Vapor Pressure and Enthalpies of Vaporization of Cerium Trichloride, Tribromide, and Triiodide

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The total vapor pressures of cerium trihalides $CeCl_3$, $CeBr_3$, and CeI_3 were measured by the torsion method, and their temperature dependence can be expressed by the following equations over the given temperature ranges: $CeCl_3(s)$, $\log(p/kPa) = (12.21 \pm 0.20) - (16443 \pm 150)K/T$, (955−1070) K; $CeBr_3(s)$, $\log(p/kPa) = (12.12 \pm 0.20) - (15332 \pm 150)K/T$, (887−1003) K; $CeBr_3(l)$, $\log(p/kPa) = (9.57 \pm 0.30) - (12745 \pm 300)K/T$, (1009−1172) K; $CeI_3(s)$, $\log(p/kPa)=(12.02 \pm 0.20) - (14843 \pm 150)K/T$, (910−1031) K. Treating the obtained results by second- and third-law methods, the standard sublimation enthalpies, $\Delta_{sub}H°$ (298 K) = {(331 ± 5), (300 ± 10), and (295 ± 10)} kJ mol^{-1} for $CeCl_3(s)$, $CeBr_3(s)$, and $CeI_3(s)$, respectively, were determined.

Introduction

There have been few studies on the vaporization of cerium trihalides. In particular the vapor pressures for $CeCl_3$ were measured using the Knudsen method by Harrison (1952), by Moriarty (1963), and by Shimazaki and Niwa (1962). Those reported by Novikov and Baev (1962) were obtained by the "dew point" method and those reported by Dudchik et al. (1969) by the "boiling point" method over the molten compound. As concerns $CeBr_3$, the only vapor pressures measured on this compound are three Knudsen values reported by Harrison (1952) and some values measured by Shimazaki and Niwa (1962) using the same method. A pressure−temperature equation obtained by the boiling point method above the molten compound was reported by Dudchik et al. (1975). Recently Gietmann et al. (1997) by using mass spectrometry to study the vapor above $CeBr_3$ found monomer and dimer species and reported their vapor pressures. Also there are few vapor pressure measurements for CeI_3. Apparently the only values are those measured by the Knudsen method by Hirayama et al. (1975), who considered the monomer as the only gaseous species in the vapor as previously observed by mass spectrometry by Hirayama and Castle (1973). As part of our ongoing program on the vaporization of lanthanide trichlorides (Brunetti et al., 1999), we have studied the vaporization of cerium trichlorides, measuring their total vapor pressures by the torsion method from which the corresponding sublimation enthalpies were derived.

Experimental Details and Results

All cerium trihalides used in this work were supplied by Aldrich, and their purity was about 99.8%, as certified by the supplier. The vapor pressures of these compounds were measured by the torsion apparatus described in a previous work (Piacente et al., 1994) using three conventional torsion cells machined from very low porosity graphite. The areas of the effusion holes of these cells were different, their diameters equal to 0.6, 1.0, and 1.8 mm for cells A, B, and C, respectively. The sample was introduced into the cell in a small alumina liner. Since all the compounds are very hygroscopic, the loading of the cell was done in a drybox and it was quickly introduced into the torsion assembly. As usual, the values of the instrument constant of the cells necessary for the conversion of the experimental torsion angles in pressure data were obtained by vaporizing a pure standard, lead in this work, having a well-known vapor pressure (Hultgreen et al., 1973). Each constant was checked during the study by vaporizing lead in runs carried out between the vaporization runs of the compounds. It was found that, for each cell, the spread of its constant is about ±5% of the value selected for the pressure calculation. The torsion assembly was suspended from a vacuum balance (Chan 1000) so that, at some temperatures, simultaneously to the torsion pressure, also the molecular weight of the vapor was determined from the mass loss rate of the sample by the Knudsen equation (Knudsen, 1909). In Tables 1−3 and Figures 1−3 are reported the total vapor pressures measured above $CeCl_3$, $CeBr_3$, and CeI_3, respectively. For $CeBr_3$ the data are referred to the solid and liquid phases, while for $CeCl_3$ and CeI_3 the data are referred only to the solid phase. Even though the vapor pressure values, especially for $CeBr_3$ and CeI_3, present a small scattering (see Figures 2 and 3), we are persuaded that this is not due to the different areas of the effusion holes of the cells. In Table 4 are reported the log p vs $1/T$ equations obtained by treating the results of each run by a linear least-squares fit. Weighting the slopes and intercepts of these equations proportionally to the experimental points, the following final pressure−temperature equations were selected as representative of the vapor pressure of the studied compounds in the reported temperature ranges:

