

# Thermodynamic Study of Sublimation of PbF<sub>2</sub> and PbF<sub>4</sub> from Torsion-Effusion Vapor Pressure Measurements

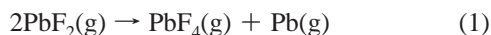
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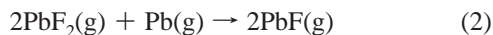
The total vapor pressures of lead di- and tetrafluoride were measured by a torsion-effusion method. The vapor above PbF<sub>2</sub>(s) is prevalently PbF<sub>2</sub>(g). The temperature dependence of the vapor pressure is represented, in the temperature range (793 to 951) K, by the expression:  $\log(p/\text{Pa}) = (12.76 \pm 0.10) - (10940 \pm 200)/(T/\text{K})$ . Treating the vapor pressures by the second and third laws, the sublimation enthalpy of PbF<sub>2</sub>,  $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (225 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$ , was selected. Lead tetrafluoride decomposes according the reaction:  $\text{PbF}_4(\text{s}) \rightarrow \text{PbF}_2(\text{s}) + \text{F}_2(\text{g})$  (a). In the range (596 to 684) K, the temperature dependence of the fluorine pressure above PbF<sub>4</sub>(s) at near unit activity is represented by the expression:  $\log(p/\text{Pa}) = (11.70 \pm 0.20) - (7450 \pm 200)/(T/\text{K})$ . In this temperature range, fluorine is partially dissociated so that, in addition to reaction a, the reaction  $1/2 \text{ PbF}_4(\text{s}) \rightarrow 1/2 \text{ PbF}_2(\text{s}) + \text{F}(\text{g})$  (b) was also studied. The second-law enthalpies at 650 K,  $\Delta H^\circ(650 \text{ K}) = (141 \text{ and } 152) \text{ kJ}\cdot\text{mol}^{-1}$  associated to the reactions a and b, respectively, were obtained with an estimated error of 6 kJ·mol<sup>-1</sup> for both enthalpies. The entropy of PbF<sub>4</sub>(s),  $S^\circ(650 \text{ K}) = (272 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , was also evaluated.

## Introduction

Apart from an old enthalpy value (113 kJ·mol<sup>-1</sup>) associated with the sublimation of PbF<sub>4</sub> estimated by Feber,<sup>1</sup> as reported by Adams et al.,<sup>2</sup> there are apparently no other thermodynamic data on the sublimation of this compound in the literature. As it concerns PbF<sub>2</sub>, the first values of its vapor pressure are old data measured above the molten compound by the boiling point method.<sup>3</sup> The vapor pressure above the solid phase was measured by Nesmeyanov and Iofa<sup>4</sup> using the Knudsen method on the assumption that PbF<sub>2</sub>(g) is the only gaseous species present in the vapor. This compound was mass spectrometrically investigated by Zmbov et al.<sup>5</sup> Contrary to the assumption of Nesmayanov and Iofa,<sup>4</sup> the appearance potentials obtained by the ionization efficiency curves for the shutterable ions show that the molecular species in the vapor above the solid and liquid phases are Pb, PbF, PbF<sub>2</sub>, and PbF<sub>4</sub>. The presence of those species led the authors<sup>5</sup> to hypothesize that PbF<sub>2</sub>(s) sublimates as PbF<sub>2</sub>(g) that partially decomposes according the disproportionation reaction:



and partially reacts with Pb(g) produced by this process according the reaction:



The second-law sublimation enthalpy of PbF<sub>2</sub>(s) was calculated from the slope of the  $\log t^+(\text{PbF}_2)T$  versus  $1/T$  line,  $\Delta_{\text{sub}}H^\circ(1000$

