Total Pressure of $ZrCl_4$ and $HfCl_4$ over Melts of NaCl-KCl(8:29*M*)-$ZrCl_4$-$HfCl_4$ Systems

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The total pressure of $ZrCl_4$ and $HfCl_4$ over the molten mixture of NaCl-KCl(8:29*M*)-$ZrCl_4$-$HfCl_4$ was determined for a tetrachloride composition of 66.0 mol % by a static method using a special metal diaphragm-liquid NaK pressure gauge. The above solutions, having $ZrCl_4$ compositions on a salt-free basis of 28.92, 54.74, 72.91, 80.83, and 93.19 mol %, had the following respective total pressure equations for log P_{mm}: $-3355/T + 8.25$; $-3434/T + 8.31$; $-3324/T + 8.12$; $-3417/T + 8.25$; and $-3604/T + 8.48$ over the general temperature range of 577–683K. The data obtained were somewhat scattered from ideality (salt-free basis); however, the results of the total pressure measurements indicate that $ZrCl_4$ and $HfCl_4$ closely followed Raoult's law-type behavior on a salt-free basis, close enough for the development of a suitable vapor-liquid equilibrium curve.

This work is part of a continuing study (*3*) for the separation of $HfCl_4$ from $ZrCl_4$ by distillation of a molten salt solution containing both tetrachlorides and selected salts (NaCl and KCl).

For a separation by distillation, isobaric vapor-liquid equilibrium data are required for the system containing $ZrCl_4$ and $HfCl_4$ in the molten salt.

For binary systems, it is now well understood that vapor-liquid equilibrium data can be obtained by measuring the total pressure and the liquid composition and then using the Gibbs-Duhem relationship to predict vapor composition (*1, 8*). The procedure can also be applied to systems composed of binary liquids and salts. In this case, the system can be treated as a binary composed of one liquid with salts as one component and the other liquid with salts as the other component (*1, 2, 6*).

However, when considering the system, $ZrCl_4$-$HfCl_4$-salt, we find that it consists of one ideal binary system, $ZrCl_4$-$HfCl_4$ (*5*), and two nonideal systems, $ZrCl_4$-salt and $HfCl_4$-salt. The total pressure of the system is then the sum of the partial pressures:

$$P_{\text{Total}} = \sum_i \gamma_i P_i^\circ X_i$$

(i = 1, 2, 3 = $ZrCl_4$, $HfCl_4$, salt). Since the salt is nonvolatile, $P_3^\circ = 0$. Therefore.

$$P_{\text{Total}} = \gamma_1 P_1^\circ (1 - X_3) X_1' + \gamma_2 P_2^\circ (1 - X_3) X_2' \quad (1)$$

Variables X_1' and X_2' in Equation 1 represent the mole fraction of components $ZrCl_4$ and $HfCl_4$ on the salt-free basis (i.e., $X_1' + X_2' = 1.0$).

Since the system is made up of one ideal binary system, $ZrCl_4$-$HfCl_4$ (*5*), and two nonideal systems, $ZrCl_4$-salt and $HfCl_4$-salt, which give nearly the same quantitative deviations from Raoult's law (*3, 4*), the activity coefficients of $ZrCl_4$ and $HfCl_4$, γ_1 and γ_2, may be assumed as functions only of the amount of salt and independent of the relative amounts of $ZrCl_4$ and $HfCl_4$ present in the mixture. Therefore, $\gamma_1 P_1^\circ(1 - X_3)$ and $\gamma_2 P_2^\circ(1 - X_3)$ in Equation 1 can be denoted as P_1' and P_2', the vapor pressure of $ZrCl_4$ over the $ZrCl_4$-salt solution and the vapor pressure of $HfCl_4$ over the $HfCl_4$-salt solution at the salt composition X_3, respectively. Accordingly, Equation 1 can be written as

$$P_{\text{Total}} = P_1' X_1' + P_2' X_2' \quad (2)$$

The partial pressure of $ZrCl_4$ and $HfCl_4$ in the system $ZrCl_4$-$HfCl_4$-salt may therefore be determined by using this equation with experimentally determined values of P_1' and P_2' and newly defined variables X_1' and X_2'. The total pressure of the system will be the sum of the partial pressures of $ZrCl_4$ and $HfCl_4$.

