J. Chem. Eng. Data **1999,** *44,* 509−515

Vaporization Studies of Dysprosium Trichloride, Tribromide, and Triiodide

Bruno Brunetti, Papirio Vassallo, Vincenzo Piacente,* and Paolo Scardala

Dipartimento di Chimica, Università di Roma “La Sapienza”, Piazzale Aldo Moro 5, 00185 Roma, Italy

The vapor pressures of $DyCl_3$, $DyBr_3$, and DyI_3 were measured by the torsion method, and the following selected equations were derived in the covered temperature ranges. $DyCl_3$: $\log(p/\text{kPa}) = 9.31 \pm 0.30 - (12523 \pm 300)(K/T)$, (924−1214 K). $DyBr_3$: $\log(p/\text{kPa}) = 11.47 \pm 0.30 - (14344 \pm 300)(K/T)$, (878−1151 K). DyI_3: $\log(p/\text{kPa}) = 11.34 \pm 0.20 - (13800 \pm 200)(K/T)$, (889−1157 K). Treating by second- and third-law methods the obtained results, the standard sublimation enthalpies, $\Delta_{\text{sub}}H°(298\text{ K}) = 283 \pm 5$, 289 ± 6, and 282 ± 4 kJ mol^{-1} for $DyCl_3$, $DyBr_3$, and DyI_3, respectively, were determined.

Introduction

Apparently, the early study on the vaporization of $DyCl_3$ was carried out by Moriarty (1963) by the Knudsen method. At high temperatures, Dudchik et al. (1969) measured the vapor pressure above the molten compound by the “boiling point” method and evaluated its vaporization enthalpy, $\Delta_{\text{vap}}H°(1472\text{ K}) = 197$ kJ mol^{-1}. Myers and Graves (1977), employing estimated thermodynamic data, calculated the standard sublimation enthalpy of this compound using the Moriarty’s vapor pressure data (244 and 297 kJ mol^{-1}, second- and third-law enthalpy values, respectively) and the Dudchik’s ones (288 and 319 ± 17 kJ mol^{-1}, second- and third-law enthalpy values, respectively). Myers and Hannay (1980) measured by the Knudsen method two vapor pressure sets from which derived the following second- and third-law standard sublimation enthalpies, $\Delta_{\text{sub}}H°(298\text{ K}) = 303$ and 313 ± 12 kJ mol^{-1}, respectively. Incidentally, these values were taken by Pankratz (1984) as source for the compilation of the thermodynamic table for this compound. A vapor pressure set was also measured by Evseeva and Zenkevich (1980) by using the same method. Recently Kudin et al. (1997) and Kuznetsov et al. (1997) using a Knudsen source coupled to a mass spectrometer found that, in addition to monomeric molecules, dimeric and very small amount of trimeric and tetramic molecules were also present in the gaseous phase in the temperature range (850−1010 K). According to their calculations, the Dy_2Cl_6 molar fraction increased with increasing temperature. Employing new thermodynamic functions, the standard enthalpies of $DyCl_3$ associated to the sublimation in both gaseous forms were derived. It is interesting to note that the standard enthalpy associated with the sublimation process as monomer, $\Delta_{\text{sub}}H°(298\text{ K}) = (272 \pm 5)$ kJ mol^{-1}, is decidedly lower than that found by Myers and Hannay (1980) and those reported by Pankratz (1984) for the other lanthanide trichlorides, ranging from 306 kJ mol^{-1} ($TbCl_3$) to 339 kJ mol^{-1} ($LaCl_3$), except for europium trichloride (278 kJ mol^{-1}).

As concerns $DyBr_3$, apparently not many studies on the vaporization of this compound were found in the literature. In particular, the only vapor pressure values were those measured at high temperatures (1220−1535 K) by boiling points (Makhmadmurodov et al., 1975; Makhmadmurodov et al., 1989) and at lower temperatures (873−1053 K), over the solid phase, by a mass spectrometer (Hilpert et al., 1995). The derived standard enthalpies, $\Delta_{\text{sub}}H°(298\text{ K}) = 273 \pm 14$ kJ mol^{-1} (second-law, Makhmadmurodov et al., 1975) and 278.4 ± 7.4 and 283.9 ± 11.3 kJ mol^{-1} (second- and third-law, respectively, Hilpert et al., 1995) are in agreement within their errors. In addition to the monomer, also the presence of a small amount of the dimer form was observed by Hilpert et al. (1995) so that the dissociation process of the dimer was also studied by these authors.

As concerns DyI_3, Hirayama and Castle (1973), from the slope of a mass spectrometric log I^+T vs $1/T$ equation, derived a second-law sublimation enthalpy of this compound equal to 290 ± 7 kJ mol^{-1} in agreement with a previous value estimated by Feber (1965) (287 kJ mol^{-1}). Later on Hirayama et al. (1975) measured by the Knudsen method new vapor pressure values in the temperature range 895−1045 K from which they derived a standard sublimation enthalpy equal to 286 ± 1.7 kJ mol^{-1}. A mass spectrometric vapor pressure set was measured by Kaposi et al. (1983). They found that also for dysprosium triiodide, in addition to DyI_3(g), also a small amount of dimer form was present in the vapor in the temperature range 970−1150 K. On the contrary, a mass spectrometric analysis of the vapor carried out by Popovic et al. (1989) showed that the monomer was practically the only gaseous species present in the vapor, but unfortunately in their paper is not reported the covered temperature range.

Considering that the vapor pressure data for dysprosium trichloride, tribromide, and triiodide are scarce, most of which derived by mass spectrometer technique with inevitable uncertainties associated with the method and in particular that the sublimation enthalpy for $DyCl_3$, recently proposed by Kudin et al. (1997), seems to be low compared to those for the other lanthanide trichlorides, we have studied again these halides and measured their total vapor pressures by the torsion method from which new sublimation enthalpies have been derived.

Experimental Section

The torsion apparatus employed in the present study was substantially the one described in detail in an our previous

---

* To whom correspondence should be addressed.

