Vaporization Studies of Lanthanum Trichloride, Tribromide, and Triiodide

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The total vapor pressures of the lanthanum trihalides $LaCl_3$, $LaBr_3$, and LaI_3 were measured by the torsion method, and their temperature dependence can be expressed by the following selected equations in the covered temperature ranges: $LaCl_3$(s): $\log(p/\text{kPa}) = (12.31 \pm 0.10) - (17012 \pm 100)\ \text{K}/T$ (1006−1122 K). $LaCl_3$(l): $\log(p/\text{kPa}) = (9.65 \pm 0.23) - (13989 \pm 272\ \text{K}/T$ (1137−1188 K). $LaBr_3$(s): $\log(p/\text{kPa}) = (11.71 \pm 0.20) - (15392 \pm 150\ \text{K}/T$ (955−1045 K). LaI_3(s): $\log(p/\text{kPa}) = (11.10 \pm 0.20) - (14098 \pm 200\ \text{K}/T$ (932−1038 K). LaI_3(l): $\log(p/\text{kPa}) = (8.39 \pm 0.15) - (11306 \pm 200\ \text{K}/T$ (1055−1123 K). Treating by second- and third-law methods the obtained results, the standard sublimation enthalpies, $\Delta_{\text{sub}}H°$(298 K)= 334 ± 5, 308 ± 5, and 285 ± 3 kJ mol^{-1} for $LaCl_3$, $LaBr_3$, and LaI_3, respectively, were determined.

Introduction

The standard sublimation enthalpy values for lanthanide trihalides, evaluated as differences between the heats of formation for their solid and gaseous phases selected by Pankratz (1984), monotonically decrease for most compounds from trifluorides to triiodides. In contrast, in a recent work from this laboratory (Brunetti et al., 1999), the standard sublimation enthalpies for dysprosium trichloride, tribromide, and triiodide derived from their vapor pressures were found practically to be the same, around 285 kJ mol^{-1}.

In view of this observation, the sublimation of other lanthanide trihalides was studied, and in particular, in the present work the results of a study on the vaporization of $LaCl_3$, $LaBr_3$, and LaI_3 are reported. Apparently, the first reported vapor pressure data for $LaCl_3$ are those measured by Harrison (1952) employing the Knudsen effusion method; later Shimazaki and Niwa (1962) and Moriarty (1963) used the same method and Novikov and Baev (1962) used the dew point method. The temperature dependencies of vapor pressure above $LaCl_3$ were also determined by the boiling point method (Dudchik et al., 1969; Nisel'son et al., 1978). A mass-spectrometric study by Hastie et al. (1968) showed that the monomer is the predominant species in the vapor.

The literature vapor pressure data of lanthanum tribromide and triiodide are more scarce. For $LaBr_3$ vapor pressures have been measured by Harrison (1952) and by Shimazaki and Niwa (1962), both employing the Knudsen method, but the obtained data are shifted by about a power. Two temperature dependence equations above solid and molten compound, respectively, were reported by Makhmadmurodov et al. (1989), employing the boiling point method. Recently, in a Knudsen effusion mass spectrometric study (Gietmann et al., 1997), the species $LaBr_3$(g) and La_2Br_6(g) were identified in the vapor and their partial pressures were measured. Enthalpies associated with sublimation and dimerization reactions have been derived.

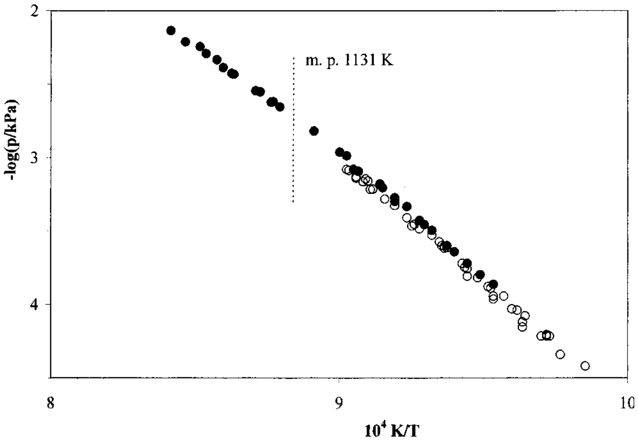

Figure 1. Torsion vapor pressures of $LaCl_3$: (○) run A,1−2−3; (●) run B,1.

