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Vapor Pressures and Sublimation Enthalpies of Copper Difluoride and Silver (I, II) Fluorides by the Torsion−Effusion Method

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The vapor pressures in equilibrium over CuF_2, AgF_2, and AgF were measured by the torsion−effusion method. CuF_2 and AgF vaporized congruently. The temperature dependences of the vapor pressure of these compounds were found to fit the following equations: CuF_2(s), $\log(p/\text{kPa}) = (9.78 \pm 0.10) - (12690 \pm 100)(T/\text{K})$ (from (881 to 1051) K) and AgF(l), $\log(p/\text{kPa}) = (7.83 \pm 0.20) - (10700 \pm 300)(T/\text{K})$ (from (880 to 1074) K). Treating the vapor pressure data by the second- and third-law methods, the standard sublimation enthalpies of these compounds, $\Delta_{\text{sub}}H°(298\ \text{K}) = (260 \pm 4)\ \text{kJ}\cdot\text{mol}^{-1}$ and $(240 \pm 10)\ \text{kJ}\cdot\text{mol}^{-1}$ for CuF_2 and AgF, respectively, were calculated. In the covered temperature range (from (655 to 776) K), AgF_2 decomposes into fluorine and solid or molten AgF so that two temperature dependences of the fluorine pressure above this compound in equilibrium with AgF(s) and AgF(l), $\log(p/\text{kPa}) = (11.39 \pm 0.30) - (11060 \pm 300)(T/\text{K})$ (from (655 to 706) K) and $\log(p/\text{kPa}) = (10.27 \pm 0.20) - (10220 \pm 200)(T/\text{K})$ (from (710 to 776) K), respectively, were determined. At these temperatures, fluorine is partially decomposed so that two partial molar standard enthalpies of AgF_2 associated to the sublimation reactions, $AgF_2(s) \rightarrow AgF(s) + F(g)$ and $AgF_2(s) \rightarrow AgF(s) + \frac{1}{2}F_2(g)$, $\Delta_{\text{sub}}H°(298\ \text{K}) = (195 \pm 10)\ \text{kJ}\cdot\text{mol}^{-1}$ and $(125 \pm 5)\ \text{kJ}\cdot\text{mol}^{-1}$, were calculated.

Introduction

Mass spectrometric studies of CuF_2[1,2] have established CuF_2(g) as the major species in its saturated vapor so that this compound sublimes without decomposition. Its vapor pressure was measured by using different cell materials: a MgO Knudsen effusion cell lined with a tantalum sheet was used by Kent et al.,[1] while Ehlert and Wang[2] vaporized CuF_2 in neutral conditions using platinum and CaF_2 cells and in reducing conditions from a copper cell. The sublimation pressures measured by the platinum cell by Ehlert and Wang[2] are lower than those reported previously by Kent et al.[1] The pressures obtained using the CaF_2 cell are decidedly lower, but this is also due to interaction with the cell. The pressures measured using the copper cell pertain to equilibria of reactions involving Cu_nF_n(g) (n from 1 to 5) gaseous species. Regarding the silver fluorides, apparently only a set of vapor pressures of silver monofluoride measured by a mass spectrometer by Zmbov and Margrave[3] have been reported in the literature.

In the present work, absolute vapor pressures above CuF_2, AgF_2, and AgF are determined by the torsion−effusion method. The torsion assembly was coupled with a thermobalance so that in the same experiments measurements of the weight loss rate of the sample were made to determine its vapor pressure also by the Knudsen−effusion technique.[4,5] From second- and third-law treatment of the vapor pressure data, the standard sublimation enthalpies of these compounds were evaluated.

Experimental Section

Anhydrous CuF_2, AgF_2, and AgF, 98 %, 98 %, and 99.9 % pure, respectively, supplied by Aldrich were used. The purities are those declared by the supplier. The vapor pressures were measured by using a torsion−effusion apparatus substantially the same as described in detail elsewhere.[6] To measure the sublimation rate of the sample, the assembly is suspended from an arm of a Chan 1000 vacuum electrobalance.

Concerning the material of the cells, preliminary experiments showed that at high temperatures CuF_2 reacted with tantalum and pyrophyllite cells. No reaction was observed when a graphite cell with and without a platinum foil as liner was used. AgF_2 was vaporized from two graphite cells, cells A and B, having different diameter effusion holes of (0.5 and 1.8) mm, respectively. AgF was vaporized from cell B lined with platinum foil. All samples were handled and loaded into the torsion cell in a drybox with the effusion holes plugged with a naphthalene pin and rapidly placed under vacuum in the torsion assembly to prevent interaction with moisture. As usual, the cell constant values necessary to convert torsion angle and weight loss of the cell into pressure values were determined by vaporizing standards with well-known vapor pressures.[7] In this work, very pure elemental lead was used as standard. Both torsion and Knudsen constant values, checked in separate experiments carried out during the study of each compound, were found reproducible within about 10 % of their average values. Practically, the vapor pressures of each run were calculated by using the torsion constant value evaluated in the next run carried out with lead.

