Vapor Pressure in Systems NaCl-KCl(8:29 Molar)-$ZrCl_4$ and NaCl-KCl(8:29 Molar)-$HfCl_4$

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The vapor pressure of $ZrCl_4$ and $HfCl_4$ over a molten mixture of NaCl-KCl(8:29 molar) was determined in the low-temperature eutectic region by a direct vapor-pressure measurement technique. Particular attention was given to the location of compositions of $ZrCl_4$ and $HfCl_4$ in the molten salt solution that would be most useful for the separation of $ZrCl_4$ from $HfCl_4$ by a distillation technique. The pseudo-binary phase diagrams for the systems of NaCl-KCl(8:29 molar)-$ZrCl_4$ and NaCl-KCl(8:29 molar)-$HfCl_4$ were drawn for the low-temperature eutectic region by using a combination of cooling curve techniques and vapor-pressure measurements. The shape and location of the liquidus in both systems were not very different, and the liquid region above ~320°C was reasonably wide for the distillation. The minimum temperatures at which homogeneous melts can be obtained were about 230°C at 62.0 mol % $ZrCl_4$(8:29 molar NaCl-KCl) and 255°C at 63.4 mol % $HfCl_4$(8:29 molar NaCl-KCl). The final solidification temperatures were 218° and 234°C in the $ZrCl_4$ and $HfCl_4$ systems, respectively, which are believed to be the true eutectic temperatures in the respective ternary systems. The volatility of $HfCl_4$ over the KCl-NaCl-$HfCl_4$ melt solution was about 1.7 times that of $ZrCl_4$ over the KCl-NaCl-$ZrCl_4$ melt solution in the range of about 63-67.5 mol % $HfCl_4$ and $ZrCl_4$.

The chemically similar elements, hafnium and zirconium, always occur together in a mixed crystal lattice. The two most important minerals from which zirconium and hafnium can be obtained are baddeleyite (ZrO_2) and zircon ($ZrSiO_4$). Zircon contains about 2% hafnium on a metal basis and is the major source for zirconium and hafnium metal. Pure zirconium metal has a low thermal neutron capture cross section in addition to exceptional corrosion resistance so that its main use has been as a fuel cladding for nuclear reactors. Zirconium has also been used by the chemical industry in severe corrosive environments.

There are presently few commercial applications using hafnium metal other than as a control-rod material in nuclear reactors, because unlike zirconium, hafnium has a high thermal neutron capture cross section. Nevertheless, the future of hafnium appears bright. Hafnium carbide melts just shy of 4000°C; thus, it is one of the most refractory materials known. Materials with such properties will find increasing demand in tomorrow's advanced materials technology (*11*). Most recently, hafnium has been superior to zirconium in flashbulbs. Another potential use of hafnium is as an alloying element in some of the "super" alloys currently being developed. The chemical behavior of hafnium and zirconium is similar, owing to the effects of the lanthanide contraction on the ionic radius of hafnium; as a result, the separation of hafnium from zirconium is the most difficult between any two elements in the periodic table and is achieved commercially only by solvent extraction methods.

The particular solvent extraction processes used involve a number of unit operations such as extraction feed makeup, liquid-liquid extraction, recovery and recycling of chemicals used in liquid-liquid extraction, precipitation, calcining, chlorination, and finally reduction to the respective metal. Furthermore, the liquid-liquid extraction process requires a large number of extraction stages. The processes involved here are complex and difficult to control; thus, it is a relatively expensive method of separation. It is, therefore, of interest to attempt to separate zirconium and hafnium in a more economical manner. The aim of this work was to determine the vapor pressure of $HfCl_4$ and $ZrCl_4$ over specific molten salt compositions thought to be useful for the separation of the two tetrachlorides by fractional distillation.

Because zirconium and hafnium tetrachloride are the starting materials for the production of zirconium and hafnium metal by the Kroll process (*7*), many attempts have been made to separate $ZrCl_4$ and $HfCl_4$ directly to obtain pure zirconium and hafnium metals.

The tetrachlorides of zirconium and hafnium sublime at reasonably low temperatures [about 334° and 315°C (*10*), respectively] at atmospheric pressure. Separation of hafnium tetrachloride from zirconium tetrachloride has therefore been attempted by fractional sublimation (*16*). Successful separation was not achieved, however, because the separation factor obtained was low.

Zirconium and hafnium tetrachlorides have vapor pressures of about 19 and 30 atm at their respective melting points (triple points) of 437° and 434°C (*10*). At least two attempts (*1, 9*) have been made to separate hafnium from zirconium tetrachloride by distillation under high pressure. However, technical difficulties at the required high pressures prevented the process from becoming commercially feasible (*8*). Furthermore, the relatively low critical temperatures of $ZrCl_4$ (503°C) and $HfCl_4$ (estimated at just below 500°C) seriously limit the useful temperature range that could be used (*12*).

To separate hafnium tetrachloride and zirconium tetrachloride, complex systems such as the double chlorides $2ZrCl_4$-$2PCl_5$ and $2HfCl_4$-$2PCl_5$ (*15*) and oxychlorides, $3ZrCl_4$-$2POCl_3$ and $3HfCl_4$-$2POCl_3$ (*4*) have been used. The difference in volatility of these compounds of hafnium and zirconium is so small ($\alpha = 1.14$) that their separation becomes difficult and expensive.