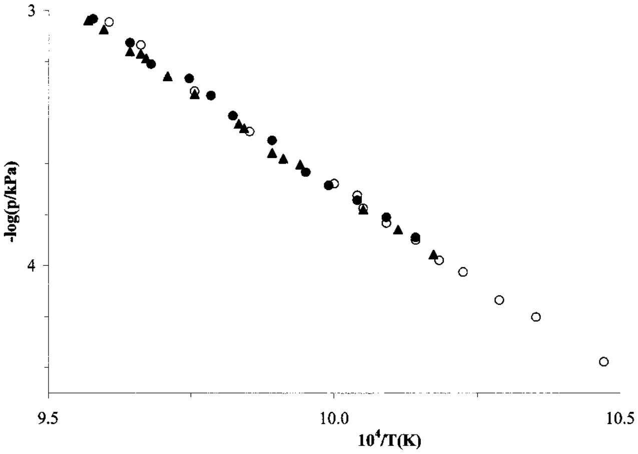

Figure 2. Torsion vapor pressures of $LaBr_3$: (○) run A,1; (●) run B,1; (▲) run B,2.

With regard to LaI_3, the only vapor pressure data are those measured by Shimazaki and Niwa (1962) using the Knudsen method and those mass-spectrometrically evaluated by Hirayama et al. (1976), but the reported data are in disagreement.

In the present work new vapor pressure data for these compounds were measured by the torsion method and compared with those found in the literature. From a

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Table 1. Torsion Total Vapor Pressure above Solid and Liquid $LaCl_3$

cell A						cell B	
run A,1		run A,2		run A,3		run B,1	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
1015	4.42	1006	4.64	1020	4.41	1049	3.86
1024	4.34	1024	4.34	1029	4.21	1054	3.80
1029	4.22	1028	4.22	1038	4.15	1059	3.72
1031	4.22	1037	4.08	1042	4.03	1064	3.64
1040	4.04	1038	4.12	1049	3.96	1067	3.60
1045	3.94	1049	3.94	1051	3.88	1073	3.49
1050	3.89	1055	3.82	1059	3.81	1076	3.46
1067	3.61	1059	3.76	1060	3.75	1078	3.43
1070	3.57	1061	3.72	1068	3.60	1083	3.33
1073	3.53	1069	3.60	1068	3.62	1088	3.27
1081	3.46	1078	3.48	1078	3.48	1088	3.30
1099	3.16	1088	3.33	1080	3.45	1093	3.20
1100	3.15	1097	3.22	1083	3.41	1094	3.18
		1108	3.08	1092	3.28	1103	3.09
		1109	3.05	1098	3.22	1105	3.08
				1101	3.16	1108	2.99
				1104	3.14	1111	2.96
				1104	3.13	1122	2.82
				1107	3.09		
						1137	2.66
						1140	2.62
						1141	2.62
						1146	2.55
						1148	2.54
						1158	2.43
						1159	2.43
						1163	2.39
						1166	2.33
						1171	2.29
						1174	2.24
						1181	2.21
						1188	2.14

second- and third-law treatment of the vapor pressure data, their standard enthalpies of sublimation were derived.

Experimental Section and Results

$LaCl_3$, $LaBr_3$, and LaI_3 samples were supplied by Aldrich. All samples are "pure" (about 99.9%, as certified by the supplier). To minimize the oxidation of the compounds, the cell was loaded in a drybox and introduced into the torsion assembly; then the system was quickly evacuated. The torsion apparatus and the procedure in the pressure measurements were described in previous works (Piacente et al., 1994; Brunetti et al., 1999). Conventional graphite torsion cells with different areas of their effusion holes (about 2.5 and 0.2 mm^2 for cells A and B, respectively) were used. Each studied sample was contained in a tantalum liner which apparently did not react with the salts. As usual, the instrument constants of both cells were measured by vaporizing very pure standards (lead and cadmium in this work) having well-known vapor pressures (Hultgren et al., 1973). The experimental vapor pressures for each compound are reported in Tables 1−3 and Figures 1−3. Vapor pressures were measured by cell B also above molten $LaCl_3$ (mp 1131 K) and LaI_3 (mp 1051 K). The few vapor pressure values measured above molten $LaBr_3$ were not taken because they were not well reproducible, probably because of interaction with the tantalum liner. The molten $LaBr_3$ data lie on a line with a slope decidedly low, compared to that obtained from the pressures determined above the solid phase corrected for the enthalpy of fusion, $\Delta H_{\mathrm{fus}} = 54$ kJ mol^{-1} (Dworkin and Bredig, 1971).

