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Sublimation Enthalpies of Neodymium Trichloride, Tribromide and Triiodide from Torsion Vapor Pressure Measurements

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The total vapor pressures of $NdCl_3$, $NdBr_3$, and NdI_3 were measured by the torsion effusion method. By a least-squares treatment of the experimental data, the following equations were selected as representative for the temperature dependence of their vapor pressures in the covered temperature ranges: $NdCl_3$(s), $\log(p/\mathrm{kPa}) = 12.20 \pm 0.30 - (16156 \pm 400)(K/T)$ (from 974 to 1031 K); $NdCl_3$(l), $\log(p/\mathrm{kPa}) = 10.18 \pm 0.20 - (14068 \pm 300)(K/T)$ (from 1063 to 1199 K); $NdBr_3$(s), $\log(p/\mathrm{kPa}) = 12.10 \pm 0.30 - (15132 \pm 300)(K/T)$ (from 866 to 954 K); $NdBr_3$(l), $\log(p/\mathrm{kPa}) = 10.09 \pm 0.20 - (13282 \pm 300)(K/T)$ (from 956 to 1019 K); NdI_3(s), $\log(p/\mathrm{kPa}) = 10.70 \pm 0.10 - (13513 \pm 200)(K/T)$ (from 906 to 1031 K). By treatment of the data by the second- and third-law methods, standard sublimation enthalpies were derived for $NdCl_3$, $NdBr_3$, and NdI_3 $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = (327 \pm 8, 298 \pm 8, 284 \pm 6)\ \mathrm{kJ{\cdot}mol^{-1}}$, respectively.

Introduction

Vapor pressure data for neodymium trihalides, $NdCl_3$, $NdBr_3$, and NdI_3, as well as for most rare of the rare-earth trihalides, are scarce. Except for some vapor pressure runs mass-spectrometrically performed by Gietmann et al.[1] above $NdBr_3$, apparently the vapor pressures of all neodymium trihalides in solid phase were measured only by the Knudsen method[2−11] and above the melting temperatures by the boiling point and dew point methods (see Table 1).

In the framework of an ongoing systematic study on the vaporization of rare-earth-metal halides,[12−15] we have carried out new measurements of the vapor pressures of these compounds by using the torsion−effusion method and derived the corresponding standard sublimation enthalpies.

Experimental Section

All neodymium trihalides samples were supplied by Aldrich with a purity of about 99.9%, as certified by the supplier. The torsion method and the apparatus used in this study for the pressure measurements was described in an our previous work.[16] On heating the sample, the equilibrium vapor effusing from the cell in the vacuum produces a torque (α) of the wire to which the cell is suspended so that its pressure (p) can be calculated through the simple relation $p = \alpha K'$. The torsion constant K' collects torsion constant and length of the wire as well as area, distances from the rotation axis, and geometrical factors of the effusion holes of the used torsion cell. During the torsion vapor pressure determinations, at some temperatures, the vapor pressures of the studied compound were also determined by the Knudsen method[17] by measuring the mass loss rates of the sample with a vacuum balance (Cahn 1000) to which was suspended the torsion assembly. For all compounds, the molecular weight of their vapor necessary to determine "Knudsen" pressure values was assumed to equal that of the monomeric species. The employed conventional torsion cells were: two cells machined from two different materials, stainless steel (cell A1) and graphite (cell A2), both with effusion holes of about 0.6 mm diameter, prevalently used for pressure measurements above molten samples, and two graphite cells, B and C, having larger effusion areas (1.5 and 2.4 mm in diameter, respectively) both used for measurements above solid compounds. No appreciable interaction of the material of the used torsion cell with the compounds was observed during their vaporization. A particular graphite cell (cell D) with two lodgings having effusion holes with different areas (0.5 and 1.8 mm in diameter) was also used in order to measure in a single experiment the vapor pressures above a solid and liquid compound. In fact, by filling both lodgings of this cell with a sample, the torsion of the assembly is due to the effusion of the vapor from both lodgings. In this experiment, when the sample in the lodging with the large effusion hole is completely vaporized, the torsion angles decrease because the torsion is due to the only effusion of the vapor from the second lodging with the smaller hole; the cell now behaves as a new cell. In this way the vapor pressure of a compound can be measured in two different temperature ranges and also above solid and liquid phases of the same experimental condition. A typical plot of the experimental torsion data obtained by using this cell during the vaporization of lead is reported in Figure 1. This element, having well-known vapor pressures[18] that are comparable with those of the studied compounds, was used in order to determine the torsion cell constants of this "double" cell (D) and of the other ones. During the lead vaporization, the Knudsen cell constants were also determined. The values of these constants were checked in some runs carried out between the vaporization runs of the compounds under investigation. The samples were loaded into the torsion cells in a drybox under an argon atmosphere and drops of naphthalene were placed over the effusion orifices to protect the samples from air during the transfer of the cell into the torsion apparatus. Under vacuum at room temperature naphthalene quickly evaporated and subsequently the samples were heated at about 600 K. Despite their certified purities for all compounds, a vaporization of about 1 to 2% of their original weights was observed in this first step of heating. When

