^{-3}$	105	181	304
1150	$3.65 \cdot 10^{-3}$	98	180	304
1200	$1.13 \cdot 10^{-2}$	91	178	305

employing new thermodynamic function.[16] By using these functions, new sublimation enthalpy values of earth rare trichlorides previously studied by us were recalculated. The final values were compared in Table 12 with those recently recommended by Kudin and Vorob'ev.[15] With the exception of $TbCl_3$ and $HoCl_3$, all our selected Δ$_{sub}H°$(298 K) values, even if not in evident conflict, are generally higher than the Kudin and Vorob'ev results. In Figure 10, the sublimation enthalpies along the lanthanide series are shown together with those of lanthanide tribromides and triiodides. As concerns trichlorides, the Δ$_{sub}H°$(298 K) values present a decreasing trend from $LaCl_3$ to $TbCl_3$ (lowest molecular weight) whereas they are comparable, ranging around 290 to 295 kJ·mol^{-1}, for the compounds at highest molecular weight.

As concerns tribromides, all Δ$_{sub}H°$(298 K) values are comparable, with a very small decreasing trend with an increase in the molecular weight of tribromides. This trend is not observed in triiodides where all their standard sublimation enthalpies, except for CeI_3 and HoI_3, were found to be comparable with the values ranging around (285 ± 10) kJ·mol^{-1}. It is interesting to observe that the decrease of Δ$_{sub}H°$(298 K) going from trichlorides to triiodides present in the earth rare trihalides at low molecular

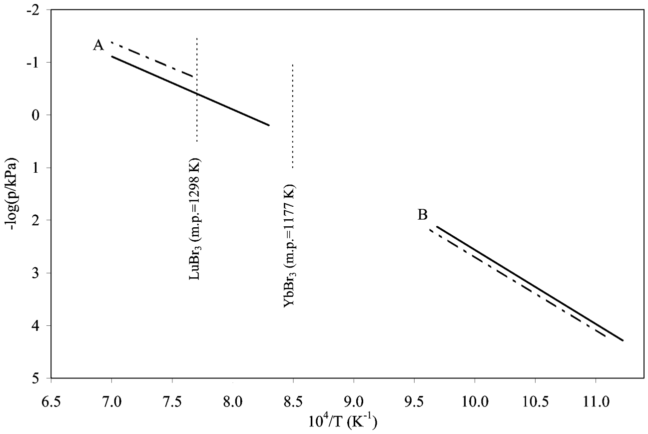

Figure 9. Comparison of $YbBr_3$ (continuous line) and $LuBr_3$ (dotted line) vapor pressures. A, Makhmadmurodov et al.;[22] B, this work.

Table 15. Temperature Dependence of Vapor Pressure Reported in Previous Works and Second- and Third-Law Standard Sublimation Enthalpies (kJ·mol^{-1}) of Solid Rare Earth Triiodide

		ΔT	$\log(p/\text{kPa}) = A - B/T$		$\Delta H°(T)$	$\Delta[H°(T) - H°(298\text{ K})]$	$\Delta H°(298\text{ K})$		
compd	ref	K	A	B	II law		II law	III law	selected
LaI_3	1	932−1038	11.10 ± 0.20	14098 ± 200	270 ± 4	18	288 ± 4	283	285 ± 3
CeI_3	2	910−1031	12.02 ± 0.20	14843 ± 150	284 ± 3	19	303 ± 8	281	295 ± 10
PrI_3	3	889−1003	11.31 ± 0.30	13766 ± 200	263 ± 4	20	283 ± 4	274	278 ± 5
NdI_3	4	906−1031	10.70 ± 0.10	13513 ± 200	259 ± 4	32[a]	291 ± 4	278	284 ± 6
SmI_3	33	815−890			258 ± 10	18[b]	276 ± 10		276 ± 10[c]
α-GdI_3	8	890−1012	10.99 ± 0.20	13651 ± 200	261 ± 4	15	276 ± 4	280	279 ± 2
α-TbI_3	8	861−1078	11.33 ± 0.30	13850 ± 400	265 ± 4	17	282 ± 4	277	279 ± 2
DyI_3	6	889−1157	11.34 ± 0.20	13800 ± 200	264 ± 4	18	282 ± 4		282 ± 4
HoI_3	7	872−1066	12.24 ± 0.10	14656 ± 150	281 ± 3	15[c]	296 ± 8		296 ± 8
ErI_3	9	871−1082	11.55 ± 0.15	13862 ± 200	265 ± 4	17[c]	282 ± 6		282 ± 6
TmI_3	10	887−1051	11.54 ± 0.20	13790 ± 200	264 ± 4	13	277 ± 4		277 ± 4
LuI_3	this work	862−1004	11.99 ± 0.40	14270 ± 300	273 ± 6	15 ± 3[c]	288 ± 9		288 ± 9