The log p versus 1/T equations obtained treating by least squares the experimental data of each run are summarized in Table 4.

Weighing the values of the slope and of the intercept of each equation reported in Table 4 proportionally to the experimental number of points, the following final ones representative of the total vapor pressures of lanthanum trihalides in the covered temperature ranges were selected:

$$LaCl_3(s)\ \log(p/\mathrm{kPa}) = (12.31 \pm 0.10) - (17012 \pm 100)\ \mathrm{K}/T\ (1006{-}1122\ \mathrm{K}) \quad (1)$$

$$LaCl_3(l)\ \log(p/\mathrm{kPa}) = (9.65 \pm 0.23) - (13989 \pm 272)\ \mathrm{K}/T\ (1137{-}1188\ \mathrm{K}) \quad (2)$$

$$LaBr_3(s)\ \log(p/\mathrm{kPa}) = (11.71 \pm 0.20) - (15392 \pm 150)\ \mathrm{K}/T\ (955{-}1045\ \mathrm{K}) \quad (3)$$

$$LaI_3(s)\ \log(p/\mathrm{kPa}) = (11.10 \pm 0.20) - (14098 \pm 200)\ \mathrm{K}/T\ (932{-}1038\ \mathrm{K}) \quad (4)$$

$$LaI_3(l)\ \log(p/\mathrm{kPa}) = (8.39 \pm 0.15) - (11306 \pm 200)\ \mathrm{K}/T\ (1055{-}1123\ \mathrm{K}) \quad (5)$$

The errors associated with the selected equations for the solid compounds and for LaI_3(l) were estimated.

These selected equations were compared with those found in the literature in Table 5 and in Figures 4−6.

Discussion and Conclusion

(A) Lanthanum Trichloride. In the covered temperature range the monomer is essentially the only gaseous species present in the vapor (Hastie et al., 1968). From the slope of the total vapor pressure equation for this compound (eq 1), the second-law sublimation enthalpies of $LaCl_3$, $\Delta_{\mathrm{sub}}H°(1064\ \mathrm{K}) = (325.6 \pm 2.0)$ kJ·mol^{-1} and $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = (346.3 \pm 2.0)$ kJ·mol^{-1}, were determined. For report-

Table 2. Torsion Total Vapor Pressure above Solid $LaBr_3$

cell A		cell B			
run A,1		run B,1		run B,2	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
955	4.38	986	3.89	983	3.96
966	4.20	991	3.81	989	3.86
972	4.13	996	3.74	995	3.78
978	4.02	1001	3.69	1006	3.60
982	3.98	1005	3.63	1009	3.58
986	3.90	1011	3.51	1011	3.56
991	3.83	1018	3.41	1016	3.46
995	3.78	1022	3.33	1017	3.44
996	3.72	1026	3.27	1025	3.33
1000	3.68	1033	3.21	1030	3.26
1015	3.47	1037	3.13	1034	3.19
1025	3.32	1044	3.03	1035	3.17
1035	3.13			1037	3.16
1041	3.04			1042	3.07
				1045	3.04

ing the enthalpy value at 298 K, the heat contents selected by Pankratz (1984) for the gaseous phase and by Gaune-Escard et al. (1996) for the solid phase were used. The difference of the slopes of eqs 1 and 2 selected for the solid and liquid compound gives an enthalpy of fusion of (58 ± 6) kJ·mol^{-1}, which is very close to that determined calorimetrically by Gaune-Escard (1994) (55.7 kJ·mol^{-1}). Though the uncertainty associated with the melting point calculated as the intersection of these equations ($T_{\mathrm{fus}} = 1136$ K) is large, the resulting value is in good agreement with those reported in the literature and summarized by Gaune-Escard (1994). Values ranging from 1119 to 1150 K were determined. This agreement is important because it shows that the errors made in the temperature measurements were not large. Moreover, the agreement of the pressure data obtained by using cells with different effusion holes and the reproducibility of their values show that the equilibrium conditions were attained in the cells and that also in the pressure measurements the error should not be too large.

