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Vapor Pressures and Sublimation Enthalpies of Praseodymium Trichloride, Tribromide, and Triiodide

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The vapor pressures for praseodymium trihalides, $PrCl_3$, $PrBr_3$, and PrI_3, were measured above solid and liquid phases by the torsion method. In the covered temperature ranges, their values can be expressed by the following equations: $PrCl_3$(s), $\lg(p/\text{kPa}) = 12.45 \pm 0.20 - (16540 \pm 200)\ \text{K}/T$ (from 963 to 1045 K); $PrCl_3$(l), $\lg(p/\text{kPa}) = 9.56 \pm 0.10 - (13422 \pm 150)\ \text{K}/T$ (from 1060 to 1131 K); $PrBr_3$(s), $\lg(p/\text{kPa}) = 12.06 \pm 0.30 - (15060 \pm 200)\ \text{K}/T$ (from 890 to 961 K); $PrBr_3$(l), $\lg(p/\text{kPa}) = 9.55 \pm 0.30 - (12698 \pm 200)\ \text{K}/T$ (from 967 to 1061 K); PrI_3(s), $\lg(p/\text{kPa}) = 11.31 \pm 0.30 - (13766 \pm 200)\ \text{K}/T$ (from 889 to 1003 K); PrI_3(l), $\lg(p/\text{kPa}) = 8.36 \pm 0.35 - (10816 \pm 300)\ \text{K}/T$ (from 1013 to 1127 K). The standard sublimation enthalpies ($\Delta_{\text{sub}}H°(298\ \text{K}) = 330 \pm 10$, 300 ± 10, and $278 \pm 5\ \text{kJ mol}^{-1}$ for $PrCl_3$, $PrBr_3$, and PrI_3, respectively) were determined by second- and third-law treatment of the vapor pressure data.

Introduction

As a continuing part of our investigation on the vaporization thermodynamic of rare-earth metal trihalides (Brunetti et al., 1999; Brunetti et al., 2000; Villani et al., 2000), the present work was undertaken in order to study the vaporization of praseodymium trihalides, $PrCl_3$, $PrBr_3$, and PrI_3.

Apparently the studies on the vaporization for these compounds, and in particular on their saturated vapor pressures, are old and scanty. The vapor pressures for $PrCl_3$ were measured employing the Knudsen effusion method by Harrison (1952), by Shimazaki and Niwa (1962), by Moriarty (1963), and by Hannay and Myers (1979). Some vapor pressures above the molten compound were measured employing the "dew point" method by Dudchik et al. (1969). For $PrBr_3$ the vapor pressures found in the literature are those measured by Shimazaki and Niwa (1962) and the more recent ones obtained by a mass spectrometer by Gietmann et al. (1997). High vapor pressures determined by the boiling point method were reported as a temperature function by Dudchik et al. (1975). The vapor pressures of PrI_3 were measured by Shimazaki and Niwa (1962) and by Hirayama et al. (1972), both using the Knudsen method. For this compound a second-law standard sublimation enthalpy, $\Delta_{\text{sub}}H°(298\ \text{K}) = (330 \pm 6)$ kJ mol^{-1}, was mass spectrometrically obtained by Hirayama and Castle (1973) from the slope of lg $I^{+}_{(PrI_2^{+})}T$, (the more abundant ion intensity in the mass spectrum) vs $1/T$.

In the present paper new vapor pressure sets of these compounds were measured by the torsion method, from which their corresponding sublimation enthalpies were derived.

Experimental Section and Results

The torsion apparatus was practically the same as that we used in previous studies (Piacente et al., 1994; Brunetti et al., 1999). The apparatus was suspended on a microbalance (Cahn model 1000) in order to measure the rate mass loss of the sample simultaneously to its torsion vapor pressure and to determine, by the Knudsen equation (Knudsen, 1909), the vapor molecular weight. To enlarge the temperature ranges, two conventional graphite torsion cells having different areas of their effusion holes (0.5 mm and 1.8 mm in diameter for cells A and B, respectively) were employed. The sample was lodged in an alumina or tantalum liner. The cell instrument constants were evaluated by vaporizing a standard element, pure lead in this study, and often their values were checked in runs carried out between the vaporization runs of the studied compounds. The temperatures were measured by a Pt−Pt(Rh 10%) thermocouple inserted in a cell placed beneath the torsion one and calibrated "in situ" by checking the zero variant point at the melting point of cadmium and silver following the procedure described in the previous work (Piacente et al., 1994) so that the error in the temperature measurements should not exceed ±2 K. To check also the reliability of the all-round apparatus, some second-law sublimation enthalpy values of lead were calculated from the slopes of the logarithm of the torsion angles versus $1/T$ equations obtained during the calibration runs. The values so obtained with both cells, (184 ± 2; 186 ± 3; 185 ± 2; and 185 ± 1) kJ mol^{-1} at the middle temperatures of the covered ranges (1005, 960, 1011, and 1007 K, respectively), were decidedly in agreement, within their standard deviations, with the sublimation enthalpy at 1000 K (184.4 kJ mol^{-1}) selected by Hultgren et al. (1973).