K) =  $238 \pm 17 \text{ kJ}\cdot\text{mol}^{-1}$ , a value comparable with that estimated by Feber,<sup>1</sup>  $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = 249 \text{ kJ}\cdot\text{mol}^{-1}$ . From the previous<sup>4</sup> weight loss data, Zmbov et al.<sup>5</sup> calculated the partial pressures of the observed gaseous species at 988 K and, employing these values, the equilibrium constants and the corresponding third-law enthalpies for the reactions involving PbF<sub>2</sub>(g) (reactions 1 and 2). In the spectrum of a subsequent mass-spectrometric work<sup>6</sup> the presence of PbF<sub>4</sub><sup>+</sup> was not observed, but in addition to Pb<sup>+</sup>, PbF<sup>+</sup>, and PbF<sub>2</sub><sup>+</sup>, small amounts of Pb<sub>2</sub>F<sub>3</sub><sup>+</sup> ion are considered derived from fragmentation of the dimer form, Pb<sub>2</sub>F<sub>4</sub>(g). The authors<sup>6</sup> report that, in the range from (830 to 930) K, the PbF<sub>2</sub>(g) amount in the gaseous phase is about 94 %, the dimer Pb<sub>2</sub>F<sub>4</sub>(g) about 1 %, and PbF(g) and Pb(g), both derived from decomposition reactions, for about 2.5 %, respectively. Temperature dependence of the partial pressures of PbF<sub>2</sub>(g) and Pb<sub>2</sub>F<sub>4</sub>(g) were reported in their work. From the PbF<sub>2</sub>(g) partial pressures reported in the work<sup>6</sup> we have calculated the second-law sublimation enthalpy of this compound,  $\Delta_{\text{sub}}H^\circ(870 \text{ K}) = 182 \text{ kJ}\cdot\text{mol}^{-1}$ . The same authors in a subsequent work<sup>7</sup> confirm that PbF<sub>2</sub> and Pb<sub>2</sub>F<sub>4</sub> are the only species present in the vapor above PbF<sub>2</sub>(s) (the first decidedly the most abundant) and determined the standard enthalpy associated to the sublimation of lead difluoride in PbF<sub>2</sub>(g) by second and third-law methods, [ $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (217 \pm 13) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(225 \pm 8) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively]. Because the absolute pressures determined by the mass-spectrometer work<sup>6,7</sup> were influenced by several parameters (sensitivity mass-spectrometric constant, abundance of the measured isotopic ion intensity, cross section for the electron ionization, fragmentation processes, gain of the electron photo multiplier), the final values may not be correct. In this work more precise absolute total pressures were measured by the torsion method. From the pressure data determined above,

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lead di- and tetra-fluoride thermodynamic data on the sublimation of  $\text{PbF}_2$  and decomposition of  $\text{PbF}_4$  were derived.

## Experimental Section

Some packages of both lead fluorides used in this study were supplied by Aldrich (purity 99.997 % for  $\text{PbF}_2$  and 99 % for  $\text{PbF}_4$ , as stated by the same supplier). The torsion-effusion technique is fully described by Freeman,<sup>8</sup> and the torsion apparatus used in the present study has practically that described in our previous work.<sup>9</sup> In particular the apparatus was suspended from an arm of a vacuum electrobalance (Cahn 1000) to measure the weight loss of a sample during its vaporization. Two conventional torsion cells were used in this study, both made of National Carbon ZT 101 grade graphite, different for the diameter of their effusion orifices, 1 mm and 1.6 mm for the cells A and B, respectively. The cell constants necessary to convert pressure data from the experimental torsion angles were obtained vaporizing very pure zinc and lead, the vapor pressures of which are well-known.<sup>10</sup> For each cell the constant values obtained using both standards were found practically equal, and the final value used for the pressure calculation, checked in runs carried out during the study of the compounds, was found reproducible within about 5 %. This uncertainty produces a very negligible shift in the intercepts of the obtained  $\log p$  versus  $1/T$  equations. Some values of the equilibrium vapor pressure of lead and zinc were also measured to test for any systematic errors in the measurements. From these pressures the second- and third-law standard sublimation enthalpies of zinc and lead were determined. Their average values,  $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (130 \pm 2) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(184 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$ , respectively, agree well with that selected by the IVTANTHERMO database<sup>10</sup> ((128.8 and 184.7)  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively). Both studied compounds are hygroscopic and easily hydrolyzed and oxidized when exposed to air so that the packages were opened and the torsion cells filled with the samples in a efficient drybox in an argon atmosphere. Moreover, both effusion holes of the cells were previously closed employing small pins of naphthalene, pins that quickly sublime when the cell was placed under vacuum in the torsion apparatus. This procedure excludes completely the contact of the sample with air. In each vaporization run the torsion angles and then the vapor pressures were measured randomly in both ascending and descending temperatures (though in the tables they are reported as ascending), and at the beginning and end of each run, the measurements were made at approximately equal temperatures.

