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Vapor Pressure of Zirconium Tetrafluoride

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ABSTRACT: Measurements were made of the vapor pressures of zirconium tetrafluoride by using a torsion effusion apparatus. The temperature dependence fit the equation: $\log(p/\text{Pa}) = (15.20 \pm 0.15) - (11\,900 \pm 200)/(T/\text{K})$ (from 685 to 828 K). The compound vaporizes congruently in the monomeric form. With treatment of the measured vapor pressures by second- and third-law methods, the standard sublimation enthalpy $\Delta_{\text{sub}}H°(298\text{ K}) = (239 \pm 2)\text{ kJ}\cdot\text{mol}^{-1}$ was obtained.

INTRODUCTION

Apparently the first vapor pressure values of solid zirconium tetrafluoride were those obtained by Lauter[1] by using a static method. Sense et al.[2,3] determined a set of vapor pressures by the transpiration method. Cantor et al.[4] studied the ZrF_4 activity in RbF-ZrF_4 mixtures by using a differential manometer measuring also the vapor pressures of the pure compound. Fischer and Petzel[5] reported a log p versus $1/T$ equation obtained by the "bell method" taking in account also the data previously obtained by Petzel.[6] Galkin et al.[7] using a Knudsen method, Akishin et al.[8] a mass-spectrometer, and last Konings and Hildenbrand[9] a torsion method measured vapor pressures at lower temperatures.

The pressure values obtained at higher temperatures are in better agreement than those measured at lower temperatures by effusion methods.[7−9] A review of all work on the vapor pressure of ZrF_4 was made by van der Vis et al.[10] and Brown et al.[11] This paper reports new torsion-effusion measurements of the vapor pressure of ZrF_4, and the sublimation enthalpy and entropy of this compound is derived from these data.

EXPERIMENTAL SECTION

The ZrF_4 sample employed for the vapor pressure measurements was supplied by Aldrich (99.9 % pure as stated by the same supplier). The measurements were carried out by the torsion-effusion method.[12] This method allows determination, at each experimental temperature, the pressure value of the vapor in equilibrium with a condensed compound by measuring the torsion angle of the fiber to which is suspended, under vacuum, a measuring cell. This cell, filled with sample, has two holes from which the vapor can effuse in the vacuum. The physical and geometrical characteristics of the used cell as a moment arm of their orifices with respect to the suspending fiber, length, and area of the holes,[13,14] etc. are included in a torsion constant K. The vapor pressure was equal to the product of this constant and the corresponding torsion angle of the fiber opportunely measured by the angular deflection of the suspended torsion assembly. Instead of obtaining the K from the different physical and geometrical constants, we prefer to determine its value from the vaporization of pure elements, the vapor pressures of which are well-known in the literature. Unfortunately this procedure does not take into account the eventual condensation coefficient of the used compound, but we believe that, if the K values obtained by using different standards are in agreement, ignoring this coefficient does not produce large errors in the absolute vapor pressure measurements. In this study two pyrophillite cells were used, cell A having two circular knife edge orifices of 1.8 mm diameter and cell B, with only one effusion orifice 1 mm in diameter and about 2 mm long. Thus, use of these cells allows for pressure measurements over a relatively large temperature range.

The particular apparatus used in the present study has been described in our previous work.[15] In order to determine the torsion constants of both cells, the well-known vapor pressures of very pure cadmium and lead[16] were used. The vaporization runs of these standards were carried out during the study of ZrF_4 in order to have frequent checks of the K values. In each run at each experimental temperature, the corresponding K was calculated and the averaged data and their corresponding temperature dependence are reported in Table 1. In each vaporization run of ZrF_4, the K used for the calculation of the pressure values was the average of those obtained in the standard vaporization runs carried out after and before the same run. In Table 2 and Figure 1 are reported the vapor pressures of ZrF_4 obtained in 11 runs and in Table 3 their temperature dependence obtained by linear least-squares treatment of the data of each run. The log p versus $1/T$ equations so obtained are in good agreement among themselves though the data obtained by cell A are slightly higher than those obtained by cell B so that a very very small orifice-size effect was observed. Weighting in proportion to the experimental number of points, the slopes and intercepts values of the log p versus $1/T$ equations in Table 3, the following representative equation of the vapor pressure of ZrF_4 over the temperature range from 685 to 828 K was selected:

$$\log(p/\text{Pa}) = (15.20 \pm 0.15) - (11900 \pm 200)/(T/\text{K}) \quad (1)$$

where the associated uncertainties were estimated. This equation is compared in Table 4 with those found in the literature and in particular in Figure 2 with those measured by the effusion method.[7−9]

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Table 1. Torsion Constants Obtained from the Vaporization Runs of Lead and Cadmium

				ΔT	$\log(a/\mathrm{rad}) = A - B/(T/\mathrm{K})$		$K = p^\circ/\alpha$[a]
cell	standard	run	no. of points	K	A[a]	B[a]	$\mathrm{Pa \cdot rad^{-1}}$
A	Pb	A01	15	825.5−971.5	9.61 ± 0.11	9636 ± 101	1.70 ± 0.09
A	Pb	A05	16	809.0−964.0	9.63 ± 0.14	9663 ± 127	1.73 ± 0.12
A	Pb	A08	18	818.0−966.0	9.62 ± 0.08	9665 ± 69	1.78 ± 0.07
A	Pb	A11	20	832.0−979.0	9.63 ± 0.13	9653 ± 119	1.72 ± 0.11
A	Cd	A03	11	449.0−508.0	10.56 ± 0.18	5727 ± 84	1.71 ± 0.09
A	Cd	A06	13	436.5−517.8	10.69 ± 0.21	5789 ± 100	1.72 ± 0.16
A	Cd	A10	14	439.0−510.0	10.59 ± 0.20	5739 ± 95	1.71 ± 0.12
B	Pb	B01	12	858.0−1008.0	8.74 ± 0.11	9643 ± 106	12.80 ± 0.61
B	Pb	B06	14	851.0−1017.0	8.77 ± 0.09	9673 ± 82	12.82 ± 0.55
B	Pb	B11	14	864.0−1022.0	8.81 ± 0.07	9657 ± 68	11.21 ± 0.37
B	Pb	B13	13	867.0−1006.0	8.76 ± 0.09	9643 ± 88	12.22 ± 0.44
B	Pb	B16	15	860.5−1027.0	8.76 ± 0.08	9653 ± 75	12.49 ± 0.46
B	Cd	B02	17	465.0−552.0	9.80 ± 0.13	5760 ± 68	11.66 ± 0.73
B	Cd	B04	17	465.0−549.0	9.80 ± 0.20	5763 ± 100	11.86 ± 1.05
B	Cd	B07	14	464.0−547.0	9.70 ± 0.12	5738 ± 61	13.33 ± 0.66
B	Cd	B09	12	468.6−538.9	9.73 ± 0.16	5741 ± 82	12.49 ± 0.65
B	Cd	B14	14	463.2−540.0	9.82 ± 0.17	5774 ± 87	11.84 ± 0.78
B	Cd	B17	15	469.6−531.0	9.80 ± 0.18	5769 ± 93	12.03 ± 0.85

[a] The quoted uncertainties are the standard deviations.