$$CeCl_3(s) \quad \log(p/kPa) = (12.21 \pm 0.20) - (16443 \pm 150)K/T \quad \text{from 955 to 1070 K} \quad (1)$$

$$CeBr_3(s) \quad \log(p/kPa) = (12.12 \pm 0.20) - (15332 \pm 150)K/T \quad \text{from 887 to 1003 K} \quad (2)$$

$$CeBr_3(l) \quad \log(p/kPa) = (9.57 \pm 0.30) - (12745 \pm 300)K/T \quad \text{from 1009 to 1172 K} \quad (3)$$

$$CeI_3(s) \quad \log(p/kPa) = (12.02 \pm 0.20) - (14843 \pm 150)K/T \quad \text{from 910 to 1031 K} \quad (4)$$

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Table 1. Torsion Total Vapor Pressure above Solid $CeCl_3$

Cell A

run A,1		run A,2		run A,3		run A,4	
T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)
1020	3.84	977	4.59	983	4.49	977	4.59
1025	3.77	985	4.47	989	4.41	984	4.47
1030	3.69	991	4.37	994	4.34	994	4.33
1037	3.59	996	4.29	1002	4.19	1003	4.17
1040	3.52	1001	4.22	1009	4.11	1014	3.99
1046	3.46	1006	4.11	1016	3.98	1024	3.84
1051	3.37	1011	4.03	1022	3.91	1030	3.75
1055	3.30	1017	3.95	1029	3.79	1040	3.59
1060	3.24	1023	3.84	1035	3.68	1052	3.39
		1027	3.79	1041	3.58	1055	3.34
		1032	3.71	1052	3.40	1059	3.28
		1038	3.62	1058	3.31	1063	3.22
		1042	3.56	1064	3.22	1070	3.13
		1048	3.46	1069	3.15		
		1057	3.31				

Cell B

run B,1		run B,2		run B,1	
T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)
983	4.52	1009	4.11	977	4.67
989	4.47	1011	4.07	982	4.59
994	4.33	1016	4.03	987	4.47
1002	4.22	1024	3.89	992	4.37
1008	4.14	1033	3.77	999	4.29
1015	4.03	1037	3.69	1004	4.22
1021	3.92	1042	3.61	1011	4.07
1026	3.84	1049	3.50	1018	3.99
1032	3.75	1055	3.41	1025	3.89
1040	3.64			1028	3.84
1048	3.50			1037	3.71
1058	3.34			1048	3.56
				1056	3.37

Cell C

run C,1		run C,2		run C,3	
T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)
959	4.89	955	5.01	967	4.79
967	4.79	960	4.89	980	4.59
975	4.64	971	4.71	995	4.31
984	4.49	981	4.53	1007	4.11
993	4.34	988	4.41	1015	4.01
1001	4.19	996	4.29	1024	3.87
1010	4.06	1004	4.15	1033	3.71
1019	3.92	1017	3.96	1042	3.58
1027	3.79	1023	3.85		
1037	3.64	1031	3.73		
1042	3.56	1041	3.56		
1051	3.41	1050	3.43		

The overall associated errors were estimated. As concerns $CeBr_3$, the slight inconsistencies among the four pressure−temperature equations obtained above this molten compound could be due to systematic errors in the data and/or to the expected failure of the least-squares treatment when applied to a too small number of points and over a small temperature range. From the pressure−temperature equations obtained above the solid and liquid phases of this compound, a rough enthalpy of fusion ($\Delta_{fus}H°$ = 50 kJ mol^{-1}) and a melting point (T_{fus} = 1014 K) close to those selected in the literature ($\Delta_{fus}H°$ =52 kJ mol^{-1}, T_{fus}=1005 K) were calculated. Even though the uncertainties associated with our results are large, this agreement is very important because it shows that large errors in the temperature measurements were not made.