The praseodymium trihalide samples were supplied by Aldrich. As certified by the supplier, their purity was greater than 99.9%. As usual, the loading of the cell was carried out in a drybox, and the cell was quickly transferred to the torsion apparatus and put under vacuum. Before starting the pressure measurements, the samples were heated for a sufficiently long time at about 700 K in order to ensure that no rotation of the cell and no mass loss of the torsion assembly occurred. In each run the pressure measurements were carried out at increasing and decreasing temperatures. The vapor pressures above the solid phase of each compound were prevalently measured by using cell B while those above the liquid phase were

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Table 1. Torsion Total Vapor Pressure above Solid and Liquid $PrCl_3$

run A1 (cell B)		run A2 (cell A)		run A3 (cell B)		run A4 (cell A)		run A5 (cell B)		run A6 (cell B)	
T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)
967	4.60	1066	2.99	963	4.66	1063	3.01	972	4.60	964	4.71
971	4.52	1074	2.89	966	4.60	1068	2.95	977	4.52	972	4.60
975	4.48	1081	2.82	975	4.45	1071	2.90	980	4.45	978	4.56
979	4.41	1090	2.72	979	4.38	1076	2.86	986	4.38	983	4.48
982	4.38	1101	2.59	985	4.28	1085	2.76	987	4.36	985	4.45
985	4.33	1111	2.48	988	4.24	1094	2.66	994	4.24	993	4.29
987	4.28	1120	2.37	993	4.13	1101	2.57	998	4.20	1002	4.14
993	4.20	1131	2.27	998	4.07	1109	2.49	1003	4.10	1003	4.11
994	4.13			1001	4.00	1115	2.43	1006	4.04	1010	3.99
998	4.11			1008	3.91	1124	2.33	1011	3.95	1012	3.98
1002	4.03			1009	3.87			1014	3.91	1018	3.86
1008	3.93			1010	3.85			1020	3.81	1022	3.80
1011	3.89			1017	3.75			1023	3.76	1026	3.73
1016	3.80			1019	3.71			1029	3.65	1031	3.65
1017	3.79			1025	3.63			1038	3.53	1043	3.48
1023	3.68			1026	3.60					1045	3.42
1025	3.65			1027	3.58						
1027	3.61							1064	3.11	1060	3.18
1029	3.56							1072	3.01	1071	3.04
								1081	2.90	1080	2.97
								1091	2.80	1090	2.84
								1101	2.68	1099	2.74
								1110	2.57	1108	2.64
								1119	2.47	1117	2.54
								1128	2.39	1126	2.43

Table 2. Torsion Total Vapor Pressure above Solid and Liquid $PrBr_3$

run B1 (cell B)		run B2 (cell A)		run B3 (cell A)		run B4 (cell B)		run B5 (cell B)		run B6 (cell B)		run B7 (cell A)	
T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)	T/K	$-$lg(p/kPa)
890	4.79	914	4.45	893	4.77	973	3.57	910	4.58	899	4.67	967	3.59
901	4.59	924	4.30	900	4.67	980	3.47	917	4.41	910	4.47	974	3.51
908	4.49	932	4.19	909	4.52	986	3.37	927	4.23	918	4.33	982	3.40
914	4.38	936	4.11	917	4.37	993	3.28	931	4.17	922	4.26	988	3.30
917	4.31	944	3.97	927	4.19	1000	3.19	939	4.02	928	4.14	992	3.25
924	4.21	951	3.83	937	4.03	1004	3.15	946	3.90	932	4.07	1002	3.15
930	4.09	961	3.66	949	3.80	1009	3.10	951	3.83	938	3.97	1009	3.06
935	4.00					1013	3.05	953	3.80	942	3.91	1017	2.96
938	3.95	972	3.51	986	3.28	1018	2.98			945	3.85	1025	2.86
943	3.86	988	3.28	991	3.21	1021	2.96	974	3.45	951	3.74	1032	2.78
948	3.76	993	3.20	997	3.14	1027	2.88	982	3.34	954	3.69	1040	2.67
953	3.67	998	3.14	1002	3.07	1035	2.81	993	3.19	958	3.63	1047	2.59
		1007	3.04	1008	3.00	1039	2.75	1001	3.08			1054	2.50
		1014	2.95	1013	2.93	1045	2.68	1011	2.97			1058	2.45
		1021	2.86	1017	2.88			1019	2.88				
		1027	2.80	1023	2.81			1027	2.79				
		1033	2.71	1029	2.73								
		1042	2.60	1033	2.68								
		1051	2.49										
		1061	2.36										