Experimental Results. A. CuF_2. The vaporization of CuF_2 was carried out in eight runs using cell A. Despite the declared purity, in the first step of the vaporization of fresh samples, the

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Table 1. Torsion Vapor Pressures of CuF_2

run 2		run 4		run 5		run 6	
graphite		graphite		graphite (Pt)		graphite	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
886	4.53	881	4.66	886	4.53	897	4.36
901	4.29	895	4.36	897	4.36	908	4.23
914	4.09	906	4.23	908	4.23	919	3.99
929	3.88	915	4.05	915	4.13	930	3.83
943	3.69	924	3.93	922	3.99	940	3.72
953	3.55	932	3.79	930	3.88	949	3.60
959	3.43	942	3.69	939	3.72	959	3.45
969	3.31	952	3.55	948	3.60	969	3.28
976	3.21	960	3.42	955	3.51	978	3.18
986	3.09	969	3.30	964	3.37	988	3.08
993	2.99	979	3.18	973	3.26	996	2.96
1003	2.91	986	3.08	983	3.13	1005	2.85
1013	2.74	996	2.95	992	3.01	1014	2.73
1023	2.61	1005	2.84	1002	2.89	1024	2.61
1032	2.51	1015	2.72	1011	2.77	1033	2.50
		1025	2.59	1020	2.66	1051	2.29
				1030	2.58		

run 8		run 10		run 11		run 13	
graphite (Pt)		graphite		graphite (Pt)		graphite (Pt)	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
902	4.29	896	4.43	900	4.36	896	4.36
911	4.18	913	4.13	908	4.23	903	4.23
922	4.02	925	3.96	918	4.13	909	4.09
928	3.93	939	3.75	931	3.96	912	4.05
934	3.83	952	3.58	944	3.72	921	3.93
941	3.75	965	3.39	956	3.55	930	3.79
948	3.63	973	3.29	969	3.39	940	3.66
956	3.53	982	3.18	984	3.17	950	3.51
965	3.42	990	3.07	989	3.10	961	3.36
974	3.29	999	2.96	998	2.99	970	3.23
982	3.18	1008	2.84	1007	2.87	979	3.13
990	3.07	1020	2.70	1016	2.76		
998	2.95			1025	2.65		
1006	2.85						
1015	2.75						
1025	2.61						

vapor pressures were not well reproducible until about 4 % of the original sample was vaporized. This initial part of the vaporization was considered to be due to volatile impurities. Going on, the pressure data were found decidedly well reproducible, and the vapor pressure data obtained by using the cell lined with platinum are in excellent agreement with those obtained without a liner. In Table 1 and Figure 1, the experimental results are reported. The log p versus $1/T$ equations obtained by a least-squares analysis of the data of each run are summarized in Table 2. By weighting slopes and intercepts of these equations proportionally to the number of points of each run, the following final equation representative of the temperature dependence of the vapor pressure above CuF_2 in the covered temperature range (881 to 1051) K was selected

$$\log(p/\mathrm{kPa}) = (9.78 \pm 0.10) - (12690 \pm 100)(T/\mathrm{K}) \quad (1)$$

The associated errors were estimated.

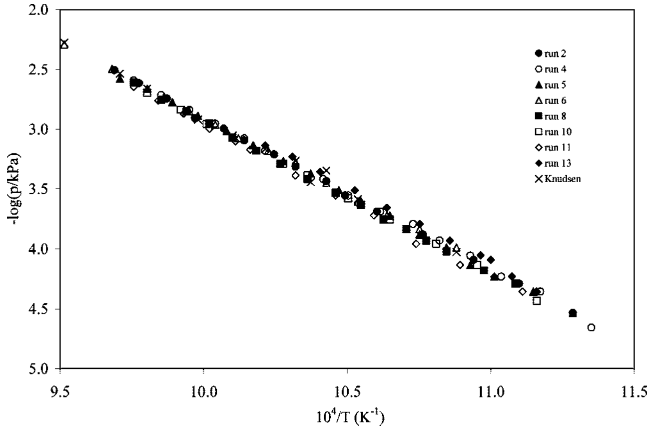

Figure 1. Torsion vapor pressures of CuF_2.

In each run, some vapor pressure values were also determined by the Knudsen−effusion method measuring, in isothermal conditions, the weight loss rate of the sample ($\Delta m/\Delta t$). The results are reported in Table 3 from the appropriate equations[4,5] on the assumption that the monomeric species CuF_2(g) is the only species present in the vapor phase. The absolute vapor pressures so determined are decidedly in agreement with those measured simultaneously by the torsion−effusion method, and this was taken as a check of the assumption. The vapor pressures measured in the present work are compared, in Table 4, with those reported in the literature. Our data are lower than those measured by Kent et al.[1] and comparable, even if with a lower slope, with those measured by Ehlert and Wang[2] (see Figure 2).

