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Vapor Pressure of $ZrCl_4$ and $HfCl_4$ over Melt Systems KCl + $AlCl_3$ (1:1.04 mol) + $ZrCl_4$ and KCl + $AlCl_3$ (1:1.04 mol) + $HfCl_4$

R. P. Tangri, D. K. Bose,* and C. K. Gupta

Materials Group, Bhabha Atomic Research Centre, Bombay 400 085, India

The vapor pressures of $ZrCl_4$ and $HfCl_4$ over a molten salt mixture of KCl + $AlCl_3$ (1:1.04 mol) + XCl_4 (X = Zr, Hf) was determined in the temperature range of 485−627 K by the transpiration technique. The compositions of $ZrCl_4$ and $HfCl_4$ in the molten salt system were chosen such that it would be useful for vapor phase separation of $ZrCl_4$ from $Zr(Hf)Cl_4$ by an extractive distillation technique employing KCl + $AlCl_3$ as the fused salt solvent. The relative volatility factor of p_{HfCl_4}/p_{ZrCl_4} over the KCl + $AlCl_3$ + XCl_4 (X = Zr, Hf) molten salt systems was determined to be 1.5 in the composition range of 16−30 mol % $HfCl_4$ or $ZrCl_4$. This indicated the possibility of separation of $ZrCl_4$ and $HfCl_4$ by extractive distillation with KCl + $AlCl_3$ molten salt solvent at ambient pressure.

Introduction

Zircon, an orthosilicate or zirconium, is the most widely distributed and abundant resource of zirconium in the world. Another mineral, baddeylite, is almost a pure oxide of zirconium and occurs only in the mountainous plateau of Brazil. In these minerals, hafnium always coexists with zirconium in a mixed crystal lattice (Blumenthal, 1958). The hafnium content varies from 2 to 2.5 mass % in these minerals on a metal basis. Zirconium, with some minor alloy addition, is primarily used in nuclear power reactors as core structural materials due to its low thermal neutron cross section (1.80×10^{-29} m^2), excellent high-temperature strength, and resistance to corrosion in water (Franklin and Lang, 1991). A small quantity of zirconium is also used as a corrosion resistance material in the chemical industry and as an alloy additive for the grain refinement of aluminum and magnesium alloys (Strieter, 1953). Hafnium, on the other hand, finds its application as a control-rod material in nuclear reactors on account of its high thermal neutron cross section (1.05×10^{-26} m^2), good mechanical strength, and corrosion resistance in hot water (Benedict and Pigford, 1957). Minor addition of hafnium inhibits grain growth in tungsten filaments used in incandescent lamps (Lomas, 1953).

Zirconium metal, used for structural applications in nuclear reactors, should be very low in hafnium content (<100 ppm) due to its high thermal neutron cross section. Thus, in the process metallurgy of zirconium, a rigorous chemical processing step is required to separate hafnium. However, due to nearly identical ionic radii, 0.080 and 0.081 nm for zirconium and hafnium, respectively, they have very similar chemical properties which makes the separation of these elements extremely difficult.

Table 1. Physical Constants of Zirconium and Hafnium Tetrachlorides

properties	$ZrCl_4$	$HfCl_4$
sublimation temperature, K	603.0	590.0
triple point		
temperature, T^t/K	710.0	705.0
pressure, P^t/kPa	2235.9	4501.3
critical point		
temperature T^c/K	770.0	722.2
pressure P^c/kPa	5766.3	5776.1

The standard processes followed industrially for the separation of zirconium from hafnium involve aqueous-based systems. In these systems, the aqueous phase containing zirconium and hafnium is contacted with organic solvents like methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), or tri-*n*-octylamine (TNOA) to effect separation (Gupta, 1987). The hafnium-free zirconium oxide product obtained from these processes is then chlorinated to zirconium tetrachloride before subjecting it to Kroll reduction to produce nuclear grade zirconium metal. Critical analysis of the operating data of these three aqueous-based processes shows that all these processes are highly energy intensive and uneconomical. A large volume of corrosive liquids is required to be handled, which create severe problems in material selection. The processes also generate huge volumes of liquid waste, which are difficult to dispose due to stringent environmental protection laws.

As tetrachlorides are the starting intermediate for the Kroll reduction to metal Zr and Hf, the process based on direct separation of $ZrCl_4$ and $HfCl_4$ has recently attracted attention. The process is expected to be better economically due to less unit operations and chemical consumption, higher overall yield, and reduction of effluents. References to the relative volatility factor of chlorides of zirconium and hafnium include Pickles and Flengas (1981) and Flengas and Dutrizac (1977). The techniques reported can be classified into (i) fractional sublimation, (ii) separation through formation of additional compounds, (iii) high-pressure liquid−vapor separation, and (iv) ambient pressure extractive distillation.