measured by using cell A. At the end of the vaporization experiments the $PrCl_3$ and $PrBr_3$ samples were completely vaporized while for PrI_3 a light gray residue was observed in the cell. In particular the vapor pressures of PrI_3 were found well reproducible till about 70−80% of the original sample had been vaporized; after that, the pressure slowly decreased till its value was not detectable. To understand if this residue is a product of a partial thermal decomposition of the compound or if it is an impurity in the original sample, a small amount of the sample was vaporized under vacuum in a separate experiment in a quartz tube and its vapor was condensed in the cold zone of the tube. The vapor pressure of this condensed material was found to be practically equal to those measured above the original sample and was well reproducible till its complete vaporization. At the end of this experiment, in fact, no appreciable residue was found in the cell, so that in spite of the certified purity, about 3−5% of a not identified impurity was present in the PrI_3 sample. The presence of this impurity influenced the pressure measurements only at the end of the experiments when the amount of the remaining sample was comparable with the amount of impurity. It

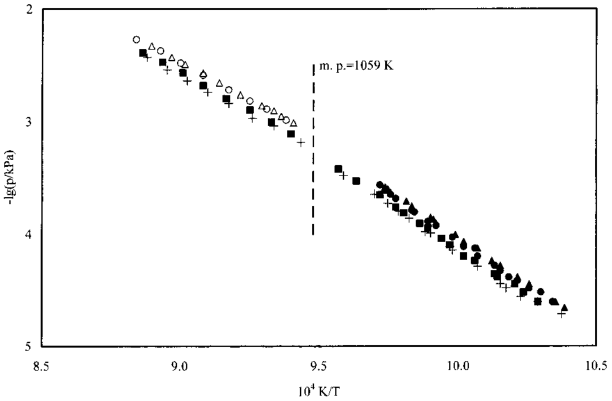

Figure 1. Torsion vapor pressure of $PrCl_3$: (●) run A1; (○) run A2; (▲) run A3; (△) run A4; (■) run A5; (+) run A6.

Table 3. Torsion Total Vapor Pressure above Solid and Liquid PrI_3

run C1 (cell B)		run C2 (cell B)		run C3 (cell A)		run C4 (cell B)		run C5 (cell A)		run C6 (cell A)	
T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$
893	4.17	903	3.94	1019	2.28	940	3.41	1018	2.19	1013	2.37
897	4.06	914	3.74	1023	2.24	944	3.32	1023	2.12	1022	2.29
904	3.94	921	3.57	1027	2.19	952	3.20	1027	2.08	1030	2.20
910	3.82	930	3.42	1032	2.13	957	3.12	1031	2.04	1034	2.17
918	3.72	949	3.15	1036	2.09	962	3.04	1035	2.00	1039	2.0.12
925	3.59	954	3.11	1040	2.04	967	2.96	1040	1.94	1046	2.05
930	3.54	962	2.98	1044	2.00	972	2.89	1044	1.91	1053	1.98
934	3.46	971	2.86	1048	1.97	976	2.83	1049	1.84	1060	1.92
941	3.37	980	2.75	1053	1.91	982	2.76	1053	1.80	1068	1.84
943	3.34	988	2.65	1058	1.86	986	2.70	1058	1.76		
945	3.27			1061	1.81	991	2.63	1062	1.72		
950	3.24			1066	1.77	994	2.57	1066	1.68		
956	3.11			1070	1.72	998	2.52	1071	1.63		
				1075	1.68			1075	1.59		

run C7 (cell A)		run C8 (cell B)		run C9 (cell A)		run C10 (cell B)		run C11 (cell B)	
T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$	T/K	$-\lg(p/\text{kPa})$
940	3.44	889	4.06	1037	2.09	923	3.64	928	3.49
945	3.32	892	3.98	1042	2.06	928	3.54	950	3.19
953	3.23	897	3.91	1045	2.02	934	3.46	959	3.05
955	3.15	903	3.82	1050	1.99	941	3.36	961	3.00
967	2.98	906	3.74	1055	1.96	947	3.27	964	2.95
970	2.96	912	3.64	1060	1.91	950	3.21	972	2.85
976	2.88	917	3.57	1065	1.89	957	3.09	977	2.78
977	2.84	922	3.49	1072	1.80	966	2.97	981	2.71
987	2.71	927	3.41	1078	1.76	969	2.92	986	2.65
998	2.57	934	3.32	1084	1.70	973	2.87	993	2.55
		942	3.19	1087	1.64	983	2.71	1000	2.44
1048	1.97	946	3.13	1097	1.59	987	2.65	1003	2.38
1055	1.92	950	3.07	1101	1.55	995	2.52		
1062	1.86			1108	1.49				
1070	1.78			1113	1.44				
1076	1.73			1121	1.37				
1083	1.67								
1088	1.62								
1095	1.57								
1102	1.50								
1109	1.45								