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Table 1. Literature Temperature Dependence of the Total Vapor Pressure of NdX_3 (X = Cl, Br, I)

compound	ref	method	no. of points	T or T limit/K	-log(P/kPa)	$\log(p/\mathrm{kPa}) = A - BK/T - C\log(T/\mathrm{K})$		
						A	B	C
$NdCl_3$(s)	2	Knudsen	2	964 and 1032	3.88 and 2.88			
$NdCl_3$(l)	2	Knudsen	1	1107	1.88			
$NdCl_3$(s)	3	Knudsen	7	from 973 to 1032		11.134	15145	
$NdCl_3$(l)	4	Knudsen	5	1093, 1138, 1203, 1233, and 1278	2.45, 1.92, 1.66, 1.55 and 1.06	6.23[a]	9430[a]	
$NdCl_3$(s)	5	Knudsen	13	from 973 to 1073		12.61 ± 0.84[b]	16250 ± 860[b]	
$NdCl_3$(l)	6	dew point	16	from 1235 to 1465		9.10	12930	
$NdCl_3$(l)	7	bp		from 1373 to 1648		40.97	17691	9.061
$NdCl_3$(l)	8	bp		?		29.96	15769	6
$NdCl_3$(l)	9	bp		?		8.53	12420	
$NdBr_3$(s)	2	Knudsen	2	849 and 908	3.88 and 2.88			
$NdBr_3$(l)	2	Knudsen	1	975	1.88			
$NdBr_3$(s)	3	Knudsen	6	from 889 to 948		11.675	14829	
$NdBr_3$(l)	10	bp		from 1258 to 1559		26.05 ± 0.44	14074 ± 57	5
$NdBr_3$(s)	1	MS	65	from 817 to 951		12.493 ± 0.182	15011 ± 169	
NdI_3(s)	3	Knudsen	8	from 953 to 1002		11.595	14495	
NdI_3(s)	11	Knudsen	32	from 857 to 1037		12.63 ± 0.13	15037 ± 125	

[a] Calculated by us from the five experimental points reported by the author. [b] This equation is reported in the work and does not taken in account that the pressures were measured above both solid and liquid phases. bp = boiling point; MS = mass-spectrometric.

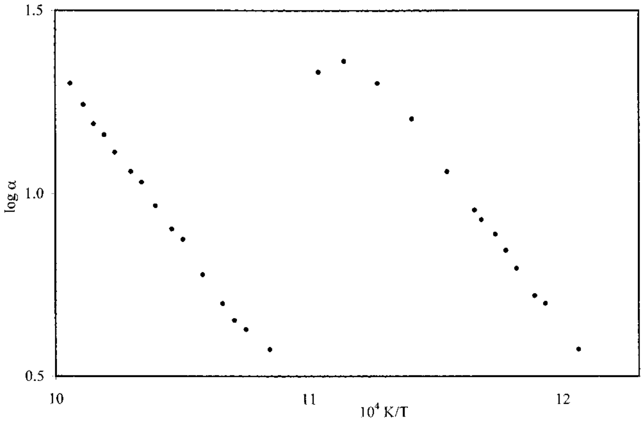

Figure 1. Typical plot of log α vs 1/T obtained by using cell D in a vaporization run of lead.

the weight of the sample was constant and the vapor pressures practically null, the torsion cell was heated at temperatures at which the pressures began to be detectable, starting the experimental measurements.

At the end of the experiments, the weight of the empty cells was found to be practically equal to the original one, showing that no significant interaction of the compounds with the cell occurred. Only when the pressure measurements were carried out above molten $NdCl_3$, despite the use of a quartz nest, a small absorption of the sample in the graphite cell (A2) occurred considering the small increase of the weight of the cell observed at the end of the experiments. However, we believe that this small absorption did not appreciably affect the measured $NdCl_3$ vapor pressures.

Results

The experimental vapor pressures for $NdCl_3$, $NdBr_3$, and NdI_3 are reported in Tables 2−4 and in Figures 2−4. To minimize systematic errors and as check of the equilibrium reached inside the cell, temperatures were increased and decreased at random. By treatment of the experimental data of each torsion experiment by linear least squares, the coefficients A and B of the equation $\log p = A - B/T$ were determined. The values obtained are reported in Table 5. By weighting for each compound these coefficients proportionally to the number of the experimental points,

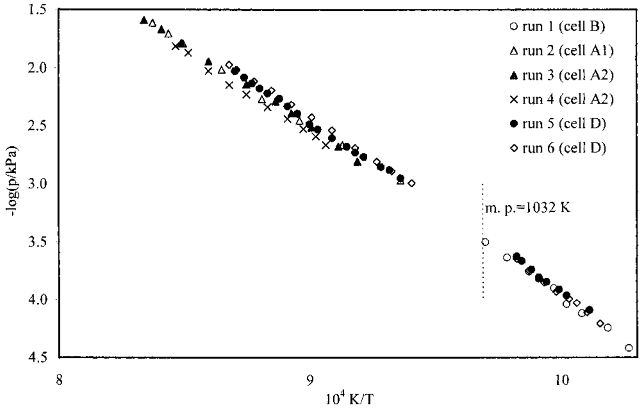

Figure 2. Torsion vapor pressures for $NdCl_3$.