When a not “fresh” $CeBr_3$ sample was used (sample kept for several days in a drybox and used in the vaporization run B,2), it was found that this sample was partially decomposed. In fact in the first step of the experiment, when the assembly was evacuated at room temperature,

Table 2. Torsion Total Vapor Pressure above Solid and Liquid $CeBr_3$

Cell A

run A,1		run A,2	
T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)
934	4.27	986	3.64
949	4.07	995	3.49
960	3.82	955	4.15
971	3.67	962	4.00
979	3.55	968	3.95
989	3.39	975	3.85
996	3.24	983	3.70
1003	3.15	960	4.07
1020	2.94	969	3.95
1030	2.81	974	3.85
1039	2.69	987	3.61
1069	2.38	1015	3.11
1086	2.20	1021	3.02
1100	2.05	1030	2.92
1114	1.94	1037	2.83
1131	1.75	1049	2.67
1139	1.68	1059	2.54
1148	1.60	1068	2.43
1155	1.53	1078	2.32
1165	1.41	1088	2.23
1172	1.35		

Cell B

run B,1		run B,2	
T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)
920	4.37	923	4.37
920	4.37	933	4.19
937	4.07	945	3.97
948	3.86	956	3.82
957	3.77	966	3.67
963	3.63	972	3.52
976	3.41	979	3.43
989	3.21	986	3.31
1001	3.03	994	3.19
		1001	3.09
		1009	2.90
		1019	2.77
		1028	2.65
		1031	2.60
		1036	2.54
		1038	2.51
		1046	2.44
		1046	2.44
		1053	2.37
		1056	2.34

Cell C

run C,1		run C,2		run C,3	
T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)	T/K	$-\log$ (p/kPa)
898	4.86	887	5.26	888	5.26
905	4.78	902	4.86	900	4.96
911	4.66	906	4.78	909	4.78
919	4.52	914	4.71	919	4.60
925	4.38	926	4.41	930	4.41
933	4.24	933	4.30	939	4.26
942	4.07	941	4.18	949	4.11
951	3.94	949	4.05	955	4.00
959	3.82	956	3.94	965	3.84
		965	3.80	975	3.69
		976	3.63	935	4.36
		983	3.52	946	4.11
		987	3.44	961	3.90
				1012	3.13
				1024	2.99
				1031	2.94
				1050	2.69
				1061	2.55
				1069	2.49

Table 3. Torsion Total Vapor Pressure above Solid CeI_3

Cell A

run A,1		run A,2	
T/K	−log (p/kPa)	T/K	−log (p/kPa)
984	3.17	976	3.17
985	3.17	993	2.92
993	3.07	1003	2.77
999	2.99	1008	2.69
1002	2.92	1015	2.59
1006	2.87	1019	2.54
1008	2.81	1027	2.43
1016	2.71	1031	2.35
1018	2.69		
1024	2.59		
1030	2.51		
1030	2.51		

Cell B

run B,1		run B,2		run B,3	
T/K	−log (p/kPa)	T/K	−log (p/kPa)	T/K	−log (p/kPa)
932	4.06	936	3.76	938	3.76
935	4.00	946	3.62	945	3.66
942	3.88	954	3.45	949	3.58
945	3.81	959	3.38	954	3.48
951	3.76	964	3.30	955	3.45
956	3.66	969	3.23	968	3.26
960	3.58	973	3.15	969	3.24
965	3.51	978	3.09	978	3.11
968	3.45			984	3.02
975	3.36				

Cell C

run C,1		run C,2		run C,3		run C,4	
T/K	−log (p/kPa)	T/K	−log (p/kPa)	T/K	−log (p/kPa)	T/K	−log (p/kPa)
925	3.96	925	3.96	922	3.96	910	4.36
930	3.88	932	3.85	935	3.76	923	4.11
935	3.76	946	3.62	947	3.54	930	3.96
942	3.66	951	3.54	954	3.43	937	3.88
944	3.62	956	3.45	960	3.34	942	3.76
947	3.58	961	3.36	966	3.24	948	3.66
954	3.48	969	3.23	969	3.18	960	3.51
957	3.40	976	3.11	972	3.14	964	3.43
963	3.34			976	3.08		

