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Vapour pressure measurement of zirconium chloride and hafnium chloride by the transpiration technique

R.P. Tangri, D.K. Bose *

Metallurgy Division, Bhabha Atomic Research Centre, Bombay-400 085, India

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Abstract

Studies on the vaporization of pure zirconium tetrachloride and hafnium tetrachloride have been conducted in the temperature range 400–520 K by the transpiration technique, using high purity argon as the carrier gas. Chemical and X-ray diffraction analyses of the condensate and of the residue confirmed the vaporization to be congruent. Assuming the vaporising species to be monomeric, the vapour pressures were calculated, and are given by the following equations

$$\log p_{(\mathrm{Pa})} = (13.51 \pm 0.058) - \frac{(5164.95 \pm 26.0)}{T} \quad (405.3 < T < 518.1\ \mathrm{K})$$

for $\langle \mathrm{ZrCl_4} \rangle \rightleftharpoons (\mathrm{ZrCl_4})$

and

$$\log p_{(\mathrm{Pa})} = (13.64 \pm 0.147) - \frac{(5112.27 \pm 63.4)}{T} \quad (398.4 < T < 500.3\ \mathrm{K})$$

for $\langle \mathrm{HfCl_4} \rangle \rightleftharpoons (\mathrm{HfCl_4})$

Keywords: Hafnium chloride; Transpiration; Vaporization; Zirconium chloride

1. Introduction

The element zirconium is always accompanied by a small amount of hafnium in nature owing to their very similar chemical properties and close atomic diameter

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* Corresponding author.

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[1]. The most important mineral from which zirconium can be extracted is either zircon (an orthosilicate) or baddeleyite. Both the minerals contain 0.5–2.0% of hafnium on a metal basis [2]. Zirconium (with minor alloying additives) finds exclusive use as a core structural material on account of its low thermal neutron cross-section (1.8×10^{-29} m^2), excellent high temperature strength and resistance to corrosion in water [3]. The associated hafnium, on the other hand, has high thermal neutron cross section (1.05×10^{-26} m^2) and is undesirable for structural use in nuclear reactors. The specification laid down for reactor grade zirconium limits the hafnium content to below 100 ppm. Therefore, in the extractive metallurgy of zirconium, a rigorous chemical processing step is essential to separate hafnium.

The conventional processes followed for the separation of zirconium and hafnium are based on aqueous systems. In these systems, the aqueous phase containing zirconium together with hafnium is contacted with an organic solvent (methyl isobutyl ketone, tributyl phosphate or tri-*n*-octylamine) to effect separation. Recently, a technique based on vapour phase separation of zirconium and hafnium has been strongly favoured over the conventional processes, as the technique is economical, it poses no pollution problems and the chlorides obtained in the process can be directly used for reduction to the metal. The development of such a technique, however, requires precise data on the relative volatility of zirconium and hafnium tetrachlorides at various temperatures. In the present investigation, an attempt has been made to determine precise vapour pressure values of these two chlorides in the temperature range 400–520 K by the transpiration technique.

The transpiration technique is a very convenient method of determining the vapour pressure of a congruently vaporizing species with known molecular mass. In this method, a carrier gas, generally inert (argon or helium), is passed over the sample ($ZrCl_4/HfCl_4$ in the present case) kept at a specific temperature at a flow rate sufficiently low for equilibrium conditions to be established. Under these conditions, the condensed vapour collected downstream is weighed to determine the vapour pressure at that temperature. The equation used for the calculation of vapour pressure (p) of the sample is as follows

$$p = \frac{n_v}{n_v + n_c} P \tag{1}$$

where n_v is the number of moles of tetrachloride transported in time t, n_c is the number of moles of inert carrier gas passed in time t, p is the vapour pressure of the tetrachloride sample in Pa, and P is the total pressure, which is 1 atm (101.325 kPa) in the present case.

2. Experimental

2.1. Materials

The zirconium and hafnium chlorides used in the present investigation were procured from the Nuclear Fuel Complex, Hyderabad. The as-received chlorides

