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Note

VAPORIZATION THERMODYNAMICS OF THORIUM TETRAFLUORIDE

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The vapour pressure of thorium tetrafluoride has been measured experimentally by Darnell and Keneshea [1]. They measured the vapour pressure of solid ThF_4 by the effusion method and that of liquid ThF_4 by the quasi-static method. In view of some discrepancies in these data, Rand has given estimated vapour pressure equations in a recent compilation [2]. In the present study, the vapour pressure of solid ThF_4 has been measured by the transpiration technique and that of liquid ThF_4 both by transpiration and boiling point methods.

EXPERIMENTAL

Transpiration technique

The apparatus and procedure used for the vapour pressure measurements of $ThF_4(l)$ have been described earlier [3]. Purified argon was used as carrier gas and the vapour pressure values were found to be independent of the carrier gas flow rate in the range 3.0×10^{-6}—5.0×10^{-6} m^3 min^{-1}. The amount of ThF_4 transported was determined from the mass change of the condenser, and the vapour pressure of ThF_4 was calculated using the relationship $p_i = x_i P$, where p_i is the partial pressure of ThF_4 in the vapour-saturated carrier gas, x_i is the mole fraction of $ThF_4(g)$ and P is the total pressure of the system.

Reproducible results for solid ThF_4 could not be obtained using this type of apparatus. A vertical assembly was therefore designed to allow better saturation of the carrier gas with ThF_4 vapour. The apparatus is shown schematically in Fig. 1. ThF_4 was loaded in the cylindrical vessel and the system was evacuated and flushed several times with purified argon. The sample was heated with a Kanthal A1 wire-wound furnace and the temperature was measured by a chromel—alumel thermocouple inside an alumina thermowell touching the top of the cylindrical vessel. Calibration experiments showed that the temperatures inside the vessel and at the thermocouple were identical. The flow rate "plateau" was obtained in the range 1.0×10^{-5}—1.5×10^{-5} m^3 min^{-1}. The vapour pressure data are reported in Table 1.

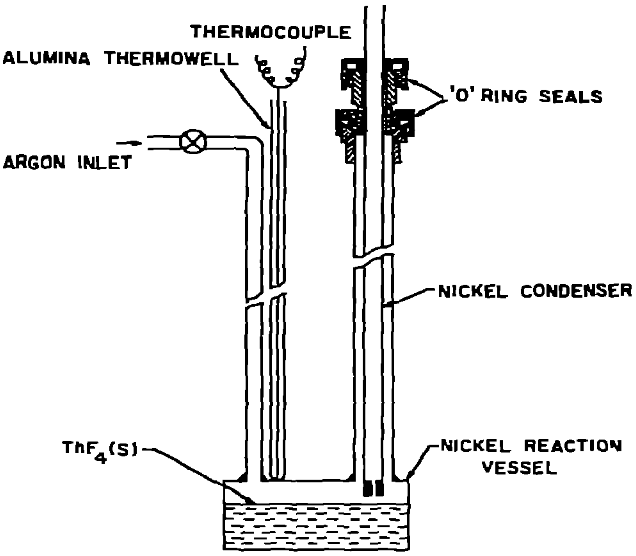

Fig. 1. Transpiration apparatus.

Boiling point technique

The experimental assembly and procedure used in these studies have been described earlier [3]. The vapour pressure data obtained using this technique are also reported in Table 1.