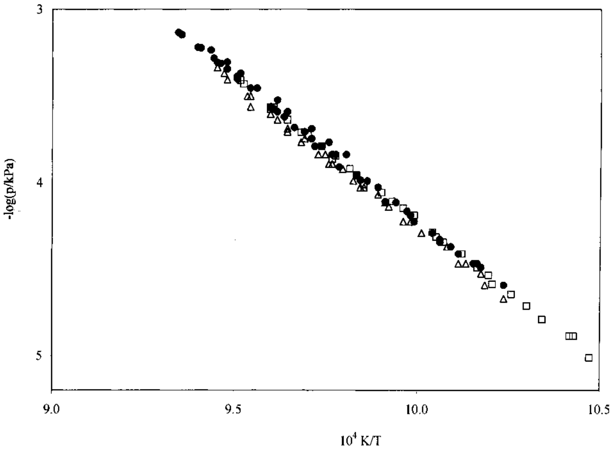

Figure 1. Torsion vapor pressure of $CeCl_3$: ●, cell A; △, cell B; □, cell C.

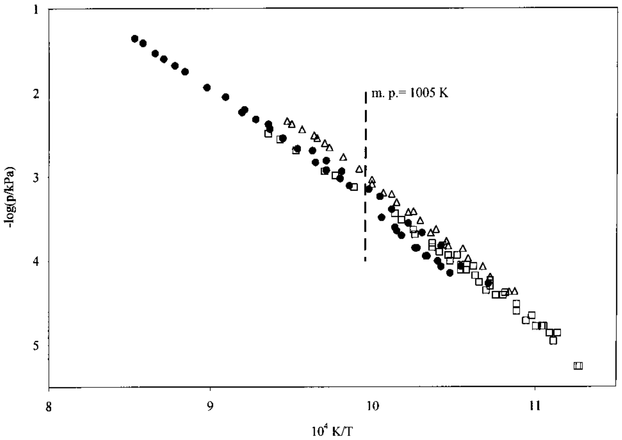

Figure 2. Torsion vapor pressure of $CeBr_3$: ●, cell A; △, cell B; □, cell C.

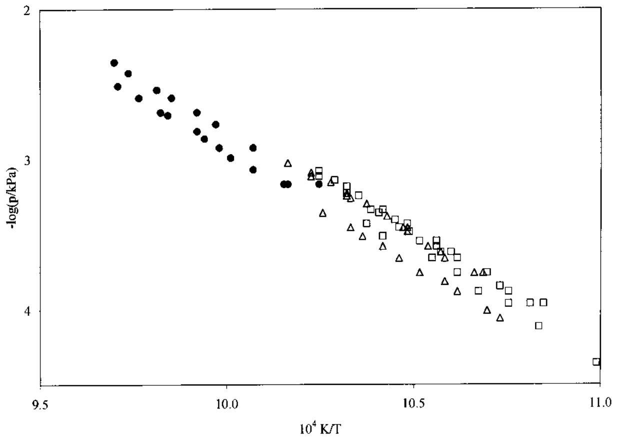

Figure 3. Torsion vapor pressure of CeI_3: ●, cell A; △, cell B; □, cell C.

the speedy sublimation of a small amount of the sample was observed. A draft value of the vapor molecular weight and the decidedly high pressures show that the vaporized substance was bromine. Moreover, at about 1080 K, a small sudden drop in the vapor pressure was also observed. This drop was justified as due to the melting (T_m = 1077 K) of the small amount of free cerium derived from the previous decomposition and its consequent mixing with the previously molten $CeBr_3$ (T_m = 1005 K). The mixing produced a small reduction in the activity of cerium tribromide in the $CeBr_3$(l)−Ce(l) mixture with a decrease of its vapor pressure. The vaporization at the start of the experiments and this drop were not observed in the other experiments, and this can be taken as proof that the employed samples had not decomposed. The torsion data measured in the run B,2 at temperatures higher than 1080 K were not taken into account. In any case at temperatures lower than 1077 K, the eventual presence of small amounts of solid cerium due to a possible small decomposition of $CeBr_3$ or, in general, of the studied cerium trihalides, does not influence the vapor pressure measurements because in the covered temperature ranges the cerium vapor pressures are decidedly negligible. Only for CeI_3 the presence of free cerium can produce cerium diiodide (Corbett et al., 1961), a stable compound that melts at 1081 K, but we are persuaded that also for CeI_3 the eventual formation of a very small amount of CeI_2 does not produce appreciable changes in the vapor pressure of the triiodide.