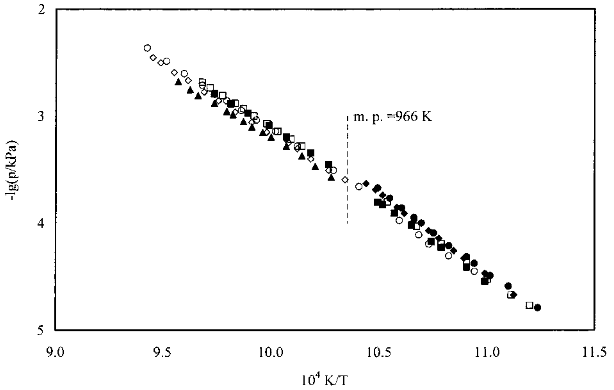

Figure 2. Torsion vapor pressure of $PrBr_3$: (●) run B1; (○) run B2; (□) run B3; (▲) run B4; (■) run B5; (◆) run B6; (◇) run B7.

was found that the impurity shows appreciable (but not reproducible) vapor pressures at higher temperatures (~1250 K), so that in the temperature ranges covered in our experiments, the contribution of the vapor pressure of this impurity to the measured pressures was negligible.

Tables 1−3 and Figures 1−3 summarize the results. The slopes and intercepts of the lg p vs $1/T$ straight lines, as evaluated by treating the experimental data of each run by least squares, are reported in Table 4. Apparently, no evident dependence on the area of the effusion holes was observed. Weighing the slope and intercept of each equation proportionally to the experimental number of points, the following final equations representative of the total vapor pressure for solid and liquid praseodymium trihalides, valid in the covered temperature ranges, were selected:

$$\text{PrCl}_3(\text{s}) \quad \lg(p/\text{kPa}) = 12.45 \pm 0.20 - (16540 \pm 200)\ \text{K}/T \quad (963-1045\ \text{K}) \tag{1}$$

$$\text{PrCl}_3(\text{l}) \quad \lg(p/\text{kPa}) = 9.56 \pm 0.10 - (13422 \pm 150)\ \text{K}/T \quad (1060-1131\ \text{K}) \tag{2}$$

$$\text{PrBr}_3(\text{s}) \quad \lg(p/\text{kPa}) = 12.06 \pm 0.30 - (15060 \pm 200)\ \text{K}/T \quad (890-961\ \text{K}) \tag{3}$$

$$\text{PrBr}_3(\text{l}) \quad \lg(p/\text{kPa}) = 9.55 \pm 0.30 - (12698 \pm 200)\ \text{K}/T \quad (967-1061\ \text{K}) \tag{4}$$

$$\text{PrI}_3(\text{s}) \quad \lg(p/\text{kPa}) = 11.31 \pm 0.30 - (13766 \pm 200)\ \text{K}/T \quad (889-1003\ \text{K}) \tag{5}$$

$$\text{PrI}_3(\text{l}) \quad \lg(p/\text{kPa}) = 8.36 \pm 0.35 - (10816 \pm 300)\ \text{K}/T \quad (1013-1127\ \text{K}) \tag{6}$$

where the associated errors were estimated. When in a single run the vapor pressures of a compound were measured above the solid and liquid phases, from the slope and the intercept of the equations obtained above these phases, the enthalpy and the temperature of fusion of this compound were calculated (see Table 5). In the same Table 5 were also reported those thermodynamic parameters calculated from the final equations selected for each compound. Considering the large uncertainties associated