**$\text{PbF}_2$ .** The vapor pressures of solid  $\text{PbF}_2$  were measured in four runs employing both torsion cells and using always fresh samples from new packages. The results are reported in Table 1 and Figure 1. The experimental data were treated by a linear least-squares method to obtain, for each run, the temperature dependence of the vapor pressure as the  $\log p$  versus  $1/T$  equation. The equations so obtained are reported in the same Table 1. From the average of their slopes and intercepts, the final equation representative of the vapor pressure above solid  $\text{PbF}_2$  in the temperature range (793 to 951) K was selected:

$$\log(p/\text{Pa}) = (12.76 \pm 0.10) - (10940 \pm 200)/(T/\text{K}) \quad (3)$$

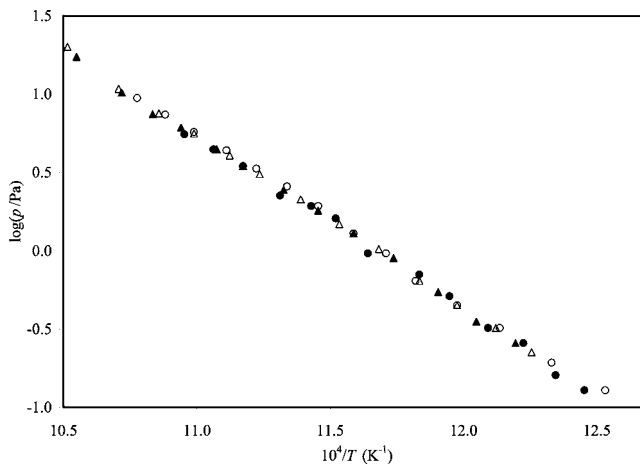
where the associated errors are estimated.

This equation presents a major slope rather than other ones reported in the literature (see Table 2 and Figure 2). The vapor pressures are slightly higher than those reported by Nesmeyanov and Iofa<sup>4</sup> but are comparable with those measured by Korenev et al.<sup>7</sup> From the slope of eq 3, the second-law sublimation

**Table 1. Torsion Total Vapor Pressures of Solid  $\text{PbF}_2$  and Their Temperature Dependence**

run 2 (cell B)		run 3 (cell B)		run 5 (cell A)	
$T/\text{K}$	$\log(p/\text{Pa})$	$T/\text{K}$	$\log(p/\text{Pa})$	$T/\text{K}$	$\log(p/\text{Pa})$
798	-0.89	793	-1.02	803	-0.89
811	-0.72	803	-0.89	816	-0.65
824	-0.49	810	-0.79	825	-0.49
835	-0.35	818	-0.59	835	-0.35
846	-0.19	827	-0.49	845	-0.19
854	-0.02	837	-0.29	856	0.01
863	0.11	845	-0.15	867	0.17
873	0.28	859	-0.02	878	0.33
882	0.41	868	0.21	890	0.49
891	0.52	875	0.28	899	0.61
900	0.64	884	0.35	910	0.75
910	0.76	895	0.54	921	0.88
919	0.87	904	0.65	934	1.03
928	0.97	913	0.74	951	1.30
run 6 (cell A)		preliminary run <sup>a</sup>			
808	-0.79	833	-0.41		
820	-0.59	841	-0.29		
830	-0.45	858	-0.02		
840	-0.26	867	0.11		
852	-0.05	876	0.25		
863	0.11	886	0.41		
873	0.25	905	0.64		
883	0.39	912	0.73		
895	0.54	931	0.98		
903	0.65				
914	0.79				
923	0.87				
933	1.01				
948	1.24				
run 2	$\log(p/\text{Pa}) = (12.76 \pm 0.14) - (10920 \pm 123)/(T/\text{K})^b$				
run 3	$\log(p/\text{Pa}) = (12.72 \pm 0.20) - (10909 \pm 173)/(T/\text{K})^b$				
run 5	$\log(p/\text{Pa}) = (12.86 \pm 0.11) - (11017 \pm 95)/(T/\text{K})^b$				
run 6	$\log(p/\text{Pa}) = (12.71 \pm 0.15) - (10898 \pm 128)/(T/\text{K})^b$				

<sup>a</sup> These values are measured above the residue of the vaporization of  $\text{PbF}_4(\text{s})$  in a preliminary run (see text and Figure 3). <sup>b</sup> The associated errors are the standard deviations from the least-squares fit.