In Table 5 and Figures 4−6 we report our selected vapor pressure equations and those found in the literature for $CeCl_3$, $CeBr_3$, and CeI_3, respectively. In general our vapor pressure data are in satisfactory agreement with those from the literature.

Discussion

The molecular weight of the vapor above the trihalides, evaluated by us at some temperatures by the Knudsen

Table 4. Temperature Dependence of the Total Vapor Pressures of CeX_3 (X = Cl, Br, and I)

				log (p/kPa) = $A - B$ K/T	
compound	run	no. of points	ΔT/K	A^a	B^a
$CeCl_3$(s)	A,1	9	1020−1060	12.23 ± 0.21	16390 ± 217
	A,2	15	977−1057	12.29 ± 0.13	16508 ± 128
	A,3	14	983−1069	12.44 ± 0.20	16679 ± 201
	A,4	13	977−1070	12.33 ± 0.11	16540 ± 111
	B,1	12	983−1058	12.23 ± 0.21	16484 ± 214
	B,2	9	1009−1055	12.06 ± 0.32	16328 ± 327
	B,3	13	977−1056	11.97 ± 0.29	16241 ± 290
	C,1	12	959−1051	12.10 ± 0.13	16319 ± 132
	C,2	12	955−1050	12.25 ± 0.09	16470 ± 95
	C,3	8	967−1042	12.11 ± 0.18	16351 ± 183
$CeBr_3$(s)	A,1	8	934−1003	12.25 ± 0.38	15453 ± 368
	A,2	11	955−995	12.18 ± 0.48	15604 ± 469
	B,1	9	920−1001	12.15 ± 0.20	15196 ± 194
	B,2	10	923−1001	12.10 ± 0.20	15203 ± 197
	C,1	9	898−959	12.17 ± 0.32	15322 ± 295
	C,2	13	887−987	12.05 ± 0.30	15282 ± 281
	C,3	13	888−975	12.00 ± 0.26	15276 ± 240
$CeBr_3$(l)	A,1	13	1020−1172	9.10 ± 0.08	12267 ± 85
	A,2	9	1015−1088	10.23 ± 0.18	13532 ± 190
	B,2	10	1009−1056	9.83 ± 0.35	12832 ± 358
	C,3	6	1012−1069	9.17 ± 0.35	12455 ± 365
CeI_3(l)	A,1	12	984−1030	11.91 ± 0.27	14861 ± 273
	A,2	8	976−1031	12.00 ± 0.15	14806 ± 155
	B,1	10	932−975	11.83 ± 0.26	14803 ± 245
	B,2	8	936−978	12.09 ± 0.29	14833 ± 281
	B,3	9	938−984	12.07 ± 0.27	14844 ± 260
	C,1	9	925−963	11.98 ± 0.43	14736 ± 405
	C,2	8	925−976	12.26 ± 0.23	15009 ± 215
	C,3	9	922−976	12.09 ± 0.12	14803 ± 118
	C,4	8	910−964	12.05 ± 0.46	14914 ± 429

[a] The errors are the standard deviations.