the following equations representative of the temperature dependence of the vapor pressures of neodymium trihalides in the covered temperature ranges were selected:

$$NdCl_3(s) \quad \log(p/\mathrm{kPa}) = 12.20 \pm 0.30 - (16156 \pm 400)(K/T) \quad \text{(from 974 to 1031 K)} \quad (1)$$

$$NdCl_3(l) \quad \log(p/\mathrm{kPa}) = 10.18 \pm 0.20 - (14068 \pm 300)(K/T) \quad \text{(from 1063 to 1199 K)} \quad (2)$$

$$NdBr_3(s) \quad \log(p/\mathrm{kPa}) = 12.10 \pm 0.30 - (15132 \pm 300)(K/T) \quad \text{(from 866 to 954 K)} \quad (3)$$

$$NdBr_3(l) \quad \log(p/\mathrm{kPa}) = 10.09 \pm 0.20 - (13282 \pm 300)(K/T) \quad \text{(from 956 to 1019 K)} \quad (4)$$

$$NdI_3(s) \quad \log(p/\mathrm{kPa}) = 10.70 \pm 0.10 - (13513 \pm 200)(K/T) \quad \text{(from 906 to 1031 K)} \quad (5)$$

The associated errors were estimated. These equations were reported in Figures 5−7 for comparison with those found in the literature.[1−11]

Discussion

As reported in the Experimental Section, during the torsion measurements, the mass-loss rate of the studied sample was also determined. From these measurements and considering that in the covered experimental temperature ranges for all the studied compounds the monomer

Table 2. Torsion Total Vapor Pressure above Solid and Liquid $NdCl_3$

run 1 (cell B)		run 2 (cell A1)		run 3 (cell A2)		run 4 (cell A2)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
974	4.42	1068	2.97	1088	2.81	1103	2.67
982	4.24	1095	2.67	1097	2.68	1108	2.59
992	4.12	1116	2.45	1110	2.51	1114	2.53
998	4.04	1135	2.27	1120	2.39	1122	2.44
1003	3.90	1156	2.01	1128	2.29	1132	2.34
1009	3.82	1177	1.79	1143	2.14	1143	2.23
1013	3.76	1185	1.70	1163	1.94	1152	2.14
1022	3.63	1194	1.61	1178	1.79	1163	2.02
1031	3.50			1189	1.67	1174	1.87
				1199	1.59	1181	1.81

run 5 (cell D)				run 6 (cell D)			
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
989	4.09	1068	2.95	985	4.21	1063	2.99
998	3.97	1073	2.88	990	4.11	1072	2.89
1001	3.91	1077	2.85	994	4.03	1079	2.81
1006	3.85	1085	2.77	997	4.00	1089	2.69
1009	3.81	1089	2.73	1002	3.93	1100	2.54
1012	3.74	1093	2.68	1007	3.85	1110	2.42
1016	3.66	1100	2.60	1013	3.75	1120	2.31
1018	3.63	1107	2.53	1018	3.65	1130	2.19
		1111	2.49			1139	2.11
		1117	2.39			1148	2.01
		1122	2.33			1152	1.97
		1126	2.26				
		1132	2.22				
		1136	2.17				
		1140	2.13				
		1144	2.08				
		1149	2.03				

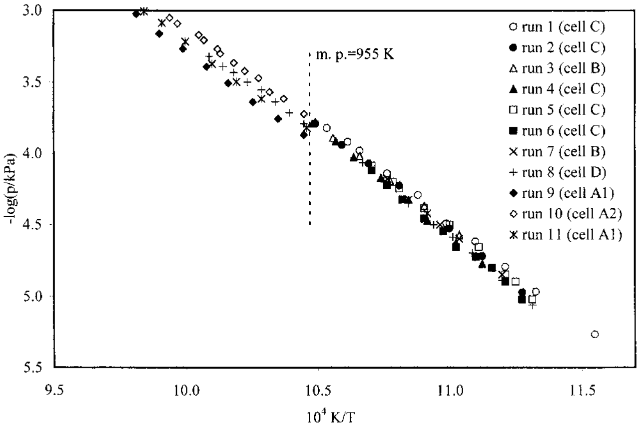

Figure 3. Torsion vapor pressures for $NdBr_3$.