Table 4. Temperature Dependence of the Vapor Pressure of PrX_3 (X = Cl, Br, I)

compd	run (cell)	no. of points	ΔT/K	$\lg(p/\text{kPa}) = A - B/(T/\text{K})$ A^a	B^a	compd	run (cell)	no. of points	ΔT/K	$\lg(p/\text{kPa}) = A - B/(T/\text{K})$ A^a	B^a
$PrCl_3$(s)	A1 (B)	19	967−1029	12.52 ± 0.21	16574 ± 209	$PrCl_3$(s)	A5 (B)	16	972−1045	12.41 ± 0.16	16543 ± 156
$PrCl_3$(l)	A2 (A)	8	106−1131	9.58 ± 0.11	13401 ± 121	$PrCl_3$(l)	A5 (B)	8	1064−1128	9.63 ± 0.14	13554 ± 148
$PrCl_3$(s)	A3 (B)	17	963−1027	12.54 ± 0.10	16568 ± 100	$PrCl_3$(s)	A6 (B)	15	964−1043	12.30 ± 0.31	16461 ± 310
$PrCl_3$(l)	A4 (A)	10	1063−1124	9.49 ± 0.10	13291 ± 109	$PrCl_3$(l)	A6 (B)	8	1060−1126	9.53 ± 0.22	13477 ± 236
$PrBr_3$(s)	B1 (B)	12	890−953	12.12 ± 0.21	15068 ± 194	$PrBr_3$(l)	B4 (B)	14	973−1045	9.09 ± 0.14	12293 ± 137
$PrBr_3$(s)	B2 (A)	7	914−961	11.96 ± 0.57	15028 ± 538	$PrBr_3$(s)	B5 (B)	8	910−953	11.98 ± 0.17	15026 ± 163
$PrBr_3$(l)	B2 (A)	12	972−1061	9.93 ± 0.09	13057 ± 93	$PrBr_3$(l)	B5 (B)	7	974−1027	9.32 ± 0.18	12436 ± 178
$PrBr_3$(s)	B3 (A)	7	893−949	11.70 ± 0.34	14730 ± 313	$PrBr_3$(s)	B6 (B)	12	899−958	12.33 ± 0.09	15287 ± 83
$PrBr_3$(l)	B3 (A)	10	986−1033	9.84 ± 0.04	12942 ± 45	$PrBr_3$(l)	B7 (A)	14	967−1058	9.59 ± 0.10	12752 ± 97
PrI_3(s)	C1 (B)	13	893−956	11.26 ± 0.28	13747 ± 257	PrI_3(s)	C7 (B)	10	940−998	11.32 ± 0.35	13846 ± 335
PrI_3(s)	C2 (B)	10	903−988	10.86 ± 0.34	13319 ± 323	PrI_3(l)	C7 (B)	10	1048−1109	7.68 ± 0.11	10121 ± 117
PrI_3(l)	C3 (A)	14	1019−1075	9.28 ± 0.08	11775 ± 82	PrI_3(s)	C8 (B)	13	889−950	11.13 ± 0.17	13483 ± 153
PrI_3(s)	C4 (B)	13	940−998	11.53 ± 0.13	14020 ± 124	PrI_3(l)	C9 (A)	17	1037−1127	7.68 ± 0.16	10161 ± 173
PrI_3(l)	C5 (A)	14	1018−1075	8.98 ± 0.07	11357 ± 71	PrI_3(s)	C10 (B)	13	923−995	11.64 ± 0.13	14103 ± 120
PrI_3(l)	C6 (A)	9	1013−1068	7.98 ± 0.10	10490 ± 109	PrI_3(l)	C11 (B)	12	928−1003	11.31 ± 0.21	13755 ± 200

[a] The errors are standard deviations.

Table 5. Heat of Fusion and Melting Point of PrX_3 (X = Cl, Br, I)

compd	source	$\Delta_{\text{fus}}H°(T_{\text{fus}})$/(kJ mol^{-1}) our	lit.	T_{fus}/K our	lit.	lit. source
$PrCl_3$	run A5 (B)	57	50	1077	1059	Pankratz (1984)
	run A6 (B)	57	52	1075	1061	Gaune-Escard et al. (1994)
	eq 1, 2	60		1077		
$PrBr_3$	run B2 (A)	38	47	972	966	Pankratz (1984)
	run B3 (A)	34		963		
	run B5 (B)	50		977		
	eq 3, 4	45		941		
PrI_3	run C7 (B)	71	53	1023	1011	Pankratz (1984)
	eq 5, 6	56		1000		

with this way of evaluating the enthalpy and temperature of fusion, the values can be considered in acceptable agreement with those selected in the literature, and this agreement is very important because it shows that there are not very large errors in the absolute vapor pressure and in the temperature measurements. The selected eqs 1 to 6 were drawn in Figures 4−6 and in Table 6 for comparison with those found in the literature.