Experimental

The apparatus and the experimental method used in this work are essentially the same as described previously (*3*) with but minor changes. In brief, the apparatus is a static vapor-pressure device which consists of a special type of liquid NaK-filled volumetric pressure element connected to the glass equilibrium chamber by a Kovar seal. The pressure element was extended to a 6-in. dial pressure indicator which was calibrated from 0 to 3000 mm Hg. The accuracy of the indicator was ±0.5%. A schematic diagram of the experimental apparatus is shown in Figure 1.

The equilibrium chamber containing the desired amounts of $ZrCl_4$, $HfCl_4$, and salts (NaCl, KCl) was connected to the diaphragm pressure gauge so that the resulting pressure over the melt in the equilibrium chamber at any temperature was read on the pressure indicator.

For the previous investigation (*3*), $ZrCl_4$ and $HfCl_4$ were introduced into the melt chamber by direct chlorination of the respective metal in situ. The metal chlorination step was not followed for the total pressure measurements made for this study. Samples were prepared which consisted of a closely fixed tetrachloride ($ZrCl_4$ + $HfCl_4$) composition (66.0 mol %) and salt composition (34.0 mol %) made of an 8:29*M* NaCl and KCl mixture. Required amounts of the highly purified tetrachlorides and salts were transferred to the equilibrium chamber in a special dry box to reduce exposure to the atmosphere.

Pure $ZrCl_4$ and $HfCl_4$ obtained by a salt scrubbing method (*7*) were used, taking all precaution necessary to keep contamination owing to moisture to an absolute minimum. Fused salt scrubbing involves the intimate contact of gaseous tetrachloride with a tetrachloride-saturated mixture of NaCl and KCl wherein most metallic impurity (Fe, Al, Ti, etc.) chlorides form nonvolatile complexes in the salt, and the intimate contact removes nonvolatile oxygen-containing species such as $ZrOCl_2$. The purified tetrachlorides of zirconium and hafnium via fused salt scrubbing were collected as dense solid deposits in an unheated upper part of the purification cell. The required amounts of pure, dense solid $ZrCl_4$ and $HfCl_4$ and sodium and potassium chloride were transferred into the equilibrium chamber which is shown in Figure 2.

The salts used (NaCl and KCl) were dried by the slow application of heat while under vacuum. The mixture of

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salts was then melted, and anhydrous HCl gas was bubbled through the liquid followed by anhydrous chlorine. The dehydration method has been described in detail (*3*). The purified $ZrCl_4$ and $HfCl_4$ used were white, dense solid products. The principal impurities in the purified $ZrCl_4$ and $HfCl_4$ were well below the normal detectable limits of the elements (nominally 10 ppm), except for hafnium impurity in zirconium which was less than 100 ppm and zirconium impurity in hafnium which was approximately 1.9% on a metal weight basis.

The equilibrium cell (Figure 2) was removed from the dry box and connected to the pressure measurement system as shown in Figure 1 by flame. The initial melt joining of the two glass tubes was performed in 10 sec in most runs, and in the worst case, it was carried out in a half minute. The blowing tube was assembled as shown in the same figure (Figure 2) to keep contamination by moisture to a negligible degree.

After the two glass tubes were joined together, the system was evacuated and gently heated. At the final stage, the system was checked for any leakage; if the system was tight, the vacuum tube was sealed off just above the chamber under continuous evacuation.

The complete system was heated slowly by two furnaces (5 in. diam and 12 in. long) to a temperature at which the pressure reached about 1500 mm Hg, after which the temperature was decreased slowly. The slow heating and cooling were repeated for a period of several days, and total pressure measurement was then initiated under equilibrium conditions. The equilibrium 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 within ±0.01 mV; hence, no corrections were used.