10.1021/je9801821 CCC: $18.00

Table 1. Instrument Constants of the Torsion Cells as Obtained in Different Experimental Runs

cell	materials	nominal diameter of the holes (mm)	$K^a \times 10^{-2}$ (kPa rad^{-1})	$K^b \times 10^{-2}$ (kPa rad^{-1})	$K \times 10^{-2}$ average (kPa rad^{-1})
As	steel	1.8	0.394; 0.381; 0.375	0.382	0.38
Bs	steel	1.0	1.22; 1.28	1.27	1.25
Cs	steel	0.3	14.0;14.8; 14.1; 14.1	14.6; 15.1	14.5
Ac	graphite	1.3	0.311; 0.296	0.292	0.30
Bc	graphite	1.0	1.51; 1.60; 1.56	1.62; 1.65; 1.59; 1.65	1.60
Cc	graphite	0.6	3.00; 3.02		3.01
Dc	graphite	0.4	8.81; 8.91; 9.09	8.68; 8.90	8.90

[a] Obtained using cadmium as standard. [b] Obtained using lead as standard.

paper (Piacente et al., 1994). Conventional torsion effusion cells, different for the materials from which were machined and for the nominal area of their effusion holes, were used. For each cell, the instrument constant necessary to convert the experimental torsion angles of the tungsten wire to which the cell is suspended in pressure data was evaluated vaporizing, in separate experiments, standards (cadmium and lead) having well-known vapor pressures (Hultgren et al., 1973). The instrument constants so determined and reported in Table 1 are reproducible within 15−20%, and this produces displacements in the log p values of about ±0.1. The calibration of the used Pt−(Pt-10% Rh) thermocouple was made following the procedure described in the previous work (Piacente et al., 1994) so that the uncertainty in the temperature measurements should not exceed ±2 K. For torsion angles smaller than about 5°, errors ranging from 20% to 5% of their values were made; errors in the measurements of larger angles were decidedly negligible.

$DyCl_3$ samples used in this work were supplied by Alfa-Johnson Matthey GmbH (Karlsruhe, Germany) 99.9% pure, $DyBr_3$ by Cerac Inc.(Milwaukee, WI), 99.9% pure, and DyI_3 by Aldrich Chem. Co., 99.99% pure, all percent purities as certified by the suppliers. To minimize oxidation and hydrolysis of the compounds, the cells were loaded in a drybox, rapidly introduced into the torsion apparatus filled with nitrogen, and then quickly evacuated.

Results

Table 2. Torsion Total Vapor Pressure of $DyCl_3$ (in kPa)

Cell As

run As, 1		run As, 2		run As, 3		run As, 4		run As, 5	
T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}
944	3.86	946	3.80	924	4.15	925	4.15	936	4.08
958	3.66	962	3.58	942	3.89	944	3.85	958	3.75
971	3.48	972	3.47	961	3.57	958	3.63	975	3.52
981	3.35	977	3.37	986	3.23	970	3.50	990	3.32
996	3.16	989	3.22	1003	3.04	983	3.33	1004	3.14
1007	3.04	1003	3.05	1019	2.85	997	3.16	1023	2.90
1016	2.92	1013	2.93	1032	2.70	1007	3.02	1043	2.69
1029	2.78	1023	2.82	1040	2.61	1020	2.82		
1045	2.58	1027	2.77	1049	2.52	1040	2.66		
		1034	2.70	1058	2.46				

Cell B_s

run Bs, 1		run Bs, 2		run Bs, 3	
T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}
964	3.65	957	3.83	987	3.37
978	3.47	969	3.65	1000	3.17
998	3.24	977	3.53	1029	2.82
1007	3.14	989	3.39	1052	2.53
1022	2.99	1002	3.24	1063	2.46
1032	2.81	1015	3.13	1073	2.33
1038	2.78	1020	3.02	1083	2.24
1048	2.64	1029	2.94	1091	2.15
1050	2.64	1035	2.84	1101	2.04
1064	2.46	1048	2.72	1109	1.97
1068	2.44	1051	2.66		
1081	2.28	1066	2.50		
1082	2.28	1068	2.47		
1090	2.19	1084	2.28		
1098	2.10	1103	2.13		

Cell Cs

run Cs, 1		run Cs, 2		run Cs, 3		run Cs, 4		run Cs, 5	
T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}	T/K	−log p_{tot}
1072	2.50	1086	2.23	1067	2.48	1044	2.80	1054	2.70
1086	2.28	1092	2.16	1096	2.22	1061	2.58	1064	2.58
1090	2.28	1095	2.11	1101	2.14	1083	2.38	1087	2.28
1102	2.08	1106	2.01	1101	2.18	1090	2.32	1107	2.10
1118	1.94	1113	1.97	1120	1.97	1103	2.13	1147	1.69
1126	1.86	1120	1.93	1123	1.95	1123	1.94	1177	1.42
1136	1.75	1128	1.81	1133	1.78	1125	1.90	1204	1.21
1139	1.72	1141	1.71	1134	1.82	1143	1.72	1212	1.14
1148	1.62	1142	1.67	1144	1.72	1158	1.55		
1155	1.56	1152	1.59	1147	1.65	1173	1.44		
1166	1.43	1160	1.53	1153	1.62	1190	1.24		
1168	1.45	1162	1.50	1161	1.52				
1176	1.34	1172	1.41	1165	1.50				
1184	1.28	1178	1.35	1176	1.39				
1192	1.22	1183	1.29	1176	1.40				
1193	1.19	1189	1.25	1185	1.31				
1201	1.14	1194	1.19	1190	1.26				
1205	1.11	1199	1.16	1198	1.20				
				1198	1.20				
				1209	1.14				
				1214	1.07				

A. Dysprosium Trichloride. The total torsion vapor pressures above molten $DyCl_3$ measured by the steel cells increasing and decreasing temperature are reported in Table 2 and Figure 1. Slopes and intercepts of the log p vs $1/T$ equations as obtained by least-squares treatment of the experimental data of each run are reported in Table 3. Some slopes of the log p vs $1/T$ equations obtained by the cell Cs (having the smallest effusion holes) are slightly higher than the slopes of the other equations obtained by the cells As and Bs. This is not thermodynamically justified (considering the negative value of the difference between the heat capacities of the vapor and liquid phase) but probably could be linked to small errors in temperature measurements when the sample was heated at high temperatures. Not evident temperature dependence of the slopes of the equations obtained using the cells As and Bs was observed. Considering the very good agreement between the absolute vapor pressure data measured by different cells, the following equation, representative of the total vapor pressure above liquid $DyCl_3$, was selected weighting proportional to the number points each slope and intercept of the equations reported in Table 3 and giving double weight to the equations obtained by the cells As and Bs:

$$\log(p/\text{kPa}) = 9.31 \pm 0.30 - (12523 \pm 300)(K/T) \quad (1)$$

where the overall associated errors were estimated. This equation was compared in Table 4 and Figure 2 with those