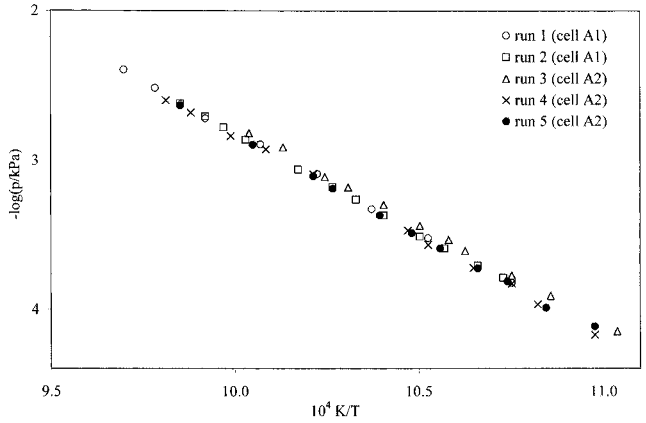

Figure 4. Torsion vapor pressures for NdI_3.

was the more abundant species present in the vapor, some "Knudsen" vapor pressures were also determined by the Knudsen method. The values so obtained were found to be decidedly in agreement with those obtained simultaneously by the torsion method, and this was taken as a check that the dimer forms in the vapor above all compounds are negligible, especially at the lowest experimental temperatures. This fact was confirmed in particular by the mass-spectrometric study for $NdBr_3$[1] in which the partial pressures of the dimer form were found to be about 1% of the total vapor pressures in the temperature range 817 to 915 K. On this basis the second-law enthalpies obtained from the slopes of the selected equations, eqs 1−5, were considered to be associated with the congruent vaporization processes:

$$NdX_3(s,l) \rightarrow NdX_3(g) \quad (X = Cl,\ Br,\ \text{and}\ I)$$

By treatment of the total vapor pressures as NdX_3(g) partial pressures, the third-law sublimation enthalpies of neodymium trihalides were also calculated and compared with the second-law results.

$NdCl_3$. The absolute total vapor pressures measured in the present work are in substantial agreement with the "Knudsen" data points found by Shimazaki and Niwa[3] and with those obtained at high temperatures[6,7] (see Figure 4). From the slopes and intercepts of the $p-T$ equations obtained in runs in which the vapor pressures were measured above both solid and liquid $NdCl_3$ (see Table 5) and of the selected ones, runs 1 and 2, approximate values of the melting point and enthalpy of fusion of this compound were calculated and reported in Table 6. In the same table, the literature data were also reported for comparison. Considering the large uncertainties associated with the procedure in our calculations, the results indicate that no large errors in the temperature measurements should be made. From eqs 1 and 2, the second-law sublimation enthalpy, $\Delta_{sub}H°$ (1003 K) = (309 ± 8) kJ·mol^{-1}, and

Table 3. Torsion Total Vapor Pressure above Solid and Liquid $NdBr_3$

run 1 (cell C)		run 2 (cell C)		run 3 (cell B)		run 4 (cell C)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
866	5.27	887	4.97	896	4.79	899	4.77
883	4.97	899	4.71	906	4.57	907	4.62
892	4.79	909	4.52	917	4.37	916	4.47
901	4.61	925	4.22	928	4.19	922	4.32
910	4.49	935	4.07	938	4.01	931	4.17
919	4.29	944	3.94	947	3.89	940	4.02
929	4.14	953	3.79	953	3.78	946	3.91
938	3.98					954	3.79
942	3.91						
949	3.82						

run 5 (cell C)		run 6 (cell C)		run 7 (cell B)		run 8 (cell D)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
884	5.02	887	5.02	893	4.84	884	5.06
889	4.90	892	4.90	900	4.72	893	4.88
892	4.84	896	4.80	906	4.60	902	4.69
900	4.65	901	4.72	912	4.50	908	4.58
909	4.50	907	4.65	916	4.42	914	4.50
917	4.38	911	4.54	922	4.32	922	4.35
925	4.24	917	4.46	929	4.18	930	4.20
927	4.20	924	4.32			937	4.06
934	4.08	929	4.22				
		934	4.12			957	3.79
						962	3.71
						967	3.64
						972	3.55
						977	3.50
						982	3.43
						986	3.39
						991	3.32

run 9 (cell A1)		run 10 (cell A2)		run 11 (cell A1)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
957	3.87	957	3.72	956	3.82
966	3.75	964	3.61	972	3.61
975	3.64	969	3.57	981	3.50
984	3.51	973	3.47	990	3.37
992	3.39	978	3.42	1000	3.22
1001	3.27	982	3.36	1009	3.09
1010	3.16	987	3.30	1016	3.01
1019	3.02	988	3.27		
		993	3.21		
		995	3.17		
		1003	3.09		
		1006	3.05		