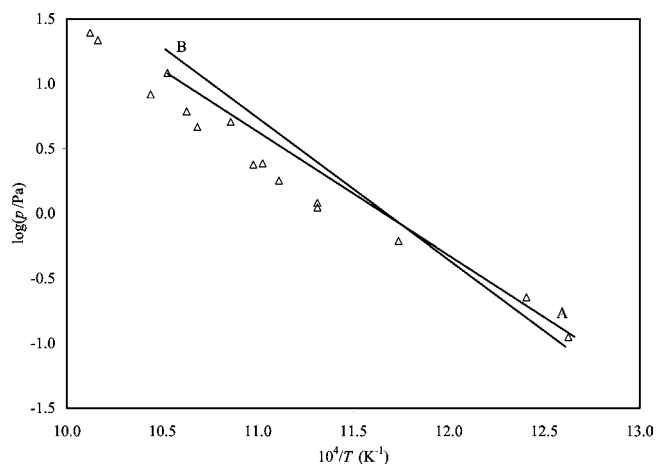
**Figure 1.** Torsion total vapor pressures of  $\text{PbF}_2(\text{s})$ .  $\circ$ , run 2;  $\bullet$ , run 3;  $\Delta$ , run 5;  $\blacktriangle$ , run 6.

enthalpy of  $\text{PbF}_2$  is  $\Delta_{\text{sub}}H^\circ(870 \text{ K}) = (209 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ , and from this an enthalpy at 298 K was calculated,  $\Delta_{\text{sub}}H^\circ(298 \text{ K}) = (216 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$  using the enthalpic increments,  $H^\circ(870 \text{ K}) - H^\circ(298 \text{ K})$ , for the solid and the gaseous phase reported by the IVTANTHERMO database,<sup>10</sup> Considering the dimer amount present in the vapor to be negligible, the total vapor pressures from eq 3 were considered equal to the partial pressures of  $\text{PbF}_2(\text{g})$  and used to evaluate, at two temperatures at the approximated extremes of the experimental range (800

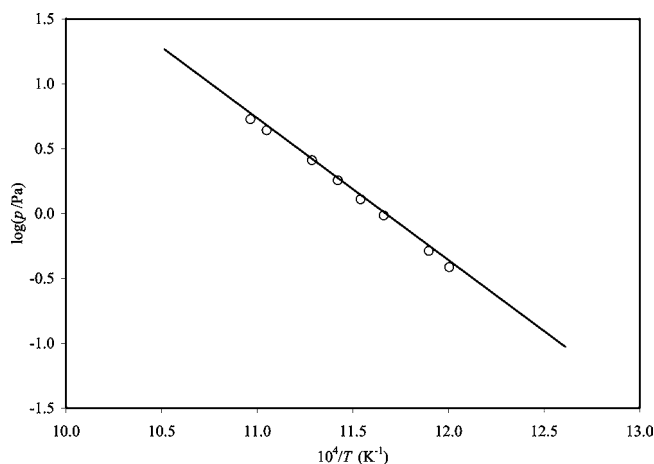
**Table 2. Total Vapor Pressures of PbF<sub>2</sub>**

author	method	$\Delta T$		phase	$\log(p/\text{Pa}) = A - B/(T/\text{K})$	
		K	K		A	B
von Wartenberg and Bosse <sup>3</sup>	boiling point	1078–1289		liq.	10.516	8627
Nesmeyanov and Iofa <sup>4</sup>	Knudsen	792–988		sol.	10.475	9096
Korenev et al. <sup>6</sup>	mass spectr.	790–950		sol.	11.10	9520
Korenev et al. <sup>7</sup>	mass spectr.	830–930		sol.	11.66 <sup>a</sup>	9976 <sup>a</sup>
this work	torsion-effusion	793–951		sol.	12.76 ± 0.10	10940 ± 200

<sup>a</sup> Calculated by us from the partial pressures of PbF<sub>2</sub>(g) and Pb<sub>2</sub>F<sub>4</sub>(g) reported in the work.<sup>7</sup>



**Figure 2.** Comparison of the torsion total vapor pressures of PbF<sub>2</sub>(s). Δ, Nesmeyanov and Iofa;<sup>4</sup> A, Korenev et al.;<sup>6,7</sup> B, this work.