The standard sublimation enthalpy of $LaCl_3$ was calculated by the third-law at two approximated extreme temperatures of the ranges covered in the experiments, 1000 and 1100 K. The $LaCl_3$(g) pressures were calculated at these temperatures by eq 1, and the necessary free energy functions, $\{[G°(T) - H°(298\ \mathrm{K})]/T\}$, for solid and gaseous phases were those selected by Pankratz (1984). The results are given in Table 6. The mean third-law standard enthalpy value, $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = (333.4 \pm 1.5)$ kJ·mol^{-1}, is lower than that obtained from the second-law procedure. This disagreement between the second- and third-law enthalpies and the small temperature trend of the third-law enthalpy values can be justified considering that a small amount of the dimer form can be present in the vapor at the highest experimental temperatures. In this case the partial pressures of monomer at these temperatures are lower than the total ones. This leads to a decreasing of the second-law sublimation enthalpy value and an increasing of the third-law $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ value calculated at 1100 K (see Table 6), reducing in this way both the temperature trend of third-law values and the disagreement between second- and third-law results. Considering negligible the dimer amount at the lowest experimental temperature, the third-law $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ value calculated at 1000 K (334.2 kJ·mol^{-1}) can be considered the more reliable value. It this interesting to note that, if this enthalpy value is used in order to evaluate by the second-law procedure the monomer partial pressure at 1100 K, this value is equal to about $0.90p_{\mathrm{tot}}$. On this basis, giving more weight to the third-law $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ value calculated at 1000 K, the standard sublimation enthalpy of $LaCl_3$, $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = 334$ kJ·mol^{-1}, was selected with an estimated error of ±5 kJ·mol^{-1}.

(B) Lanthanum Tribromide. The mass spectrum of the vapor above $LaBr_3$ observed in our laboratory at 986 K has shown that the predominant ion species were Br^+, La^+, $LaBr^+$, $LaBr_2{}^+$, $LaBr_3{}^+$, and $La_2Br_5{}^+$, and their relative intensities were about 14, 20, 20, 100, 6, and ~0.7, respectively. The appearance potentials for these ions, 17.0, 19.7, 15.1, 10.2, and 9.4 eV for Br^+, La^+, $LaBr^+$, $LaBr_2{}^+$, and $LaBr_3{}^+$, respectively (for $La_2Br_5{}^+$ the value was not measurable), were comparable with those found for similar

Table 3. Torsion Total Vapor Pressure above Solid and Liquid LaI_3

cell A								cell B			
run A,1		run A,2		run A,3		run A,4		run B,1		run B,2	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
952	3.66	946	3.81	932	4.00	935	4.01	970	3.47	966	3.58
962	3.51	955	3.66	944	3.81	956	3.65	982	3.28	974	3.45
969	3.40	957	3.62	949	3.76	969	3.46	987	3.21	981	3.34
978	3.26	963	3.54	954	3.66	982	3.27	994	3.11	990	3.21
984	3.17	969	3.45	958	3.58	998	3.04	1001	3.00	997	3.11
989	3.10	976	3.34	964	3.48	1007	2.94	1007	2.93	1005	3.00
999	2.97	982	3.28	970	3.40	1016	2.80	1016	2.79	1019	2.82
1006	2.87	989	3.15	975	3.32	1027	2.65			1026	2.71
1009	2.83	996	3.06	980	3.26	1038	2.52	1055	2.30	1032	2.65
1017	2.70	1003	2.97	986	3.17			1062	2.23		
1023	2.61	1009	2.89	993	3.08			1071	2.13	1061	2.30
1030	2.52	1014	2.81	999	3.00			1079	2.05	1065	2.25
		1017	2.77	1004	2.93			1087	1.99	1069	2.21
		1022	2.71	1009	2.85			1096	1.90	1070	2.18
				1016	2.75			1106	1.81	1074	2.14
				1020	2.69			1114	1.73	1079	2.11
				1026	2.61			1123	1.66	1080	2.08
				1030	2.56					1087	2.03
										1089	2.01
										1091	1.99
										1098	1.94
										1100	1.93
										1105	1.85
										1110	1.82
										1111	1.78