A critical analysis of the results led us to consider our absolute vapor pressure data more reliable than those determined in the previous mass spectrometric measurements[1,2] considering the instrumental uncertainties inherent to this method (in particular, estimation of the ionization cross sections and multiplier gains for the species involved).

Table 2. Temperature Dependence of Torsion Vapor Pressures and Sublimation Enthalpies of CuF_2[a]

			ΔT		$\log(p/\text{kPa}) = A - B/(T/\text{K})$		$\Delta_{\text{sub}}H(T)^b$	$\Delta_{\text{sub}}H°(298\text{ K})^c$
comp.	run	cell	K	no. of points	A^b	B^b	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
CuF_2	2	graphite	886 to 1032	15	9.71 ± 0.08	12623 ± 80	241.6 ± 1.5	257 ± 2.5
	4	graphite	881 to 1025	16	9.78 ± 0.11	12679 ± 105	242.7 ± 2.0	258 ± 3.0
	5	graphite (Pt)	886 to 1030	17	9.76 ± 0.10	12673 ± 94	242.6 ± 1.8	258 ± 3.0
	6	graphite	897 to 1051	16	9.75 ± 0.11	12654 ± 105	242.2 ± 2.0	258 ± 3.0
	8	graphite (Pt)	902 to 1025	16	9.77 ± 0.09	12709 ± 85	243.2 ± 1.6	259 ± 2.5
	10	graphite	896 to 1020	12	9.73 ± 0.08	12669 ± 79	242.5 ± 1.5	258 ± 2.5
	11	graphite (Pt)	900 to 1025	13	9.81 ± 0.14	12773 ± 132	244.5 ± 2.5	260 ± 3.5
	13	graphite (Pt)	896 to 979	11	9.94 ± 0.19	12784 ± 179	244.7 ± 3.4	259 ± 4.5
							average	259 ± 4

[a] In the runs 1, 3, 7, 9, and 12, pure lead was vaporized. [b] The quoted errors are standard deviations. [c] The errors are obtained allowing about ± 1 $\text{kJ}\cdot\text{mol}^{-1}$ as a result of the correction to 298 K.

Table 3. Knudsen Vapor Pressures of CuF_2 Compared with the Torsion Data

	T	a	$\Delta t \pm 20$	$\Delta m \pm 0.1$	pressures (in kPa)		
run	K	rad	s	mg	Knudsen[a]	torsion[b]	torsion[c]
2	959	0.073	8400	7.5	$4.52\cdot10^{-4}$	$3.68\cdot10^{-4}$	$3.49\cdot10^{-4}$
2	969	0.096	5400	5.8	$5.46\cdot10^{-4}$	$4.85\cdot10^{-4}$	$4.78\cdot10^{-4}$
4	979	0.131	3720	5.0	$6.87\cdot10^{-4}$	$6.62\cdot10^{-4}$	$6.50\cdot10^{-4}$
5	964	0.084	6600	4.7	$3.61\cdot10^{-4}$	$4.27\cdot10^{-4}$	$4.09\cdot10^{-4}$
5	1002	0.256	3000	7.0	$1.21\cdot10^{-3}$	$1.29\cdot10^{-3}$	$1.29\cdot10^{-3}$
5	1030	0.524	1800	10.0	$2.91\cdot10^{-3}$	$2.65\cdot10^{-3}$	$2.85\cdot10^{-3}$
6	919	0.020	8400	1.6	$9.44\cdot10^{-5}$	$1.03\cdot10^{-4}$	$9.26\cdot10^{-5}$
6	949	0.049	11400	5.9	$2.61\cdot10^{-4}$	$2.50\cdot10^{-4}$	$2.53\cdot10^{-4}$
6	1051	1.012	840	8.4	$5.30\cdot10^{-3}$	$5.12\cdot10^{-3}$	$5.02\cdot10^{-3}$
8	990	0.169	5400	9.3	$8.85\cdot10^{-4}$	$8.53\cdot10^{-4}$	$9.06\cdot10^{-4}$
10	1020	0.399	2400	10.0	$2.17\cdot10^{-3}$	$2.02\cdot10^{-3}$	$2.16\cdot10^{-3}$

[a] Calculated considering $CuF_2(g)$ as the only gaseous species in the vapor. [b] Calculated using the torsion angle measured during the weight loss of the sample. [c] Calculated from eq 1.

Table 4. Comparison of the Vapor Pressures and Sublimation Enthalpy of CuF_2

			$\log(p/\text{kPa}) = A - B/(T/\text{K})$		$\Delta_{\text{sub}}H°(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$		
ref	method	$\Delta T/\text{K}$	A	B	II law	III law	selected
1	Knudsen−mass spectr.	897 to 1026	10.59 ± 0.14	13000 ± 130	263 ± 3 264[a]	267 ± 4 253[a]	267 ± 4
2	Knudsen−mass spectr.	874 to 1005	10.67 ± 0.16	13586 ± 146	276 ± 4 275[a]	272 ± 2 263[a]	272 ± 2
this work	torsion	881 to 1051	9.78 ± 0.10	12690 ± 300	258 ± 4	261 ± 1	260 ± 2

[a] Recalculated by using the vapor pressure reported in the work and the IVTANTHERMO[9] database thermodynamic parameters.