[a] In this enthalpy value the solid α → β transition, $\Delta_{\text{trans}}H°(847\text{ K}) = 14$ kJ·mol^{-1},[26] is included. [b] Value obtained by us in a recent work and submitted for publication in *J. Chem. Eng. Data*. [c] Estimated value.

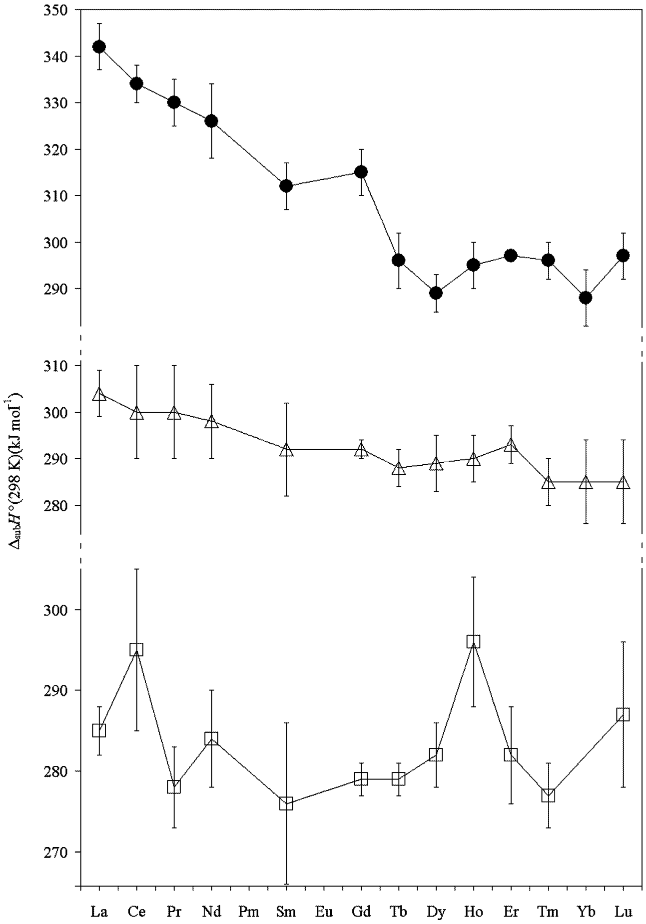

Figure 10. Comparison $\Delta_{\text{sub}}H°(298\text{ K})$ of lanthanides halides: ●, chlorides; △, bromides; □, iodides.

weight is practically absent in the corresponding trihalides of heavy lanthanides. In particular as concerns HoI_3, a critical analysis of the results reported in the previous work[7] lead us to conclude that the $\Delta_{\text{sub}}H°(298\text{ K}) = 296$ kJ·mol^{-1} obtained from second-law treatment of the data could be considered an upper limit. In confirmation of this, the fef values for solid HoI_3 derived from third-law treatment of this enthalpy value and the vapor pressures are decidedly higher for about 20 J·K^{-1}·mol^{-1} than those reported by Pankratz[26] for other solid triiodides. Difference of 20 J·K·mol^{-1} for fef of the solid compound at 1000 K can be also justified with an variation of factor 10 of the absolute vapor pressures, but a such error in our experimental pressure measurements is decidedly too high, and the vapor pressures are in agreement with those reported in the literature. This leads to the conclusion that probably the slope of log p versus $1/T$ equation and the derived second-law sublimation enthalpy value are upper limits so that, considering the $\Delta_{\text{sub}}H°(298\text{ K})$ evaluated for other triiodides, we believe that the standard sublimation enthalpy for HoI_3 is minor and probably equal to about (285 ± 10) kJ·mol^{-1}. Of course, further experiments are necessary in order to confirm this.

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