TABLE 1

Vapour pressure data for ThF_4

$ThF_4(s)$ Transpiration		$ThF_4(l)$			
		Transpiration		Boiling point	
T (K)	p ($\times 10^2$ kPa)	T (K)	p ($\times 10$ kPa)	T (K)	p ($\times 10$ kPa)
1293	2.05	1394	1.59	1395	1.71
1302	2.27	1412	2.18	1425	2.47
1311	2.88	1420	2.52	1429	2.82
1317	3.33	1424	2.70	1447	3.88
1324	3.90	1442	3.49	1473	5.80
1331	4.82	1459	4.24	1476	6.06
1343	5.60	1459	4.72	1501	8.70
1350	6.63	1459	4.49	1501	8.96
1359	7.94	1463	5.30	1515	10.92
1366	9.45	1470	5.49	1526	12.46
1366	9.31	1470	5.51	1531	12.97
1375	11.38	1482	7.14	1541	15.70
		1499	8.49	1554	18.26
		1510	9.36		

Materials

The thorium tetrafluoride used in these experiments was prepared by reaction of anhydrous hydrogen fluoride with reactive ThO_2 at 750—800 K. Analysis of the ThF_4 sample indicated its purity to be better than 99.5%.

RESULTS

The vapour pressure of solid ThF_4 was measured using the transpiration technique in the temperature range 1293—1375 K. The vapour pressure of liquid ThF_4 was measured using the transpiration technique in the temperature range 1394—1510 K and the boiling point method in the temperature range 1395—1554 K. The experimental data are given in Table 1. Least-squares analysis of the vapour pressure data for $ThF_4(s)$ gave eqn. (1)

$$\log_{10}(p) = (10.99 \pm 0.22) - (16416 \pm 300)\,(1/T) \tag{1}$$

where p is measured in kPa and T is the Kelvin temperature. Similarly, vapour pressure data for $ThF_4(l)$ obtained using transpiration and boiling point methods can be represented by eqns. (2) and (3), respectively

$$\log_{10}(p) = (9.50 \pm 0.21) - (14352 \pm 305)\,(1/T) \tag{2}$$

$$\log_{10}(p) = (9.49 \pm 0.09) - (14343 \pm 135)\,(1/T) \tag{3}$$

Since the vapour pressure data for liquid ThF_4 obtained using these two techniques are in excellent agreement (±2%), the two sets of data were combined to give eqn. (4)

$$\log_{10}(p) = (9.48 \pm 0.09) - (14320 \pm 135)\,(1/T) \tag{4}$$

The constants for the vapour pressure equations obtained in the present work and those reported in the literature are given in Table 2. From eqns. (1) and (4), the melting point, the normal boiling point and the enthalpy of

TABLE 2

Comparison of vapour pressure data for ThF_4 represented by $\log_{10}(p) = A - B(1/T)$

Ref.	Technique and temp. range (K)	A	B
$ThF_4(s)$			
1	Effusion (1055—1297)	(11.11 ± 0.16)	(16 860 ± 190)
2	Suggested equation (298—1383)	11.34	17 076
Present study	Transpiration (1293—1375)	(10.99 ± 0.22)	(16 416 ± 300)
$ThF_4(l)$			
1	Boiling point (1427—1595)	(9.95 ± 0.21)	(15 270 ± 310)
2	Suggested equation (1383—2055)	8.39	13 070
Present study	Transpiration (1394—1510)	(9.50 ± 0.21)	(14 352 ± 305)
	Boiling point (1395—1554)	(9.49 ± 0.09)	(14 343 ± 138)
	Combined (1394—1554)	(9.48 ± 0.09)	(14 320 ± 135)

TABLE 3

Comparison of thermodynamic and vapour pressure data for ThF_4 obtained in this study with data from the literature

Ref.	ΔH^0_{vap}(298.15 K) (kJ mole^{-1})		ΔS^0_{vap} (298.15 K) (JK^{-1} mole^{-1})	p (×10^2 kPa)			
				ThF_4(s)		ThF_4(l)	
	Second law	Third law		1290 K	1350 K	1400 K	1500 K
1	347.4	338.0	225.4	1.09	4.18 [a]	10.9 [a]	58.3
2	351.5	335.9	229.7	1.27	4.91	13.5	48.1
Present study	334.4	330.0	197.8	1.83	6.76	17.9	85.8

[a] Extrapolated.