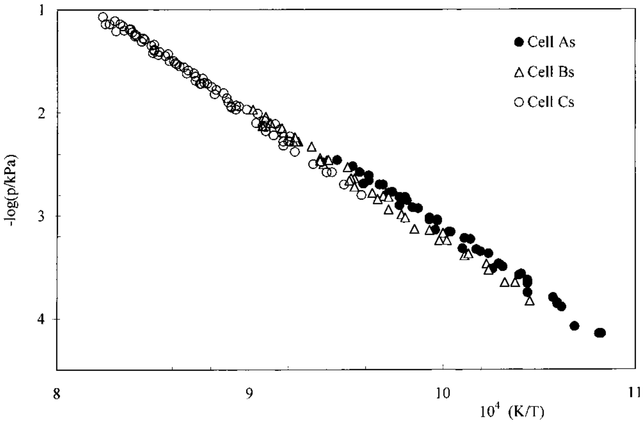

Figure 1. Torsion total vapor pressures of $DyCl_3$.

Table 3. Temperature Dependence of the Total Vapor Pressure of DyX_3 (X = Cl, Br, I)

compound	run	no. of points	ΔT (K)	$\log(p/\text{kPa}) = A - B/(T/\text{K})$	
				A^a	B^a
$DyCl_3$ (liq)	As, 1	9	944−1045	9.26 ± 0.08	12376 ± 81
	As, 2	10	946−1034	9.24 ± 0.13	12337 ± 130
	As, 3	10	924−1058	9.37 ± 0.22	12460 ± 216
	As, 4	9	925−1040	9.43 ± 0.25	12539 ± 242
	As, 5	7	936−1043	9.60 ± 0.12	12795 ± 122
	Bs, 1	15	964−1098	9.04 ± 0.12	12248 ± 122
	Bs, 2	15	957−1103	8.99 ± 0.12	12258 ± 119
	Bs, 3	10	987−1109	9.18 ± 0.16	12353 ± 167
	Cs, 1	18	1072−1205	9.95 ± 0.14	13304 ± 161
	Cs, 2	18	1086−1199	9.07 ± 0.13	12276 ± 153
	Cs, 3	21	1067−1214	9.49 ± 0.14	12815 ± 160
	Cs, 4	11	1044−1190	9.83 ± 0.17	13201 ± 194
	Cs, 5	8	1054−1212	9.20 ± 0.17	12518 ± 190
$DyBr_3$ (sol)	Ac, 1	7	936−1043	11.56 ± 0.13	14308 ± 125
	Ac, 2	11	878−1038	11.14 ± 0.14	13922 ± 138
	Ac, 3	8	919−1038	11.43 ± 0.07	14223 ± 67
	Bc, 1	9	950−1040	11.22 ± 0.11	14729 ± 107
	Bc, 2	10	917−1039	11.23 ± 0.10	13951 ± 103
	Cc, 1	9	965−1043	12.01 ± 0.09	14651 ± 87
	Cc, 2	10	954−1060	11.44 ± 0.31	14207 ± 312
	Cc, 3	10	965−1062	11.75 ± 0.31	14546 ± 310
	Cc, 4	8	956−1036	11.64 ± 0.21	14403 ± 206
	Dc, 1	9	1030−1151	11.34 ± 0.13	14307 ± 138
	Dc, 2	8	1037−1145	11.60 ± 0.26	14692 ± 282
DyI_3 (sol)	Ac, 1	14	889−1015	11.18 ± 0.08	13648 ± 79
	Ac, 2	11	898−1000	11.15 ± 0.14	13664 ± 130
	Ac, 3	15	936−1023	11.30 ± 0.05	13795 ± 45
	Bc, 1	12	940−1027	11.29 ± 0.19	13871 ± 184
	Bc, 2	8	987−1060	11.78 ± 0.22	14086 ± 223
	Cc, 1	9	1002−1078	11.34 ± 0.10	13713 ± 108
	Cc, 2	12	982−1089	11.30 ± 0.16	13832 ± 173
	Cc, 3	10	996−1081	11.41 ± 0.20	13995 ± 210
	Cc, 4	11	981−1086	11.35 ± 0.16	13960 ± 168
	Dc, 1	15	1026−1157	11.28 ± 0.12	13517 ± 130
	Dc, 2	8	1013−1123	11.67 ± 0.18	13998 ± 187

[a] The quoted errors are standard deviations.

reported in the literature. Our pressure data are in better agreement with those reported by Dudchik et al. (1969) and by Evseeva and Zenkevich (1980).

B. Dysprosium Tribromide. In Table 5 and Figure 3 are reported the total vapor pressure values measured above solid $DyBr_3$ by graphite cells. In Table 3 are reported log(p) vs 1/T equations obtained in each experimental run. Contrary to trichloride, all the slopes of the equations determined by different torsion cells in different temperature ranges were found comparable enough within their standard deviations. The pressures measured by the cell Dc are slightly lower than those measured by other cells. In the overall temperature range covered in our experiments (878 to 1151 K), the total vapor pressure of tribromide can be expressed by the following equation evaluated as for $DyCl_3$:

$$\log(p/\text{kPa}) = 11.47 \pm 0.30 - (14344 \pm 300)(K/T) \quad (2)$$

where the associated errors were estimated. This equation was compared in Table 4 and Figure 4 with those reported in the literature. Taking into account the contribution of the heat of fusion, our data seem to be in better agreement with the results reported by Makhmadmurodov et al. (1975).

C. Dysprosium Triiodide. Despite the certified purity, the vaporization of about 4−5% of the original weight of the sample due to the vaporization of unidentified impurities was observed at about 500 K; of course, this vaporization step was neglected in the subsequent runs. On increasing the temperature, the vapor pressure falls below the instrument sensitivity so that the pressures measured at higher temperatures were considered representative of the vapor pressures above practically pure DyI_3. In Tables 3 and 6 and in Figure 5 were reported the obtained results. The log p vs 1/T equations so determined are in agreement between themselves even though, contrary to that observed in the measurements above $DyBr_3$, the pressures measured by the cell Dc are slightly higher than those measured by the other cells. From these equations, the following one, representative of the total vapor pressure of DyI_3 in the temperature range 889 to 1157 K, was selected:

$$\log(p/\text{kPa}) = 11.34 \pm 0.20 - (13800 \pm 200)(K/T) \quad (3)$$

where the associated errors were estimated. This equation and those found in the literature were reported in Table 4 and in Figure 6 for comparison. Even though the absolute pressure data are decidedly in agreement with those found in the previous works [Hirayama et al. (1975) and Kaposi et al. (1983)], the slope of our selected eq 3 seems to be slightly lower.