**Figure 3.** Vapor pressures measured above the residue of PbF<sub>4</sub> (see text). The line represents eq 3.

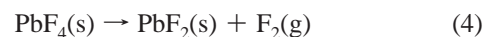
**Table 3. Third-Law Standard Sublimation Enthalpies of PbF<sub>2</sub><sup>a</sup>**

T	p	fef/J·K <sup>-1</sup> ·mol <sup>-1</sup>					
		PbF <sub>2</sub> solid		PbF <sub>2</sub> gas		$\Delta_{\text{sub}}H^\circ(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
		A	B	A	B	A	B
800	0.124	140.0	135.6	311.9	310.8	228.1	230.6
950	17.88	147.5	146.7	316.2	317.0	227.1	230.0

<sup>a</sup>A and B are referred to values obtained by using free energy function (fef) reported by Pankratz<sup>11</sup> and IVTANTHERMO database,<sup>10</sup> respectively.

to 950) K, two third-law values of the standard sublimation enthalpy of PbF<sub>2</sub>. The free energy functions (fef),  $[G^\circ(T) - H^\circ(298\text{ K})]/T$ , for solid and gaseous compounds used for these calculations were taken from the IVTANTHERMO database<sup>10</sup> and from Pankratz.<sup>11</sup> The fef of the solid PbF<sub>2</sub> found in the literature<sup>10,11</sup> are different (see Table 3) because they are calculated using different values of the standard entropy,  $S^\circ(298\text{ K}) = (110.5^{10}$  and  $106.0^{11}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Both third-law sublimation standard enthalpies calculated at (800 and 950) K using the fef from refs 10 and 11 present a small descending temperature trend. It is difficult to choose between their values, so by giving equal weight to these values, we propose  $(229 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$  as the third-law result. This value is higher than that obtained by the second-law method  $(216 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$  and than those reported by Nesmeyanov and Iofa<sup>4</sup> [ $\Delta_{\text{sub}}H^\circ(0\text{ K}) = (207$  and  $223) \text{ kJ}\cdot\text{mol}^{-1}$  from the second- and third-law methods, respectively] and by Koronev et al.<sup>6,7</sup> [ $182 \text{ kJ}\cdot\text{mol}^{-1}$  from the second-law<sup>6</sup> method and  $[(217 \pm 13)$  and  $(225 \pm 8)] \text{ kJ}\cdot\text{mol}^{-1}$  from the second- and third-law<sup>7</sup> methods, respectively] but lower with that proposed by Zmbov et al.<sup>5</sup> at 1000 K,  $\Delta_{\text{sub}}H^\circ(1000\text{ K}) = (238 \pm 17) \text{ kJ}\cdot\text{mol}^{-1}$  [ $\Delta_{\text{sub}}H^\circ(298\text{ K}) = (245 \pm 17) \text{ kJ}\cdot\text{mol}^{-1}$ , employing the enthalpic increments reported in the literature<sup>10</sup>]. On this basis we believe and propose  $225 \text{ kJ}\cdot\text{mol}^{-1}$  as the more reliable value of the sublimation enthalpy of PbF<sub>2</sub> with an estimated error of  $5 \text{ kJ}\cdot\text{mol}^{-1}$ .

**PbF<sub>4</sub>.** Because apparently no data on the vaporization behavior of this compound were found in the literature, a run was carried out to have preliminary information. Heating a small amount of a sample, after the sublimation of the pins of naphthalene at room temperature and of a very small amount of impurity ( $\sim 0.5\%$  of the sample) at about (330 to 350) K, heating the cell at 650 K, the vapor pressures were detectable, but their values, going on the sublimation of the sample, were found to be poorly reproducible. When about 15 % of the employed sample was vaporized, the residue does not present appreciable vapor pressure. At 800 K the vapor pressures were found again to be appreciable and the values comparable with those measured above PbF<sub>2</sub>(s). This vaporization behavior and the amount vaporized in the first step suggested that, when the sample was heated at about 650 K, PbF<sub>4</sub> decomposes according the reaction:



so that at the end of this step the residue was practically PbF<sub>2</sub>.