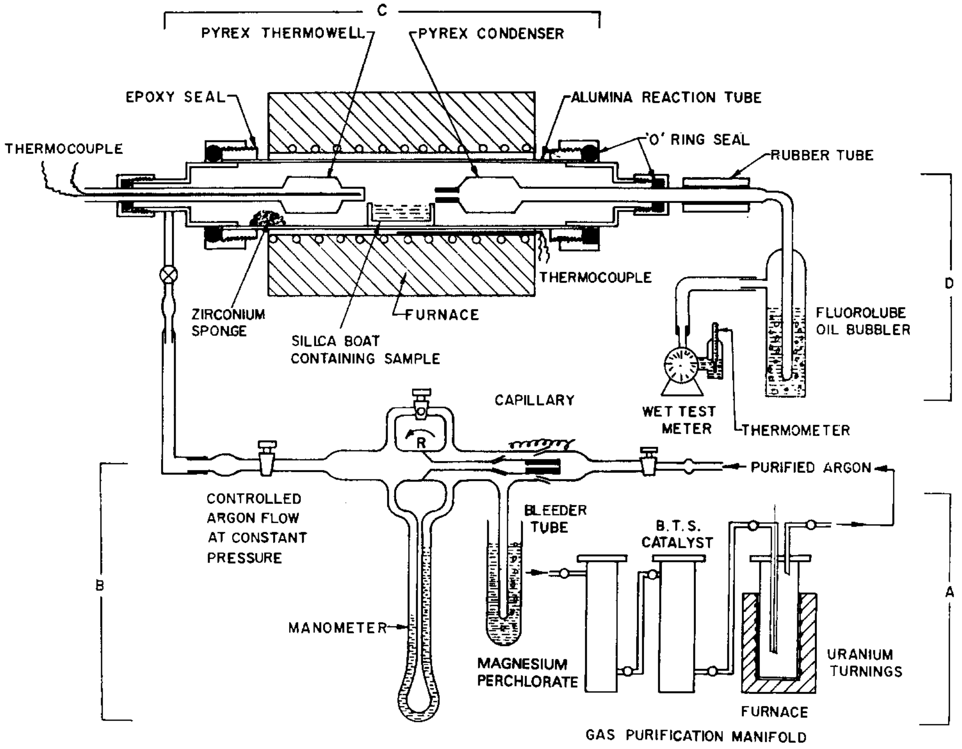

Fig. 1. Transpiration apparatus for vapour pressure measurement.

were purified by fused salt (NaCl:KCl:$ZrCl_4$, 8:29:63 mol%) scrubbing [4]. This treatment removed oxides or oxychlorides formed during handling and other metallic chloride contaminants such as $FeCl_3$, $NiCl_2$ etc. The purified chlorides were stored in a dry box, in which the pressure of high purity argon, having levels of H_2O and O_2 of 5 and 50 ppm, respectively, was kept slightly above the atmospheric pressure. Chemical and X-ray diffraction analyses of the salts confirmed these to be in the required phase and having purity of > 99.99 mass%.

2.2. Equipment

The transpiration apparatus reported elsewhere [5,6] has been modified to suit the present investigation. The apparatus as shown in Fig. 1 comprises essentially of the following major sections.

Section A: carrier gas purification assembly

High purity argon, used as a carrier gas, is obtained by passing IOLAR grade argon through a series of absorbents and getters kept in 5 cm diameter, 60 cm high stainless steel towers.

Section B: constant pressure flow meter
In this unit a horizontal capillary made of ground glass is employed to achieve constant pressure. Any pressure drop across the capillary is indicated by a sensitive U-tube manometer filled with the low vapour pressure compound dibutyl phthalate.

Section C: vapour saturation chamber
An alumina sample boat of length 80 mm is inserted into a 40 mm ID, 750 mm long alumina tube fitted with "VEECO type" fittings at each end. A thermowell and a condenser, both made of Pyrex tubing, are placed on either side of the sample boat. The bulbous ends of these two tubes, the condenser bulb having a 0.5 mm orifice for passage of vapour saturated gas, served as a diffusion barrier for the sublimate vapours. The boat containing the sample was located in the isothermal zone (± 1 K) of the furnace. A chromel to alumel thermocouple was used for the temperature measurement, which was calibrated against the melting temperature of bismuth, antimony and silver. The precision of the temperatures was better than ± 1 K.

Section D: carrier gas quantity measurement
A GCA Corporation Inc. (USA) wet test meter was used to measure the total volume of the carrier gas that passed through the transpiration tube. This wet test meter was calibrated with a soap bubble meter prior to use in the vapour pressure measurement experiments.

2.3. Standardization of the apparatus

The appropriate range of carrier gas flow rates, as mentioned in the Introduction, was determined for the present system by vaporizing high purity magnesium ($>99.9\%$, from Johnson Matthey Chemical Co., USA) at a fixed temperature of 999 K while varying the flow rate of purified argon from 1.0×10^{-5} to 8.0×10^{-5} m^3 min^{-1}. The mass of magnesium condensate per unit volume of carrier gas passed was plotted against the gas flow rate to determine the "plateau" region. In this region of carrier gas flow rate, as pointed out earlier, vaporization of the sample is independent of kinetic and diffusion effects. Based on repeated experiments conducted with magnesium, the plateau region for pure argon has been found to extend from 2.5×10^{-5} to 6.5×10^{-5} m^3 min^{-1}.