Results and Discussion

From previous work (*3*), the optimum composition range of the tetrachlorides for the separation appeared to be about 65–67 mol % tetrachloride in the 8:29*M* NaCl–KCl salt system if the distillation operation is to be conducted at 1 atm. As described earlier (*3*), the amount of tetrachloride in the vapor phase is different at different temperatures; thus, the vapor-pressure curves presented were not strictly at constant composition. The true composition differs from the average composition by a maximum of 0.4 mol % (*3*). To develop the vapor pressure as a function of temperature and constant composition, corrections of composition owing to the tetrachloride in the vapor phase were made (*4*).

The total pressure of $ZrCl_4$ and $HfCl_4$ over various NaCl-KCl(8:29*M*)-$ZrCl_4$-$HfCl_4$ melts were measured in the present work. The composition for the total pressure measurement was 66.0 mol % tetrachlorides ($ZrCl_4$ + $HfCl_4$) and 34.0 mol % salts (NaCl + KCl). The amounts of $ZrCl_4$ and $HfCl_4$ varied for the different runs, but the composition of the combined tetrachlorides of $ZrCl_4$ and $HfCl_4$ was kept at 66.0 mol % in the salt system. The compositions studied are shown in Table I. The total pressure of $ZrCl_4$ and $HfCl_4$ over the salt systems was measured at temperatures varying from about 300° to 400°C. In this temperature range, the system completely melted and consisted only of a liquid and vapor phase. The dependence of the total pressure on temperature, based on the linear relationship between log P and $1/T$, is shown in Table II. The collection of data for the determination of the best fitted curve can be seen in Table III.

The measured total pressure over the salt system was compared with the total pressure which was calculated from the individual vapor pressures of $ZrCl_4$ and $HfCl_4$

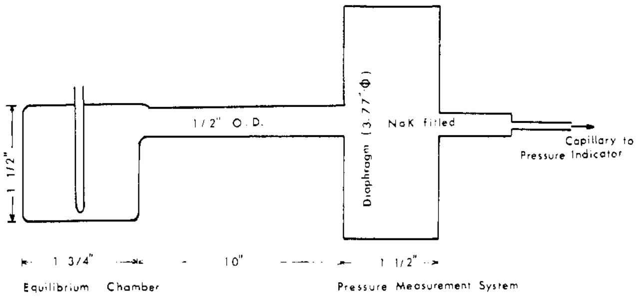

Figure 1. Schematic diagram of experimental apparatus

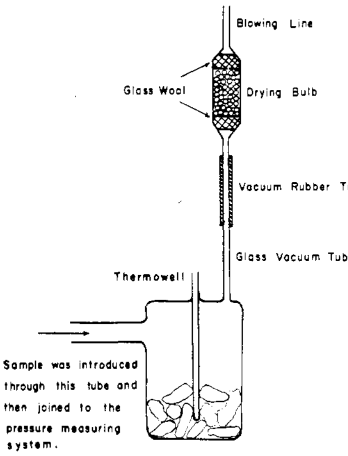

Figure 2. Equilibrium chamber for total pressure measurements

Table I. Compositions for Total Pressure Determination of System 34.0 Mol % NaCl and KCl(8:29*M*)-66.0 Mol % $ZrCl_4$ and $HfCl_4$

Expt no.	Weight of sample, g				$ZrCl_4$ and $HfCl_4$ compn on salt-free basis, mol %	
	$ZrCl_4$	$HfCl_4$[a]	NaCl	KCl	$ZrCl_4$	$HfCl_4$
1	12.524	15.097	0.660	3.053	54.74	45.26
2	18.919	6.395	0.660	3.053	80.83	19.17
3	16.977	9.038	0.660	3.053	72.91	27.09
4	6.195	23.710	0.660	3.053	28.92	71.08
5	21.948	2.271	.0.660	3.053	93.19	6.81

[a] $HfCl_4$ contained 2.68 wt % of $ZrCl_4$ (i.e., 1.9 wt % Zr on a metal basis). For calculation of the composition, corrections were made for the content of $ZrCl_4$ in the $HfCl_4$.