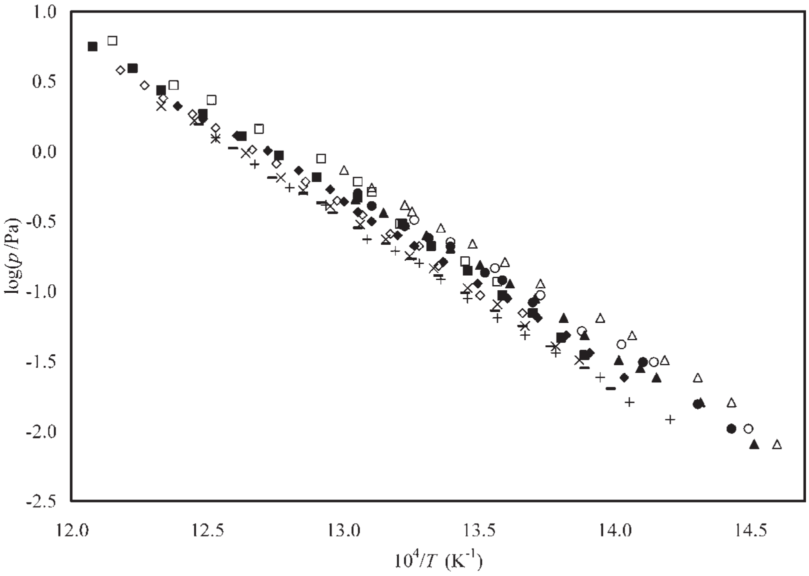

Figure 1. Torsion vapor pressures of $ZrF_4(s)$. ○, run A02; ●, run A04; △, run A07; ▲, run A09; □, run B03; ■, run B05; ◇, run B08; ◆, run B10; ×, run B12; −, run B15; +, run B18.

The very excellent agreement of our results, calculated by using torsion constants obtained from well-known vapor pressures of standards, and the results obtained by Konings and Hildebrand[9] using torsion-effusion constants derived by geometrical and physical parameters lead to the conclusion that the procedure used by us to obtain the torsion constant is valid and allows a frequent check of its value throughout the study of a compound.

Zirconium tetrafluoride vaporizes congruently in the monomeric form.[8] From the slope and intercept of our selected (eq 1) and the enthalpic increments reported by the IVTANTHERMO database,[16] the standard second-law sublimation enthalpy, $\Delta_{\mathrm{sub}}H^\circ(298\ \mathrm{K}) = 237\ \mathrm{kJ \cdot mol^{-1}}$, and entropy, $\Delta_{\mathrm{sub}}S^\circ(298\ \mathrm{K}) = 213\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, were calculated, with overall uncertainties estimated to be $\pm\ 4\ \mathrm{kJ \cdot mol^{-1}}$ and $\pm\ 3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. The obtained sublimation entropy is comparable with that selected by the IVTANTHERMO database[16] ($218\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$). The standard sublimation enthalpy was also calculated at two extreme temperatures of the experimental range (680 and 830 K) by a third-law procedure using vapor pressures from eq 1 (see Table 5). The necessary free energy function, $[G^\circ(T) - H^\circ(298\ \mathrm{K})]/T$, of

Table 2. Torsion Vapor Pressures of Solid ZrF_4

cell A							
run A02		run A04		run A07		run A09	
T	log(p	T	log(p)	T	log(p	T	log(p)
K	Pa	K	Pa	K	Pa	K	Pa
690.0	−1.98	693.0	−1.98	685.0	−2.09	689.0	−2.09
707.0	−1.51	699.0	−1.81	693.0	−1.79	698.5	−1.79
713.0	−1.38	709.0	−1.51	699.0	−1.62	706.5	−1.62
720.5	−1.28	730.0	−1.08	705.0	−1.49	709.5	−1.55
728.5	−1.03	736.0	−0.92	711.0	−1.31	713.5	−1.49
737.5	−0.84	739.5	−0.87	717.0	−1.19	720.0	−1.31
746.5	−0.65	746.5	−0.68	728.5	−0.95	724.0	−1.19
754.0	−0.49	751.0	−0.62	735.5	−0.79	729.5	−1.05
		756.0	−0.54	742.0	−0.66	734.5	−0.95
		763.0	−0.39	748.5	−0.55	740.5	−0.81
		766.0	−0.30	754.5	−0.43	746.5	−0.69
				756.0	−0.38	751.5	−0.60
				763.0	−0.26	756.0	−0.52
				769.0	−0.13	760.5	−0.44
						766.5	−0.34