Discussion

A. Dysprosium Trichloride. Considering that a small dimer amount is present in the vapor in the temperature range covered in our experiments, the partial pressures of the monomer were calculated at 50 K intervals in the temperature range 1000−1200 K from the total vapor pressures derived from eq 1 and the dimer percents evaluated from the mass spectrometric results reported by Kuznetsov (1997). These pressures are in Table 7. The second-law vaporization enthalpy of this compound in monomer form, $\Delta_{\text{vap}}H°(1069\text{ K}) = 238 \pm 6$ kJ mol^{-1}, was derived from the slope of the equation, $\log(\bar{p}DyCl_3/\text{kPa}) = 9.19 \pm 0.30 - (12425 \pm 300)(K/T)$, obtained treating the $DyCl_3$ partial pressures by least squares. The errors were considered equal to those associated to the selected eq 1. The enthalpic value was reported to 298 K, $\Delta_{\text{sub}}H°(298\text{ K}) = 287 \pm 6$ kJ mol^{-1}, by 9 kJ mol^{-1} (needed to convert $\Delta_{\text{vap}}H°$ from 1069 K to melting point 924 K), by the heat of fusion equal to 25.5 kJ mol^{-1} [value calorimetrically obtained by Dworkin and Bredig, 1971 (25.5 kJ mol^{-1}), and from the second-law sublimation and vaporization enthalpies reported by Kudin et al., 1997, both corrected at 924 K (25.4 ± 6 kJ mol^{-1})] and by 14.6 kJ mol^{-1} [difference of the enthalpic increments for solid and gaseous compound from the melting point to 298 K, Pankratz, 1984]. The standard sublimation enthalpy of $DyCl_3$ was also calculated by the third-law method using two sets of free energy function, $\Delta\{[G°(T) - H°(298\text{ K})]/T\} = \Delta\text{fef}$, those reported in Pankratz's tables and those derived from the Kudin's

Table 4. Temperature Dependence of the Total Vapor Pressure of DyX_3 (X = Cl, Br, I)

compound	method	ΔT/K	total vapor pressure
$DyCl_3$	Knudsen	1023–1123	$\log(p/\text{kPa})^a = 8.56 - 11025(K/T)$
	boiling point	1325–1620	$\log(p/\text{kPa})^b = 29.873 - 15066(K/T) - 6.0 \log(T/\text{K})$
	Knudsen	924–1031	$\log(p/\text{kPa})^c = 10.06 - 13459(K/T)$
	Knudsen	973–1073	$\log(p/\text{kPa})^d = 7.65 - 10668(K/T)$
	mass spectrom.	850–924	$\log(p/\text{kPa})^{e,1} = 10.84 - 13458(K/T)$
	mass spectrom.	924–1010	$\log(p/\text{kPa})^{e,2} = 9.18 - 11922(K/T)$
	this work	924–1214	$\log(p/\text{kPa}) = 9.31 \pm 0.30 - (12523 \pm 300)(K/T)$
$DyBr_3$	boiling point	1220–1535	$\log(p/\text{kPa})^f = 26.02 \pm 0.11 - (13349 \pm 72)(K/T) - 5 \log(T/\text{K})$
	mass spectrom.	803–1053	$\log(p/\text{kPa})^g = 11.54 - 13942(K/T)$
	this work	878–1151	$\log(p/\text{kPa}) = 11.47 \pm 0.30 - (14344 \pm 300)(K/T)$
DyI_3	Knudsen	843–1060	$\log(p/\text{kPa})^h = 11.80 \pm 0.14 - (14085 \pm 133)(K/T)$
	mass spectrom.	970–1150	$\log(p/\text{kPa})^i = 12.704 - 15023(K/T)$
	this work	889–1157	$\log(p/\text{kPa}) = 11.34 \pm 0.20 - (13800 \pm 200)(K/T)$

[a] Evaluated by us from four points reported by Moriarty (1963). [b] Dudchik et al. (1969). [c] Evaluated by us from the vapor pressure data reported by Myers and Hannay (1980). [d] Evseeva and Zenkevich (1980). [e,1;e,2] Calculated by us from the slopes and intercepts of the temperature-partial pressure equations for $DyCl_3$(g) and Dy_2Cl_6(g) reported by Kudin et al. (1997) and Kuznetsov et al. (1997) over the solid (e,1) and molten $DyCl_3$ (e,2), respectively. [f] Makhmadmurodov et al. (1975). [g] Calculated by us from slopes and intercepts of the temperature–partial pressure equations for $DyBr_3$(g) and Dy_2Br_6(g) reported by Hilpert et al. (1995). [h] Hirayama et al. (1975). [i] Calculated by us from the vapor pressure values reported by Kaposi et al. (1983).

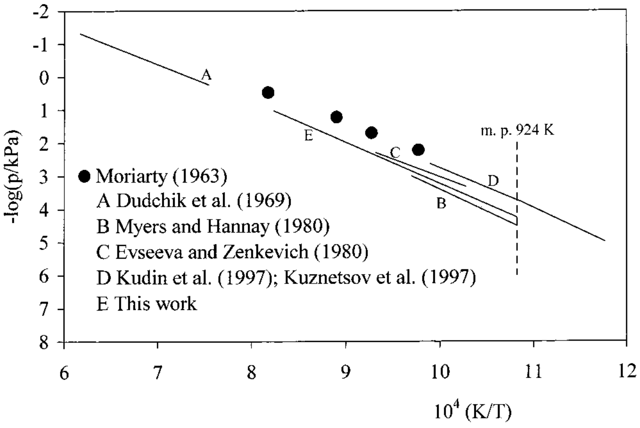

Figure 2. Comparison of the total vapor pressures of $DyCl_3$ with the literature data.