In light of this hypothesis, a new run was carried out employing a large amount of sample. The vapor pressures measured in the first step of the sublimation at about 650 K were found to be reproducible the first time, but going on the vaporization, their values tend to decrease. This is probably connected to the decrease in the PbF<sub>4</sub> activity for the formation, on its surface, of a PbF<sub>2</sub> film produced by decomposition reaction 4. Heating the sample at about 800 K, the values were found decidedly well reproducible when ascending and descending the temperatures and practically equal to the vapor pressures of PbF<sub>2</sub> (see Figure 3). These values were included in Table 1 but not used for the calculation of eq 3. All of the subsequent experiments were carried out employing a large amount of fresh compound ( $\sim 1 \text{ g}$ ), and the torsion measurements were stopped when about 5 % of the original weight was

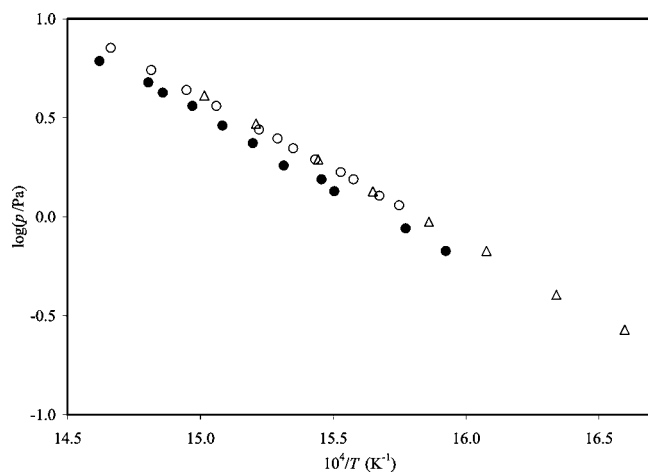
**Table 4. Torsion Total Vapor Pressures of Solid PbF<sub>4</sub> and Their Temperature Dependence**

run 2 (cell A)		run 4 (cell A)		run 5 (cell B)	
T/K	log(p/Pa)	T/K	log(p/Pa)	T/K	log(p/Pa)
635	0.06	628	-0.17	603	-0.57
638	0.11	634	-0.06	612	-0.39
644	0.23	645	0.13	622	-0.17
648	0.29	647	0.19	631	-0.03
654	0.40	653	0.26	639	0.11
664	0.56	658	0.37	648	0.29
669	0.64	663	0.46	657	0.47
675	0.74	668	0.56	666	0.61
682	0.85	673	0.63	670	0.68
		676	0.68		
		684	0.79		

run	log(p/Pa) = (11.56 ± 0.05) - (7306 ± 34)/(T/K) <sup>a</sup>
run	log(p/Pa) = (11.78 ± 0.16) - (7510 ± 107)/(T/K) <sup>a</sup>
run	log(p/Pa) = (11.89 ± 0.13) - (7512 ± 83)/(T/K) <sup>a</sup>

<sup>a</sup> The associated errors are the standard deviations from the least-squares fit.



**Figure 4.** Torsion total vapor pressures of PbF<sub>4</sub>. ○, run 2; ●, run 4; △, run 5.

sublimed to measure vapor pressures above PbF<sub>4</sub>(s) at near unit activity, when the amount of PbF<sub>2</sub> produced during the decomposition of the sample was negligible. The total vapor pressures above PbF<sub>4</sub>(s) are reported in Table 4 and Figure 4. The experimental data of each run were treated as usual by the linear least-squares method to represent the temperature dependence of the vapor pressures as the log *p* versus 1/*T* equation. Slopes and intercepts of the obtained equations are reported in the same Table 4. Weighting the reported slopes and intercepts proportionally to the corresponding experimental points, the following final equation representative of fluorine pressures

above solid PbF<sub>4</sub> in the temperature range (603 to 684.0) K was selected:

$$\log(p/\text{Pa}) = (11.75 \pm 0.20) - (7450 \pm 200)/(T/\text{K}) \quad (5)$$

where the associated uncertainties are estimated.