The development of a new method to separate hafnium tetrachloride from zirconium tetrachloride by a distillation operation under ambient pressure is highly desirable. The only system thought to be useful was a eutectic mixture of $ZrCl_4$, $HfCl_4$, and certain fused salts. However, no information regarding the vapor-liquid equilibrium existed; it was therefore felt to be desirable to accumulate such data. As a first step, the vapor-pressure data for $HfCl_4$ and $ZrCl_4$ over the molten salt solution of specified compositions have been accumulated in this study.

Certain fused salts have a high solubility for $ZrCl_4$ and $HfCl_4$ at elevated temperature, and the solutions exhibit low vapor pressure, low viscosity, and the ability to dissolve many different materials (*13*). Although other salt systems could be used, the fused salt mixture of NaCl

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and KCl was selected for use with $ZrCl_4$ and $HfCl_4$ for this study.

Regardless of the salt system selected, the lowest temperatures which can be used for the distillation step must be higher than the sublimation temperature of $HfCl_4$ (315°C) if a separation of $ZrCl_4$ and $HfCl_4$ over the salt solution is to be conducted at atmospheric pressure. Howell et al. (*5*) presented the phase diagram for the pseudo-binary system, NaCl-KCl(1:1 molar)-$ZrCl_4$, in the composition range of 48-65.5 mol % $ZrCl_4$. This information shows that a homogeneous liquid phase exists at temperatures above the normal sublimation temperatures of $ZrCl_4$ and $HfCl_4$. The true eutectic composition for the NaCl-KCl-$ZrCl_4$ system has been reported to be close to 8 mol % NaCl, 29 mol % KCl, and 63 mol % $ZrCl_4$ (*6*). By use of this latter system, we could expect to formulate a homogeneous melt easily at low temperature, and the liquid phase would also exist over a reasonably wide range of composition at a temperature above 320°C.

The chemical properties of $ZrCl_4$ and $HfCl_4$ are similar; therefore, it could also be expected that the shape of the phase diagram of NaCl-KCl(8:29 molar)-$HfCl_4$ would be similar to that of the corresponding $ZrCl_4$ system. For these reasons, a mixture of NaCl-KCl(8:29 molar) was chosen for the homogeneous salt solution in this work.

Information on the melt properties such as phase diagrams, vapor-pressure data, and activity behavior of $ZrCl_4$ and $HfCl_4$ in the melt solution is necessary to carry out the distillation calculations. In this study, vapor-pressure data for the two selected systems have been collected, and their respective phase diagrams have been drawn.

Experimental

$ZrCl_4$ and $HfCl_4$ are difficult to handle as they are exceptionally reactive with moisture, exothermically forming the respective oxychlorides ($ZrCl_4 + H_2O \rightarrow ZrOCl_2 + 2HCl$). Therefore, stringent precautions must be taken to eliminate any contamination owing to hydrolysis. To accomplish this for vapor-pressure measurement studies, a known amount of pure zirconium or hafnium metal was chlorinated in situ (within the melt chamber), thereby obviating the need to handle the tetrachloride and its consequent exposure to air. Double salt-scrubbed and resublimed tetrachlorides were used for the cooling curve determinations.

For the development of the phase diagrams, two different procedures were used: phase diagrams were developed by analyzing the vapor-pressure data; and phase diagrams were developed from the cooling curve data.

In determination of the cooling curves, known amounts of purified $ZrCl_4$ (or $HfCl_4$) and the salts (NaCl and KCl) were transferred into 5-cc heart-shaped ampuls which had a thermowell near the center of each ampul. The transferring step was carried out under an inert atmosphere in a dry box. The ampuls were then evacuated while being heated to ~150°C, and vacuum sealed. The cells were placed in an Inconel metal sheath and loaded into the furnace. The temperature in the furnace was controlled by means of a transformer driven by an electric motor through a combination of gears to provide a uniform linear cooling rate. A cooling rate of 0.7°C per minute or less was used for all of the cooling curve studies. The temperatures were measured by chromel-alumel thermocouples which were calibrated at the freezing points of zinc, lead, and tin. The emf responses were accurate to ±0.01 mV; hence, no corrections were used. The calibration of the thermocouples was checked from time to time during the course of the studies.

Preparation of Materials

Reagent grade NaCl and KCl were dried initially under vacuum at 400°C and then were melted slowly under a stream of dry hydrogen chloride gas. When the salts were molten, the hydrogen chloride was flushed out with a stream of argon. Chlorine gas was then bubbled through the molten salt for 30 min. The salt was then flushed with dry argon and allowed to cool under an argon atmosphere.

Zirconium metal powder as obtained from Amax Specialty Metals, Inc., was essentially hafnium free (<70 ppm Hf). Other impurities were, by spectroanalysis: 30 ppm Al, 10 ppm Cu, 200 ppm Fe, 15 ppm Ti, 15 ppm Mg, 0.2 ppm B, <10 ppm Mn, <10 ppm Pb, <5 ppm Sn, and <10 ppm Mo.

Some samples of hafnium metal were prepared by heating hafnium hydride (obtained from Teledyne Wah Chang) at 900°C for 12 hr in a continuously evacuated silica bulb, allowing the product to cool under argon. Metallic impurities in the hafnium were in the ppm range, except for zirconium which was 3.7 wt % on a metal basis. The principal impurities were: 30 ppm Al, 200 ppm Fe, 20 ppm Ti, 10 ppm Mg, 0.3 ppm B, 20 ppm Mn, 15 ppm Pb, <5 ppm Sn, <10 ppm Mo, and <10 ppm Cu. Pure hafnium metal was also obtained from Teledyne Wah Chang which contained less than 100 ppm zirconium; this pure metal was used for the vapor-pressure experiments for the $HfCl_4$-NaCl-KCl system.

