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Vapor Pressures and Sublimation Enthalpies of Mercury(I, II) Fluorides by the Torsion-Effusion Method

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The vapor pressures in equilibrium over HgF_2 and Hg_2F_2 were measured by the torsion-effusion method. HgF_2 vaporized congruently. The temperature dependence of the vapor pressure of this compound was found to fit the following equation: HgF_2(s), $\log(p/\text{kPa}) = (9.00 \pm 0.30) - (6750 \pm 200)(\text{K}/T)$ (from (496 to 629) K). Treating the vapor pressure data by the second- and third-law methods, the standard sublimation enthalpy, $\Delta_{\text{sub}}H°(298\ \text{K}) = (136 \pm 4)\ \text{kJ}\cdot\text{mol}^{-1}$, and entropy, $\Delta_{\text{sub}}S°(298\ \text{K}) = (145 \pm 6)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, were selected. In the covered temperature range (from (457 to 589) K), Hg_2F_2(s) decomposes into HgF_2(s) and Hg(g) so that the temperature dependence of the mercury pressure above this compound, $\log(p/\text{kPa}) = (7.90 \pm 0.50) - (5400 \pm 300)(\text{K}/T)$, was determined. Also, for this compound, the standard sublimation enthalpy, $\Delta_{\text{sub}}H°(298\ \text{K}) = (105 \pm 4)\ \text{kJ}\cdot\text{mol}^{-1}$, and entropy, $\Delta_{\text{sub}}S°(298\ \text{K}) = (114 \pm 10)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, were determined.

Introduction

The vapor pressures and the data of the thermodynamics of sublimation of mercury mono- and difluoride are not available in the literature. A matrix isolation infrared and Raman study of HgF_2 trapped in solid krypton carried out by Givan and Loewenschuss[1] showed HgF_2 is the only gaseous species in the vapor. In the present work, the absolute total vapor pressures of these compounds were measured by the torsion-effusion method, and by the second- and third-law treatment of these data, the standard sublimation enthalpies and entropies of these compounds were calculated.

Experimental Section

The HgF_2 and Hg_2F_2 used had a nominal purity of 95 % and 97 %, respectively, as certified by the supplier (Alfa Aesar items # 11533 and 40130 for HgF_2 and Hg_2F_2, respectively). Both samples and in particular HgF_2, easily contaminable with HgFOH produced in the presence of steam (as observed by XRD analysis), were loaded into the torsion cell in a drybox. The cell, with effusion holes closed with a drop of naphthalene, was transported into the torsion assembly and rapidly evacuated. The absolute vapor pressures of these compounds were measured by a torsion assembly described in detail in a previous work.[2] The conventional torsion cell, having the nominal diameter of the effusion holes of 1 mm, was machined by graphite at low porosity. The torsion constant of this cell necessary to convert the torsion angles measured at different temperatures in vapor pressures was determined and checked by vaporizing very pure cadmium or mercury, standards having well-known vapor pressures,[3] in several runs carried out between the vaporization runs of the studied compounds. The torsion constant was found well reproducible, and their values ranged within about 5 % of the mean. This uncertainty produced a negligible displacement of the logarithm of the derived pressure value.

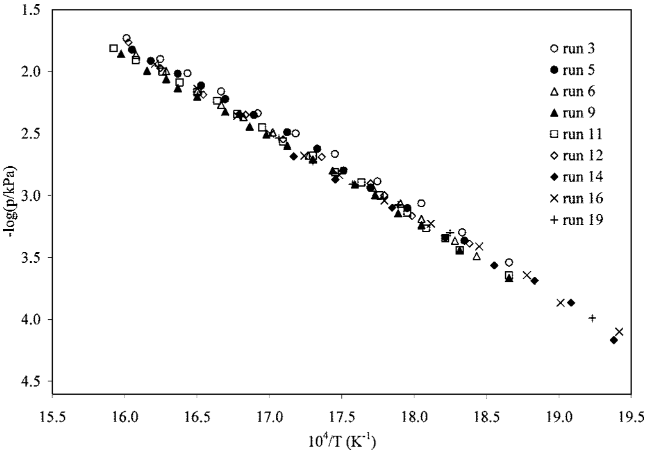

Figure 1. Vapor pressures of HgF_2.

Experimental Results

A. HgF_2. Heating the samples, a weight loss of about (6 to 10) % was always observed at about (350 to 400) K, and this was considered due to the vaporization of a large amount of impurities. The vapor pressures of this compound so purified were measured in several runs and are reported in Table 1 and Figure 1. In Table 2 are reported slopes and intercepts of the log p versus $1/T$ equations obtained by treating with least-squares the experimental data measured in each run. Weighting these values proportionally to the experimental points, the following final equation valid over the temperature range (496 to 629) K was selected

$$\log(p/\text{kPa}) = (9.00 \pm 0.30) - (6750 \pm 200)(\text{K}/T) \quad (1)$$

where the associated errors were estimated.