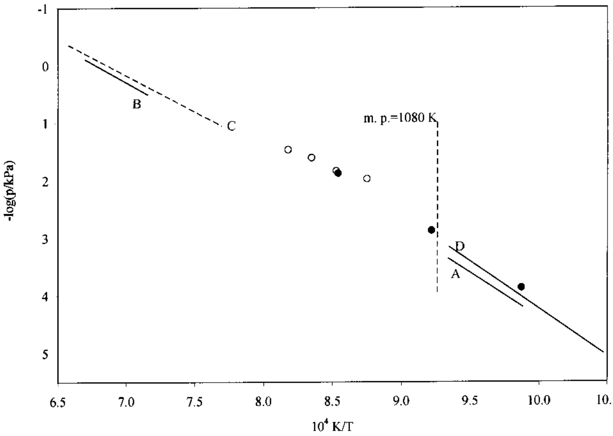

Figure 4. Comparison of the vapor pressure of $CeCl_3$: ●, Harrison (1952); ○, Moriarty (1963); A, Shimazaki and Niwa (1962); B, Novikov and Baev (1962); C, Dudchik et al. (1969); D, this work.

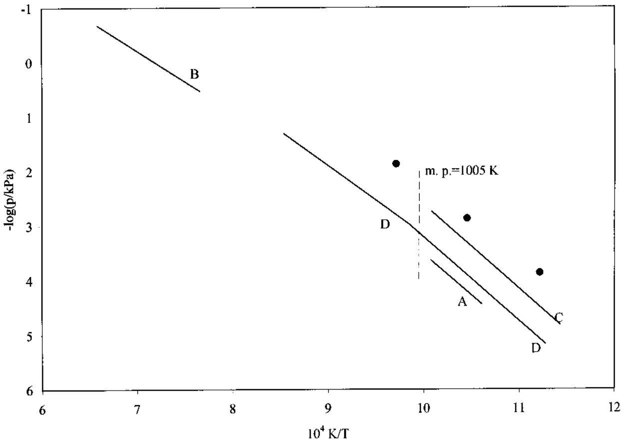

Figure 5. Comparison of the vapor pressure of $CeBr_3$: ●, Harrison (1952); A, Shimazaki and Niwa (1962); B, Dudchik et al. (1969); C, Gietmann et al. (1997); D, this work.

method, shows that, in the temperature ranges covered in our experiments, the amount of the dimer form in the gaseous phases can be considered negligible so that the partial pressures of the monomer form can be considered equal to those measured. In this way, the second-law enthalpies associated with the sublimation for these compounds in the monomer form at the experimental middle temperatures were derived from the slopes of the corresponding pressure−temperature equations selected above the solid compounds: $\Delta_{sub}H°$(1012 K) = (314.7 ± 3.0) kJ mol^{-1}, $\Delta_{sub}H°$(945 K) = (293.4 ± 3.0) kJ mol^{-1}, and $\Delta_{sub}H°$(970 K) = (284.1 ± 3.0) kJ mol^{-1} for $CeCl_3$, $CeBr_3$, and CeI_3, respectively. As concerns $CeCl_3$ our sublimation enthalpy value is slightly higher than that found by Shimazaki and Niwa (1962), $\Delta_{sub}H°$(1040 K) = 297 kJ mol^{-1}. For $CeBr_3$ our sublimation enthalpy agrees both with the Knudsen value, $\Delta_{sub}H°$ (967 K) = 287 kJ mol^{-1}, reported by Shimazaki and Niwa (1962) and with that recently found by Gietmann et al. (1997), $\Delta_{sub}H°$(933 K) = (295 ± 4) kJ mol^{-1}.

Table 5. Comparison of the Temperature Dependence of the Total Vapor Pressures of CeX_3 (X = Cl, Br, I)