Physical constant data for zirconium and hafnium tetrachlorides, given in Table 1 (Denisova et al., 1967), show the possibility of separation by fractional distillation at a reasonably low temperature of 570−670 K. Though the relative volatility factor of pure hafnium tetrachloride and zirconium tetrachloride is reasonably high (1.9) at 523 K under 0.1 MPa of pressure, several earlier attempts (Plucknett et al., 1949; Jacque and Dumez, 1967; Gillot and Goldberger, 1969) have not gained industrial importance as the separation is dependent on solid−vapor contact which is generally very inefficient.

The separations through the formation of oxy chloride compounds like {$3Zr(Hf)Cl_4$ + $2POCl_3$} (VanArkel and deBoer, 1927) and alkoxides (Bradley and Wardlaw, 1951) make up some of the classical methods used for preparing hafnium-free zirconium on a small scale. The processes, however, have very limited applications due to a low separation factor (α = 1.4), poor throughput, and problems

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encountered in the handling of chlorides at high temperatures.

Liquid–vapor distillation is more efficient than solid–vapor distillation. However, a high pressure on the order of 4–6 MPa (see Table 1) is required to maintain the liquid–vapor condition needed for separation. Bromberg (1958) and Ishizuka (1982) successfully separated purified $ZrCl_4$ by this technique. However, technical difficulties to maintain such a high pressure in the distillation column prevented its application in large-scale production (Kim and Spink, 1974).

Vapor phase separation by extractive distillation with a fused salt solvent is considered as a serious alternative to the solvent extraction route. In this technique, the separation is achieved via sublimination from a solution of $Zr(Hf)Cl_4$ in molten salt which selectively decreases the activity of one of the tetrachlorides and permits separation at ambient pressure at a reasonably lower temperature. The first trial in this direction was made by Eaton (1956) using a $NaCl + ZrCl_4$ solution at 623 K. Another well-established method for the preparation of pure $HfCl_4$ was carried out by Plucknet (1957). Spink and Jonasson (1981) carried out detailed studies on the physicochemical as well as applied aspects of the separation of zirconium and hafnium tetrachlorides with $NaCl + KCl + Zr(Hf)Cl_4$ (8:29:63 mol %) solvent.

The present investigation is concerned with the determination of the vapor pressure of $ZrCl_4$ and $HfCl_4$ over the fused salt systems $KCl + AlCl_3$ (1:1.04 mol) $+ ZrCl_4$ and $KCl + AlCl_3$ (1:1.04 mol) $+ HfCl_4$ in the temperature range of 485–627 K by a transpiration technique. The $KCl + AlCl_3$ binary eutectic was chosen because (i) it has a high solubility for $ZrCl_4$ and $HfCl_4$ at temperatures above 590 K, (ii) the solutions thus formed have a low vapor pressure of the tetrachlorides, and (iii) the solution has a low viscosity. All these properties are highly desirable for the solvent needed for extractive distillation.

The transpiration technique is a very convenient method for determining the vapor pressure of a congruently vaporizing species with known molecular mass (Alcock and Hooper, 1961). In this method, an inert carrier gas (argon, helium) is passed over the $KCl + AlCl_3 + ZrCl_4$ or $KCl + AlCl_3 + HfCl_4$ solution kept at a specific temperature at a flow rate sufficiently low for equilibrium conditions to be established. Under this condition, the mass of the condensed vapor collected downstream determines the vapor pressure at a given temperature. The equation used for calculation of the vapor pressure (p) of the sample at a given temperature is

$$p = n_V P/(n_V + n_C)$$

where n_V = moles of tetrachloride transported in time t, n_C = moles of inert carrier gas passed in time t, p = vapor pressure of the tetrachloride, and P = total pressure, 101.32 kPa.

Experimental Section

Materials. Nuclear grade $ZrCl_4$ ([Hf] < 100 ppm), procured from Nuclear Fuel Complex, Hyderabad, India, was used. Pure $HfCl_4$ was prepared by the chlorination of electrolytic grade hafnium containing 3.8% zirconium on a metal basis. Other impurities present were <50 ppm Al, <50 ppm Fe, <25 ppm Ti, and <25 ppm Mg. Both zirconium and hafnium tetrachlorides were further purified by scrubbing with a fused salt mixture of $NaCl + KCl$ prior to use. This step removed traces of oxides and oxy chlorides formed during handling (Kim and Spink, 1974). Chemical and X-ray diffraction analyses of the purified chlorides confirmed the presence of the required phase ($ZrCl_4$, $HfCl_4$) only. Because of high reactivity of the tetrachlorides with moisture and oxygen, extreme care was taken to avoid contact with atmospheric air. Handling of these tetrachlorides like their weighing, mixing with known masses of $KCl + AlCl_3$ and finally transferring the mixture in a sample boat was carried out inside a glovebox, where the pressure of high-purity argon (moisture, <5 ppm, and oxygen, <20 ppm) was kept slightly above atmosphere pressure so as to prevent diffusion of moisture into the glovebox.