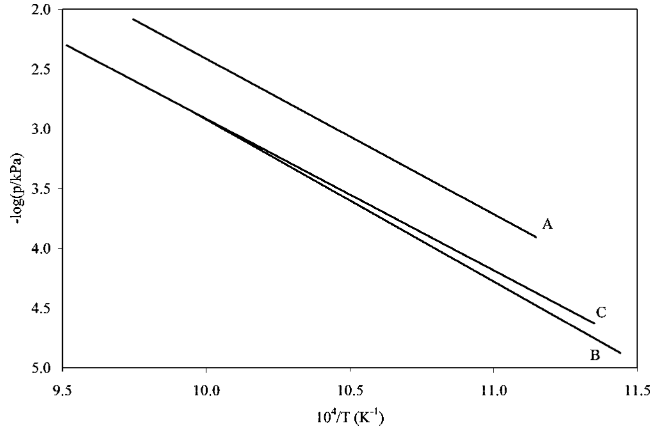

Figure 2. Comparison of the vapor pressure of CuF_2. A, ref 1; B, ref 2; C, this work.

B. AgF_2 and AgF. In a preliminary experiment, the vaporization of AgF_2 was carried out by using a graphite cell. After an initial sublimation of a very small amount of the sample (about 0.2 %) at low temperatures (~ 450 K) probably due to volatile impurities, in a first short step (~(650 to 700) K), the vapor pressure values were found to be well reproducible. When about (4 to 5) % of the original sample weight was vaporized, the vapor pressure became no longer reproducible and decreased, initially at a slow rate and progressively at a more rapid rate, until their values were not measurable by the torsion assembly. At the end of this first step, the sample had vaporized about 15 % of its original weight. With increasing temperature, at about 870 K, the vapor pressure of the residue was again detectable, but after the first points the values were not reproducible. The few pressure values were found to be approximately comparable with those measured by Zmbov and Margrave[3] above AgF. This observation and the weight loss of the sample after the first vaporization step led us to hypothesize that $AgF_2(s)$ decomposes to solid or molten AgF, considering its melting point (708 K), and fluorine. The increase of molten AgF on the AgF_2 surface produced a decrease of its activity, and this justifies the decrease in the vapor pressures observed in the first step of the vaporization. The second step of the preliminary experiment was stopped when the pressures suddenly dropped rapidly. When the torsion cell was open, small drops of practically pure silver, as determined by SEM analysis, were observed at the bottom and on the inner walls. In our experiment, in contrary to the previous one[3] in which the compound was studied in a platinum cell, AgF in contact with the graphite cell decomposed partially taking into account the amount of silver produced and evaluated by weighing the empty cell at the end of the experiment.

Table 5. Torsion Total Vapor Pressures of AgF_2 Measured by Using the Cell B Considering the Sublimation Reaction $AgF_2(s) \rightarrow AgF(s) + xF(g) + (1 - x)/2F_2(g)$

run 2		run 3		run 5		run 6		run 8	
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	$-\log(p/\text{kPa})$
655	5.44	656	5.44	658	5.44	663	5.31	657	5.61
665	5.21	663	5.31	663	5.31	672	5.07	663	5.44
673	5.01	672	5.01	670	5.14	675	4.96	668	5.31
680	4.83	679	4.83	677	4.91	678	4.87	673	5.14
685	4.71	686	4.71	684	4.77	681	4.80	678	5.01
689	4.61	689	4.61	688	4.66	685	4.71	684	4.91
693	4.53	693	4.53	695	4.50	689	4.61	689	4.77
698	4.44	696	4.47	701	4.41	694	4.53	695	4.66
701	4.36	700	4.38	706	4.31	700	4.41	699	4.57
705	4.29	704	4.31			703	4.36		

Table 6. Torsion Vapor Pressures of AgF_2 Measured by Using the Cell A Considering the Sublimation Reaction $AgF_2(s) \rightarrow AgF(l) + xF(g) + (1 - x)/2F_2(g)$

run 10		run 11		run 13		run 15		run 17	
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	$-\log(p/\text{kPa})$
711	4.05	710	4.21	711	4.12	713	4.09	714	3.98
716	3.93	714	4.12	716	4.02	720	3.98	721	3.85
724	3.83	719	4.02	719	3.94	729	3.79	727	3.70
739	3.51	728	3.78	726	3.79	732	3.68	733	3.62
750	3.30	736	3.72	728	3.77	737	3.61	739	3.50
757	3.18	745	3.50	733	3.68	742	3.53	745	3.40
768	2.99	753	3.39	739	3.58	747	3.44	751	3.28
776	2.87	762	3.20	744	3.48	752	3.37	757	3.17
		769	3.10						