Discussion and Conclusion

As reported in previous literature and as checked by the values of the vapor molecular weight determined during the torsion pressure measurements, for all compounds the monomer was practically the only gaseous species present in the vapor. The contribution of the dimer partial pressures to the total pressures would be on the order of the magnitude of the uncertainties of the pressure values. On this basis, from the slopes of the selected eqs 1−6, the second-law sublimation and vaporization enthalpies of each compound, at approximately the middle temperatures of the covered range, were calculated and reported in Table 7. These enthalpies were corrected at 298 K by the differences of the enthalpic increments for the condensed and gaseous compounds reported by Pankratz (1984). The obtained average values are $\Delta_{\text{sub}}H°(298\text{ K}) = \{(338 \pm 4), (309 \pm 4), \text{and } (283 \pm 4)\}$ kJ mol^{-1} for $PrCl_3$, $PrBr_3$, and PrI_3, respectively, where the errors have been estimated. These standard sublimation enthalpies were also calculated by the third-law method at (900, 1000, and 1100) K by the vapor pressures above solid and liquid phases evaluated at these temperatures from eqs 1−6 and by the corresponding free energy functions, $[G°(T) - H°(298\text{ K})]/T$,

Table 6. Comparison of the Temperature Dependence of the Total Vapor Pressures of PrX_3 (X = Cl, Br, I)

compd	ref	method	no. of points	T or T limit K	$\lg(p/\text{kPa}) = A - B/T - C \lg T$ A	B	C
$PrCl_3$(s,l)	Harrison (1952)	Knudsen	3	T = 991, 1061, 1142	$-\lg(p/\text{kPa})$ = 3.88, 2.88, 1.88		
$PrCl_3$(s)	Shimazaki and Niwa (1962)	Knudsen	9	from 1002 to 1061	12.211	15439	
$PrCl_3$(l)	Moriarty (1963)	Knudsen	4	T = 1108, 1173, 1218, 1273	$-\lg(p/\text{kPa})$ = 2.17, 1.77, 1.48, 1.01		
$PrCl_3$(s)	Hannay and Myers (1979)	Knudsen	18	from 914 to 1056	11.78^a	16031^a	
$PrCl_3$(s)	Hannay and Myers (1979)	Knudsen	12	from 914 to 1056	11.63^a	15980^a	
$PrCl_3$(l)	Novikov and Baev (1962)	dew point	14	from 1314 to 1465	10.131	14860	
$PrCl_3$(l)	Dudchik et al. (1975)	boiling point	24	from 1374 to 1636	28.15	16100	6
$PrCl_3$(l)	Nieselson et al. (1978)	boiling point		∼1310	8.32	14419	
$PrCl_3$(s)	this work	torsion	67	from 963 to 1045	12.45 ± 0.20	16540 ± 200	
$PrCl_3$(l)	this work	torsion	34	from 1060 to 1131	9.56 ± 0.10	13422 ± 150	
$PrBr_3$(s)	Shimazaki and Niwa (1962)	Knudsen	8	from 924 to 973	12.508	14916	
$PrBr_3$(s)	Gietmann et al. (1997)	mass spectr	39	from 812 to 956	12.223 ± 0.235	14995 ± 220	
$PrBr_3$(l)	Dudchik et al. (1969)	boiling point		from 1280 to 1560	23.93 ± 0.13	14080 ± 84	5
$PrBr_3$(s)	this work	torsion	46	from 890 to 961	12.06 ± 0.30	15060 ± 200	
$PrBr_3$(l)	this work	torsion	57	from 967 to 1061	9.55 ± 0.30	12698 ± 200	
PrI_3(s)	Shimazaki and Niwa (1962)	Knudsen	9	from 933 to 1002	12.703	14640	
PrI_3(s)	Hirayama et al. (1972)	Knudsen	30	from 841 to 1032^b	10.878 ± 0.32	15281 ± 302	
PrI_3(s)	this work	torsion	84	from 889 to 1003	11.31 ± 0.30	13766 ± 200	
PrI_3(l)	this work	torsion	64	from 1013 to 1127	8.36 ± 0.35	10816 ± 300	

[a] Calculated by us using the results reported in the Hannay paper. [b] Only one point (at 1032 K) measured above the liquid phase.

Table 7. Second-Law Standard Sublimation Enthalpies for PrX_3 (X = Cl, Br, I)

compd	T K	$\Delta_{sub}H°(T)$ kJ mol^{-1}	$\Delta_{sub}H°(298\ K)^a$ kJ mol^{-1}
$PrCl_3$(s)	1000	317 ± 4	340 ± 4
$PrCl_3$(l)	1100	257 ± 3	336 ± 3
$PrBr_3$(s)	900	288 ± 4	306 ± 4
$PrBr_3$(l)	1000	243 ± 3	313 ± 4
PrI_3(s)	900	263 ± 4	280 ± 4
PrI_3(l)	1000	207 ± 6	286 ± 6

[a] Obtained by the enthalpic increments reported by Pankratz (1984).