Zirconium and hafnium tetrachlorides were provided by Teledyne Wah Chang and Amax Specialty Metals, Inc. $ZrCl_4$ was free of hafnium (i.e., <100 ppm), and $HfCl_4$ contained about 3% of zirconium on a metal basis. These tetrachlorides were purified via a fused-salt (NaCl-KCl) scrubbing method (*13*) to eliminate oxides, oxychlorides, and other metal impurities. The tetrachlorides were double scrubbed, and the purified tetrachlorides were resublimed prior to use. The resulting products were white zirconium and hafnium tetrachlorides, substantially free of impurities as substantiated by spectrographic analysis which indicated that all extraneous elements were below the normal detectable limits of the elements, nominally <10 ppm.

Chlorine and argon gases used for the chlorination of the metals were supplied by Canada Laboratory Supplies and Union Carbide Canada Ltd., respectively. The purity of chlorine was 99.5 vol % Cl_2, and the argon was of high purity containing only several ppm of N_2, O_2, and hydrocarbons. The gases were used after drying via a concentrated sulfuric acid bubbler and a drying bulb containing anhydrous calcium sulfate.

Apparatus for Vapor-Pressure Measurement

The direct chlorination and vapor-pressure measurement apparatus is shown schematically in Figure 1a. The apparatus contains three major sections, A, gas flow and vacuum system; B, equilibrium chamber; C, pressure measurement section.

The gas flow system consisted of chlorine and argon cylinders which were connected to the equilibrium chamber through a concentrated sulfuric bubbler S_1, and a drying bulb, D, which contained anhydrous calcium sulfate.

The vacuum system consisted of a vacuum pump connected to the equilibrium chamber via a cold trap, t.

The equilibrium section (Figure 1b) consisted of a pyrex glass chamber (1¾-in. diam × 1¾-in. high) with a thermowell, T. Through tube, M_1, the dried NaCl-KCl mixture was introduced. One side of the vessel was con-

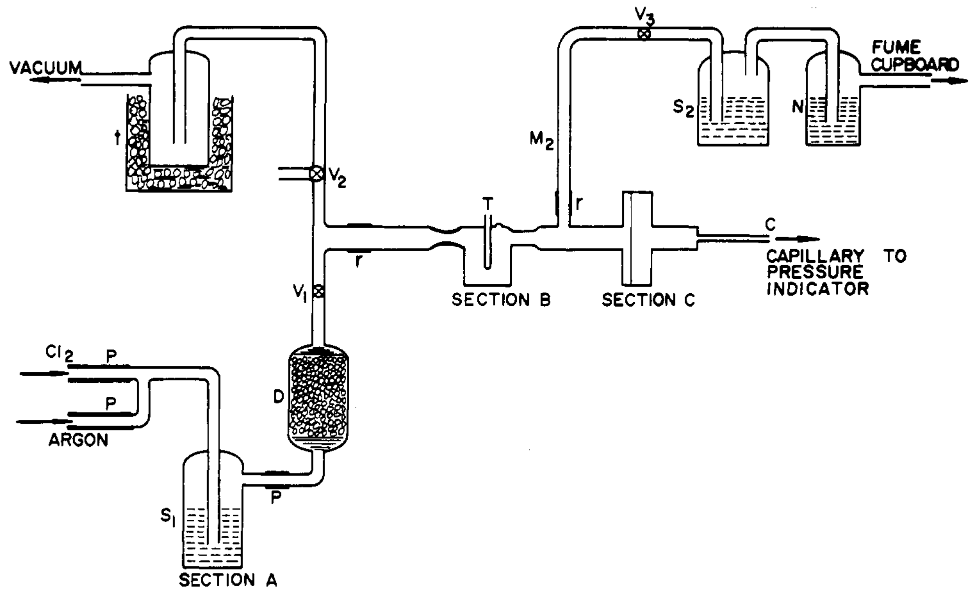

Figure 1a. Schematic diagram of experimental apparatus

Section A:	gas flow/vacuum system
Section B:	equilibrium chamber
Section C:	pressure measurement system
S:	sulfuric acid bubbler
t:	cold trap
D:	drying tube
P:	polyethylene tubing
r:	vacuum rubber tubing
N:	absorber
V:	stopcock
T:	thermocouple well