Apparatus. The transpiration apparatus, reported earlier (Prasad et al., 1977; Tangri et al., 1989) was modified for use in the present investigation. The apparatus, shown in Figure 1, had four major sections, viz., (a) a carrier gas purification assembly, (b) a constant pressure flow meter, (c) a vapor saturation chamber with a resistance heating furnace, and (d) a carrier gas measuring device.

An alumina boat of length 85 mm was used to load the sample. The sample was heated with a nichrome wire wound resistance furnace having a constant temperature (±1 K) zone of length 120 mm. A thermocouple well and a condenser tube, both Pyrex, were placed on either side of the sample boat. Wider (bulblike) ends of these two tubes, as shown in the figure, acted as reflectors. The constriction in front of the condenser tube served as a diffusion barrier and also minimized heat loss.

Vapor Pressure. Prior to the measurement of the vapor pressure of $ZrCl_4$ or $HfCl_4$ in the $KCl + AlCl_3 + XCl_4$ (X = Zr, Hf) melt, the equipment was standardized by measuring the vapor pressure of high-purity magnesium (>99.99% procured from Johnson and Matthey Chemical Co.). The condenser as well as thermowell used for magnesium was made of recrystallized alumina. The "plateau" region in the plot of mass per unit volume of the condensate (at a fixed temperature) against the carrier gas flow rate is the region where the vaporization is independent of the kinetic and diffusion effects. Hence, experiments performed in the plateau region need no correction for these effects. On the basis of a number of experiments conducted with magnesium, the plateau region was found to extend from 2.5×10^{-5} to 6.5×10^{-5} $m^3\ min^{-1}$ of argon. The vapor pressure of pure magnesium was measured in the temperature range 945–1100 K. From the experimental vapor pressure data of magnesium, $\Delta_f H°(298.15\ K)$ of magnesium vapor was calculated using the free energy function values from Stull and Sinke (1956), and the value obtained was (147.62 ± 0.38) kJ mol^{-1}. This agreed well with the reported value of (147.1 ● 0.80) kJ mol^{-1} (CODATA, 1978).

Reagent grade KCl dried under vacuum at 725 K was mixed with reagent grade anhydrous $AlCl_3$ in the molar ratio 1:1.04. This mixture was melted under dry argon to give the eutectic mixture $KAlCl_4$ having a well-defined melting point of 533 K. Mixing of this fused salt with either $ZrCl_4$ or $HfCl_4$ at room temperature and loading into an alumina boat were carried out in the argon-filled dry glovebox. Usually about 10 g of intimately mixed $ZrCl_4$ (or $HfCl_4$) and $KAlCl_4$ powder was charged into the alumina boat inside the glovebox. The amount of tetrachloride in the charge was varied from 16.5 to 30.0 mol %. The boat was subsequently placed inside a Pyrex tube having a cone and socket closure at both ends. After keeping the sample tray inside the tube with both the ends of the tube closed with sockets, the assembly was taken out of the glovebox for transferring to the transpiration tube.

Prior to inserting the sample boat, the reaction tube was heated under vacuum to remove moisture and adsorbed