fusion at the melting point were calculated to be 1388 K, 1916 K and 36.6 kJ mole^{-1}, respectively. The data were used to calculate the standard enthalpy of vaporization ΔH^0_{vap}(298.15 K) by second- and third-law methods. The "Σ" method reported by Darken et al. [4] was used in the second-law calculations. The relation between Σ and temperature for ThF_4(s) may be represented by

$$\Sigma = -(76.67 \pm 1.03) + (82228 \pm 1374)\,(1/T)$$

where

$$\Sigma = [-R\ln(p) + \Delta a \ln(T) + \Delta b/2(T) + \Delta c/2(1/T)^2]/\mathrm{JK^{-1}\ mole^{-1}}$$

p is measured in kPa and T is the Kelvin temperature. The constants Δa, Δb and Δc were obtained from the heat capacity data for ThF_4(s) and ThF_4(g) reported by Wagman et al. [5]. The procedure gave a value of 334.5 ± 5.7 kJ mole^{-1} for ΔH^0_{vap}(298.15 K) and 197.8 ± 0.3 J K^{-1} mole^{-1} for ΔS^0_{vap}-(298.15 K). Third-law analysis of the data was carried out using the free-energy functions reported by Wagman et al. [5], and the values of ΔH^0_{vap}-(298.15 K) obtained by using vapour-pressure data for solid and liquid are 330.0 ± 0.3 and 329.5 ± 0.4 kJ mole^{-1}, respectively. The vapour-pressure values and thermodynamic data obtained in the present study are compared with those reported in the literature in Table 3.

DISCUSSION

No other data for ThF_4(s) are available in the temperature range of the present study. The earlier effusion measurements by Darnell and Keneshea [1] lie in the temperature range 1055—1297 K. As seen from Table 3, the present data are 40% higher than the extrapolated data of Darnell and Keneshea and about 30% higher than the estimated data of Rand [2].

The vapour-pressure data for ThF_4(l) obtained by transpiration and boiling point techniques agree within 2% throughout the temperature range. As seen from Table 3, the vapour pressures of ThF_4(l) obtained in the present study are about 30% higher than the values of Darnell and Keneshea [1] and the estimated values of Rand [2].

The melting point obtained in the present study (1388 K) is in good agreement with the reported values of Asker et al. [6] (1384 K), Dergunov and Bergman [7] (1387 K), Thoma et al. [8] (1383 K) and Dworkin and Bredig [9] (1383 K). The enthalpy of fusion calculated at 1388 K is 36.6 kJ $mole^{-1}$. Using the data of Darnell and Keneshea, a melting temperature of 1365 K was obtained and the enthalpy of fusion at 1365 K was calculated to be 21.7 kJ $mole^{-1}$, which is very small compared to the present value. Rand [2] has estimated a value of 43.9 kJ $mole^{-1}$ for ΔH_{fus}(1383 K), which is higher than the present value. Since the vapour pressure of ThF_4(l) has been measured by two independent techniques in the present study and the two sets of data are in excellent agreement, we regard the present data as reliable. It can be seen from Table 3 that the values of ΔH^0_{vap}(298.15 K) obtained from ThF_4(s) vapour pressure data using second- and third-law methods, are in good agreement. ΔH^0_{vap}(298.15 K) obtained from the third-law analysis of ThF_4(s) vapour pressure data is in excellent agreement with the value obtained by a similar analysis of the vapour pressure data of ThF_4(l). ΔS^0_{vap}(298.15 K) obtained from ThF_4(s) vapour-pressure data (198.8 J $K^{-1}mole^{-1}$) is in very good agreement with the value reported by Wagman et al. [5] (199.6 J $K^{-1}mole^{-1}$). This, combined with the fact that the two vapour-pressure equations give a melting point of ThF_4 in good agreement with the reported value, show that the vapour pressure data obtained for ThF_4(s) is accurate.

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