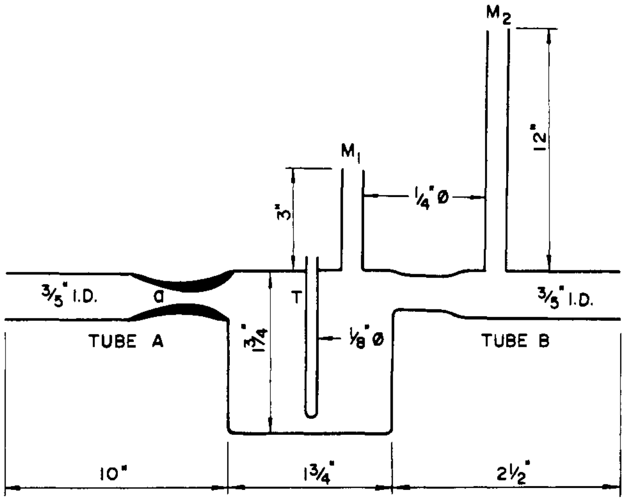

Figure 1b. Equilibrium chamber

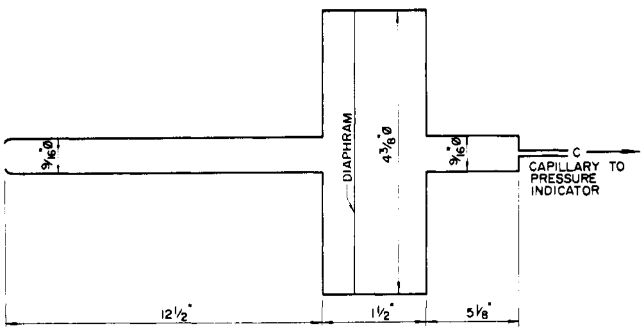

Figure 1c. Volumetric pressure element

nected to the gas flow and vacuum system, and the other side connected to the pressure measurement system. Between the vessel and the pressure measurement system, there was a glass tube, M_2, which was connected to a second acid bubbler, S_2. Unreacted chlorine and argon gas from the system passed first through the acid bubbler and then through another bubbler, N, which contained a saturated solution of sodium hydroxide. Unreacted gases were let out in the fume cupboard. Connecting tubes A and B were 3/5-in. glass tubing, 10-in. and 2½-in. long, respectively. At point, a, the tube wall was made somewhat thicker (smaller inside diameter) to facilitate sealing under vacuum.

A special type of the NaK filled volumetric pressure element (Figure 1c) was connected to the equilibrium chamber by welding a kovar seal between tube B and the pressure system. There was a diaphragm (0.005-in. thick and 3.776-in. diam) welded in the pressure element which did not permit contact of $ZrCl_4$ (or $HfCl_4$) vapor with NaK. The equilibrium chamber was connected to the diaphragm pressure gauge so that the resulting pressure over the melt in the chamber at any temperature placed a force on the diaphragm which in turn transferred the impulse to a pressure indicator through a liquid NaK filled capillary. Therefore, the vapor pressures of the tetrachlorides were read directly. NaK is a eutectic mixture of sodium and potassium metals which melts at −12.3°C, is stable when properly contained, and has a low vapor pressure at the highest temperature studied (about 1 mm Hg at 420°C). This special type of volumetric pressure element was made of stainless steel (type 316) by Taylor Instrument Co., Rochester, N.Y. (Model 103). Capillary, C, of the pressure element was extended to the 6-in. dial pressure indicator which was calibrated from 0 to 3000 mm Hg absolute. Precision of the pressure was ±0.5% of the indicated values, and pressures on the indicator were read within ±5 mm Hg accuracy.

After chlorination of the metal was completed in tube A, the gas flow and vacuum system were disconnected by sealing off at the points indicated.

The sections of the volumetric pressure element and the melt chamber were heated by two furnaces. The two furnaces were of identical dimensions (5-in. diam and 12-in. long) and were wound with resistance heating wire of the same resistance.

The melt chamber was heated by one of the heaters. The melt temperature was controlled by means of a temperature controller actuated by a thermocouple placed outside the melt chamber. By this arrangement, a 2-in. constant temperature zone (±0.5°C) could be attained at the melt.

To prevent the condensation of zirconium and hafnium tetrachloride in the pressure element, the diaphragm of the element was heated to a somewhat higher temperature than the sublimation temperature of tetrachloride. Temperatures at several positions of the system were measured by calibrated chromel-alumel thermocouples for proper control.

Procedure

The following procedure was followed for all experiments. The pyrex glass equilibrium chamber was cleaned with acid, washed with distilled water, and finally dried. The glass tube, B, of the chamber was connected to the pressure element by joining a Kovar seal between the chamber and the pressure element. The glass tube, M_2, was connected to a sulfuric acid bubbler, S_2.

A weighed amount of the metal was placed in tube A at a position about 3 in. from point a, and the tube was connected to the gas flow and vacuum system.

A weighed amount of dry salt was placed in the equilibrium chamber through tube M_1. Tube M_1 was then closed by flame.

With stopcocks V_1 and V_3 closed and V_2 opened, the system was evacuated and checked for leaks. After closing stopcock V_2, the argon flow was started and stopcock V_1 opened. When the inside argon pressure was greater than 1 atm, stopcock V_3 was opened. The inside system was then flushed with continuously flowing argon gas. The equilibrium chamber was heated for 20 min with an oxygen-natural gas torch to a low temperature (150-200°C) to eliminate free moisture. After this, the system was again evacuated. The salt in the chamber was heated again to a relatively high temperature (about 400°C) for an hour under a vacuum of 0.1 torr.

After drying of the system was completed, argon was allowed to flow at a rate of 100-200 cc/min. The chlorine flow rate was regulated next. By carefully regulating the flow rates and amount of heat applied to the metal, chlorination proceeded in a slow but controlled manner. The tetrachloride formed condensed as a fluffy solid in the equilibrium chamber. The temperature of chlorination used was about 300-350°C so that the reaction rate was slow. Most of the metal chlorinated; however, there always remained what appeared to be a fragile oxide shell.

After conversion appeared to be complete, the chlorine flow was stopped, but the argon was allowed to flow for several minutes to remove any unreacted chlorine from the system. At this point, tube M_2 was closed off by fusing at the lower part. The equilibrium chamber was evacuated again and tube A was closed off by fusion at point a. Thus, the chamber contained a known amount of salt (NaCl-KCl) and of pure tetrachloride. At the conclusion of the run, the mixture was analyzed for confirmation of the composition. The amount of tetrachloride was thus determined by two methods which gave results in excellent agreement: the amount of tetrachloride was calculated from the amount of metal chlorinated; and the salt was analyzed for zirconium or hafnium by a gravimetric procedure.