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Table 1. Torsion Vapor Pressures of HgF_2

run 3		run 5		run 6		run 9		run 11	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
536	3.54	545	3.36	543	3.49	536	3.67	536	3.64
546	3.30	557	3.10	547	3.36	546	3.44	546	3.44
554	3.06	565	2.94	554	3.19	554	3.24	549	3.34
564	2.89	571	2.80	559	3.06	559	3.14	553	3.26
573	2.67	577	2.62	565	2.94	564	3.00	557	3.14
582	2.50	584	2.49	572	2.80	569	2.91	563	3.00
591	2.34	592	2.35	579	2.68	574	2.80	567	2.90
600	2.16	599	2.22	588	2.49	578	2.71	573	2.81
609	2.02	605	2.11	595	2.36	584	2.60	578	2.68
616	1.90	611	2.02	600	2.27	589	2.51	585	2.57
625	1.73	618	1.91	606	2.16	593	2.44	590	2.45
		623	1.82	614	2.00	599	2.32	596	2.34
				622	1.86	606	2.20	601	2.24
						611	2.13	606	2.17
						614	2.06	611	2.09
						619	1.99	615	2.00
						626	1.86	622	1.91
								628	1.81

run 12		run 14		run 16		run 19	
T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$	T/K	$-\log(p/\mathrm{kPa})$
544	3.39	509	4.34	496	4.64	503	4.47
556	3.17	516	4.17	508	4.24	520	3.99
562	3.00	524	3.86	515	4.10	531	3.69
565	2.90	531	3.69	526	3.86	539	3.56
576	2.69	539	3.56	533	3.64	548	3.30
585	2.55	549	3.34	542	3.41	559	3.07
594	2.35	560	3.10	552	3.23	569	2.91
605	2.19	573	2.87	562	3.04	578	2.72
616	1.97	583	2.68	572	2.84	586	2.54
624	1.76	596	2.34	580	2.68	595	2.36
		629	1.71	588	2.50	605	2.17
				596	2.36	616	1.96
				606	2.14		
				617	1.94		

Table 2. Temperature Dependence of the Torsion Total Vapor Pressures above HgF_2 and Hg_2F_2

		ΔT		$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
compound	run	K	no. of points	A^a	B^a
HgF_2	3	536 to 625	11	9.06 ± 0.13	6733 ± 75
	5	545 to 623	12	9.04 ± 0.17	6754 ± 101
	6	543 to 622	13	9.02 ± 0.13	6766 ± 73
	9	536 to 626	17	8.83 ± 0.11	6685 ± 67
	11	536 to 628	18	9.04 ± 0.12	6789 ± 70
	12	544 to 624	10	9.04 ± 0.21	6768 ± 119
	14	509 to 629	11	9.14 ± 0.24	6846 ± 133
	16	496 to 617	14	8.86 ± 0.12	6677 ± 66
	19	503 to 616	12	9.01 ± 0.12	6766 ± 69
Hg_2F_2	2	498 to 552	8	7.65 ± 0.17	5232 ± 88
	4	483 to 557	9	8.03 ± 0.13	5470 ± 67
	5	457 to 518	8	7.91 ± 0.27	5359 ± 128
	7	480 to 568	10	7.54 ± 0.11	5197 ± 60
	8	496 to 589	12	7.28 ± 0.05	5102 ± 28
	9	487 to 544	8	8.74 ± 0.17	5821 ± 87
	11	473 to 528	10	8.70 ± 0.23	5812 ± 115
	13	464 to 560	13	7.69 ± 0.07	5290 ± 37

[a] The quoted errors are standard deviations.

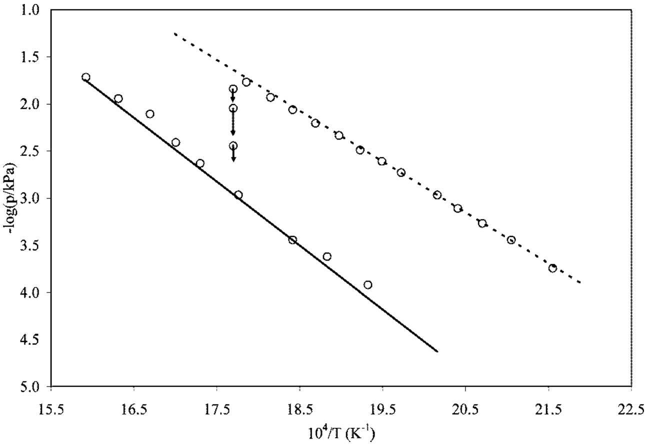

Figure 2. Typical vaporization behavior of Hg_2F_2. ○, Vapor pressures measured in run 13; the continuous line represents eq 1; the dotted line represents eq 3.