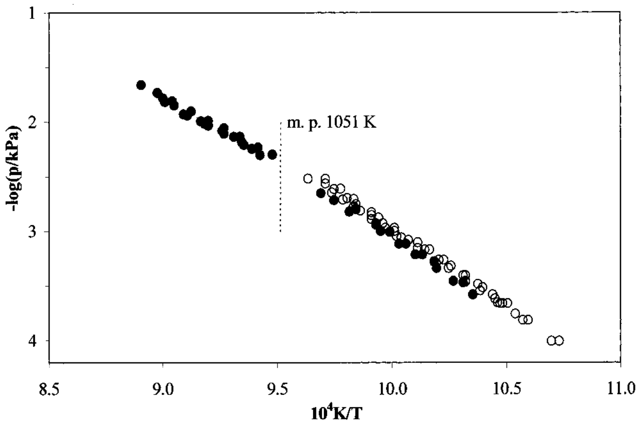

Figure 3. Torsion vapor pressures of LaI_3: (○) run A,1−2−3−4; (●) run B,1−2.

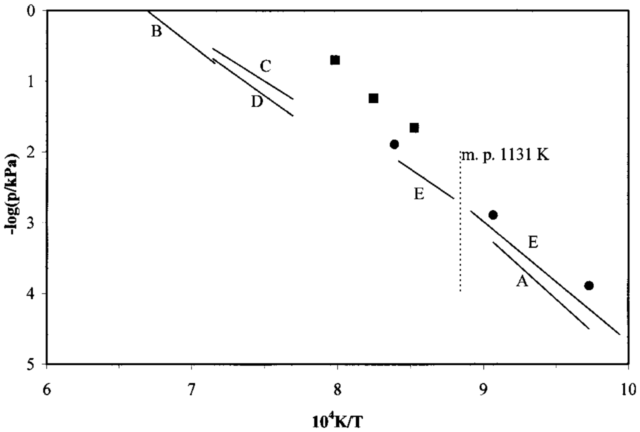

Figure 4. Comparison of vapor pressures of $LaCl_3$: (●) Harrison (1952); (■) Moriarty (1963); (A) Shimazaki and Niwa (1962); (B) Novikov and Baev (1962); (C) Dudchik et al. (1969); (D) Niesel'son et al. (1978); (E) this work.

Table 4. Temperature Dependence of the Total Vapor Pressure above LaX_3 (X = Cl, Br, I)

		no. of		$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
compound	run	points	ΔT/K	A	B
$LaCl_3$(s)	A,1	13	1015−1100	12.38 ± 0.26	17078 ± 272
	A,2	15	1006−1109	12.33 ± 0.20	17043 ± 213
	A,3	19	1020−1107	12.30 ± 0.23	17027 ± 244
	B,1	18	1049−1122	12.27 ± 0.19	16923 ± 207
$LaCl_3$(l)	B,1	13	1137−1188	9.65 ± 0.23	13989 ± 272
$LaBr_3$(s)	A,1	14	955−1041	11.74 ± 0.21	15421 ± 208
	B,1	12	986−1044	11.74 ± 0.28	15425 ± 280
	B,2	15	983−1045	11.64 ± 0.15	15339 ± 154
LaI_3(s)	A,1	12	952−1030	11.36 ± 0.11	14305 ± 108
	A,2	14	946−1022	10.90 ± 0.10	13910 ± 96
	A,3	18	932−1030	11.14 ± 0.08	14116 ± 81
	A,4	9	935−1038	10.95 ± 0.10	13968 ± 104
	B,1	7	970−1016	11.30 ± 0.12	14325 ± 117
	B,2	9	966−1032	10.96 ± 0.13	14030 ± 132
LaI_3(liq)	B,1	9	1055−1123	8.26 ± 0.07	11140 ± 74
	B,2	15	1061−1111	8.46 ± 0.24	11406 ± 263