Table 8. Third-Law Standard Sublimation Enthalpies for PrX_3 (X = Cl, Br, I)

compd	T K	$-$lg $(p/\text{kPa})^a$	$-R \ln p$ J K^{-1} mol^{-1}	$-\Delta\text{fef}^b$ J K^{-1} mol^{-1}	$\Delta_{sub}H°(298\ K)$ kJ mol^{-1}
$PrCl_3$(s)	900	5.93	152	209	325
$PrCl_3$(s)	1000	4.09	117	207	323
$PrCl_3$(l)	1100	2.65	89	202	320
				average	323
$PrBr_3$(s)	900	4.67	128	197	292
$PrBr_3$(l)	1000	3.15	99	193	292
$PrBr_3$(l)	1100	1.99	77	187	290
				average	291
PrI_3(s)	900	3.99	115	191	275
PrI_3(s)	1000	2.46	85	188	274
PrI_3(l)	1100	1.48	67	182	274
				average	274

[a] Calculated from the selected eqs 1−6 above both phases of each compound. [b] $\Delta\text{fef} = \Delta[G°(T) - H°(298\ K)]/T$, from Pankratz (1984).

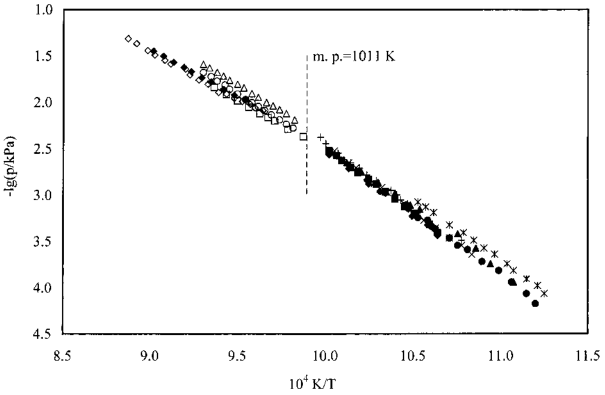

Figure 3. Torsion vapor pressure of PrI_3: (●) run C1; (▲) run C2; (○) run C3; (■) run C4; (Δ) run C5; (□) run C6; (◆) run C7; (∗) run C8; (◇) run C9; (×) run C10; (+) run C11.

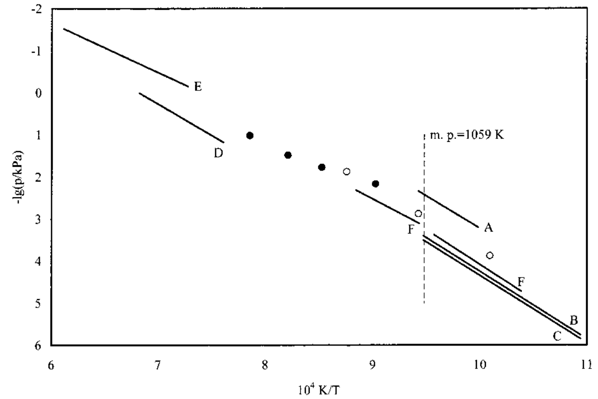

Figure 4. Comparison of vapor pressure of $PrCl_3$: (●) Harrison (1952); (○) Moriarty (1963); (A) Shimazaki and Niwa (1962); (B) Hannay and Myers (1979); (C) Hannay and Myers (1979); (D) Novikov and Baev (1962); (E) Dudchik et al. (1969); (F) this work.

reported in Pankratz's tables. The enthalpy values so obtained are reported in Table 8. Considering the large temperature range, the results do not present an appreciable trend (except perhaps for $PrCl_3$), but their average values, $\Delta_{sub}H°(298\ K) = (323, 291, \text{and } 274)$ kJ mol^{-1} for $PrCl_3$, $PrBr_3$, and PrI_3 respectively, are lower than those derived by the second-law method. Second- and third-law sublimation enthalpies of these compounds were also calculated from the vapor pressures found in the literature above the only solid phase and employing the Pankratz's thermodynamic functions. The results are in Table 9. Also, these second-law enthalpies are generally higher than the third-law values. A critical analysis to explain this difference led to a possible presence in the vapor of the dimer form in small but different amounts at different temperatures in the covered ranges. This in fact does not produce appreciable changes of the third-law enthalpies but can influence the second-law values. To justify the difference found in the present work, in particular for $PrCl_3$ and $PrBr_3$, the dimer concentration in the vapor at the highest temperatures could be so high as to affect the molecular weight. This is in contrast with the value experimentally found, which was close to the monomer value, and mainly with its constancy at very different temperatures. On this basis this error source was considered negligible. Considering that the sublimation enthalpies are tied both to the inevitable errors associated with pressure and temperature measurements and to the uncertainties of the used ther-