Table 4. Torsion Total Vapor Pressure above Solid NdI_3

run 1 (cell A1)		run 2 (cell A1)		run 3 (cell A2)		run 4 (cell A2)		run 5 (cell A2)	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
930	3.82	932	3.79	906	4.15	911	4.17	911	4.11
950	3.52	938	3.71	921	3.91	924	3.97	922	3.99
964	3.33	946	3.59	930	3.77	930	3.83	931	3.81
978	3.09	952	3.51	941	3.61	939	3.72	938	3.73
993	2.89	961	3.37	945	3.54	950	3.57	947	3.59
1008	2.71	968	3.26	952	3.44	955	3.47	954	3.49
1022	2.51	974	3.18	961	3.30	979	3.09	962	3.37
1031	2.39	983	3.06	970	3.18	992	2.92	974	3.19
		997	2.86	976	3.11	1001	2.84	979	3.11
		1003	2.78	987	2.91	1012	2.68	995	2.89
		1008	2.70	996	2.82	1019	2.60	1015	2.63
		1015	2.62						

vaporization enthalpy, $\Delta_{vap}H°$ (1131 K) = (269 ± 6) kJ·mol^{-1}, were derived. These values were reported at 298 K by using the heat capacities for the condensed phase calorimetrically measured by Gaune-Escard et al.,[20] the enthalpy of fusion, $\Delta_{fus}H° = 48.1$ kJ·mol^{-1}, determined by Gaune-Escard et al.[21] and the enthalpic increments reported by Pankratz [19] for the gaseous phase. The values obtained were: $\Delta_{sub}H°(298\ \text{K}) = (332 \pm 8)$ and (348 ± 6) kJ·mol^{-1} from the sublimation and vaporization enthalpies, respectively. The standard sublimation enthalpy was also determined by third-law treatment of the vapor pressures above both solid and liquid phases by using the corresponding free energy functions, $[G°(T) - H°(298\ \text{K})]/T$, reported in Pankratz's tables.[19] The third-law enthalpies so obtained are reported in Table 7. The values calculated at the lowest temperatures for the vaporization of the solid

Table 5. Temperature Dependence of the Total Vapor Pressure of NdX_3 (X = Cl, Br, I)

compound	phase	run (cell)	no. of points	ΔT/K	$\lg(p/\text{kPa}) = A - B/(T/\text{K})$ A^a	 B^a
$NdCl_3$	solid	run 1 (B)	9	974−1031	12.13 ± 0.42	16105 ± 416
	liquid	run 2 (A1)	8	1068−1194	9.90 ± 0.21	13768 ± 234
	liquid	run 3 (A2)	10	1088−1199	10.23 ± 0.17	14149 ± 196
	liquid	run 4 (A2)	10	1103−1181	10.01 ± 0.22	13973 ± 246
	solid	run 5 (D)	8	989−1018	12.17 ± 0.62	16099 ± 620
	liquid	“	17	1068−1149	10.27 ± 0.18	14143 ± 199
	solid	run 6 (D)	8	985−1018	12.32 ± 0.48	16272 ± 480
	liquid	“	11	1063−1152	10.35 ± 0.10	14183 ± 115
$NdBr_3$	solid	run 1 (C)	10	866−949	11.53 ± 0.16	14554 ± 143
	solid	run 2 (C)	7	887−953	12.00 ± 0.31	15035 ± 290
	solid	run 3 (B)	7	896−953	11.84 ± 0.32	14877 ± 297
	solid	run 4 (C)	8	899−954	12.45 ± 0.22	15479 ± 206
	solid	run 5 (C)	9	884−934	12.18 ± 0.35	15183 ± 321
	solid	run 6 (C)	10	887−934	12.24 ± 0.38	15291 ± 347
	solid	run 7 (B)	7	893−929	12.24 ± 0.25	15262 ± 230
	solid	run 8 (D)	8	884−937	12.41 ± 0.21	15443 ± 194
	liquid	“	8	957−991	9.81 ± 0.31	13007 ± 303
	liquid	run 9 (A,1)	8	957−1019	10.04 ± 0.18	13324 ± 176
	liquid	run 10 (A,2)	12	957−1006	10.24 ± 0.25	13358 ± 243
	liquid	run 11 (A,1)	7	956−1016	10.20 ± 0.29	13418 ± 286
NdI_3	solid	run 1 (A1)	8	930−1031	10.79 ± 0.14	13595 ± 140
	solid	run 2 (A1)	12	932−1015	10.69 ± 0.08	13506 ± 74
	solid	run 3 (A2)	11	906−996	10.68 ± 0.13	13442 ± 124
	solid	run 4 (A2)	11	911−1019	10.77 ± 0.17	13604 ± 161
	solid	run 5 (A2)	11	911−1015	10.61 ± 0.14	13442 ± 138

[a] The quoted errors are standard deviations.