Therefore, the vapor effused in this step was constituted by a gaseous mixture. To avoid this decomposition, the vaporization of AgF_2 was carried out, in a second preliminary experiment, using the graphite cell lined with platinum. Now the vapor pressures measured in the first vaporization step of AgF_2 were found not to be reproducible and were decidedly lower than those measured without platinum, while those measured in the second step above the "residue" were found reproducible until all the sample was vaporized. The pressure values were comparable with those reported by Zmbov and Margrave.[3] At the end of the experiment, no silver was observed in the cell, but the platinum liner was found to be corroded. In the first step, fluorine due to the decomposition of AgF_2 reacted with the platinum liner producing probably solid PtF_4 and a volatile fraction, $PtF_6(g)$, as observed by Weinstock et al.;[8] therefore, the pressures that were not reproducible were not significant. When AgF_2 was completely decomposed in AgF, the vapor pressures measured in the second step referred to the congruent vaporization of molten AgF. As a consequence of these observations, AgF_2 and AgF were studied in separate experiments, AgF_2 using the graphite cells without the platinum liner and AgF using the graphite cell B with a platinum liner.

AgF_2. This compound was vaporized using the graphite cells A and B in two temperature ranges. Some runs were carried out in cell B, with the larger effusion holes, in temperature ranges having as an upper limit the melting point of AgF (708 K), and some runs were carried out by cell A, having 708 K as the lowest temperature. In this way, two vapor pressure sets above solid AgF_2 involving equilibrium with solid or molten silver monofluoride, respectively, were obtained. All the experiments, carried out employing always fresh samples, were stopped and considered concluded when about (4 to 5) % of the original weight was vaporized. In this way, the number of pressure values was limited, but those were considered representative of the vapor in equilibrium with AgF_2 at near unit activity, that is, before the pressure decreased due to the production of a consisting AgF layer on the sample surface. In Tables 4, 5, and 6 and Figure 3, the results obtained are reported. The log p versus $1/T$ equations are summarized in Table 7. From these equations, two final ones were selected representative of

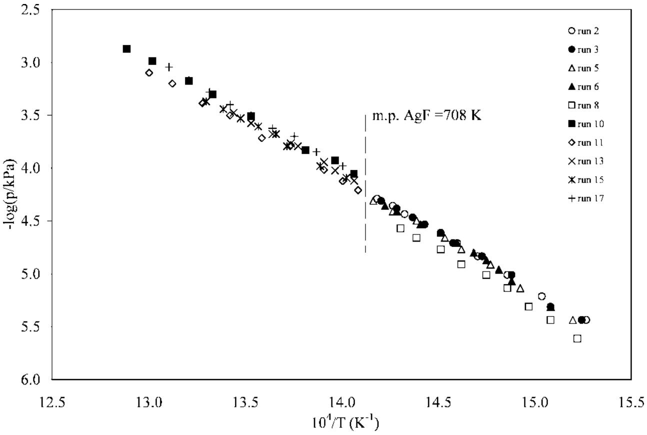

Figure 3. Torsion total vapor pressures of AgF_2.

Table 7. Temperature Dependence of the Torsion Total Vapor Pressures for AgF_2[a]

		ΔT		$\log(p/\text{kPa}) = A - B/(T/\text{K})$	
run	cell	K	no. of points	A^b	B^b
2	B	655 to 705	10	11.05 ± 0.18	10802 ± 122
3	B	656 to 704	10	11.49 ± 0.36	11104 ± 249
5	B	658 to 706	9	11.44 ± 0.40	11096 ± 270
6	B	663 to 703	10	11.35 ± 0.54	11017 ± 370
8	B	657 to 699	9	11.67 ± 0.45	11335 ± 307
10	A	711 to 776	8	10.19 ± 0.23	10130 ± 168
11	A	710 to 769	9	10.23 ± 0.33	10244 ± 241
13	A	711 to 744	8	10.27 ± 0.30	10221 ± 217
15	A	713 to 752	8	10.29 ± 0.49	10253 ± 361
17	A	714 to 763	9	10.35 ± 0.20	10231 ± 165

[a] In the runs 1, 4, 7, 9, 12, 14, 16, and 18, pure lead was vaporized. [b] The quoted errors are standard deviations.