The equilibrium chamber and the diaphragm pressure element were heated slowly to a temperature at which the pressure reached about 1500 mm Hg, and the system was kept at that temperature for approximately a week to attain a homogeneous melt. In taking vapor-pressure measurement, the melt solution was maintained at constant temperature for at least 3 hr by means of a temperature controller (Thermac Controller, Model D30).

For the study of vapor pressures corresponding to different compositions, a new equilibrium chamber was connected, and the same procedure repeated as detailed above.

Results, Discussion, and Conclusions

As mentioned earlier, a pyrex glass apparatus was used for the phase diagram studies and vapor-pressure measurements. The pyrex glass was not visibly attacked by the solutions used in this study. Further, a sample of NaCl-KCl-$HfCl_4$ melt, when heated in a pyrex container at 380°C over several months, did not visibly attack the pyrex glass.

No corrosion was evident on the stainless-steel (type 316) pressure element diaphragm used for the vapor-pressure measurements; this diaphragm has been used for about a year in fairly continuous service.

The melts obtained in both systems studied ($ZrCl_4$ and $HfCl_4$ with a mixture of NaCl-KCl) were clear, colorless, and very fluid. The vapors over the melt were condensed by cooling with air and taken for analysis for salt content (NaCl and KCl). The tetrachlorides were completed salt free. From the vapor density measurements of $ZrCl_4$ (*3*) and of $ZrCl_4$ and $HfCl_4$ (*2*), there is no evidence of association or dissociation in the vapor state. Also, tetrachloride vapor is unimolecular in the vapor phase (Spiridonov et al., *14*). Therefore, the pressure measured represents the equilibrium pressure of the $ZrCl_4$ (or $HfCl_4$) species over the system.

The compositions studied in the ternary systems NaCl-KCl-$ZrCl_4$ and NaCl-KCl-$HfCl_4$ consisted of an 8:29 molar mixture of NaCl-KCl with the balance consisting of the particular tetrachloride. Figures 2a and 2b show the location of the liquidus as a function of temperature and composition for each system. Isobars showing the vapor pressure of the tetrachloride in equilibrium with the melt are also shown in Figures 2a and 2b.

A narrow range of composition, between 50 and 70 mol % $ZrCl_4$ for the $ZrCl_4$-salt system and 54 and 70 mol % $HfCl_4$ for the $HfCl_4$-salt system, was investigated; beyond that composition range, the vapor pressures were relatively high and not amenable to study in a glass apparatus. However, the composition ranges studied were adequate for the purposes of this study.

It was extremely difficult to thermally detect liquidus breaks near the lowest melt composition (located far below 320°C). The liquidus was extrapolated to the lowest melt composition of the tetrachlorides. Since only the limited composition range was studied in the ternary systems, a conclusion on the nature of solid phases was not made. However, this is not felt to detract from the work since the aim was to obtain the properties of the homogeneous melt for a distillation operation.

The following information was obtained from the phase diagram studies. The minimum temperatures at which homogeneous melts can be obtained are about 230°C at 62.0 mol % $ZrCl_4$ for the 8:29 molar NaCl-KCl and $ZrCl_4$ system and 255°C at 63.4 mol % $HfCl_4$ for the NaCl-KCl(8:29 molar)-$HfCl_4$ system.

The final solidification temperatures of all melts of $ZrCl_4$ and $HfCl_4$ with salts were 218° and 234°C, respectively. These temperatures are believed to be the true eutectic temperatures of the NaCl-KCl-$ZrCl_4$ and NaCl-KCl-$HfCl_4$ systems.

The minimum melt composition and the location of the liquidus curves are close together in both systems. The width of the liquidus regions is 5–6 mol % tetrachloride at 320°C, 9–10 mol % at 350°C, and 14–15 mol % at 375°C.

For compositions above about 65.5 mol % tetrachloride ($ZrCl_4$ or $HfCl_4$), the initial solid phase forming at the liquidus is $ZrCl_4$ and $HfCl_4$ in each respective system. This information was found from the vapor-pressure study. For compositions below 63 mol % tetrachloride ($ZrCl_4$ or $HfCl_4$), the vapor pressure at the liquidus temperature is far below that of the pure tetrachlorides at the same temperature from which it can be concluded that the initial solid phase in this region is a complex salt.

To check whether the vapor-pressure apparatus gave accurate values, vapor pressures in the range of 130–2000 mm Hg with pure $ZrCl_4$ were measured. The results obtained are compared in Figure 3 with the data obtained by Palko et al. (*10*). Data obtained were fitted with a least-squares method for a straight line; the resulting equation was

$$\log_{10} P\,\mathrm{mm} = \frac{-5317}{T} + 11.605 \quad (561.6\mathrm{K} < T < 641.3\mathrm{K}) \tag{1}$$

$$(\text{mean square error } 0.6 \times 10^{-4})$$

The heats of sublimation in the temperature range were calculated from the slope of the curve to be 24.33 ± 0.05 kcal/mol. The entropy of sublimation varies from 38.0 to 43.3 cal/mol deg in the studied temperature range, and that value at 336°C (1 atm) was estimated to be 40.0 cal/mol deg.