ions above $DyBr_3$ (Hilpert et al., 1995) and show that all the observed ion species originated from $LaBr_3$(g) whereas $La_2Br_5^+$ was an ion fragment probably originating from La_2Br_6(g). We considered that the amount of the dimer over the vapor in the temperature range covered in our measurements was negligible. From the slope of the selected eq 2, the second-law enthalpies associated with the sublimation of lanthanum tribromide in the monomer form were $\Delta_{sub}H°(1000\ K) = (295 \pm 4)\ kJ{\cdot}mol^{-1}$ and $\Delta_{sub}H°(298\ K) = (315 \pm 4)\ kJ{\cdot}mol^{-1}$; the $H°(T) - H°(298\ K)$ values necessary to obtain the sublimation enthalpy value at 298 K were those selected by Pankratz (1984). At 950 and 1050 K, approximately the extreme temperatures of the covered temperature range, two third-law standard sublimation enthalpy values were calculated employing the $LaBr_3$(g) pressures from eq 3 and the necessary free energy functions from Pankratz (1984) (see Table 6). The enthalpy values are in agreement, but their average value $\Delta_{sub}H°(298\ K) = (302.1 \pm 0.5)\ kJ{\cdot}mol^{-1}$ is slightly lower than that obtained by the second-law procedure, $(315 \pm 4)\ kJ{\cdot}mol^{-1}$. Considering that at higher temperatures the partial pressures of the dimer form can be not negligible and using the same considerations used for $LaCl_3$, the average $\Delta_{sub}H°(298\ K) = 304\ kJ{\cdot}mol^{-1}$ with an estimated error of ±5 $kJ\ mol^{-1}$ was selected as the standard sublimation enthalpy of $LaBr_3$, giving more weight to the third-law $\Delta_{sub}H°(298\ K)$ value calculated at 950 K (see Table 6).

(C) Lanthanum Triiodide. The vaporization of LaI_3 was characterized by a first step in which the vapor pressures were very reproducible but, going on with the vaporization, the pressure was observed to decrease slowly.

At the end of the measurement, when the pressure was not detectable (below the instrument sensitivity), a dark residue was observed in the cell. Vaporizing a LaI_3 sample in a quartz tube under vacuum, it was condensed opportunely its vapor. The condensate so obtained was picked and introduced in the torsion assembly and studied. The vaporization behavior of this condensate was found to be practically equal to that observed for the original one, including also the production of the final residue at the end of the measurement. This showed that the residue (about 5% of the sample) was not an impurity included in the original sample but a product of a partial decomposition of LaI_3. The energy dispersion microanalysis (EDS) of the original sample and of the residue showed that the iodine amount on the surface of the residue was minor compared to that in the original sample. X-ray analysis of the residue showed that this was completely amorphous. The phase diagram of the system LaI_3−La, studied by differential thermal analysis (Corbett et al., 1961), showed the existence of stable LaI_2 (black, melting congruently at 1103 K) and a stoichiometric intermediate compound $LaI_{2.4}$ (with an incongruent melting point at 1023 K). On this basis, in addition to the principal sublimation reaction

$$LaI_3(s) \rightarrow LaI_3(g)$$

as mass-spectrometrically observed by Hirayama et al. (1976) (the dimer form La_2I_6(g) is negligible), we believe that at temperatures below 1023 K a small amount of lanthanum triiodide partially decomposes to give $LaI_{2.4}$. According to the phase diagram, at about 1023 K this compound melts (this explains the amorphous phase) and decomposes to I_2(g) and LaI_2, which probably is the final residue observed at the end of each experiment. Because free lanthanum was never directly observed on the residues by SEM analysis, the important decomposition of LaI_3 to lanthanum and iodine does not occur during the heating. The formation on the sample surface of a film of the intermediate compound explains the small pressure decrease observed during the vaporization. On this basis, for each run only the pressures measured in the first step of the vaporization above the "fresh" sample were considered representative of the vapor pressures above LaI_3 at unit activity and used in the calculation of the equations in Table 4. It is interesting to note that, as for $LaCl_3$, the slopes of the selected eqs 4 and 5 and their intersections give both an enthalpy of fusion ($\Delta_{fus}H° = 53 \pm 8\ kJ\ mol^{-1}$) and a melting point (about 1030 K) in agreement with those