Table 9. Comparison of Sublimation Enthalpies of PrX_3 (X = Cl, Br, I) Obtained from Vapor Pressure Data Measured above the Solid Phase

compd	ref	T K	$\Delta_{sub}H°(T)$ kJ mol^{-1}	$\Delta_{sub}H°(298\ K)$/(kJ mol^{-1}) II law^a	 III law^b	Δ(II−III) kJ mol^{-1}
$PrCl_3$	Shimazaki and Niwa (1962)	1031	295	319	307	12
	Hannay and Myers (1979)	984	306	329	327	2
	this work	1000	317 ± 4	340 ± 4	324	17
$PrBr_3$	Shimazaki and Niwa (1962)	950	285	302	280	22
	Gietmann et al. (1997)	884	291	309	289	20
	this work	900	288 ± 4	306 ± 4	292	14
PrI_3	Shimazaki and Niwa (1962)	967	280	298	265	33
	Hirayama et al. (1972)	936	292	310	311	−1
	Hirayama and Castle (1973)			330 ± 6^c		
	this work	900	263 ± 4	280 ± 4	275	5

[a] Calculated using enthalpic increments reported by Pankratz (1984). [b] Calculated at the average temperature by free energy functions reported by Pankratz (1984). [c] Derived from the slope of the mass spectrometric lg $I^+_{(PrI_2^+)}T$ vs $1/T$ equation.

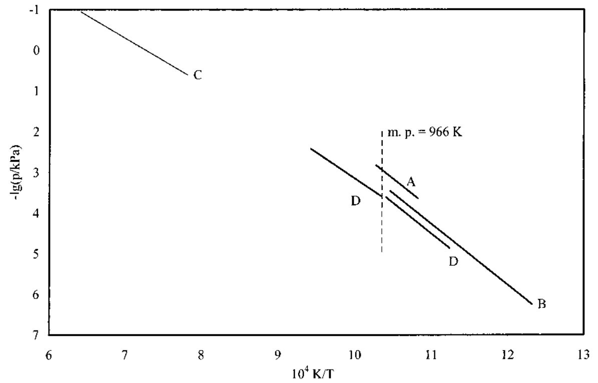

Figure 5. Comparison of vapor pressure of $PrBr_3$: (A) Shimazaki and Niwa (1962); (B) Gietmann et al. (1997); (C) Dudchik et al. (1969); (D) this work.

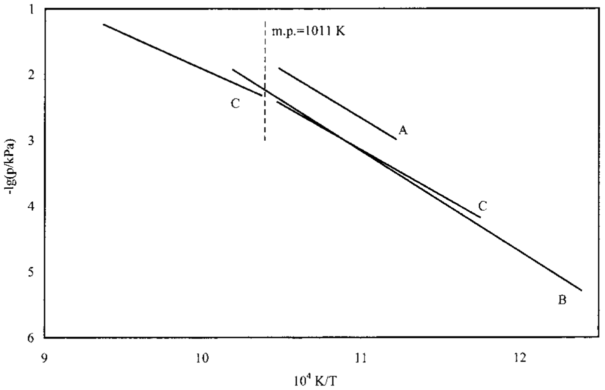

Figure 6. Comparison of vapor pressure of PrI_3: (A) Shimazaki and Niwa (1962); (B) Hirayama et al. (1972); (C) this work.

modynamic functions (free energy functions in the third-law calculations and the enthalpic increments in reporting the second-law enthalpies at 298 K), we believe that each enthalpy should be associated a real uncertainty comparable with the difference of the second- and third-law values. On this basis, giving for each compound equal weight to both enthalpy values found in the present work, we propose as the standard sublimation enthalpy of the praseodymium trihalides the values $\Delta_{sub}H°(298\ K) = (330, 300, \text{and } 278)\ kJ\ mol^{-1}$ for $PrCl_3$, $PrBr_3$, and PrI_3, respectively, with an overestimated error of $\pm 10\ kJ\ mol^{-1}$ for $PrCl_3$ and $PrBr_3$ and $\pm 5\ kJ\ mol^{-1}$ for PrI_3. Within these errors, our enthalpies agree with those evaluated as differences between the selected standard enthalpies of formation for solid and gaseous compounds, (325, 297, and 275) $kJ\ mol^{-1}$ (Pankratz, 1984). As observed for lanthanum (Brunetti et al., 2000) and cerium (Villani et al., 2000) trihalides, and for praseodymium trihalides going from trichlorides to triiodides, the standard sublimation enthalpy presents a trend. Such a trend is not observed for dysprosium halides (Brunetti et al., 1999).

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