Table 8. Torsion Vapor Pressures of Molten AgF Measured by Using the Cell B Lined with Platinum

run 2		run 4		run 5		run 7		run 8	
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	$-\log(p/\text{kPa})$
913	3.87	931	3.76	880	4.24	894	4.11	910	3.81
921	3.76	941	3.62	897	4.11	917	3.81	920	3.64
928	3.63	948	3.51	914	3.81	938	3.57	939	3.43
936	3.57	956	3.37	931	3.60	958	3.30	949	3.28
947	3.39	965	3.27	948	3.37	978	3.07	968	3.05
958	3.30	975	3.17	966	3.16	996	2.87	986	2.84
967	3.17	985	3.06	984	2.98	1013	2.70	995	2.77
979	3.05	994	2.96	1000	2.80	1036	2.48	1008	2.65
990	2.93	1004	2.84	1019	2.62			1017	2.58
1000	2.83	1014	2.76	1037	2.45				
1010	2.73	1025	2.63						
		1034	2.59						

run 10		run 11		run 13		run 14	
T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$	T/K	$-\log(p/\text{kPa})$
893	4.24	910	4.01	910	3.98	891	4.28
915	3.93	920	3.81	920	3.78	904	4.08
933	3.63	929	3.71	929	3.68	912	3.98
955	3.39	949	3.46	949	3.43	925	3.78
976	3.14	958	3.33	958	3.30	933	3.68
996	2.93	977	3.14	977	3.11	942	3.57
1016	2.72	985	3.04	985	3.01	955	3.43
1035	2.53	994	2.96	994	2.93	965	3.30
1054	2.35	1012	2.78	1012	2.75	974	3.19
1074	2.17	1022	2.68	1022	2.65	987	3.05
		1031	2.61	1031	2.58	996	2.97
		1040	2.51	1040	2.48	1005	2.91
		1049	2.43	1049	2.40	1013	2.85
		1057	2.35	1057	2.32	1026	2.70

the total vapor pressures above AgF_2(s) in the presence of solid and molten AgF, respectively:

$$\log(p/\text{kPa}) = (11.39 \pm 0.30) - (11060 \pm 300)(T/\text{K}) \quad \text{(from (655 to 706) K)} \quad (2)$$

$$\log(p/\text{kPa}) = (10.27 \pm 0.20) - (10220 \pm 200)(T/\text{K}) \quad \text{(from (710 to 776) K)} \quad (3)$$

where the errors are estimated.

From the difference of the slopes of these equations, a value of the heat of fusion of AgF was evaluated equal to 16 kJ·mol^{-1}. This value, with a decidedly large error of about 10 kJ·mol^{-1}, is equal with that estimated by Zmbov and Margrave[3] [(17 ± 4) kJ·mol^{-1}].

AgF. This molten compound was vaporized by using the graphite cell B lined with platinum.

The vapor pressures measured in nine runs are reported in Table 8 and Figure 4. Treating as usual by least-squares the experimental results of each run, slopes and intercepts of the log p versus $1/T$ equations were calculated and are reported in Table 9. From these equations, the following one representative of the vapor pressure of molten AgF in the temperature range (880 to 1074) K was selected:

$$\log(p/\text{kPa}) = (7.83 \pm 0.50) - (10700 \pm 300)(T/\text{K}) \quad (4)$$

The vapor pressures measured in the present work are slightly lower than those reported by Zmbov and Margrave[3] (see Figure 4), but considering that these were evaluated from only one absolute pressure value determined by the Knudsen method, we believe that our absolute vapor pressure could be more reliable.

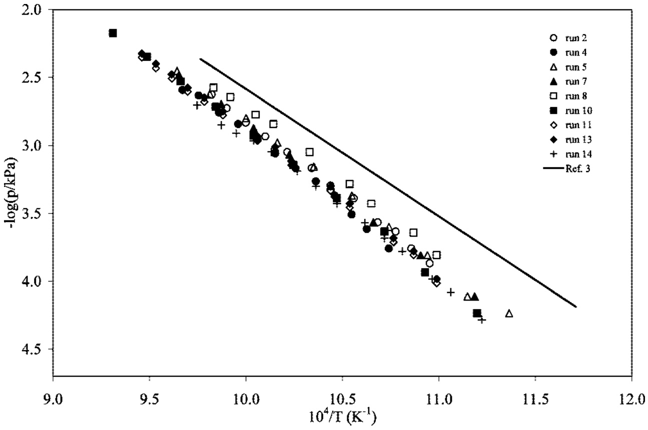

Figure 4. Torsion vapor pressures of AgF.

Discussion and Conclusion

A. CuF$_2$. The standard sublimation enthalpy of CuF_2 was calculated by second- and third-law treatment of the vapor pressure data. The second-law value, $\Delta_{\text{sub}}H°(298\ \text{K}) = 259$ kJ·mol^{-1}, was evaluated as the average of the corresponding values (see Table 2) obtained by reducing to 298 K the sublimation enthalpies determined at the experimental mid temperature of each run by using the enthalpic increments for solid and gaseous phases reported by the IVTANTHERMO database.[9] Considering the good agreement of these values, the error associated to the final standard sublimation enthalpy value was estimated to be ± 4 kJ·mol^{-1}. Employing the vapor pressure values calculated by eq 1 at 50 K intervals across the temperature range from (850 to 1050) K, the third-law standard sublimation enthalpies reported in Table 10 were evaluated. The necessary free energy functions (fef), $[G°(T) - H°(298\ \text{K})]/T$, were also taken from the IVTANTHERMO database.[9] The obtained values do not present any appreciable temperature trend. The average third-law value, $\Delta_{\text{sub}}H°(298\ \text{K}) = 261 \pm 1$ kJ·mol^{-1}, is in agreement with the second-law one. Giving equal weight to second- and third-law results, the final standard