						log (p/kPa) = $A - B(K/T) - C$ log(T/K)		
compound	ref	method	no. of points	T or T/K limit	−log (p/kPa)	A	B	C
$CeCl_3$(sol)	Harrison (1952)	Knudsen	2	1013, 1085	3.87, 2.87			
$CeCl_3$(liq)	Harrison (1952)	Knudsen	1	1171	1.87			
$CeCl_3$(liq)	Moriarty (1963)	Knudsen	4	1143, 1173, 1198, 1223	1.97, 1.83, 1.60, 1.46			
$CeCl_3$(sol)	Shimazaki and Niwa (1962)	Knudsen	18	from 1012 to 1071		11.160	15544	
$CeCl_3$(liq)	Novikov and Baev (1962)	dew point	11	from 1397 to 1493		10.11	14860	
$CeCl_3$(liq)	Dudchik et al. (1969)	boiling point		?		30.209	16347	6
$CeCl_3$(sol)	this work	Torsion	117	from 955 to 1070		12.21 ± 0.20	16443 ± 150	
$CeBr_3$(sol)	Harrison (1952)	Knudsen	2	892, 957	3.87, 2.87			
$CeBr_3$(liq)	Harrison (1952)	Knudsen	1	1030	1.87			
$CeBr_3$(sol)	Shimazaki and Niwa (1962)	Knudsen	7	from 943 to 992		11.459	14990	
$CeBr_3$(liq)	Dudchik et al. (1969)	boiling point		from 1306 to 1518		26.005	14300	5
$CeBr_3$(sol)	Gietmann et al. (1997)	mass spectrom	87	from 875 to 992		12.810 ± 0.207	15418 ± 200	
$CeBr_3$(sol)	this work	torsion	73	from 887 to 1003		12.12 ± 0.20	15332 ± 150	
$CeBr_3$(liq)	this work	torsion	38	from 1009 to 1172		9.57 ± 0.30	12745 ± 300	
CeI_3(sol)	Hirayama et al. (1975)	Knudsen	32	from 870 to 1015		12.28 ± 0.23	14858 ± 222	
CeI_3(sol)	this work	torsion	81	from 910 to 1031		12.02 ± 0.20	14843 ± 150	

Table 6. Third-Law Sublimation Enthalpies in (kJ mol^{-1}) for CeX$_3$ (X = Cl, Br, I)

	CeCl$_3$			CeBr$_3$			CeI$_3$		
T/K	p/kPa	$-\Delta$fef^a	$\Delta_{sub}H°$ (298 K)	p/kPa	$-\Delta$fef^a	$\Delta_{sub}H°$ (298 K)	p/kPa	$-\Delta$fef^a	$\Delta_{sub}H°$ (298 K)
950	7.94×10^{-6}	208.6	327.3	9.42×10^{-5}	179.9	280.6	2.46×10^{-4}	189.3	281.9
1000	5.82×10^{-5}	207.5	327.0	6.04×10^{-4}	178.9	278.9	1.49×10^{-3}	188.4	280.9

[a] Δfef = $\Delta[\{G°(T) - H°(298\text{ K})\}/T]$ in J K^{-1} mol^{-1} (Pankrarz, 1984).

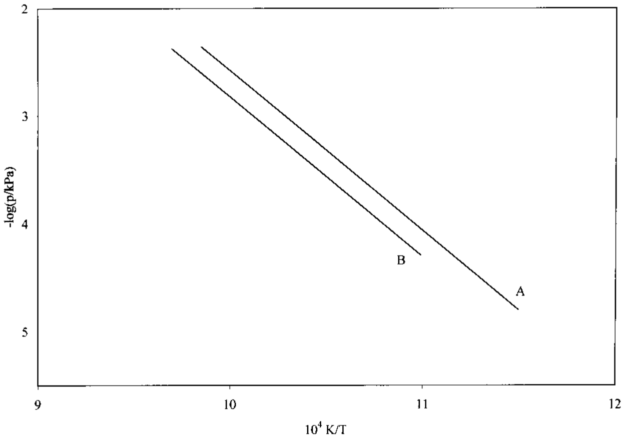

Figure 6. Comparison of the vapor pressure of CeI$_3$: A, Hirayama et al. (1975); B, this work.

For CeI$_3$ our sublimation enthalpy, (284 ± 3) kJ mol^{-1}, is equal to that reported by Hirayama et al. (1975), $\Delta_{sub}H°$(943 K) = (284 ± 4) kJ mol^{-1}. These sublimation enthalpy values were reported at 298 K by the enthalpic increments for the solid and gaseous compounds found in Pankratz's tables (1984): $\Delta_{sub}H°$ (298 K) = {(336 ±8), (310 ± 8), and (303.5 ± 8)} kJ mol^{-1} for CeCl$_3$, CeBr$_3$, and CeI$_3$, respectively. The associated errors were estimated.