Palko et al. measured $ZrCl_4$ vapor pressure in the temperature range of $480\mathrm{K} < T < 689\mathrm{K}$. The equation was given by $\log_{10} P\,\mathrm{mm} = -5400/T + 11.766$. The Palko et al. data in the same temperature range as the present work were selected and compared with the present work. The equation of the line which fits the Palko et al. data in a temperature range 567.7–642.2K is given below.

$$\log_{10} P\,\mathrm{mm} = \frac{-5234}{T} + 11.486 \quad (567.7\mathrm{K} < T < 642.2\mathrm{K}) \tag{2}$$

$$(\text{mean square error } 9 \times 10^{-4})$$

The results from the present work agree well with the Palko et al. data as shown in Figure 3; the present data appear to be much less scattered. The sublimation temperature of $ZrCl_4$ at which the equilibrium pressure reaches 1 atm is 336°C from Equation 1 and is 335°C from Equation 2.

The vapor-pressure data obtained for the system NaCl-KCl(8:29 molar)-$ZrCl_4$ are shown in Figure 4, and those of Figure 5 represent the system NaCl-KCl(8:29 molar)-$HfCl_4$ with the pure $HfCl_4$ vapor-pressure data (*10*).

Since the amount of the tetrachloride of the metal in the vapor phase is different at different temperatures, the vapor-pressure curves shown in Figures 4 and 5 are not strictly at constant composition. The true composition differs from the average composition shown in Figures 4 and 5 by a maximum of 0.4%.

For tetrachloride compositions above 65 mol %, the vapor-pressure curves changed at the liquidus and followed along with the vapor-pressure curves of the pure tetrachloride. For tetrachloride compositions below 63