Table 9. Temperature Dependence of the Torsion Vapor Pressures and Sublimation Enthalpies of Molten AgF

	ΔT		$\log(p/\text{kPa}) = A - B/(T/\text{K})$		$\Delta_{\text{sub}}H(T)^a$	$\Delta_{\text{sub}}H°(298\text{ K})^b$
run	K	no. of points	A^a	B^a	kJ·mol^{-1}	kJ·mol^{-1}
2	913 to 1018	12	7.94 ± 0.14	10762 ± 136	206.0 ± 2.6	237 ± 4.5
4	931 to 1034	12	8.04 ± 0.25	10946 ± 248	209.5 ± 4.7	241 ± 6.5
5	880 to 1037	10	7.87 ± 0.20	10680 ± 192	204.4 ± 3.7	235 ± 5.5
7	894 to 1036	8	7.90 ± 0.09	10736 ± 87	205.5 ± 1.7	236 ± 3.5
8	910 to 1017	9	7.98 ± 0.21	10697 ± 199	204.7 ± 3.8	236 ± 6.0
10	893 to 1074	10	7.99 ± 0.14	10882 ± 141	208.3 ± 2.7	239 ± 4.5
11	910 to 1057	14	7.62 ± 0.14	10528 ± 137	201.5 ± 2.6	233 ± 4.5
13	910 to 1057	14	7.65 ± 0.14	10528 ± 137	201.5 ± 2.6	233 ± 4.5
14	891 to 1026	14	7.67 ± 0.19	10607 ± 179	203.0 ± 3.4	234 ± 5.5
					average	236 ± 4

[a] The quoted errors are standard deviations. [b] The errors are obtained allowing about 2 kJ·mol^{-1} as a result of the correction to 298 K.

Table 10. Third-Law Standard Sublimation Enthalpies of CuF_2

T	p	$\Delta_{\text{sub}}G°(T)/T$	$-\Delta$fef	$\Delta H°(298\text{ K})$
K	kPa	J·mol^{-1}	J·K^{-1}·mol^{-1}	kJ·mol^{-1}
850	$7.01 \cdot 10^{-6}$	137.0	169.4	260.5
900	$4.73 \cdot 10^{-5}$	121.2	168.6	260.8
950	$2.61 \cdot 10^{-4}$	107.0	167.8	261.0
1000	$1.22 \cdot 10^{-3}$	94.2	166.9	261.1
1050	$4.89 \cdot 10^{-3}$	82.6	166.1	261.1
			average	261 ± 1

sublimation enthalpy of CuF_2, $\Delta_{\text{sub}}H°(298\text{ K}) = 260$ kJ·mol^{-1}, was selected with an estimated error not exceeding ± 4 kJ·mol^{-1}.

Our results are compared in Table 4 with those proposed by Kent et al.[1] and by Ehlert and Wang[2] and with those by us, recalculated using the vapor pressures reported in their works[1,2] and the IVTANTHERMO database[9] thermodynamic functions.

B. AgF₂. In the covered temperature range, the fluorine produced from the decomposition of AgF_2 is partially dissociated. From the total vapor pressures obtained by eqs 2 and 3 and the equilibrium constants of the dissociation reaction, $F_2(g) = 2\,F(g)$, given in the IVTANTHERMO database,[9] [$\log(p/\text{kPa}) = 8.48 - 8511(T/\text{K})$], the F(g) partial pressures were determined at two extreme temperatures of the covered ranges in the presence of solid and molten AgF. From $F_2(g)$ and F(g) partial pressures, the third-law standard partial molar enthalpies of the sublimation of AgF_2 according to the reactions

$$AgF_2(s) \rightarrow AgF(s,l) + F(g) \qquad (5)$$

$$AgF_2(s) \rightarrow AgF(s,l) + \tfrac{1}{2}F_2(g) \qquad (6)$$

were calculated by using for $AgF_2(s)$ and AgF(s,l) the fef of $CuF_2(s)$ and CuF(s) and the fef of F(g) and $F_2(g)$ reported in the IVTANTHERMO database.[9]

The obtained values reported in Table 11 do not present any temperature trend. Their average values are (190 ± 4) kJ·mol^{-1} and (124 ± 4) kJ·mol^{-1} for reactions 5 and 6, respectively, when the overestimated errors include the additional uncertainty in the thermodynamic functions.