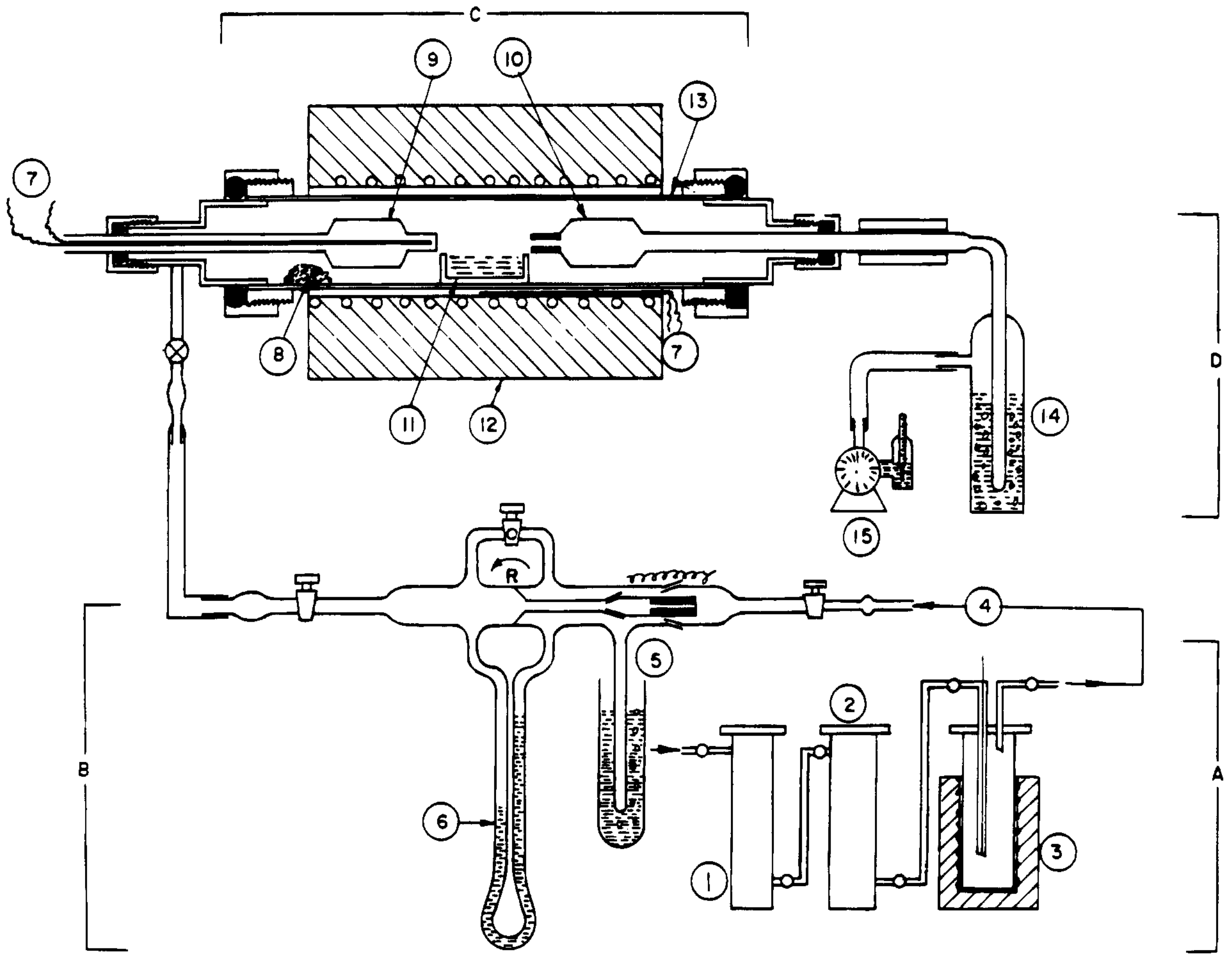

Figure 1. Transpiration apparatus for vapor pressure measurement: (1) magnesium perchlorate, (2) BTS catalyst, (3) uranium turnings, (4) purified argon, (5) bleeder tube, (6) manometer, (7) thermocouple, (8) zirconium sponge, (9) Pyrex thermowell, (10) Pyrex condenser, (11) sample, (12) furnace, (13) alumina reaction tube, (14) oil bubbler, (15) wet test meter.

gases. The alumina tray containing the mixture of $ZrCl_4$ or $HfCl_4$ and $KAlCl_4$ was then pushed from the enclosed Pyrex tube to the isothermal zone of the vapor saturation chamber under a positive pressure of argon. Loading the sample in this manner reduced exposure of the sample to the atmosphere.

After placing the sample boat in the central isothermal region, the system was gradually heated in a rapid stream of argon at 322 K to ensure the system was free from any moisture and adsorbed gases. During this period, the condenser was kept in the cooler region to avoid any possible diffusion of the sample vapor into the condenser tube. After removal of moisture, the gas flow was stopped and the system heated to the required temperature and kept there for some time to attain thermal equilibrium. When the system attained thermal equilibrium, the condenser was pushed to the position shown in Figure 1. At this stage, the carrier gas was admitted at a rate corresponding to the plateau region for the tetrachloride systems (2.5×10^{-5} to 4.5×10^{-5} m^3 min^{-1}). At the end of the experiment, the heating was discontinued and the carrier gas flow stopped. The total volume of carrier gas passed was measured on the wet test meter. The condenser was also withdrawn to its initial position in the cooler region of the reaction tube. When the system cooled to room temperature, the condenser tube was removed from the reaction tube and its mass determined. The quantity of vapors deposited was determined by the mass gain of the condenser tube.