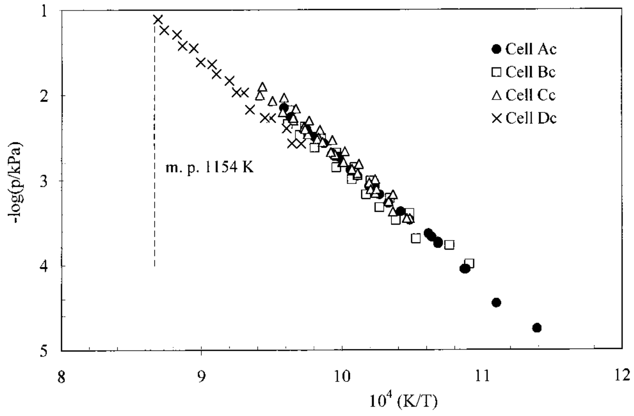

Figure 3. Torsion total vapor pressures of $DyBr_3$.

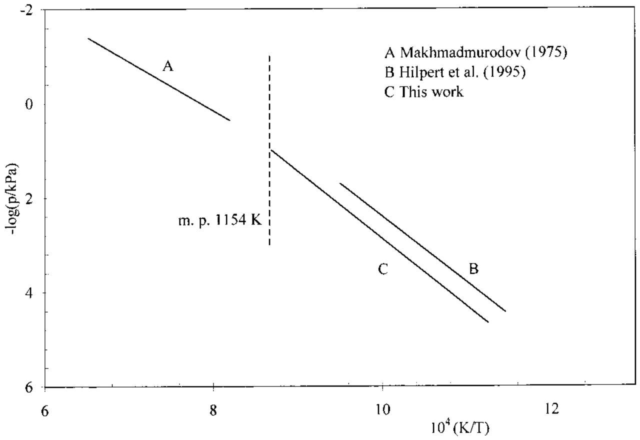

Figure 4. Comparison of the total vapor pressures of $DyBr_3$ with the literature data.

thermodynamic data. The obtained results are in Table 7. The third-law sublimation enthalpies obtained using Kudin's free energy functions do not present an appreciable temperature trend and their average value, $\Delta_{vap}H°(298\ K) = 281\ kJ\ mol^{-1}$, agrees within the uncertainties with the second-law one. Giving more weight to the third-law results, we propose as the standard sublimation enthalpy of $DyCl_3$ the value 283 kJ mol^{-1} with an estimated error that could not exceeded ±5 kJ mol^{-1}. This selected value is slightly higher than the Kudin's results (270 ± 4 and 272 ± 6 kJ mol^{-1} second- and third-law values, respectively) and then the standard enthalpy values obtained treating the previous vapor pressure data reported in the literature by Kudin's thermodynamic functions [272 ± 10 kJ mol^{-1} (second-law), Moriarty (1963); 278 ± 9 and 277 ± 10 kJ mol^{-1} (second- and third law, respectively), Dudchik et al. (1969); 250 ± 7 and 275 ± 10 kJ mol^{-1} (second- and third-law, respectively), Evseeva and Zenkevich (1980)].

B. Dysprosium Tribromide. Also, the monomer partial pressures of this compound were calculated from selected eq 2 and the dimer amount present in the vapor was evaluated from the data reported by Hilpert (1995). The $DyBr_3$ pressures so calculated at 100 K intervals in the temperature range 800–1100 K are in Table 8. These values fit well on the linear equation: $\log(\bar{p}DyBr_3/\text{kPa}) = 11.29 \pm 0.30 - (14200 \pm 300)(K/T)$. The associated errors are those in eq 2. From the slope of this equation, the second-law sublimation enthalpies of $DyBr_3$, $\Delta_{sub}H°(1015\ K) = 272 \pm 6\ kJ\ mol^{-1}$ and $\Delta_{sub}H°(298\ K) = 289 \pm 6\ kJ\ mol^{-1}$, were obtained. The enthalpic increment value, $\Delta[H°(1015\ K) - H°(298\ K)](\text{gas} - \text{cr})$ equal to -17 kJ mol^{-1}, was evaluated as the difference of the enthalpic increment reported by Pankratz (1984) for the gaseous compound, and the enthalpy increment for the solid compound obtained by the heat capacities, $C_p/(J\ mol^{-1}\ K^{-1}) = 95.02 \pm 0.11 + (17.5 \pm 0.2)\ 10^{-3}T$, calorimetrically measured by Elsam and Preston (1992). The standard enthalpy so obtained is within the error comparable with that selected by Hilpert et al. (1995) [$\Delta_{sub}H°(298\ K) = 281.1 \pm 6.2\ kJ\ mol^{-1}$]. It is interesting to note that previously Myers and Graves

Table 5. Torsion Total Vapor Pressure of $DyBr_3$ (in kPa)

Cell Ac

run Ac, 1		run Ac, 2		run Ac, 3	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
936	3.73	878	4.75	919	4.05
942	3.63	901	4.45	936	3.75
977	3.07	920	4.05	960	3.37
1002	2.73	940	3.67	974	3.17
1013	2.57	954	3.47	989	2.95
1026	2.40	968	3.27	1005	2.72
1043	2.15	981	3.07	1025	2.44
		994	2.88	1038	2.26
		1007	2.69		
		1020	2.49		
		1038	2.26		

Cell Bc

run Bc, 1		run Bc, 2	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
950	3.69	917	3.99
963	3.47	929	3.77
974	3.32	954	3.39
983	3.17	967	3.21
993	2.99	980	3.01
1004	2.85	991	2.85
1020	2.62	1004	2.68
1031	2.47	1015	2.51
1040	2.34	1027	2.37
		1039	2.18

Cell Cc

run Cc, 1		run Cc, 2		run Cc, 3		run Cc, 4	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
965	3.17	954	3.45	965	3.37	956	3.45
977	2.99	981	3.03	977	3.15	968	3.25
988	2.81	993	2.87	989	2.94	976	3.11
998	2.66	1005	2.70	980	3.11	989	2.92
1007	2.53	1017	2.50	1000	2.79	999	2.79
1016	2.41	1025	2.46	1008	2.67	1014	2.55
1024	2.30	1036	2.30	1018	2.52	1027	2.40
1034	2.16	1044	2.20	1028	2.38	1036	2.27
1043	2.03	1052	2.07	1036	2.26		
		1060	1.90	1062	2.00		