These standard enthalpies were also calculated by third-law treatment of the data using the free enthalpy functions, $[G°(T) - H°(298\text{ K})]/T$, reported in Pankratz's tables (1984). The third-law $\Delta_{sub}H°$(298 K) values calculated at 950 K and 1000 K, approximated extreme temperatures at which the vapor pressures were determined above the compounds in the solid phase, are reported in Table 6. Apart from the standard sublimation enthalpy for CeCl$_3$, comparable within the uncertainty with the second-law value, the third-law standard enthalpies for CeBr$_3$ and CeI$_3$ are lower than those obtained by the second-law treatment of the vapor pressures. It is difficult to justify this disagreement. A critical analysis of the uncertainty associated with the second-law $\Delta_{sub}H°$(T) value shows that this would be minor. In fact considering the agreement among the results obtained in a large number of experimental runs, and the substantial agreement between our final results with those found in the literature, we believe that the error associated with a second-law sublimation enthalpy value does not exceed 4 kJ mol^{-1}. A comparable uncertainty was found during the calibration runs (runs carried out to determine the instrument constant of the cells) in which all the sublimation enthalpy values of lead (standard used in the calibrations) obtained from the slopes of the logarithm of the measured torsion angles vs 1/T equations were in agreement among themselves, and their average value, $\Delta_{sub}H°$(1012 K) = (185 ± 2) kJ mol^{-1}, was practically equal to that selected in the literature, $\Delta_{sub}H°$(1000 K) = 184.4 kJ mol^{-1} (Hultgreen et al., 1973). The major error (±8 kJ mol^{-1}) associated with the standard sublimation enthalpies of the compounds was estimated to take into account the uncertainties tied with the used enthalpic increments. Errors of the temperatures excepted, the principal error sources in the third-law $\Delta_{sub}H°$(298 K) are those associated with the absolute vapor pressures and with the used free energy functions. The observed spread of the vapor pressures of CeBr$_3$ and CeI$_3$, overestimated by a factor of 2, produces, at 1000 K, an uncertainty of the final $\Delta_{sub}H°$(298 K) value of about 6 kJ mol^{-1}. An evaluation of the error associated with the enthalpy value for the use of erroneous $\Delta\{(G°(T) - H°(298))/T\}$ values is not possible. Of course the possible presence of the dimer form in the vapor and its eventual different amount at the extreme experimental temperatures (greater at the higher temperatures) is a considerable cause of the disagreement between the second- and third-law enthalpy values. In this case the partial pressures of the monomer are lower (much more at the highest temperatures) than those used equal to the total ones, and this leads both to a decrease of the second-law enthalpy value and to an increase of the third-law enthalpy, reducing their small temperature trend and the disagreement between the second- and third-law data. But considering that no evident changes of the Knudsen vapor molecular weight at different temperatures were observed and that the mass-spectrometric analysis of the vapor above CeBr$_3$ (Gietmann et al., 1997) shows that the dimer amount in the vapor is about 1% of the monomer, we are persuaded that the presence of the dimer form could not be the principal cause of the observed disagreement. In light of these observations, and considering also the trend found in the third-law $\Delta_{sub}H°$ (298 K) values calculated at two not much different temperatures, we believe that, for CeBr$_3$ and CeI$_3$, in addition to the possible small uncertainty associated with the pressure data, the principal error source could be due to the used free energy functions selected by Pankratz (1984). The suspicion that these functions may be not correct was also hypothesized in our previous work (Brunetti et al., 1999). On this basis, we propose as standard sublimation enthalpy for CeCl$_3$ the value (331± 5) kJ mol^{-1}, the average of the second- and third-law results, while for CeBr$_3$ and CeI$_3$ the values 300 and 295 kJ mol^{-1}, respectively, were obtained giving more weight to the second-law results, both with an error of about 10 kJ mol^{-1}. These selected values present a trend going from trichloride to triiodide, but this trend is less evident than that of the sublimation enthalpies evaluated as the difference of the enthalpies of formation of solid and gaseous cerium trihalides reported by Pankratz (1984), 330, 286, and 278 kJ mol^{-1}, respectively. However, the free energy functions for CeBr$_3$ and CeI$_3$ can bias these values.

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