Table II. Total Pressure Results of System 34.0 Mol % NaCl and KCl(8:29*M*)-66.0 Mol % $ZrCl_4$ and $HfCl_4$

Expt no.	$ZrCl_4$ and $HfCl_4$ compn on salt-free basis, mol %		Temp range, T, K	Total press equation, log P_{mm}
	$ZrCl_4$	$HfCl_4$		
1	54.74	45.26	578.0–679.2	$-3434/T + 8.31$
2	80.83	19.17	582.1–676.4	$-3417/T + 8.25$
3	72.91	27.09	590.0–669.0	$-3324/T + 8.12$
4	28.92	71.08	578.1–662.2	$-3355/T + 8.25$
5	93.19	6.81	577.1–683.0	$-3604/T + 8.48$

Table III. Comparison of Experimental and Ideal Total Pressure of System 34.0 Mol % NaCl and KCl(8:29M)–66.0 Mol % $ZrCl_4$ and $HfCl_4$

Temp, °C	Exptl total press, mm Hg	Tet. compn in melt, cor	$ZrCl_4$ vp at cor melt compn, mm Hg	$HfCl_4$ vp at cor melt compn, mm Hg	Ideal total press, mm Hg	% Dev, $\frac{p_{\text{exptl}} - p_{\text{ideal}}}{p_{\text{ideal}}}$
	Overall composition of combined $ZrCl_4$ and $HfCl_4$ (uncorrected) = 66.0 mol % Composition of $ZrCl_4$ (salt-free basis) = 54.74 mol % Composition of $HfCl_4$ (salt-free basis) = 45.26 mol %					
353.1	693	65.55	505	885	677	2.36
385.8	1305	65.19	848	1600	1188	9.85
385.8	1275	65.21	860	1605	1197	6.52
401.2	1653	65.00	1275	2100	1648	0.30
393.6	1454	65.11	1105	1755	1399	3.93
405.6	1797	64.95	1375	2225	1760	−0.74
394.3	1442	65.12	1120	1855	1453	−0.76
386.9	1274	65.21	981	1635	1277	−0.23
377.3	1112	65.30	820	1365	1067	4.22
361.3	832	65.46	597	1030	793	4.92
406.0	1764	64.94	1380	2240	1769	−0.28
361.8	841	65.46	601	1038	799	5.26
353.9	723	65.53	510	900	687	5.24
354.0	659	65.59	512	912	693	−4.91
337.9	500	65.66	365	653	495	1.01
321.8	359	65.75	254	470	352	1.99
305.0	246	65.82	168	325	239	2.93
305.5	219	65.84	173	328	243	−9.88
354.3	716	65.53	514	910	693	3.32
304.8	230	65.83	168	325	239	−3.77
						Absolute mean deviation = 3.62%
	Overall composition of combined $ZrCl_4$ and $HfCl_4$ (uncorrected) = 66.0 mol % Composition of $ZrCl_4$ (salt-free basis) = 80.83 mol % Composition of $HfCl_4$ (salt-free basis) = 19.17 mol %					
382.8	1149	65.29	915	1535	1034	11.12
390.5	1305	65.20	1035	1740	1170	11.54
398.5	1455	65.12	1212	2015	1366	6.52
403.2	1550	65.06	1315	2160	1477	4.94
398.3	1433	65.13	1207	2010	1361	5.22
390.4	1300	65.20	1045	1750	1180	10.17
390.8	1272	65.22	1055	1775	1193	6.62
383.8	1117	65.31	916	1562	1040	7.40
367.0	810	65.48	675	1150	766	5.74
358.8	713	65.54	572	995	653	9.19
359.1	700	65.55	575	1000	656	6.70
351.0	617	65.59	485	848	555	11.17
342.9	515	65.65	410	725	470	9.57
334.8	425	65.71	342	618	395	7.59
325.5	360	65.75	277	508	321	12.15
317.0	285	65.79	228	425	266	7.14
308.9	240	65.82	186	354	218	10.19
						Absolute mean deviation = 8.31%
	Overall composition of combined $ZrCl_4$ and $HfCl_4$ (uncorrected) = 66.0 mol % Composition of $ZrCl_4$ (salt-free basis) = 72.91 mol % Composition of $HfCl_4$ (salt-free basis) = 27.09 mol %					
388.9	1295	65.20	1025	1700	1208	7.20
375.9	1040	65.35	805	1340	950	9.47
388.9	1275	65.21	1025	1700	1208	5.55
395.5	1435	65.12	1150	1900	1353	6.06
376.0	1040	65.35	796	1347	745	10.05
329.5	405	65.72	302	549	369	9.76
318.9	323	65.77	235	440	291	11.00
328.5	400	65.72	299	538	362	10.50
351.3	615	65.59	490	855	589	4.41
376.0	970	65.39	805	1360	955	1.57
377.0	950	65.40	821	1380	972	−2.26
389.3	1250	65.23	1030	1730	1220	2.46
389.0	1232	65.24	1025	1725	1215	1.40