Cell Dc

run Dc, 1		run Dc, 2	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
1030	2.57	1037	2.567
1041	2.39	1058	2.266
1053	2.27	1070	2.169
1075	1.97	1081	1.965
1087	1.83	1098	1.754
1102	1.64	1112	1.613
1118	1.45	1128	1.421
1133	1.29	1145	1.235
1151	1.11		

Table 6. Torsion Total Vapor Pressure of DyI_3 (in kPa)

Cell Ac

run Ac, 1		run Ac, 2		run Ac, 3	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
889	4.17	898	4.06	936	3.44
900	3.98	906	3.90	946	3.29
912	3.79	917	3.74	952	3.20
924	3.56	932	3.53	956	3.13
937	3.39	940	3.41	963	3.02
945	3.26	946	3.31	968	2.95
954	3.14	949	3.23	973	2.89
962	3.01	958	3.10	979	2.79
971	2.89	977	2.85	986	2.70
980	2.75	991	2.63	991	2.62
989	2.63	1000	2.51	997	2.54
997	2.50			1004	2.45
1006	2.38			1009	2.37
1015	2.25			1016	2.27
				1023	2.19

Cell Bc

run Bc, 1		run Bc, 2	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
940	3.49	987	2.47
952	3.27	999	2.35
958	3.19	1010	2.17
966	3.09	1019	2.05
973	2.97	1029	1.91
980	2.84	1040	1.77
987	2.75	1051	1.63
995	2.65	1060	1.50
1003	2.53		
1010	2.49		
1019	2.34		
1027	2.22		

Cell Cc

run Cc, 1		run Cc, 2		run Cc, 3		run Cc, 4	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
1002	2.31	982	2.77	996	2.57	981	2.91
1015	2.16	995	2.61	1007	2.46	992	2.71
1028	2.01	1006	2.46	1020	2.27	1001	2.61
1038	1.88	1016	2.31	1030	2.16	1010	2.46
1045	1.79	1028	2.16	1040	2.01	1021	2.31
1053	1.70	1039	2.01	1047	1.91	1029	2.23
1060	1.60	1046	1.93	1054	1.83	1038	2.10
1070	1.48	1056	1.79	1063	1.71	1050	1.97
1078	1.38	1064	1.68	1072	1.60	1061	1.82
		1073	1.63	1081	1.48	1071	1.68
		1081	1.46			1086	1.50
		1089	1.41				

Cell Dc

run Dc, 1		run Dc, 2	
T/K	$-\log p_{tot}$	T/K	$-\log p_{tot}$
1026	1.87	1013	2.15
1039	1.72	1028	1.97
1050	1.60	1043	1.75
1053	1.56	1058	1.56
1062	1.44	1072	1.37
1073	1.34	1085	1.22
1085	1.20	1102	1.03
1096	1.08	1123	0.82
1103	0.99		
1115	0.85		
1123	0.76		
1132	0.64		
1141	0.55		
1149	0.49		
1157	0.39		

(1977), using the pressure−temperature equation reported by Makhmadmurodov et al. (1975) and estimated thermodynamic functions, derived two standard sublimation enthalpy values, $\Delta_{sub}H°(298\ K) = 278\ kJ\ mol^{-1}$ and $294 \pm 17\ kJ\ mol^{-1}$ (second- and third-law, respectively) also comparable with our result. Treating by third-law procedure $\Delta_{sub}H°(298\ K)$ determined in the present work and the $DyBr_3$ partial pressures, the free energy function changes, $\Delta fef = \Delta\{[G°(T) - H°(298\ K)]/T\}(gas - cr)$, associated to the sublimation reaction were calculated. Knowing the fef selected by Barin (1993) for $DyBr_3$ (g), the fef values for solid $DyBr_3$ were so evaluated at the temperature range 800−1100 K and reported in Table 8. It is interesting to note that a rough extrapolation at 1400 K of Δfef, gave a value ($-185 \pm 2\ J\ K^{-1}\ mol^{-1}$) equal to that estimated by Myers and Graves (1977) ($-186\ J\ K^{-1}\ mol^{-1}$). From the fef

Table 7. Third-Law Partial Standard Sublimation Enthalpy of $DyCl_3$ in Monomeric Form

T (K)	p_{tot}[a] (kPa)	xDy_2Cl_6[b]	$\bar{p}DyCl_3$ (kPa)	Δfef (Kudin) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_{sub}H°$ (298 K) ($kJ\ mol^{-1}$)	Δfef (Pankratz) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_{sub}H°$ (298 K) ($kJ\ mol^{-1}$)
1000	6.1×10^{-4}	4.7	5.8×10^{-4}	−180.7	281.0	−209.15	309.4
1050	2.4×10^{-3}	5.5	2.3×10^{-3}	−178.8	281.1	−206.95	310.7
1100	8.4×10^{-3}	6.4	7.9×10^{-3}	−176.9	281.1	−204.82	311.8
1150	2.6×10^{-2}	7.3	2.4×10^{-2}	−175.1	281.0	−202.74	312.8
1200	7.5×10^{-2}	8.2	6.9×10^{-2}	−173.3	280.7	−200.74	313.7

[a] As calculated from eq 1. [b] Dy_2Cl_6 % from Kuznetsov partial pressure data (1997).

Table 8. Thermodynamic Functions, fef = $[G°(T) - H°(298\ K)]/T$ and $S°(298\ K)$ for Solid $DyBr_3$ from Third-Law Treatment of Its Vapor Pressures [$\Delta_{sub}H°(298\ K) = (289 \pm 6)\ J\ K^{-1}\ mol^{-1}$]

T (K)	p_{tot}[a] (kPa)	xDy_2Br_6[b]	$\bar{p}DyBr_3$ (kPa)	Δfef ($J\ K^{-1}\ mol^{-1}$)	fef$DyBr_3$ (g)[c] ($J\ K^{-1}\ mol^{-1}$)	fef$DyBr_3$(s) ($J\ K^{-1}\ mol^{-1}$)	$S°$(298 K) ($J\ K^{-1}\ mol^{-1}$)
800	3.47×10^{-7}	1.3	3.42×10^{-7}	−199.1	−433.3	−234.19	197.2
900	3.41×10^{-5}	3.0	3.30×10^{-5}	−197.0	−439.6	−242.64	197.7
1000	1.34×10^{-3}	7.0	1.24×10^{-3}	−195.0	−445.6	−250.60	198.0
1100	2.69×10^{-2}	12.0	2.37×10^{-2}	−193.2	−451.2	−257.97	198.1

[a] As calculated from eq 2. [b] Dy_2Cl_6 % from Kuznetsov partial pressure data (1997). [c] Selected by Barin (1993).