From the F(g) and $F_2(g)$ partial pressure values calculated at the extreme temperatures by eq 2 above AgF_2 and AgF, the second-law enthalpies of the reaction 5 and 6 were determined and reported at 298 K using the enthalpy increments from the same source of the fef. The obtained values were $\Delta_{\text{sub}}H°(298\text{ K}) = 205$ kJ·mol^{-1} and $\Delta_{\text{sub}}H°(298\text{ K}) = 127$ kJ·mol^{-1} for reaction 5 and 6, respectively. Considering that, owing to the small temperature ranges covered, the uncertainties associated to the second-law results are considerably high, these values can be considered in agreement with those obtained by the third-law procedure. On this basis, we propose as $\Delta_{\text{sub}}H°(298\text{ K})$ for the sublimation reactions of AgF_2 according to reactions 5 and 6 the average values [(195 ± 10) and (125 ± 5)] kJ·mol^{-1}, respectively, where the errors were estimated.

C. AgF. From the slopes of the selected equations reported in Table 9, the second-law vaporization enthalpy of AgF(l) at 1000 K was calculated and reported at 298 K employing for AgF(l) the enthalpic increment of CuF(s)[9] and its heat of fusion evaluated in the present work and for AgF(g) that of CuF(g).[9] The average value, $\Delta_{\text{sub}}H°(298\text{ K}) = (236 \pm 10)$ kJ·mol^{-1}, was obtained allowing for 2 kJ·mol^{-1} uncertainty as a result of the correction to 298 K. The third-law standard sublimation enthalpy was calculated at 50 K intervals across the temperature range (900 to 1150) K, employing the fef of copper monofluoride reported in the IVTANTHERMO database[9] and the vapor pressures calculated at these temperatures by eq 4. The results, reported in Table 12, present a very small temperature trend. The average value 244 kJ·mol^{-1}, where the associated error was estimated as 6 kJ·mol^{-1} taking into account the observed trend, is comparable with that obtained by the second-law, so we propose as the standard sublimation enthalpy of AgF the final value of (240 ± 10) kJ·mol^{-1}. This value is decidedly higher than that proposed by Zmbov and Margrave,[3] [(197 ± 20) kJ·mol^{-1}]. By using the vapor pressures reported in their paper at the extreme of the covered temperature range (854 to

Table 11. Third-Law Standard Partial Molar Enthalpies of Sublimation of AgF_2 According the Reactions A, $AgF_2(s) \rightarrow AgF(s,l) + F(g)$, and B, $AgF_2(s) \rightarrow AgF(s,l) + \tfrac{1}{2}F_2(g)$

		pressure		reaction A			reaction B		
T	Kp^a	total^b	F(g)	$R \cdot \ln(p_{-F})$	$-\Delta$fef	$\Delta_{\text{sub}}H°(298\text{ K})$	$R \cdot \ln(p_{-F_2})^{1/2}$	$-\Delta$fef	$\Delta_{\text{sub}}H°(298\text{ K})$
K	kPa	kPa	kPa	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	kJ·mol^{-1}
655	$3.05 \cdot 10^{-5}$	$3.16 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$	144	147	191	101	88	124
706	$2.65 \cdot 10^{-4}$	$5.24 \cdot 10^{-5}$	$4.48 \cdot 10^{-5}$	122	147	190	87	88	124
710	$3.10 \cdot 10^{-4}$	$7.52 \cdot 10^{-5}$	$6.26 \cdot 10^{-5}$	119	147	189	85	88	123
776	$3.24 \cdot 10^{-3}$	$1.26 \cdot 10^{-3}$	$9.70 \cdot 10^{-4}$	96	147	189	72	88	124
					average	190		average	124

[a] Equilibrium constant of the dissociation reaction $F_2(g) \rightarrow 2\,F(g)$ from the IVTANTHERMO database.[9] [b] Obtained from the selected eqs 2 and 3.

Table 12. Third-Law Standard Sublimation Enthalpies for AgF

T	p	$\Delta_{sub}G°(T)/T$	$-\Delta$fef	$\Delta H°(298\text{ K})$
K	kPa	$J \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
900	$8.85 \cdot 10^{-5}$	116.0	152.2	241.3
950	$3.73 \cdot 10^{-4}$	104.0	151.4	242.6
1000	$1.36 \cdot 10^{-3}$	93.2	150.5	243.8
1050	$4.41 \cdot 10^{-3}$	83.5	149.7	244.9
1100	$1.28 \cdot 10^{-2}$	74.6	148.9	245.9
1150	$3.39 \cdot 10^{-2}$	66.5	148.2	246.9
			average	244

1024) K ($2.4 \cdot 10^{-4}$ kPa and $1.8 \cdot 10^{-2}$ kPa, respectively) and the fef of CuF as used in this work, we calculated two standard sublimation enthalpy values at these temperatures, of $\Delta_{sub}H°(298\text{ K}) = 235\ kJ \cdot mol^{-1}$ and $243\ kJ \cdot mol^{-1}$, respectively. These values, though more comparable with our results, present a more evident temperature trend.

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