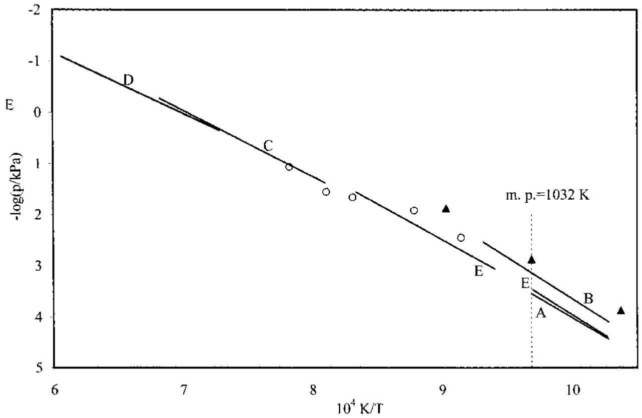

Figure 5. Comparison of vapor pressures for $NdCl_3$: (▲) Harrison;[3] (○) Moriarty;[4] (A) Shimazaki and Niwa;[3] (B) Evseeva and Zenkevich;[5] (C) Novikov and Baev;[6] (D) Polyachenok and Novikov;[7] (E) this work;

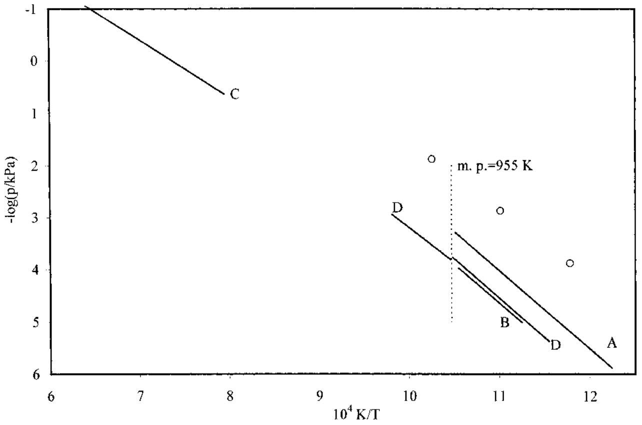

Figure 6. Comparison of vapor pressures for $NdBr_3$: ○, Harrison;[2] (A) Gietmann et al.;[1] (B) Shimazaki and Niwa;[3] (C) Dudchik et al.;[10] (D) this work.

phase present a negligible temperature trend with an average enthalpy value of 322 kJ·mol^{-1} and an estimated error limit of ±2 kJ·mol^{-1}. More evident is the temperature trend of the enthalpy values obtained from the vapor pressures measured above the liquid phase. It is interesting to note that also the two second-law $\Delta_{\text{sub}}H°(298\text{ K})$ values obtained from the vapor pressures measured above molten and solid phases are not in good agreement. Considering that the enthalpy of fusion derived from the slopes of the selected eqs 1 and 2 (~40 kJ·mol^{-1}) is lower by about 8 kJ·mol^{-1} than the calorimetric value measured by Gaune-Escard et al.,[21] we believe that the slopes of the $p-T$ equations determined above the molten $NdCl_3$ should be slightly higher (see comments in the conclusion section). On this basis, taking into account the second- and third-law results obtained from the only vapor pressures measured above $NdCl_3$ in solid phase, we propose as standard sublimation enthalpy for this compound the average value 327 kJ·mol^{-1} with an estimated error of 8 kJ·mol^{-1}. This value agrees with that of 323 kJ·mol^{-1}, obtained as difference between the standard enthalpies of formation for solid and gaseous $NdCl_3$ reported by Pankratz,[19] and the value of 318 ± 8 kJ·mol^{-1} mass spectrometrically determined by Ciach et al.[22] from a ($\log I^+T$) vs $1/T$ equation (I^+ is the ion current of $NdCl_2^+$) obtained in a small temperature range, 1055 to 1093 K. Considering that the absolute vapor pressures measured by Shimazaki and Niwa[3] and Evseeva and Zenkevich[5] above the solid phase (see Figure 4) are in substantial agreement with our pressure data, the third-law sublimation enthalpies determined with these pressures are bound to be in substantial agreement with our result.

$NdBr_3$. The vapor pressures of this compound were measured above both molten and solid phases. The absolute total pressure values obtained above solid-phase agree with the few Knudsen points measured by Shimazaki and Niwa,[3] but are slightly lower than those obtained by mass-spectrometry reported by Gietmann et al.[1] The slope of our selected eq 3 agrees with that selected by Gietmann et al.[1] The enthalpy of fusion and the melting point determined

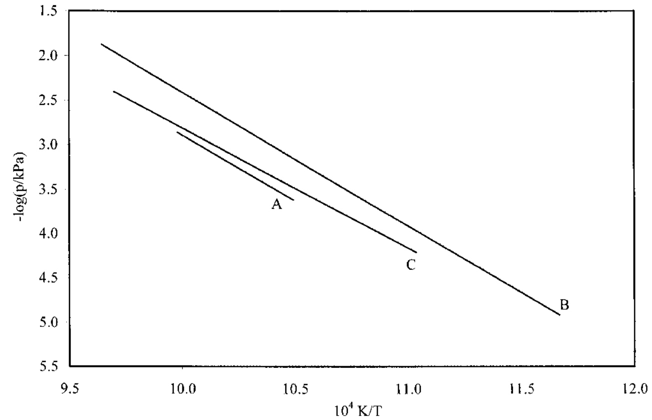

Figure 7. Comparison of vapor pressures for NdI_3: (A) Shimazaki et al.;[3] (B) Hirayama et al.;[11] (C) this work.