cell B							
run B03		run B05		run B08		run B10	
T	log(p)	T	log(p)	T	log(p)	T	log(p)
K	Pa	K	Pa	K	Pa	K	Pa
737.0	−0.93	720.0	−1.46	724.0	−1.33	712.5	−1.62
743.5	−0.79	724.5	−1.33	732.0	−1.16	719.0	−1.44
757.0	−0.52	730.0	−1.16	740.5	−1.03	723.5	−1.31
763.0	−0.29	736.0	−1.03	749.0	−0.82	729.0	−1.19
766.0	−0.22	743.0	−0.85	753.0	−0.68	735.0	−1.05
774.0	−0.05	750.5	−0.68	759.0	−0.59	741.0	−0.95
788.0	0.16	756.5	−0.52	765.0	−0.46	748.0	−0.79
799.0	0.37	766.0	−0.33	770.5	−0.35	754.0	−0.68
808.0	0.47	775.0	−0.19	777.5	−0.22	757.5	−0.60
823.0	0.79	783.5	−0.03	784.0	−0.09	763.0	−0.50
		792.0	0.11	789.5	0.01	766.0	−0.43
		801.0	0.27	798.0	0.17	769.0	−0.36
		811.0	0.44	803.5	0.27	772.0	−0.27
		818.0	0.59	810.5	0.38	779.0	−0.14
		828.0	0.75	815.0	0.47	786.0	0.00
				821.0	0.58	793.0	0.11
						801.0	0.23
						807.0	0.32

cell B					
run B12		run B15		run B18	
T	log(p)	T	log(p)	T	log(p)
K	Pa	K	Pa	K	Pa
721.0	−1.49	715.0	−1.69	704.0	−1.92
725.5	−1.39	720.0	−1.55	711.5	−1.79
731.5	−1.25	726.5	−1.39	717.0	−1.62
737.0	−1.09	732.0	−1.25	725.5	−1.44
743.0	−0.98	737.5	−1.14	731.5	−1.31
750.0	−0.84	743.5	−1.01	737.0	−1.19
755.0	−0.75	749.0	−0.89	743.0	−1.05
760.0	−0.63	754.5	−0.77	748.5	−0.92
765.5	−0.52	760.0	−0.66	753.0	−0.80
772.0	−0.39	766.0	−0.55	758.0	−0.71
778.0	−0.28	771.5	−0.44	764.0	−0.63
783.0	−0.19	774.0	−0.37	773.0	−0.38
791.0	−0.01	778.0	−0.30	781.0	−0.26
798.0	0.09	785.0	−0.19	789.0	−0.09
803.0	0.22	794.0	0.02	798.0	0.10
811.0	0.32	802.0	0.19		

Table 3. Temperature Dependence of ZrF_4 Vapor Pressures

		ΔT		log(p/Pa)= $A - B/(T/\text{K})$	
cell	run	K	no. of points	A[a]	B[a]
A	A02	690.0−754.0	8	15.41 ± 0.40	11 988 ± 291
A	A04	693.0−766.0	11	15.25 ± 0.25	11 914 ± 181
A	A07	685.0−769.0	14	15.17 ± 0.28	11 756 ± 203
A	A09	689.0−766.5	15	15.28 ± 0.23	11 943 ± 170
B	B03	737.0−823.0	10	15.35 ± 0.47	11 973 ± 361
B	B05	720.0−828.0	15	15.17 ± 0.23	11 922 ± 179
B	B08	724.0−821.0	16	14.92 ± 0.13	11 772 ± 97
B	B10	712.5−807.0	18	15.00 ± 0.14	11 813 ± 108
B	B12	721.0−811.0	16	14.92 ± 0.10	11 819 ± 79
B	B15	715.0−802.0	16	15.27 ± 0.12	12 106 ± 91
B	B18	704.0−798.0	15	15.28 ± 0.10	12 128 ± 107

[a] The quoted uncertainty are standard deviations.