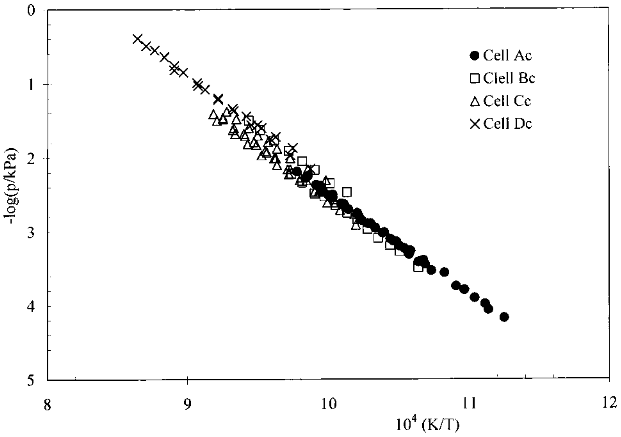

Figure 5. Torsion total vapor pressures of DyI_3.

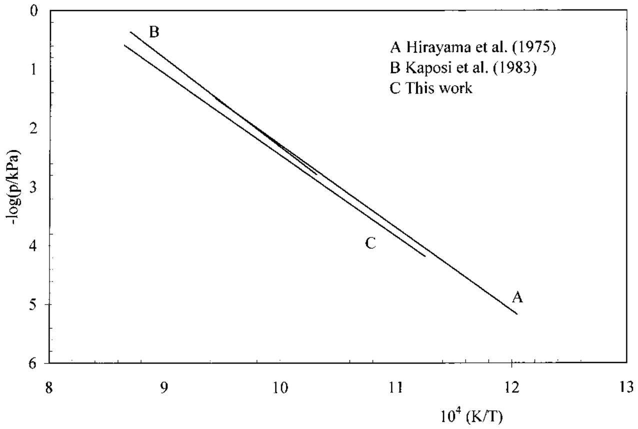

Figure 6. Comparison of the total vapor pressures of DyI_3 with the literature data.

Table 9. Standard Sublimation Enthalpies of Lanthanide Trihalides Derived from the Enthalpies of Formation Reported by Pankratz (See Text)

	$\Delta_{sub}H°(298\ K)/kJ\ mol^{-1}$			
Ln	LnF_3	$LnCl_3$	$LnBr_3$	LnI_3
La	435	338	303	279
Ce	440	330	286	278
Pr	431	325	297	275
Nd	440	323	295	273
Sm	428			
Eu	436	278		
Gd	452	312	297	277
Tb	445	306		274
Dy	446	313		
Dy		287 ± 5[a]	289 ± 6[a]	282 ± 4[a]
Ho	455	323	292	
Er	449	320		
Tm	440			
Yb	444			
Lu	435			

[a] This work.

of solid $DyBr_3$ so determined and C_p measured by Elsam and Preston (1992), the absolute entropy at 298 K of this compound was derived (see Table 8). The average value, $S°(298\ K) = 198\ J\ mol^{-1}\ K^{-1}$, was selected with an error of $\pm 10\ J\ mol^{-1}\ K^{-1}$ roughly estimated considering the uncertainties in the standard sublimation enthalpy value, in the fef for $DyBr_3$(g) and in the evaluation of $DyBr_3$(g) partial pressures (linked both to errors in our experimental total vapor pressures and in the evaluation of the monomer amount present in the vapor). This entropy value is comparable with those reported by Pankratz (1984) for tribromides of some lanthanides, values ranging from 178 $J\ mol^{-1}\ K^{-1}$ (lanthanum) to 207 $J\ mol^{-1}\ K^{-1}$ (cerium).

C. Dysprosium Triiodide. For this compound, the presence of dimer form in the vapor in the covered temperature range was considered negligible so that its second-law sublimation enthalpies, $\Delta_{sub}H°(1023\ K) = 264 \pm 4\ kJ\ mol^{-1}$ and $\Delta_{sub}H°(298\ K) = 282 \pm 4\ kJ\ mol^{-1}$, were determined from the slope of the selected eq 3. ΔC_p equal to $-24\ J\ mol^{-1}\ K^{-1}$ (Kaposi et al., 1983) was used in the extrapolation of the sublimation enthalpy to 298 K. The enthalpy value selected in the present work is comparable with that estimated by Feber (1965) 287 $kJ\ mol^{-1}$ and with those measured by Hirayama and Castle (1973) (290.4 ± 6.7 $kJ\ mol^{-1}$) Hirayama et al. (1975) (286.2 ± 2.5 $kJ\ mol^{-1}$), and Kaposi et al. (1983) (292 ± 12 $kJ\ mol^{-1}$). The value is comparable also with the standard sublimation enthalpies for triiodides of some lanthanides (see Table 9) as derived from the Pankratz's Tables.

Conclusion

The standard sublimation enthalpies of $DyCl_3$, $DyBr_3$, and DyI_3 determined in the present work, $\Delta_{sub}H°(298\ K) = 283 \pm 5$, 289 ± 6, and $282 \pm 4\ kJ\ mol^{-1}$, respectively, are decidedly comparable. This is in contrast with the evident trend of the standard sublimation enthalpies for trihalides of some lanthanides (going from trifluorides to triiodides) evaluated as the difference between the heats of formation of solid and gaseous compounds reported by Pankratz (1984) (see Table 9). It is interesting to note that the standard sublimation enthalpy value of $DyCl_3$ is also lower than those for trichlorides of other lanthanides. Considering that the major difference with the Pankratz data was observed for $DyCl_3$, we have further studied this compound and carried out several vaporization runs. The obtained results (see Figure 1) are decidedly reproducible, and a critical analysis of the errors associated with the standard sublimation enthalpy values determined by second- and third-law treatment of the vapor pressure data shows that those are minor. In fact, as concerns the second-law $\Delta_{sub}H°(298\ K)$ value, taking into account the large number of the experimental points obtained by different cells and the negligible uncertainties in temperature and torsion angle measurements, the error associated with the vaporization enthalpy of liquid $DyCl_3$ is very small (decidedly smaller than that overestimated, ± 6 kJ mol^{-1}). Also minor could be the errors associated with the heat of fusion (considering the agreement of the data reported in the literature) and the enthalpic increment (comparable enough with those for other lanthanide trichlorides) used to report the vaporization enthalpy at 298 K. On this basis, we believe that an overall error of 10 kJ mol^{-1} is decidedly the maximum uncertainty in the second-law enthalpy.