From this equation, the second-law thermodynamic changes associated with the congruent sublimation of HgF_2 at the middle of the experimental temperature range [$\Delta_{\mathrm{sub}}H°(560\ \mathrm{K}) = (129 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{sub}}S°(560\ \mathrm{K}) = (134 \pm 6)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$] were calculated and reported at 298 K [$\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = (134 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_{\mathrm{sub}}S°(298\ \mathrm{K}) = (145 \pm 6)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$] using the enthalpic increments [$H°(500\ \mathrm{K}) - H°(298\ \mathrm{K})$] selected by the IVTANTHERMO database[4] for HgF_2(s) and by Givas and Loewenschuss[1] for HgF_2(g). It is interesting to note that the entropy change obtained at 560 K is slightly lower than that obtained from the difference in the absolute entropies reported by the IVTANTHERMO database[4] for the compound in the solid and gaseous phases, $\Delta_{\mathrm{sub}}S°(560\ \mathrm{K}) = 143\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. Employing the vapor pressure values calculated by eq 1 at (500 and 600) K, two extreme temperatures of the experimental ranges covered, two third-law values of the standard sublimation enthalpy of HgF_2 were calculated. The free energy functions [$G°(T) - H°(298\ \mathrm{K})]/T$ necessary for this calculations were taken from the same source as the enthalpic increments. The two enthalpy values so obtained (reported in Table 3) are comparable showing that these do not have appreciable temperature dependence. The average value 138.5 $\mathrm{kJ \cdot mol^{-1}}$, with an associated overestimated error of about ± 4 $\mathrm{kJ \cdot mol^{-1}}$, agrees with the second-law result. On this basis, we propose as $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ for the sublimation of HgF_2 the average value of $(136 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$ and as $\Delta_{\mathrm{sub}}S°(298\ \mathrm{K})$ the value of $(145 \pm 6)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

B. Hg_2F_2. Also for this compound, the vaporization of about 5 % of the samples was observed at about room temperature. Upon heating the samples so purified, initially the vapor pressures were found to be decidedly well reproducible, but in all experiments, going on the vaporization, when the sample in the cell was about (70 to 80) % of the original amount, the pressure values showed a decreasing trend. Going on the heating of the sample, the vapor pressures were found again reproducible and very similar to those measured above HgF_2. A typical vaporization behavior of Hg_2F_2 (run 13) is reported in Figure 2. A rough experiment was carried out vaporizing this compound under vacuum in a test tube and condensing the vapor on the cooled top of the test tube. Going on the vaporization, the condensation of a yellow layer and drops of mercury were observed. After the vaporization of about half of the sample, the XRD analysis of the residue and the condensed layer showed that both were HgF_2. This observation and the vapor pressures measured in the second step of the vaporization lead to the conclusion that this compound vaporizes according to the reaction

$$Hg_2F_2(s) \rightarrow HgF_2(s) + Hg(g) \qquad (2)$$

Considering that the small amount of HgF_2(s) produced in this step is not at unit activity, the pressures calculated from eq 1 are an upper limit, and the contribution of the vapor pressures of HgF_2(g) at the operating temperatures in the first step of the vaporization of Hg_2F_2 is decidedly negligible. Therefore, the

Table 3. Third-Law Standard Enthalpies for the Reactions[a]

	T	p	$-R\cdot\ln p$	$[G°(T) - H°(298\ \mathrm{K})]/T/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$					$\Delta H°(298\ \mathrm{K})$
reaction	K	kPa	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$	$HgF_2(s)$	$HgF_2(g)$	$Hg_2F_2(s)$	Hg(g)	Δ	$\mathrm{kJ\cdot mol^{-1}}$
A	500	$3.11\cdot 10^{-5b}$	124.6	−120.2	−271.8			−151.6	138.1
	600	$5.53\cdot 10^{-3b}$	81.6	−126.3	−276.5			−150.2	139.1
B	450	$8.28\cdot 10^{-5c}$	116.5	−117.4		−177.4	−176.4	−116.3	104.8
	600	$8.20\cdot 10^{-2c}$	59.2	−126.3		−190.3	−178.9	−115.0	104.5

[a] Reaction A: $HgF_2(s) \rightarrow HgF_2(g)$. Reaction B: $Hg_2F_2(s) \rightarrow HgF_2(s) + Hg(g)$. [b] HgF_2 vapor pressures calculated by eq 1. [c] Hg(g) pressures considered equal to the total vapor pressures calculated by eq 3.