Table 2. Composition of the $ZrCl_4$ (or $HfCl_4$) + KCl + $AlCl_3$ Mixture used for Measurement of the Vapor Pressure of $ZrCl_4$ (or $HfCl_4$) over the Ternary Salt Melt

set no.	$[ZrCl_4]$/(mol %)	[KCl]/(mol %)	$[AlCl_3]$/(mol %)	set no.	$[HfCl_4]$/(mol %)	[KCl]/(mol %)	$[AlCl_3]$/(mol %)
Zr-1	16.50	40.93	42.57	Hf-1	16.50	40.93	42.57
Zr-2	23.40	37.55	39.05	Hf-2	23.40	37.55	39.05
Zr-3	26.20	36.18	37.62	Hf-3	26.20	36.18	37.62
Zr-4	30.00	34.31	35.69	Hf-4	30.00	34.31	35.69

Results and Discussion

The composition studied in the ternary systems KCl + $AlCl_3$ + $ZrCl_4$ and KCl + $AlCl_3$ + $HfCl_4$ was a 1:1.04 molar mixture of KCl + $AlCl_3$, with the balance consisting of the particular tetrachloride. Four different compositions in the range of 16.5−30 mol % $ZrCl_4$ for the $ZrCl_4$ salt system and 16.5−30.0 mol % $HfCl_4$ for the $HfCl_4$ salt system as shown in Table 2 were measured in the temperature range 485−627 K. Results of these vapor pressure studies are presented in Tables 3 and 4.

The KCl + $AlCl_3$ in a 1:1.04 mole ratio formed a low melting (533 K) eutectic, and this binary salt melt had a very good solubility of $ZrCl_4$ or $HfCl_4$ (>40 mass %), forming a homogenous colorless solution. The ternary melt of either KCl + $AlCl_3$ + $ZrCl_4$ or KCl + $AlCl_3$ + $HfCl_4$ could be thermally stripped to almost free of zirconium or hafnium chloride at 773 K. These dissolution and stripping characteristics were considered to be very helpful in the separation of zirconium and hafnium chlorides by distillation. Analyses of thermally stripped vapor of $ZrCl_4$ or $HfCl_4$ revealed no evidence of the presence of potassium

Table 3. Vapor Pressure of $ZrCl_4$ over the KCl + $AlCl_3$ (1:1.04 mol) + $ZrCl_4$ Salt System

set no.	$[ZrCl_4]$/(mol %)	$10^3K/T$	log(*p*/Pa)	set no.	$[ZrCl_4]$/(mol %)	$10^3K/T$	log(*p*/Pa)
Zr-1	16.5	2.06	2.49	Zr-3	26.2	2.15	2.40
		1.98	2.76			2.10	2.67
		1.89	3.05			2.04	2.98
		1.82	3.34			1.97	3.28
		1.75	3.55			1.92	3.48
		1.70	3.75			1.87	3.67
		1.64	3.99			1.83	3.78
		1.61	4.06			1.79	3.93
Zr-2	23.4	2.09	2.59	Zr-4	30.0	2.16	2.34
		2.02	2.81			2.14	2.51
		1.95	3.09			2.07	2.80
		1.88	3.34			2.02	3.09
		1.81	3.62			1.95	3.46
		1.72	3.94			1.88	3.76
		1.65	4.15			1.83	3.93
		1.62	4.27			1.78	4.13

Table 4. Vapor Pressure of $HfCl_4$ over the KCl + $AlCl_3$ (1:1.04 mol) + $HfCl_4$ Salt System

set no.	$[HfCl_4]$/(mol %)	$10^3K/T$	log(*p*/Pa)	set no.	$[HfCl_4]$/(mol %)	$10^3K/T$	log(*p*/Pa)
Hf-1	16.5	2.03	2.75	Hf-3	26.2	2.20	2.31
		1.98	2.91			2.16	2.51
		1.94	3.07			2.05	3.11
		1.88	3.30			1.96	3.54
		1.83	3.46			1.91	3.70
		1.79	3.59			1.88	3.80
		1.75	3.72			1.83	3.95
		1.72	3.86			1.81	4.06
		1.67	4.01			1.79	4.10
		1.65	4.11				
Hf-2	23.4	2.04	3.03	Hf-4	30.0	2.15	2.59
		1.97	3.21			2.11	2.80
		1.91	3.45			2.01	3.35
		1.86	3.61			1.93	3.77
		1.82	3.72			1.89	3.90
		1.79	3.85			1.87	4.01
		1.74	4.04			1.85	4.07
		1.68	4.24			1.82	4.17

or aluminum salts. Therefore, the measurements of the vapor pressure of $ZrCl_4$ or $HfCl_4$ over the respective ternary salt system by the transpiration technique represented the true equilibrium pressure of $ZrCl_4$ or $HfCl_4$.

Vapor pressure studies of $ZrCl_4$ or $HfCl_4$ over the salt system KCl + $AlCl_3$ + XCl_4 (X = Zr, Hf) were carried out by varying the tetrachloride content from 16.5 to 30 mol %. The vapor pressure over the ternary salt system containing more than 30 mol % $ZrCl_4$ or $HfCl_4$ was relatively high and was not amenable to study in this apparatus.