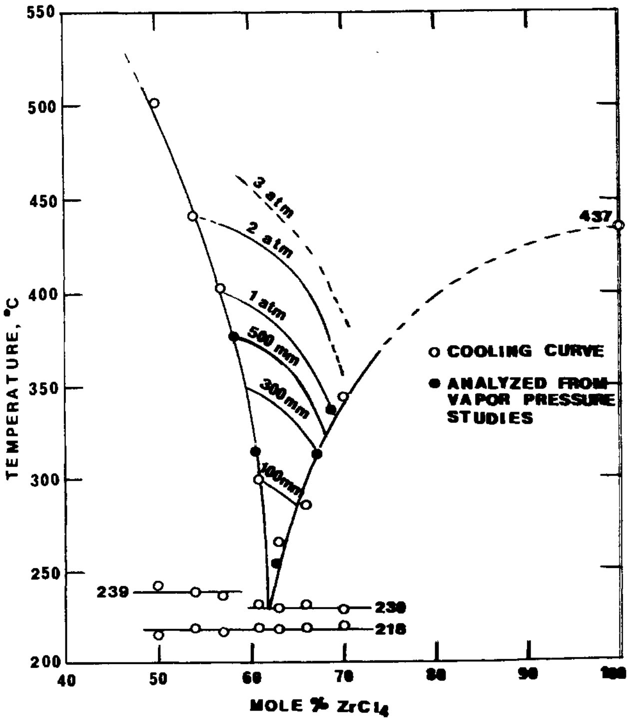

Figure 2a. Pseudo-binary phase diagram of NaCl-KCl(8:29)-$ZrCl_4$ system

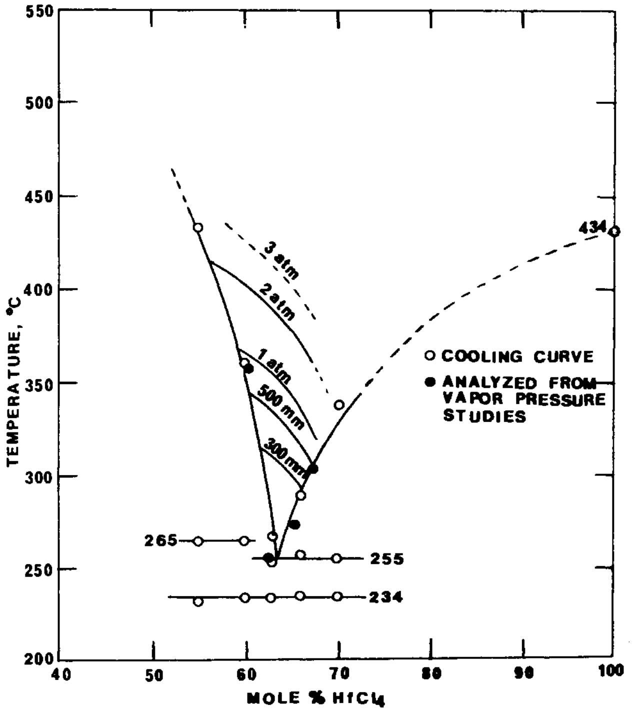

Figure 2b. Pseudo-binary phase diagram of NaCl-KCl(8:29)-$HfCl_4$ system

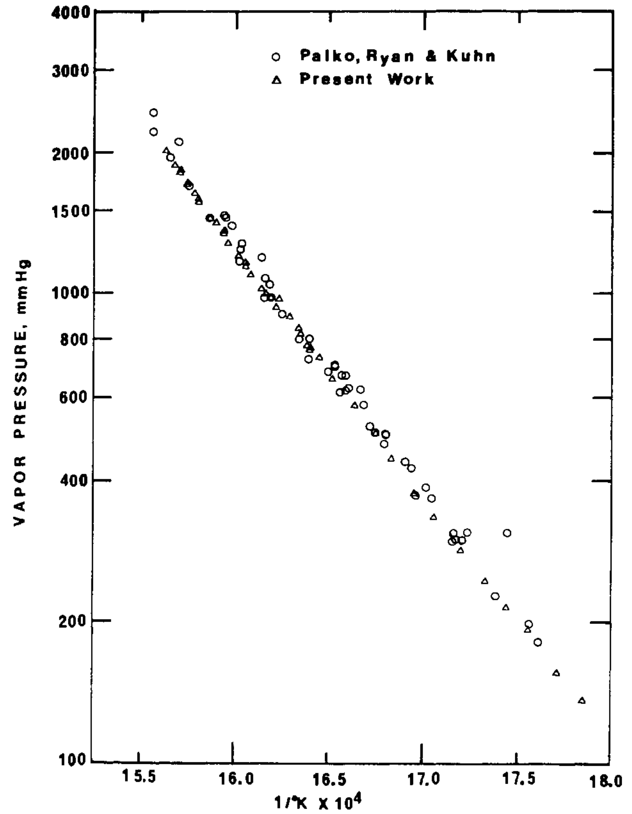

Figure 3. Vapor pressure of $ZrCl_4$

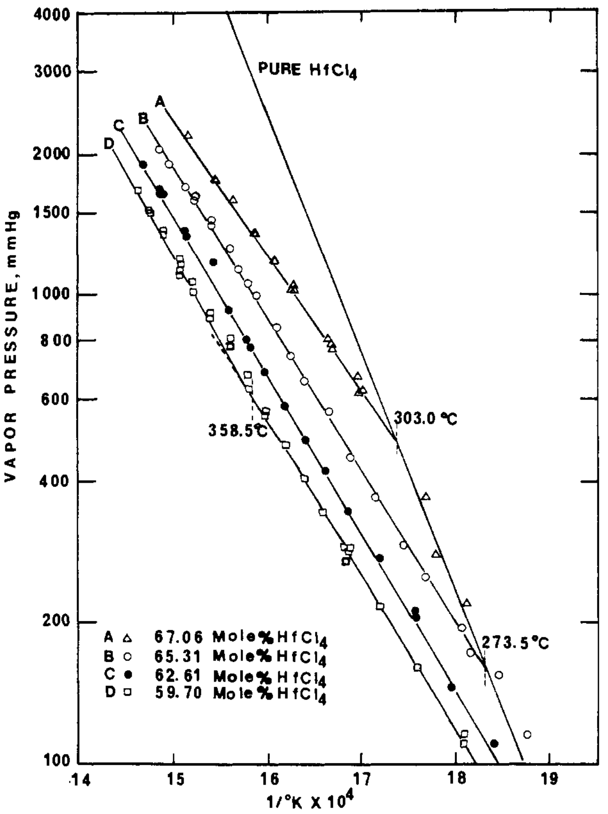

Figure 5. Vapor pressure of $HfCl_4$ in NaCl-KCl(8:29)-$HfCl_4$ system

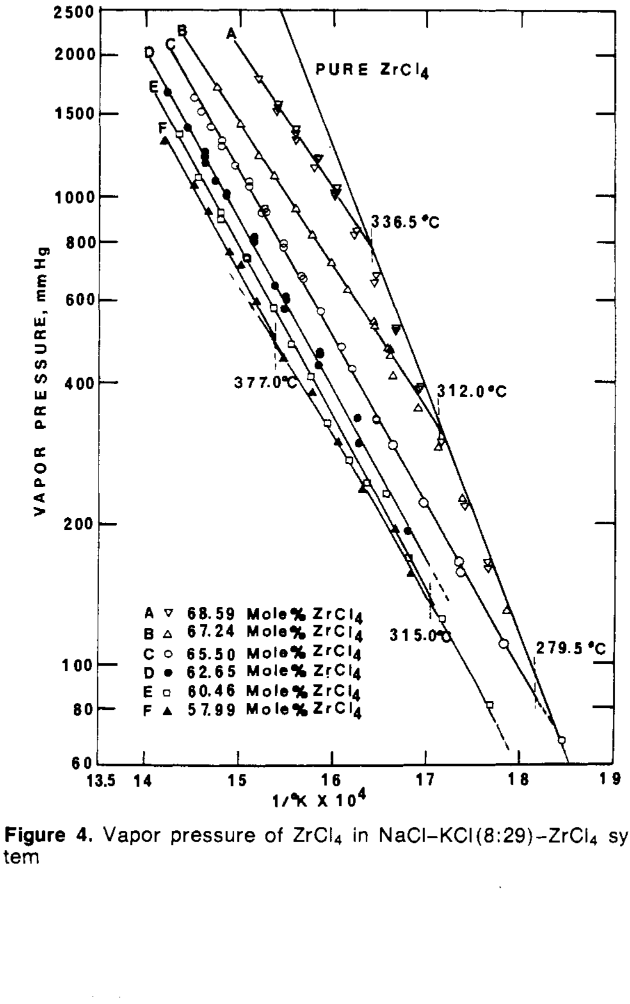

Figure 4. Vapor pressure of $ZrCl_4$ in NaCl-KCl(8:29)-$ZrCl_4$ system

mol %, the vapor pressure at the liquidus is considerably lower than that of pure tetrachloride of zirconium or hafnium at that temperature.