Table 6. Enthalpies and Temperatures of Fusion for $NdCl_3$ and $NdBr_3$

compound	source	$\Delta_{fus}H$/kJ·mol^{-1}	T_{fus}/K
$NdCl_3$	run 5	37	1030
$NdCl_3$	run 6	40	1058
$NdCl_3$	eqs 1 and 2	40	1031
$NdCl_3$	Gaune-Escard et al.[21]	48.1	1032
$NdBr_3$	run 8	47	937
$NdBr_3$	eqs 3 and 4	35	918
$NdBr_3$	Dworkin and Bredig[23]	45.3	955

Table 7. Third-Law Standard Sublimation Enthalpies for NdX_3 (X = Cl, Br; I)

compound	phase	T/K	-log(p/kPa)	($-\Delta$[G°(T) − H°(298 K)]/T)/ J·K^{-1}·mol^{-1}	ΔH°(298)/ kJ·mol^{-1}
$NdCl_3$	solid	900	5.75[a]	209.9	322.5
$NdCl_3$	solid	1000	3.95[a]	207.7	321.7
$NdCl_3$	solid	1032	3.45[a]	207.0	321.4
$NdCl_3$	liquid	1032	3.45[b]	206.9	321.4
$NdCl_3$	liquid	1100	2.61[b]	202.6	320.1
$NdCl_3$	liquid	1200	1.54[b]	196.4	317.2
$NdBr_3$	solid	850	5.70[c]	198.5	294.1
$NdBr_3$	solid	900	4.71[c]	197.6	293.5
$NdBr_3$	solid	955	3.74[c]	196.5	292.7
$NdBr_3$	liquid	955	3.82[d]	196.5	294.1
$NdBr_3$	liquid	1000	3.19[d]	193.5	293.0
$NdBr_3$	liquid	1050	2.56[d]	190.4	291.7
NdI_3	solid	800	6.19[e]	191.9	279.0
NdI_3	solid	900	4.31[e]	188.6	278.5
NdI_3	solid	1000	2.81[e]	185.3	277.5

[a−e] Calculated from the selected eqs 1−5, respectively.

from the $p-T$ equations for solid and molten compound obtained in the single experiment (run 8) and from the selected ones, eqs 3 and 4, are reported in Table 6. Even if our results are affected by heavy uncertainties, the comparison with the literature data[23] (see Table 6) shows that the results obtained in the single experiment agree with those selected in the literature better than those derived from the selected equations, these last obtained from runs carried out with different torsion cells. The second-law treatment of the vapor pressures give the following vaporization and sublimation enthalpies, $\Delta_{vap}H$° (987 K) = 254 kJ·mol^{-1} and $\Delta_{sub}H$° (910 K) = 290 kJ·mol^{-1}, respectively, both with an estimated error of ±6 kJ·mol^{-1}. These values, reported at 298 K by using the enthalpic increments selected by Pankratz[19] and calculated by the calorimetric enthalpy of fusion of 45.3 kJ·mol^{-1} [23], give two standard sublimation enthalpy values, $\Delta_{sub}H$°(298 K) = 319 and 305 kJ·mol^{-1}, respectively. Considering, as observed for $NdCl_3$, that the enthalpy of fusion (~35 kJ·mol^{-1}) calculated by our pressure data is about 10 kJ·mol^{-1} lower than the calorimetric value, we believe that the slope of the $p-T$ equation determined above the molten compound could be an upper limit. On this basis, by giving more weight to the results obtained from the vapor pressures on the solid phase, we propose as second-law $\Delta_{vap}H$°(298 K) the value of 307 kJ·mol^{-1} with an estimated error of 8 kJ·mol^{-1}. The third-law treatment of the vapor pressures calculated by the selected eqs 3 and 4 in the temperature range 850 to 1050 K gives the standard sublimation enthalpy values reported in Table 7. The employed free energy function are those selected by Pankratz.[19] These values present small trends both in the temperature range above the solid phase and in the range above the liquid phase. The average third-law value of $\Delta_{vap}H$°(298 K) = 293 kJ·mol^{-1}, with an overestimated error of 4 kJ·mol^{-1} (considering the only uncertainties on the temperature and torsion angle measurements), was selected. This value is lower than that obtained by the second-law method but agrees well with that proposed by Gietmann et al.[1] (291.6 ± 7.2 kJ·mol^{-1}) and with that obtained as difference between the enthalpies of formation of solid and gaseous compound reported by Pankratz[19] (295 kJ·mol^{-1}). On this basis, giving a slightly higher weight to the third-law result, we propose as standard sublimation enthalpy of $NdBr_3$ the value of 298 kJ·mol^{-1} with an error of 8 kJ·mol^{-1}.