The vapor pressure data obtained for KCl + $AlCl_3$ + $ZrCl_4$ were plotted in Figure 2 as log *p* vs 1/*T*. The vapor pressure of $HfCl_4$ over the KCl + $AlCl_3$ (1:1.04 mol) + $HfCl_4$ system is shown in Figure 3.

For the less volatile $ZrCl_4$ with the solvent KCl + $AlCl_3$ (1:1.04 mol), for a composition of more than 23.4 mol %, Figure 2 shows that the vapor pressure curve changes at the liquidus and follows the vapor pressure of pure tetrachloride. This indicates that the $ZrCl_4$ concentration in the solvent salt melt should not be increased beyond 23.4 mol % (40 mass %) during extractive distillation.

A similar phenomenon was also observed with $HfCl_4$ with the solvent KCl + $AlCl_3$ (1:1.04 mol) as shown in Figure 3. However, the vapor pressure of $HfCl_4$ is always relatively higher than $ZrCl_4$ at the corresponding temperature and composition.

From the present studies on the vapor pressure measurements, the volatility of $HfCl_4$ over KCl + $AlCl_3$ (1:1.04 mol) was found to be on an average 1.5 times that of $ZrCl_4$ in the composition range of tetrachloride of 16.5–23.4 mol % or below. Therefore, at this relative volatility factor (α = 1.5) over the KCl + $AlCl_3$ (1:1.04 mol) + $ZrCl_4$ (or $HfCl_4$) salt system, it may be possible to separate $HfCl_4$ from $ZrCl_4$ by extractive distillation at ambient pressure.

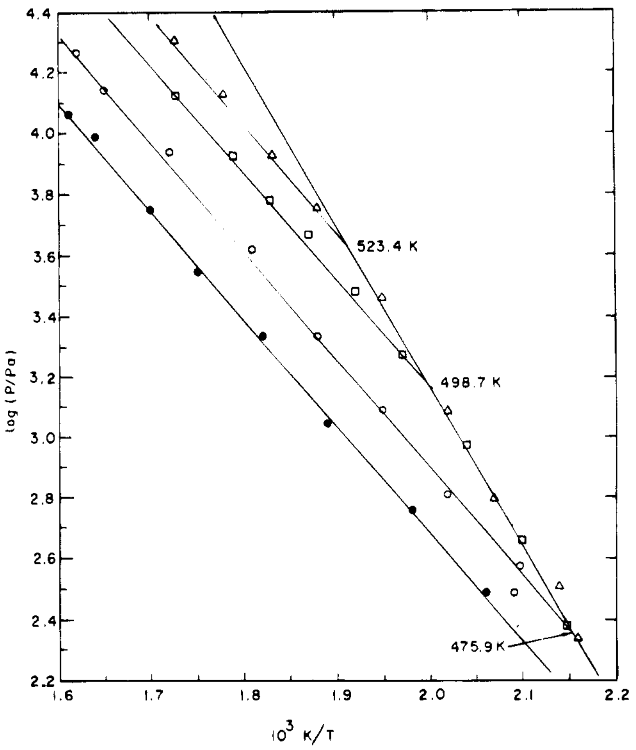

Figure 2. Vapor pressure of $ZrCl_4$ in the KCl + $AlCl_3$ (1:1.04 mol) + $ZrCl_4$ system: (△) 30.0 mol % $ZrCl_4$, (□) 26.2 mol % $ZrCl_4$, (○) 23.4 mol % $ZrCl_4$, (●) 16.5 mol % $ZrCl_4$.

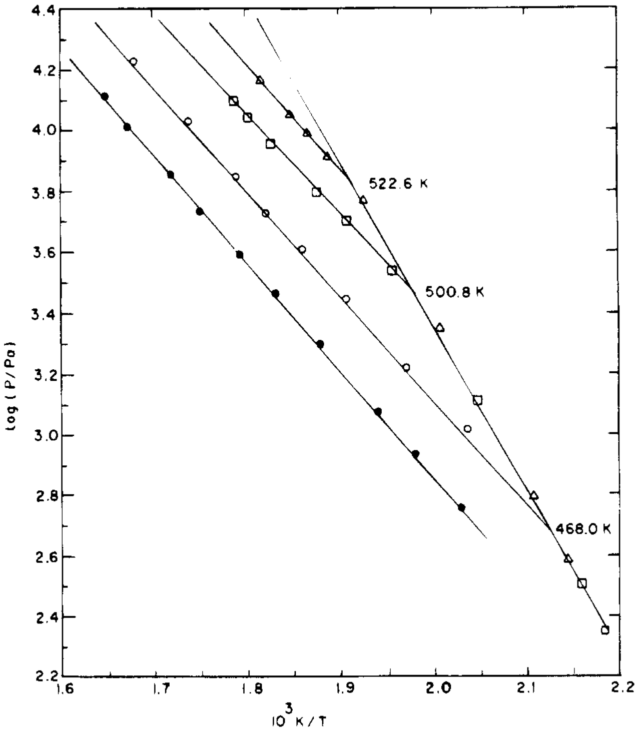

Figure 3. Vapor pressure of $HfCl_4$ in the KCl + $AlCl_3$ (1:1.04 mol) + $HfCl_4$ system: (△) 30.0 mol % $HfCl_4$, (□) 26.2 mol % $HfCl_4$, (○) 23.4 mol % $HfCl_4$, (●) 16.5 mol % $HfCl_4$.