From the vapor-pressure study, the volatility of $HfCl_4$ over the KCl-NaCl-$HfCl_4$ melt solution was 1.7 times that of $ZrCl_4$ over the KCl-NaCl-$ZrCl_4$ melt solution in the range of 63-67.5 mol % $HfCl_4$ and $ZrCl_4$. It is therefore theoretically possible to separate $HfCl_4$ and $ZrCl_4$ in the molten salt solution by a distillation technique at 1 atm.

The workable composition range of the tetrachlorides for the separation is felt to be between 63 and 67.5 mol % in the 8:29 molar NaCl-KCl salt system if a distillation operation is conducted at 1 atm. The optimum composition range appears to be about 65-67 mol % tetrachloride. These ranges are established from the phase diagram and the vapor-pressure studies.

To prepare an accurate vapor-liquid equilibrium curve for $ZrCl_4$–$HfCl_4$ in the melt, one would need either activity values of $ZrCl_4$ and $HfCl_4$ in the salt solution or experimentally determined equilibrium data. A sample of 65.5 mol % tetrachlorides (52.5 mol % $ZrCl_4$, 47.5 mol % $HfCl_4$ on a NaCl-KCl free basis) and 34.5 mol % NaCl-KCl(8:29 molar) was prepared, and the total pressure was measured. The experimentally measured total pressure was close to the calculated total pressure from the individual vapor pressures of $ZrCl_4$ and $HfCl_4$ systems by use of Raoult's Law. For this particular mixture, the system would appear to be close to an ideal solution, which if it can be proven, would greatly simplify further experimental work.

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Studies on Aqueous HF System

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The thermodynamic properties of equilibria $H^+ + F^- = HF$ and $HF + F^- = HF_2^-$ were evaluated at 15°, 25°, and 35°C in water. $NaNO_3$ was used to maintain a constant ionic strength of 0.5000*m*. No evidence was found to indicate the presence of complexes higher than HF_2^- or of polynuclear complexes.

This paper is concerned with the complex equilibria of fluoride ions in acidic aqueous solution. There are two predominant equilibria in this system represented by the three relationships

$$H^+ + F^- = HF \qquad (K_1 \text{ or } \beta_1) \tag{1}$$

$$HF + F^- = HF_2^- \qquad (K_2) \tag{2}$$

$$H^+ + 2F^- = HF_2^- \qquad (\beta_2) \tag{3}$$

The values in parentheses denote either a stability constant (β) or an equilibrium constant (K). These equilibria have received considerable attention for almost 80 years (e.g., *1–10*), and values for K_1 and K_2 appear to be fairly consistent (Table I). Broene and DeVries (*6*) were the only investigators to study these reactions as a function of temperature, and their work is the most widely quoted one today. There are, however, two problems associated with their results. First is the fact that their measurements included liquid junction potentials which had to be approximated. Second is the fact that their results for K_2 at 15° and 25°C were, within experimental error, identical.

With the development of the solid state LaF_3 electrode, it became possible to make measurements on the HF system in a constant ionic strength medium where the liquid junction potential effectively cancels out. This was first demonstrated by Srinivasan and Rechnitz (*10*) and later by Neumann and Sillén (*9*). In the present work, the solid state LaF_3 electrode has been employed in the study of the HF system at three temperatures.

Experimental

The salts NaF and $NaNO_3$ (reagent grade) were air dried at 125°C for 24 hr and stored in a desiccator over P_2O_5 before use. Reagent grade HNO_3 was used to prepare a 4.402*m* stock solution. Stock solutions of 0.5000*m* NaF and $NaNO_3$ were prepared at 25.0°C. Mixtures of these three solutions were made by titrating aliquots into polypropylene bottles in proportions such that the total ionic strength was maintained at 0.5000*m*. Water jacketed burets maintained at 25.0°C were used throughout these preparations. All densities (except that of 0.5000*m* NaF) were obtained from standard tables (*12*). The density of 0.5000*m* NaF was determined pycnometrically to be equal to 1.0184 g/ml at 25.00°C. All solutions were stored in polypropylene bottles until used. Three solutions were stored in 125-ml Pyrex vessels but had to be discarded for the following reasons: In two flasks of high fluoride concentration (0.1 and 0.2*m*), some precipitation occurred upon cooling. In a third flask for $[F^-] = 0.003m$ and $[H^+] = 0.001m$, one experimental point was obtained at 35°C before inconsistent behavior occurred, presumably due to adsorption of F^- on the Pyrex. The experimental points for this solution at 15° and 25°C were discarded.

All measurements were carried out in a temperature bath at 14.95 ± 0.05, 25.00 ± 0.01, and 35.00 ± 0.02°C. The electrochemical cell was a polypropylene vessel of ~125-ml capacity. The reference electrode was a saturated (25°C) calomel sealed in a $^7\!/_{20}$ standard taper Pyrex joint. The entire joint was immersed into the study solution, and the liquid junction was formed around the ground joint sleeve. An Orion Model 94-09A solid state fluoride electrode was used as the indicator electrode and an Orion Model 801 pH meter was used for the emf measurements. This instrument has an accuracy of ±0.1 mV. All emf measurements were recorded after at least 10 min, the minimum time required to obtain steady values in these unstirred solutions.

Results

The potential of the fluoride electrode vs. the calomel is given by

$$E = E_0' - \frac{2.3\,RT}{F}\log[F^-] \tag{4}$$

In Equation 4, E_0' is a formal potential which includes activity coefficient effects and a liquid junction potential, both of which are invariant in the present work because

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