(Continued on page 176)

Table III. (Continued)

Temp, °C	Exptl total press, mm Hg	Tet. compn in melt, cor	$ZrCl_4$ vp at cor melt compn, mm Hg	$HfCl_4$ vp at cor melt compn, mm Hg	Ideal total press, mm Hg	% Dev, $\frac{P_{\text{exptl}} - P_{\text{ideal}}}{P_{\text{ideal}}}$
	Overall composition of combined $ZrCl_4$ and $HfCl_4$ (uncorrected) = 66.0 mol %					
	Composition of $ZrCl_4$ (salt-free basis) = 72.91 mol %					
	Composition of $HfCl_4$ (salt-free basis) = 27.09 mol %					
395.8	1380	65.16	1160	1920	1366	1.03
376.0	950	65.40	810	1350	956	−0.63
351.3	590	65.61	490	855	589	0.17
328.6	402	65.72	299	838	364	10.44
316.8	295	65.79	226	420	279	5.73
					Absolute mean deviation = 5.54%	
	Overall composition of combined $ZrCl_4$ and $HfCl_4$ (uncorrected) = 66.0 mol %					
	Composition of $ZrCl_4$ (salt-free basis) = 28.92 mol %					
	Composition of $HfCl_4$ (salt-free basis) = 71.08 mol %					
383.7	1408	65.13	915	1520	1345	4.68
389.0	1568	65.03	1006	1680	1485	5.59
375.9	1220	65.23	795	1330	1175	3.83
346.2	730	65.52	432	765	669	4.43
354.6	830	65.46	515	900	789	5.20
362.5	935	65.40	610	1045	919	1.74
360.5	1070	65.32	710	1215	1069	0.09
378.2	1240	65.22	830	1390	1228	0.98
370.0	1080	65.31	703	1195	1053	2.56
362.4	968	65.38	610	1045	919	5.33
354.3	832	65.46	510	900	789	5.72
346.4	680	65.55	435	772	675	0.74
338.1	602	65.59	364	647	565	6.54
354.6	792	65.48	515	907	794	−0.25
369.8	1035	65.34	704	1200	1057	−2.08
352.3	690	65.55	495	865	759	−8.97
329.6	478	65.67	303	545	475	0.63
320.4	405	65.71	243	450	390	3.85
320.3	395	65.72	244	450	390	1.28
304.9	275	65.80	169	325	280	−1.79
					Absolute mean deviation = 3.31%	
	Overall composition of combined $ZrCl_4$ and $HfCl_4$ (uncorrected) = 66.0 mol %					
	Composition of $ZrCl_4$ (salt-free basis) = 93.19 mol %					
	Composition of $HfCl_4$ (salt-free basis) = 6.81 mol %					
402.5	1405	65.15	1310	2160	1368	2.70
397.8	1250	65.24	1212	2020	1267	−1.34
404.7	1455	65.12	1370	2230	1429	1.82
409.8	1672	65.00	1500	2420	1563	6.97
398.9	1345	65.18	1220	2030	1275	5.49
378.8	964	65.40	852	1435	892	8.07
370.8	795	65.49	730	1240	765	3.92
363.3	687	65.56	614	1085	646	6.35
354.9	565	65.63	530	930	557	1.44
345.8	452	65.70	437	775	460	−1.74
331.0	363	65.75	315	570	332	9.33
315.2	217	65.84	218	410	231	−6.06
361.8	640	65.59	608	1055	638	0.31
369.6	750	65.52	715	1225	750	0.00
377.4	860	65.46	835	1420	875	−1.71
385.8	1010	65.37	980	1625	1024	−1.36
394.3	1125	65.31	1142	1900	1194	−5.98
402.4	1315	65.21	1320	2175	1378	−4.57
370.0	715	65.54	700	1230	736	−2.85
344.8	440	65.70	427	760	450	−2.22
345.5	435	65.71	433	770	456	−4.60
328.9	300	65.79	302	546	319	−5.96
303.9	170	65.87	167	319	177	−3.95
					Absolute mean deviation = 4.22%	