In the covered temperature range fluorine is partially dissociated so that the second-law enthalpy value derived from the slope of eq 5,  $\Delta H(650 \text{ K}) = (142 \pm 4) \text{ kJ} \cdot \text{mol}^{-1}$ , is referred to the vaporization of one mole of the F<sub>2</sub>(g) and F(g) mixture. From the total vapor pressures of eq 5 and the temperature dependence of the equilibrium constants of the dissociation reaction: F<sub>2</sub>(g) = 2F(g), given in the IVTANTHERMO database,<sup>10</sup> [log(*p*/kPa) = 8.48 - 8511(K/*T*)], the F(g) and F<sub>2</sub>(g) partial pressures above PbF<sub>4</sub> at near unity activity were determined at (600, 650, and 700) K. From the calculated F(g) and F<sub>2</sub>(g) partial pressures, their temperature dependence were opportunely evaluated as log *p* versus 1/*T* equations. From the slopes of these equations the second-law enthalpies associated with reactions 4 and 6:



were determined,  $\Delta_{\text{sub}}H^\circ(650 \text{ K}) = 141 \text{ kJ} \cdot \text{mol}^{-1}$  and  $152 \text{ kJ} \cdot \text{mol}^{-1}$ , respectively, with an error estimated as  $\pm 6 \text{ kJ} \cdot \text{mol}^{-1}$  for both enthalpies. Because no thermodynamic data of solid PbF<sub>4</sub> are found in the literature, the entropy of this compound was calculated from  $\Delta S^\circ(T)$  of reactions 4 and 6 obtained by the Gibbs-Helmholtz equation:  $\Delta S^\circ(T) = R \ln p + \Delta H^\circ(T)/T$ , where *p* are the partial pressures of F<sub>2</sub> or F. The corresponding entropies for PbF<sub>2</sub>(s), F<sub>2</sub>(g), and F(g) were those selected by the IVTANTHERMO database.<sup>10</sup> The results are in Table 5. The entropy values of PbF<sub>4</sub>(s) obtained from thermodynamic data of the reactions 4 and 6 agree, but their values at the middle temperature 650 K, (273.0 and 272.3) J·K<sup>-1</sup>·mol<sup>-1</sup>, are higher than those of other solid tetrafluorides as TiF<sub>4</sub> [ $\Delta S^\circ(650 \text{ K}) = 184 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ] and ZrF<sub>4</sub> [ $\Delta S^\circ(650 \text{ K}) = 124 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ] as reported by Pankratz.<sup>11</sup> A critical analysis leads to the conclusion that the errors (i) in the absolute vapor pressures measured above PbF<sub>4</sub>(s), (ii) in the temperature dependence of the dissociative equilibrium constant of F<sub>2</sub>(g) reported by the IVTANTHERMO database<sup>10</sup> and then in the derived F<sub>2</sub>(g) and F(g) partial pressures, (iii) in the second law enthalpies associated to reactions 4 and 6, and (iv) in the entropies of PbF<sub>2</sub>(s) and of gaseous species could produce an overestimated uncertainty of about  $15 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Even taking into account this uncertainty, we believe that the value  $\Delta S^\circ(650 \text{ K}) = 272 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for solid PbF<sub>4</sub> must be considered as an upper limit.

**Table 5. Entropy Values of Solid PbF<sub>4</sub>**

<i>T</i> K	PbF <sub>4</sub> (s) → PbF <sub>2</sub> (s) + F <sub>2</sub> (g)					
	$-R \ln p(\text{F}_2)$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta H^\circ(T)$ kJ·mol <sup>-1</sup>	$\Delta S^\circ(T)$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S^\circ(T) \text{ PbF}_2(\text{s})^a$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S^\circ(T) \text{ F}_2(\text{g})^a$ J·K <sup>-1</sup> ·mol <sup>-1</sup>	$S^\circ(T) \text{ PbF}_4(\text{s})$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
600	109.3	141.4	126.4	162.5	226.0	262.1
650	89.5	141.4	126.4	170.6	228.8	273.0
700	75.6	141.4	126.4	179.8	231.4	284.8

<i>T</i> K	1/2PbF <sub>4</sub> (s) → 1/2PbF <sub>2</sub> (s) + F(g)					
	$-R \ln p(\text{F})$	$\Delta H^\circ(T)$	$\Delta S^\circ(T)$	$S^\circ(T) \text{ PbF}_2(\text{s})^a$	$S^\circ(T) \text{ F}(\text{g})^a$	$S^\circ(T) \text{ PbF}_4(\text{s})$
600	128.4	152.2	125.2	162.5	174.6	261.3
650	107.1	152.2	125.2	170.6	176.0	272.2
700	92.2	152.2	125.2	179.8	177.6	284.7

<sup>a</sup> From the IVTANTHERMO database.<sup>10</sup>

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