The relative volatility factor (α = 1.5) determined by the present technique is very useful to predict *X*–*Y* data (where

X is the mole fraction of a component in the liquid phase in a binary solution and Y is the corresponding mole fraction of the same in the vapor phase) at equilibrium conditions. It should be mentioned here that in chemical engineering practice, in the analysis of vapor–liquid equilibrium, X–Y data are essential to obtain the required equilibrium data and plot the equilibrium curve. The equilibrium plot is used for the prediction of the number of stages required for achieving the desired level of separation by fractional distillation. McCabe and Thiele (1925) developed a graphical method, widely used to predict the number of equilibrium stages from the equilibrium curve. An attempt has been made to use a similar method to separate $HfCl_4$ from $ZrCl_4$ to a desired level from their binary solution $ZrCl_4$ + $HfCl_4$ in the presence of a fused salt solvent, KCl + $AlCl_3$, at ambient pressure. The theoretically calculated data provide valuable guidelines in the engineering design of a multistage distillation tower for the separation of $HfCl_4$ from $HfCl_4$ + $ZrCl_4$. In this computation method it has been assumed that the determined relative volatility factor of these two chlorides over the solvent KCl + $AlCl_3$ is nearly constant ($a = 1.5$) over the operating temperature of the distillation column, 573–598 K, and also over each fractional distillation stage.

Generally, the zirconium tetrachloride obtained by direct chlorination of either zircon or ZrO_2 contains 2.5 mass % hafnium on a metal basis. Starting with this feed material ($x_F = 2.5$ mass % $HfCl_4$) and aiming for the extractive distillation to result in a bottom product containing <0.01 mass % $HfCl_4$ and overhead product containing 96 mass % $HfCl_4$, a graphical computation by the McCabe and Thiele diagram (with $a = 1.5$) predicted 49 theoretical stages.

Conclusion

(1) The vapor pressures of $ZrCl_4$ and $HfCl_4$ over the halide salt system KCl + $AlCl_3$ (1:1.04 mol) + XCl_4 (X = Zr or Hf), respectively, were determined in the temperature range 485–627 K by the transpiration technique.

(2) The KCl + $AlCl_3$ (1:1.04 mol) binary salt solvent has a melting point as low as 533 K. It has a very high solubility (>40 mass %) of tetrachlorides ($ZrCl_4$ or $HfCl_4$) and excellent stripping characteristics as demanded for vapor phase separation by extractive distillation.

(3) The vapor pressure of $ZrCl_4$ or $HfCl_4$ was found to be substantially low over the KCl + $AlCl_3$ (1:1.04 mol) + XCl_4 (X = Zr, Hf) system having a tetrachloride concentration below <23.4 mol %.

(4) The volatility of $HfCl_4$ over KCl + $AlCl_3$ + $HfCl_4$ was 1.5 times that of $ZrCl_4$ over the KCl + $AlCl_3$ + $ZrCl_4$ melt solution on average in the temperature and composition ranges studied, indicating the possibility of separation of $HfCl_4$ and $ZrCl_4$ by extractive distillation.

(5) Starting with a material containing 2.5 mass % $HfCl_4$ on a metal basis and considering the relative volatility factor of $HfCl_4$ to be 1.5 times that of $ZrCl_4$ in the solvent KCl + $AlCl_3$, the McCabe and Thiele diagram predicted 49 theoretical stages to produce a bottom product of $ZrCl_4$ containing <0.01 mass % $HfCl_4$ and a top overhead condensate containing 96 mass % $HfCl_4$ using a extractive distillation technique employing KCl + $AlCl_3$ as the solvent.

Literature Cited

Alcock, C. B.; Hooper, J. T. Measurement of Vapour Pressures at High Temperatures by Transpiration Method. In *Physical Chemistry of Process Metallurgy*; St. Pierre, G. R., Ed.; Interscience: New York, 1961; Part I, pp 325–340.

Benedict, M.; Pigford, T. *Nuclear Chemical Engineering*; McGraw-Hill: New York, 1957.

Blumenthal, W. B. *The Chemical Behaviour of Zirconium*; Van Nostrand: New York, 1958.

Bradley, D. C.; Wardlaw, W. Zirconium Alkoxides. *J. Chem. Soc.* **1951**, 280–285.