The third-law $\Delta_{sub}H°(298\ K)$ values evaluated employing Kudin's Δfef could be decidedly more reliable than those obtained using Pankratz's Δfef, considering their comparison with the second-law result and the evident temperature trend of Pankratz's enthalpies (see Table 7). This could be due to the use of erroneous Δfef values, and it should cause the suspicion that also the sublimation enthalpies of other trichlorides derived from Pankratz's table may be in error primarily for erroneous Δfef. Also, the corrections of the total pressure values for the presence in the vapor of different amounts of dimer in the evaluation of $DyCl_3$ partial pressures do not produce appreciable change of the final third-law enthalpy value. On this basis, we are persuaded that the error associated with the third-law sublimation enthalpy could be considered more minor than that overestimated for the second-law enthalpy.

This critical analysis of our results on $DyCl_3$ and the agreement of our final enthalpy value with those of other authors (see previous discussion) induce us to believe that the proposed sublimation enthalpy of $DyCl_3$, $\Delta_{sub}H°(298\ K) = 283 \pm 5$ kJ mol^{-1}, is reliable enough and that those of other trichlorides derived from Pankratz's table could be considered upper limits so that new measurements of sublimation enthalpies of these compounds are necessary.

Literature Cited

Barin, I. *Thermochemical Data for Pure Substances*; Springer: Berlin, 1993.

Dworkin, A. S.; Bredig, M. A. Enthalpy of Lanthanide Chlorides, Bromides, and Iodides from 298 to 1300 K: Enthalpies of Fusion and Transition. *High Temp. Sci.* **1971**, *3*, 81−90.

Dudchik, G. P.; Polyachenok, O. G.; Novikov, G. I. Saturated Vapour Presures of Yttrium, Praseodymium, Gadolinium, Terbium, and Dysprosium Chlorides. *Russ. J. Inorg. Chem.* **1969**, *14* (11), 1969−1970.

Elsam, L. E.; Preston, S. R. The High Temperature Heat Capacity of Dysprosium(III) Bromide by Differential Scanning Calorimetry. *Thermochim. Acta* **1992**, *205*, 319−321.

Evseeva, G. V.; Zenkevich, L. V. Determination of Vapor Pressure of Dysprosium Chloride.*Vestn. Mosk. Univ., Ser. 2: Khim* **1980**, *21* (4), 400.

Feber, R. C. *Heats of Dissociation of Gaseous Halides*, 40th ed.; LA-3164, TID-4500, Los Alamos Scientific Laboratory: Los Alamos, 1965.

Hilpert, K.; Miller, M.; Ramondo, F. Vaporization of $DyBr_3$(s) and thermochemistry of the dimer homocomplex $(DyBr_3)_2$(g). *J. Chem. Phys.* **1995**, *102* (15), 6194−6197.

Hirayama, C.; Castle, P. M. Mass spectra of rare earth triiodides. *J. Phys. Chem.* **1973**, *77* (26), 3110−3114.

Hirayama, C.; Rome, J. F.; Camp, F. E. Vapor pressures and thermodynamic properties of lanthanide triiodides. *J. Chem. Eng. Data* **1975**, *20* (1), 1−6.

Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metals Park, OH, 1973.

Kaposi, O.; Lelik, L.; Balthazàr, K. High-temperature mass spectrometric investigation of the evaporation properties of dysprosium triiodide. *High Temp. Sci.* **1983**, *16*, 299−310.

Kudin, L. S.; Pogreboy, A. M.; Kuznetsov, A. Yu.; Butman, M. F.; Burdukovskaya, G. G. Vaporisation Studies of Dysprosium and Ytterbium Chlorides. *High Temp. High Pressures* **1997**, *29*, 389−396.

Kuznetsov, A. Yu.; Butman, M. F.; Kudin, L. S.; Pogreboy, A. M.; Burdukovskaya, G. G. The Composition of Saturated Vapor over Dysprosium Trichloride: The Thermodynamic Characteristics of the Ionic and Neutral Components. *High Temp.* **1997**, *35* (5), 719−727.

Makhmadmurodov, A.; Dudchik, G. P.; Polyachenok, O. G. Saturated vapor pressure of rare earth and yttrium bromides. *Zh. Fiz. Khim.* **1975**, *49* (10), 2714−2715.

Makhmadmurodov, A.; Temurova, M.; Sharipov, A. Thermodynamics of vaporization of rare earth bromides. *Izv. Akad. Nauk. Tadzh. SSR, Otd. Fiz.-Mater., Khim. Geol. Nauk.* **1989**, *1*, 39−42.

Moriarty, J. L. Vapor Pressures of Yttrium and Rar Earth Chlorides Above Their Melting Points. *J. Chem. Eng. Data* **1963**, *8* (3), 422−424.

Myers, C. E.; Graves, D. T. Thermodynamic Properties of Lanthanide Trihalide Molecules. *J. Chem. Eng. Data* **1977**, *22* (4), 436−439.

Myers, C. E.; Graves, D. T. Vaporization Thermodynamics of Lanthanide Trihalides. *J. Chem. Eng. Data* **1977**, *22* (4), 440−445.

Myers, C. E.; Hannay, M. H. Vapor Pressures and Sublimation Thermodynamics of $GdCl_3$, $TbCl_3$ and $DyCl_3$. *J. Less-Common Met.* **1980**, *70*, 15−24.

Piacente, V.; Fontana, D.; Scardala, P. Enthalpies of Vaporization of a Homologous Series of *n*-Alkanes Determined from Vapor Pressure Measurements. *J. Chem. Eng. Data* **1994**, *39* (2), 231−237.

Popovic, A.; Muhic, S.; Marsel, J. Determination of appearance energy for ions formed in the gaseous phase over alkali iodide and rare earth iodide systems. *Rapid Commun. Mass Spectrom.* **1989**, *3* (7), 207−211.

Pankratz, L. B. *Thermodynamic Properties of Halides*; Bulletin/U.S. Department Int., Bureau of Mines 674: Washington, DC, 1984.

Received for review August 6, 1998. Accepted January 21, 1999.

JE9801821