Table 4. Torsion Total Vapor Pressures of Hg_2F_2

run 2		run 4		run 5		run 7	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
498	2.87	483	3.29	457	3.82	480	3.32
504	2.75	490	3.12	466	3.62	496	2.94
513	2.54	493	3.04	469	3.52	502	2.79
516	2.46	499	2.95	474	3.38	511	2.61
526	2.32	514	2.64	481	3.18	525	2.36
535	2.12	527	2.36	488	3.05	542	2.06
543	1.98	533	2.24	504	2.75	555	1.86
552	1.84	551	1.88	518	2.44	560	1.73
		557	1.78			565	1.66
						568	1.61

run 8		run 9		run 11		run 13	
T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)	T/K	−log(p/kPa)
496	3.02	487	3.22	473	3.62	464	3.75
502	2.88	494	3.05	481	3.38	475	3.44
507	2.79	503	2.82	487	3.22	483	3.27
523	2.48	512	2.65	492	3.11	490	3.11
525	2.44	521	2.40	498	2.97	496	2.97
539	2.19	529	2.26	505	2.76	507	2.73
549	2.03	537	2.12	510	2.68	513	2.61
557	1.88	544	1.97	515	2.59	520	2.49
561	1.79			521	2.47	527	2.34
570	1.69			528	2.34	535	2.21
580	1.53					543	2.06
589	1.39					551	1.93
						560	1.77

total vapor pressures measured in the first step are practically mercury partial pressures in equilibrium with Hg_2F_2. In light of this vaporization behavior, all the experiments were carried out utilizing always fresh samples and were stopped when these were vaporized for about (10 to 15) % of the original amounts so that the measured vapor pressures referred to the compound practically at unit activity. The vapor pressures so measured are reported in Table 4 and Figure 3. The temperature dependence of the experimental points linearized by least-squares treatment of the data measured in each run is expressed by a log p versus $1/T$ equation and the obtained equations reported in Table 3. Weighting slopes and intercepts of these equations proportionally to the number of experimental points, the following equation representative of the total vapor pressure above Hg_2F_2 in the temperature range ((457 to 589) K) was selected

$$\log(p/\mathrm{kPa}) = (7.90 \pm 0.50) - (5400 \pm 300)(\mathrm{K}/T) \quad (3)$$

where the associated errors were estimated.

Because the total vapor pressures were practically equal to the partial pressure of mercury, from the slope and intercept of this equation, the second-law enthalpy and entropy associated with the sublimation reaction at the middle temperature of all the experiment ranges were calculated: $\Delta_{\mathrm{sub}}H°(520\ \mathrm{K}) = (103 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}$ and $\Delta_{\mathrm{sub}}S°(520\ \mathrm{K}) = (113 \pm 10)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. This entropy change agrees within the error of that obtained as the difference of the absolute 114 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ entropy reported by the IVTANTHERMO database.[4] From this source were taken the enthalpy increment data, enabling us to report these values at 298 K: $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = (105 \pm 6)\ \mathrm{kJ\cdot mol^{-1}}$ and $\Delta_{\mathrm{sub}}S°(298\ \mathrm{K}) = (115 \pm 10)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. From pressure values calculated at two extreme experimental temperatures [(450 and 600) K] by eq 3, two third-law standard enthalpy values of the sublimation reaction 2 were calculated. The free energy functions necessary for this calculation were taken from the same source as the enthalpic increments. The third-law values so obtained have no temperature trend, and its average value, $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K}) = 104.7\ \mathrm{kJ\cdot mol^{-1}}$ with an estimated error of ± 2 $\mathrm{kJ\cdot mol^{-1}}$, is equal to that derived from the second-law treatment.

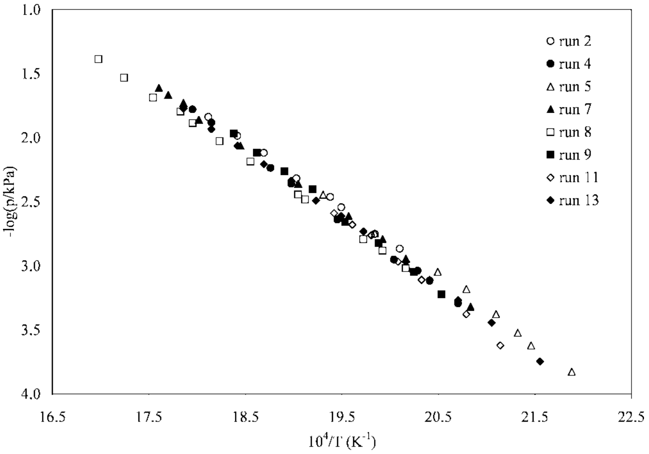

Figure 3. Torsion total vapor pressures over Hg_2F_2.

On this basis, we propose as the standard enthalpy change associated to the sublimation of $Hg_2F_2(s)$ according to reaction 2 the value of 105 $\mathrm{kJ\cdot mol^{-1}}$ with an overestimate error limit of ± 4 $\mathrm{kJ\cdot mol^{-1}}$.

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