After the determination of the flow rate plateau region, the apparatus was standardized by measuring the vapour pressure of the high purity magnesium metal at different temperatures. The vapour pressure measured by this apparatus compares very well with the values determined by Hoenig and Kramer [7].

2.4. Procedure for measurement of vapour pressure

After establishing the reliability of the apparatus, experiments were conducted using zirconium and hafnium tetrachlorides. As these salts are extremely reactive and hygroscopic. An inert gas-filled glove box, having oxygen and moisture levels maintained at < 20 ppm and < 5 ppm respectively, was used for storing, handling and loading of the tetrachlorides. Normally, about 10 g of purified $ZrCl_4$/$HfCl_4$ sample was charged into the alumina tray inside the dry glove box. The tray was subsequently placed inside a small Pyrex tube having cone and socket closures at each end. After keeping the sample tray inside the Pyrex tube, both the ends were closed with the sockets. The assembly was finally taken out of the glove box for transfer of the sample tray into the reaction tube.

Before inserting the sample tray, the reaction tube was heated under vacuum to remove moisture and adsorbed gases. The alumina tray with the tetrachloride sample was then pushed into the reaction tube by opening the sockets of the assembly, maintaining a positive pressure of argon inside the reaction tube. Loading of the sample tray in this manner completely prevented exposure of the sample to the atmosphere.

After placing the sample tray at the central isothermal region of the reaction tube, the system was gradually heated to about 350 K, to ensure that the system was free from any adsorbed gases or moisture. The condenser capillary was kept in the cooler region to avoid any possible diffusion of the sample vapour into the condenser tube. After removal of moisture, the gas flow was stopped and the system was heated further to the required temperature. The system was operated for a sufficient time to allow it to attain thermal equilibrium. After ensuring thermal equilibrium, the condenser tube was pushed to the position as shown in Fig. 1 and a flow of carrier gas at a rate corresponding to the established "plateau region" was started through the wet test meter. At the end of the experiment, after discontinuing heating, the carrier gas flow was stopped and the condenser was withdrawn to its initial position in the cooler part of the reaction tube. The total volume of gas and the temperature were noted on the wet test meter. When the system temperature had cooled to room temperature, the condenser tube was removed from the reaction tube. The amount of vapour deposited into the condenser was quickly determined from its weight gain. The vapour pressure of the tetrachloride sample was calculated using Eq. (1) given in the Introduction.

Wet chemical and X-ray diffraction (XRD) analyses of the condensate and residue after vaporization under argon as carrier gas confirmed the congruency of vaporization of $ZrCl_4$ and $HfCl_4$ for the samples studied in the present investigation, and there was no association or dissociation of the molecules.

3. Results and discussion

The transpiration data together with the calculated pressure are given in Table 1. The temperature value given in the third column is the temperature at which the gas volume was measured. The pressure values reported are the average of the experimental runs, and the temperatures for the two runs were within ±1 K.

Table 1
Transpiration data and vapour pressures of $\langle ZrCl_4 \rangle$ and $\langle HfCl_4 \rangle$

Compound	Temperature in K	Carrier gas		Quantity of condensate $\times 10^2$ in g	p in Pa
		Volume in dm^3	Temperature in K		
$\langle ZrCl_4 \rangle$	405.3	15.0	301.5	0.83	5.95
	410.7	13.0	300.0	1.06	8.72
	420.2	11.0	299.5	1.68	16.30
	427.9	10.0	301.0	2.49	26.71
	436.7	8.5	300.5	3.65	45.99
	448.4	7.0	302.0	6.10	93.73
	458.8	9.0	302.0	15.29	182.57
	469.5	9.0	300.0	26.85	318.05
	485.4	8.5	301.0	57.91	725.80
	500.0	7.0	301.0	102.57	1548.24
$\langle HfCl_4 \rangle$	398.4	14.0	300.5	1.11	6.18
	402.4	14.5	300.0	1.62	8.69
	408.2	6.5	298.0	1.07	12.72
	411.9	8.0	301.5	1.77	17.30
	420.6	9.2	300.0	3.44	29.09
	429.2	7.3	297.0	5.70	60.12
	438.8	8.6	300.5	9.82	88.93
	450.5	7.0	299.0	19.03	210.43
	464.8	7.5	299.5	37.48	386.78
	475.9	6.0	296.5	64.10	815.10
	485.9	4.8	296.0	83.50	1318.37

The data thus obtained were fitted by a least squares method to a straight line and the resulting equations are given below.

$$\log p_{(\mathrm{Pa})} = (13.51 \pm 0.058) - \frac{(5164.95 \pm 26.0)}{T}; \quad 405.3 < T < 518.1\ \mathrm{K}$$

for $\langle ZrCl_4 \rangle \rightleftharpoons (ZrCl_4)$

and

$$\log p_{(\mathrm{Pa})} = (13.64 \pm 0.147) - \frac{(5112.27 \pm 63.4)}{T}; \quad 398.4 < T < 500.3\ \mathrm{K}$$

for $\langle HfCl_4 \rangle \rightleftharpoons (HfCl_4)$.