Bromberg, M. L. Zirconium Tetrachloride. U.S. Patent 2,852,446, Sept 16, 1958.

CODATA. Recommended Key Values for Thermodynamics. *J. Chem. Thermodyn.* **1978**, *10*, 903–906.

Denisova, N. D.; Safronov, E. K.; Pustil'nik, A. I.; Bystrova, O. N. Boundary Liquid-Vapour Curve and Saturated Vapour Pressure of $ZrCl_4$ and $HfCl_4$. *Russ. J. Phys. Chem.* **1967**, *41*, 30–33.

Eaton, R. B. Separation of Hafnium Tetrachloride. U.S. Patent 2,744,060, May 1, 1956.

Flengas, S. N.; Dutrizac, J. E. A New Process for the Separation of Hafnium from Zirconium. *Metall. Trans. B* **1977**, *8B*, 377–383.

Franklin, D. G.; Lang, P. M. Zirconium-Alloy Corrosion: A Review Based on an IAEA Meeting. In *Zirconium in Nuclear Industry*, Ninth International Symposium, ASTM STP-1132; Eucken, C. M., Garde, A. M., Eds.; American Society for Testing and Materials: Philadelphia, PA, 1991; pp 3–32.

Gillot, J.; Goldberger, W. M. Separation by Thin Film Fractional Sublimation. *Chem. Eng. Prog. Symp. Ser.* **1969**, *65* (91), 36–42.

Gupta, C. K. *Materials in Nuclear Energy Application*; CRC Press: Boca Raton, FL, 1987; Vol. II, pp 10–34.

Ishizuka, H. Separation of Zirconium and Hafnium Tetrachlorides from a Mixture Comprising Such Chlorides and Apparatus for the Process. Eur. Pat. Appl. EP 45,270, Feb 3, 1982.

Jaeque, L.; Dumez, P. Continuous Fractional Sublimation Without Reflux and its Use in the Separation of Zirconium and Hafnium. *Chim. Ind., Genie Chim.* **1967**, *97* (11), 1677–84.

Kim, J. D.; Spink, D. R. Vapor Pressure in Systems NaCl–KCl (8:29 Molar)–$ZrCl_4$ and NaCl–KCl(8:29 Molar)–$HfCl_4$. *J. Chem. Eng. Data* **1974**, *19* (1), 36–42.

Lomas, J. Hafnium. *Can. Min. J.* **1953**, *74* (11), 80–82.

McCabe, W. L.; Thiele, E. W. Graphical Design of Fractionating Column. *Ind. Eng. Chem.* **1925**, *17*, 605.

Pickles, C. A.; Flengas, S. N. The Separation of $HfCl_4$ from $ZrCl_4$ by Selective Reactivity of $HfCl_4$ Vapour with Solid or Molten Alkali Chlorides and their Mixtures. In *Extractive Metallurgy of Refractory Metals*; Sohn, H. Y., Carlson, O. N., Smith, J. T., Eds.; The Metallurgical Society of AIME: Warrendale, PA, 1981; pp 315–339.

Plucknett, W. K.; Hansen, R. S.; Duke, F. R. Progress Report in Physical and Inorganic Chemistry; Gr II, III, and IV; Iowa State College, ISC-51, April 30, 1949.

Plucknett, W. K. Separation of Zirconium and Hafnium Halides. U.S. Patent 2,816,814, Dec 17, 1957.

Prasad, R.; Venugopal, V.; Sood, D. D. Vapour Pressure of Bismuth Calculated from Mg–Bi and Pb–Bi Alloys Using Transpiration Technique. *J. Chem. Thermodyn.* **1977**, *9*, 593–601.

Spink, D. R.; Jonasson, K. A. Separation of $HfCl_4$ and $ZrCl_4$ by Fractional Distillation. In *Extractive Metallurgy of Refractory Metals*; Sohn, H. Y.; Carlson, O. N.; Smith, J. T., Eds.; The Metallurgical Society of AMIE: Warrendale, PA, 1981; pp 297–314.

Strieter, F. P. Magnesium Casting Alloys Containing Zirconium. *Met. Prog.* **1953**, *63* (3), 75–82.

Stull, D. R.; Sinke, G. C. *Thermodynamic Properties of Elements*; Advances in Chemistry Series 18; American Chemical Society: Washington, DC, 1956.

Tangri, R. P.; Venugopal, V.; Bose, D. K.; Sundaresan, M. Thermodynamics of Vaporisation of Caesium Molybdate. *J. Nucl. Mater.* **1989**, *167*, 127–130.

Van Arkel, A. E.; deBoer, J. H. Mixtures of Zirconium and Hafnium Halides. Dutch Patent No. 15,390, Feb 15, 1927.

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