NdI_3. The vapor pressures of this compound were determined above β solid phase (α−β transition point at 847 K). From the selected eq 5, the second-law enthalpies associated to the sublimation of this compound in the monomer form, $\Delta_{sub}H$° (968 K) = (259 ± 4) kJ·mol^{-1} and $\Delta_{sub}H$°(298 K) = (291 ± 4) kJ·mol^{-1}, were derived. As usual the enthalpic increments necessary to reducing to 298 K were those selected by Pankratz.[19] From the same source were taken the free energy function used in the third-law treatment of the vapor pressures. The standard sublimation enthalpy values so determined and reported in Table 6 present a negligible temperature trend. Their average value, $\Delta_{sub}H$°(298 K) = 278 kJ·mol^{-1}, with an estimated error of 4 kJ·mol^{-1}, is lower than that determined by the second-law. The agreement of the constants of five $p-T$ equations (see Table 5) and the very small trend of the third-law results lead us to conclude that both results should be reliable, and therefore we propose as $\Delta_{sub}H$°(298 K) for NdI_3 an average value of 284 kJ·mol^{-1} with an error of 6 kJ·mol^{-1}. This value is higher than that obtained from the enthalpies of formation for solid and gaseous NdI_3 (273 kJ·mol^{-1})[19] but decidedly lower than that found from Knudsen vapor pressures by Hirayama and Camp[11] (325 ± 3 kJ·mol^{-1}).

Conclusion

The total vapor pressures of $NdCl_3$, $NdBr_3$, and NdI_3 were measured by the torsion−effusion method. From the second- and third-law treatment of the pressure data the vaporization and sublimation enthalpies of these compounds were determined. A critical analysis of the obtained results leads to the following two considerations: (i) the final second-law standard sublimation enthalpies derived by using the vapor pressures measured above molten $NdCl_3$ and $NdBr_3$ are higher than those obtained above the solid compounds; (ii) the enthalpies obtained by the second-law method for all compounds in solid phase are higher than those derived by the third-law treatment of the experimental data, the differences being 10 to 15 kJ·mol^{-1}.

As concerns the first consideration, the low values for the enthalpies of fusion derived from the slopes of our selected $p-T$ equations compared to the calorimetric values could be due either to a too low slope of the equations evaluated for the solid phase or to a too high value of the slope of the equations for the molten compounds, or both of course. The better agreement of the second- and third-law results obtained above the solid $NdCl_3$ and $NdBr_3$ than those obtained above the molten compounds leads one to hypothesize that the more probable cause of the low value of the enthalpy of fusion is due to too high values for the slopes of the $p-T$ equations determined above the liquid phases. This can be due to a small temperature dependence errors at their highest values or/and the presence in the vapor of small amount of dimer form at these temperatures. On this basis, we considered more reliable the results obtained by the vapor pressures measured above both compounds in solid phase. As concerns the second consideration, even if the differences between the second- and third-law results obtained above the solid compounds are comparable with the sum of their estimated errors, a critical analysis of the uncertainties associated with the second-law standard sublimation enthalpy shows that those are minor taking into account (i) that the large number of the experimental points obtained by using different cells, (ii) that the second-law lead vaporization enthalpy values (standard used in the instrument calibration) obtained from the slopes of some log α vs $1/T$ equations (α are the experimental torsion angles) determined in temperature ranges comparable with those covered in neodymium trihalides sublimations agree within about 3% with that selected,[18] and (iii) that the measured pressures are reproducible (see Figures 2−4) when these were measured in a same run on increasing and decreasing the temperature (not activity change for interaction of the sample occurs during its vaporization). On this basis, we believe that the overall estimated error of 8 $kJ\cdot mol^{-1}$ is decidedly the maximum uncertainty for the second-law enthalpy. The analysis of the errors associated with the third-law results shows that while the uncertainties connected to the absolute vapor pressure values necessary in the calculation of the change of the standard Gibbs free energy are minor (because of those were evaluated as logarithm), those connected to the used free energy functions could be decidedly more important considering the presence of temperature trends in the $\Delta_{sub}H°(298\ K)$ values. On this basis, probably the errors of 4 $kJ\cdot mol^{-1}$ associated with the third-law sublimation enthalpies for $NdBr_3$ and NdI_3 and of 2 $kJ\cdot mol^{-1}$ for $NdCl_3$ could be underestimated. In any case, the selected final standard enthalpies proposed in the present work were obtained giving more weight to the second- or third-law result according to the studied compound.

The final selected sublimation enthalpy values found in the present work present, just like as observed for lanthanum, cerium, and praseodymium trihalides in our previous works,[13−15] a trend going from trichloride to triiodides in contrast with the values found for dysprosium[12] and holmium trihalides[24] which were comparable (288 ± 5, 289 ± 6, and 282 ± 4 $kJ\cdot mol^{-1}$ for $DyCl_3$, $DyBr_3$, and DyI_3 and 297 ± 10, 290 ± 5, and 296 ± 8 $kJ\cdot mol^{-1}$ for $HoCl_3$, $HoBr_3$, and HoI_3, respectively).

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