The vapour pressures for the two salts are shown in Fig. 2. The heats of sublimation for $ZrCl_4$ and $HfCl_4$ as determined from the slopes of the curves in the temperature ranges 405–500 K and 398–486 K are calculated to be 99.24 kJ mol^{-1} and 99.12 kJ mol^{-1} respectively. The entropy of sublimation in the studied temperature range for $ZrCl_4$ and $HfCl_4$ is calculated to be 163.59 J mol^{-1} K^{-1} and 168.28 J mol^{-1} K^{-1}.

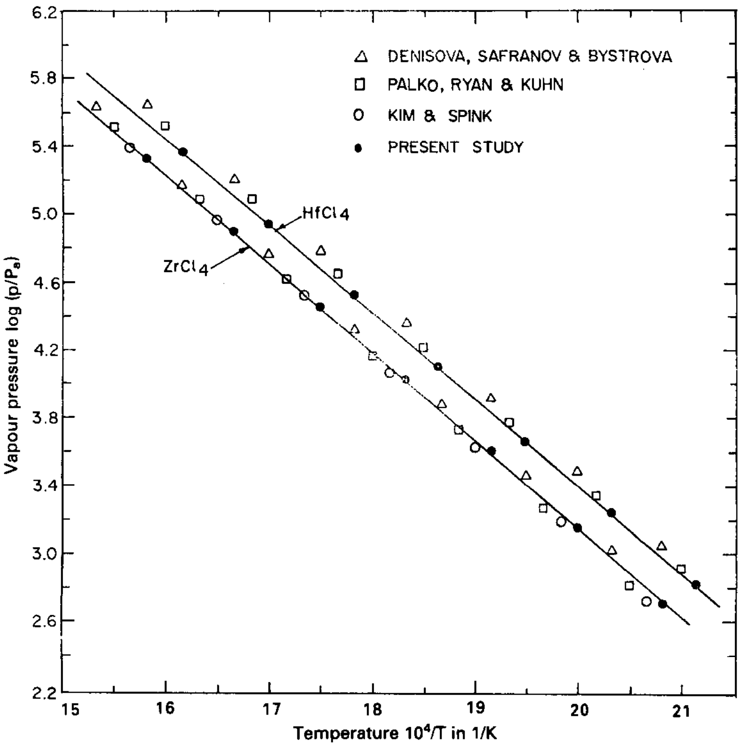

Fig. 2. Vapour pressure of $ZrCl_4$ and $HfCl_4$.

Table 2
Comparison of vapour pressure data for $ZrCl_4$ and $HfCl_4$

Sample No.	Temperature in K		Vapour pressure of $ZrCl_4$ ($\log p_{(Pa)}$)				Vapour pressure of $HfCl_4$ ($\log p_{(Pa)}$)		
	T	$1/T(\times 10^4)$	Ref. 9	Ref. 8	Ref. 4	Present	Ref. 9	Ref. 8	Present
1	475.0	21.1	2.66	2.52	2.54	2.64	2.96	2.90	2.88
2	500.0	20.0	3.21	3.09	3.10	3.18	3.50	3.44	3.42
3	525.0	19.0	3.70	3.61	3.60	3.67	3.99	3.94	3.90
4	550.0	18.2	4.15	4.07	4.06	4.12	4.44	4.39	4.34
5	575.0	17.4	4.56	4.50	4.48	4.53	4.84	4.80	4.75
6	600.0	16.7	4.94	4.89	4.87	4.90	5.22	5.18	5.12

As can be seen from Table 2, the results of the present work agree well with those reported in the literature by Kim and Spink [4], Palko et al. [8] and Denisova et al. [9]. The comparison is also shown in Fig. 2.

4. Conclusions

(1) The saturated vapour pressure of $ZrCl_4$ and $HfCl_4$ has been measured by the transpiration technique. The temperature dependence of the vapour pressure and the heat of sublimation and entropy of sublimation for the studied temperature range are discussed.

(2) It has been observed that, in the temperature range 400–520 K, log p for the salts varies linearly as a function of $1/T$. The vapour pressure rises sharply with a rise in temperature. The measured vapour pressure values agree very well with the data reported in the literature [4,8,9].

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