Table 5. Comparison of the Temperature Dependence of the Total Vapor Pressures of LaX_3 (X = Cl, Br, I)

						$\log(p/\mathrm{kPa}) = A - B/T - C \log T$		
compound	ref	method	no. of points	T or T limit/K	$-\log(p/\mathrm{kPa})$	A	B	C
$LaCl_3$ (s)	Harrison (1952)	Knudsen	2	1028, 1103	3.89, 2.89			
$LaCl_3$ (liq)	Harrison (1952)	Knudsen	1	1192	1.89			
$LaCl_3$ (s)	Shimazaki (1962)	Knudsen	15	from 1022 to 1110		10.96	15796	
$LaCl_3$ (liq)	Moriarty (1963)	Knudsen	3	1173, 1213, 1253	1.66, 1.24, 0.70			
$LaCl_3$ (liq)	Novikov (1962)	dew point	11	from 1397 to 1493		10.66	15940	
$LaCl_3$ (s)	Hastie (1968)	mass spec	17	from 990 to 1098			16500[a]	
$LaCl_3$ (liq)	Dudchik (1969)	boiling point		?		30.1	16463	6
$LaCl_3$ (liq)	Nisel'son (1978)	boiling point		?		9.80	14671	
$LaCl_3$ (s)	this work	torsion	65	1006−1122		12.31 ± 0.10	17012 ± 100	
$LaCl_3$ (liq)	this work	torsion	13	1137−1188		9.65 ± 0.23	13989 ± 272	
$LaBr_3$ (s)	Harrison (1952)	Knudsen	3	915, 981, 1057	3.89, 2.89, 1.89			
$LaBr_3$ (s)	Shimazaki (1962)	Knudsen	6	from 1002 to 1052		11.70	15446	
$LaBr_3$ (s)	Makhmadmurodov (1989)	boiling point(?)[b]		?		25.78 ± 0.42	17206 ± 328	4
$LaBr_3$ (liq)	Makhmadmurodov (1989)	boiling point[b]		from 1305 to 1526		26.21 ± 0.24	14830 ± 150	5
$LaBr_3$ (s)	Gietmann (1997)	mass spec	44	from 873 to 1029		13.836 ± 0.057	16146 ± 58	
$LaBr_3$ (s)	this work	torsion		from 955 to 1045		11.71 ± 020	15392 ± 150	
LaI_3 (s)	Shimazaki (1962)	Knudsen	7	from 953 to 1012		11.97	15397	
LaI_3 (s)	Hirayama (1976)	mass spec	35	from 897 to 1008		13.00 ± 0.23	15784 ± 220	
LaI_3 (s)	this work	torsion	69	from 932 to 1038		11.10 ± 0.20	14098 ± 150	
LaI_3 (l)	this work	torsion	24	from 1055 to 1123		8.39 ± 0.15	11306 ± 200	

[a] Value obtained from the second-law sublimation enthalpy value, $\Delta_{sub}H°(T) = 310 \pm 8$ kJ mol^{-1}, calculated by the authors from the slope of the log $I^+(LaCl_2^+)T$ versus $1/T$ curve. [b] No pressure data are reported in the original work. The constants of the pressure−temperature equation are those reported in a table of Makhmadmurodov's paper.

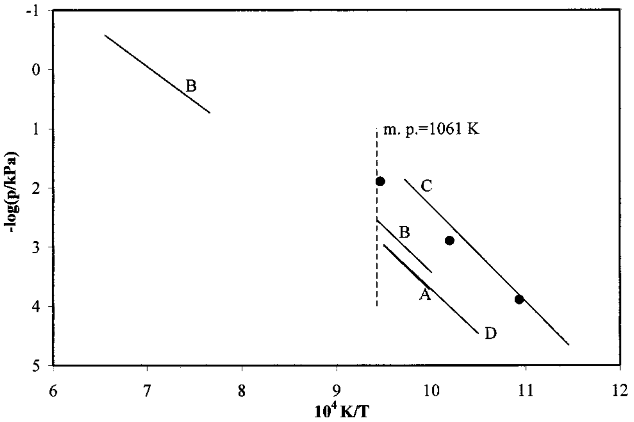

Figure 5. Comparison of vapor pressures of $LaBr_3$: (●) Harrison (1952); (A) Shimazaki and Niwa (1962); (B) Makhmadmurodov et al. (1989); (C) Gietmann (1997); (D) this work.