Table 4. Comparison of the Temperature Dependence of the Vapor Pressure of ZrF_4

		ΔT	log (p/Pa) = $A - B/(T/\text{K})$	
author	method	K	A	B
Lauter[1]	static	913−1178	14.673	11 413
Sense[2]	transpiration	961−1099	15.346	12 146
Sense[3]	transpiration	890−1154	15.524	12 376
Cantor[4]	diff. manometer	983−1081	14.667	11 360
Fischer[5,6]	static	983−1213	14.82	11 597
Galkin[7]	Knudsen	713−873	14.275	10 722
Akishin[8]	mass spectrometry	681−913	15.682	12 430
Konings[9]	torsion-effusion	697−856	15.260 ± 0.062	11 974 ± 26[a]
this work	torsion-effusion	685−828	15.20 ± 0.15	11 900 ± 200

[a] The quoted uncertainties are statistical values.

Table 5. Third-Law Standard Sublimation Enthalpy of ZrF_4

T	p	$-R \ln p$	$-\Delta(G^\circ(T) - H^\circ(298\ \text{K}))/T$	$\Delta_{\text{sub}}H^\circ(298\ \text{K})$
K	Pa	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
680	6.0×10^{-3}	138.3	213.7	239.4
830	8.70	77.8	211.2	239.8

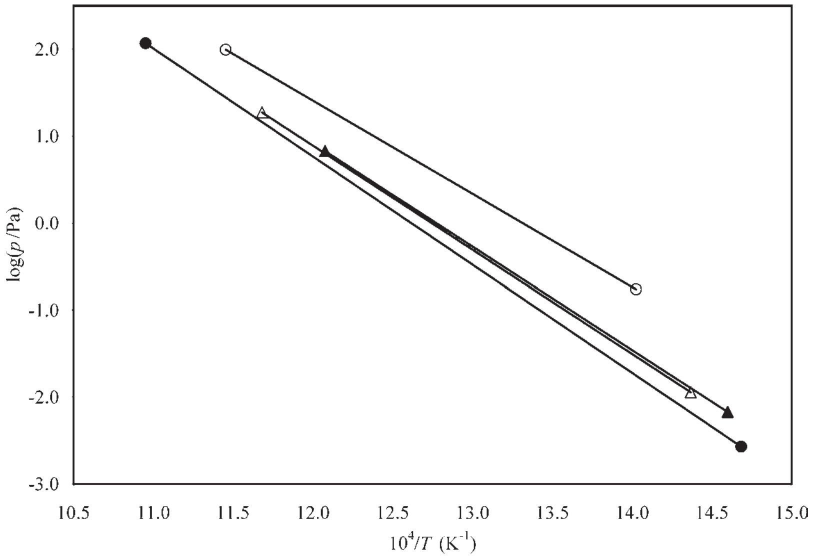

Figure 2. Comparison of the torsion total vapor pressures of ZrF_4. ○, Galkin et al.;[7] ●, Akishin et al.;[8] Δ, Konings and Hildebrand;[9]▲, this work.

solid and gaseous ZrF_4 were those selected by the IVTANTHERMO database, and the difference between the values for the gas and condensed phases were $-213.7\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $-211.2\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 680 and 830 K, respectively.[16] The two sublimation enthalpy values ($239.4\ \text{kJ}\cdot\text{mol}^{-1}$ and $239.8\ \text{kJ}\cdot\text{mol}^{-1}$) are practically equal without a temperature trend and in reasonable agreement with the second-law value ($237 \pm 4\ \text{kJ}\cdot\text{mol}^{-1}$). On this basis, we propose as the standard sublimation enthalpy of ZrF_4 $\Delta_{\text{sub}}H^\circ(298\ \text{K}) = 239\ \text{kJ}\cdot\text{mol}^{-1}$ with an overestimated uncertainty of $\pm 2\ \text{kJ}\cdot\text{mol}^{-1}$, in excellent agreement with that found in the previous torsion study[9] [$(239 \pm 3)\ \text{kJ}\cdot\text{mol}^{-1}$ and $(240 \pm 1)\ \text{kJ}\cdot\text{mol}^{-1}$ as second- and third-law results respectively].

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