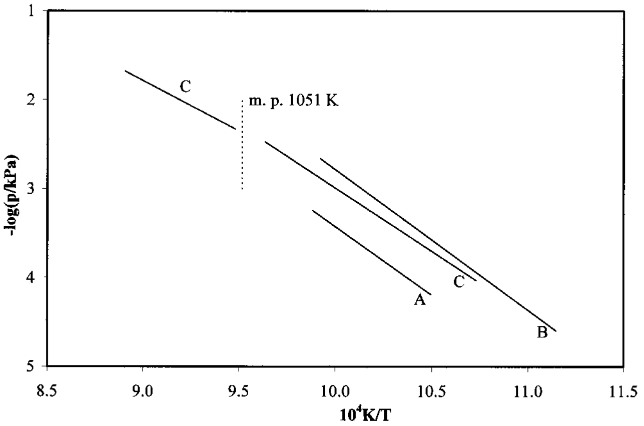

Figure 6. Comparison of vapor pressures of LaI_3. (A) Shimazaki and Niwa (1962); (B) Hirayama et al. (1976); (C) this work.

calorimetrically measured by Dworkin and Bredig (1971) (56 kJ mol^{-1} and 1051 K, respectively).

From the slope of the selected eq 4, the second-law sublimation enthalpies of LaI_3, $\Delta_{sub}H°(985\ \mathrm{K}) = (270 \pm 4)$ kJ mol^{-1} and $\Delta_{sub}H°(298\ \mathrm{K}) = (288 \pm 4)$ kJ mol^{-1}, were derived. Enthalpic increments measured by Dworkin and Bredig (1971) for solid LaI_3 and selected by Pankratz (1984) for the gaseous phase were used in reporting the value at 298 K. The standard sublimation enthalpy was calculated by the third-law at 950 and 1050 K using the LaI_3(g) pressures from eq 4 and the free energy functions from Pankratz (1984) (see Table 6). The presence in the vapor of a small amount of I_2(g) from the decomposition of LaI_3 in the intermediate compounds was not taken into account. The obtained results do not show a temperature dependence, and their average value, (282.5 ± 0.2) kJ mol^{-1}, agrees well with the second-law result. From these values, the average $\Delta_{sub}H°(298\ \mathrm{K}) = (285 \pm 3)$ kJ mol^{-1} was selected as standard sublimation enthalpy for LaI_3.

Table 6. Third-Law Standard Sublimation Enthalpies of LaX_3 (X = Cl, Br, I)

compound	T/K	$-R \ln(p/p°)$[a]/ J K^{-1} mol^{-1}	$-\Delta$fef[b]/ J K^{-1} mol^{-1}	$\Delta_{sub}H°(298\ \mathrm{K})$/ kJ mol^{-1}
$LaCl_3$	1000	128.5	205.7	334.2
	1100	98.6	203.5	332.6
$LaBr_3$	950	124.4	194.2	302.7
	1050	94.9	192.3	301.6
LaI_3	950	110.0	187.6	282.7
	1050	83.0	186.0	282.4

[a] $p°$=101325 Pa. [b] $\Delta\mathrm{fef} = \Delta(G°_T - H°_{298})/T$.

In conclusion, the standard sublimation enthalpies of $LaCl_3$, $LaBr_3$, and LaI_3 determined in the present work, $\Delta_{sub}H°(298\ \mathrm{K}) = 334 \pm 5$, 304 ± 5, and 285 ± 3 kJ mol^{-1}, respectively, are decidedly in agreement with those evaluated as the difference between the enthalpies of formation of solid and gaseous compounds selected by Pankratz (1984) (338, 303, and 279 kJ mol^{-1}, respectively) and present a trend going from trichloride to triiodide, which was not observed in the previous study on dysprosium halides (Brunetti et al., 1999).

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