over the salt system obtained earlier (*3*). To calculate the total pressure, the following equation was used:

$$P_T = P_{\mathrm{ZrCl_4}}{}^\circ X_{\mathrm{ZrCl_4}} + P_{\mathrm{HfCl_4}}{}^\circ X_{\mathrm{HfCl_4}} \qquad (3)$$

where P_T is the calculated total pressure of $ZrCl_4$ and $HfCl_4$ over the salt system; $P(ZrCl_4)^\circ$ and $P(HfCl_4)^\circ$ are the vapor pressures of pure $ZrCl_4$ and $HfCl_4$ over the salt system at the corrected melt composition and the given temperature at which the experimental total pressure was taken; and $X(ZrCl_4)$ and $X(HfCl_4)$ are the mole fractions of $ZrCl_4$ and $HfCl_4$ in the melt, free of salt; i.e., $X(ZrCl_4) + X(HfCl_4) = 1.0$.

Since the vapor does not have the same composition of $ZrCl_4$ and $HfCl_4$ as the liquid phase (salt-free basis), the actual composition of $ZrCl_4$ and $HfCl_4$ (salt-free basis) in the melt solution is not exactly the same as the originally mixed composition, i.e., the amount of $ZrCl_4$ and $HfCl_4$ in the vapor phase slightly alters the composition of $ZrCl_4$ and $HfCl_4$ in the liquid phase (salt-free basis). However, the effect of the amount of the tetrachlorides in the vapor phase on the composition of $ZrCl_4$ and $HfCl_4$ (salt-free basis) in the liquid phase is much less than our ability to make the indicated solutions. Therefore, the initially mixed $ZrCl_4$ and $HfCl_4$ compositions (salt-free basis) were used as the compositions of the solution.

The vapor pressures of $ZrCl_4$ and $HfCl_4$ and the total pressure calculated are also shown in Table III with the experimental total pressures for comparison. The results of this study show that the experimental data deviated slightly from the calculated values. The absolute mean deviation from Raoult's law for the systems studied was in the range of 3.3–8.3%. The reasons for the deviations are most probably related to the small differences in the stabilities and solubilities of $ZrCl_4$ and $HfCl_4$ in the salt solution and to inherent experimental error, although the consistency of the deviations would seem to negate the latter cause.

The experimental and calculated total pressure results at 343° and at 369°C are compared in Figure 3 and presented in Table IV. At 343°C the vapor pressure of $HfCl_4$, and at 369°C the vapor pressure of $ZrCl_4$ reach 1 atm when the respective tetrachloride composition in the NaCl–KCl(8:29*M*)-tetrachloride ($ZrCl_4$ or $HfCl_4$) is 66.0 mol % (*3, 4*). Because the volatilities of $ZrCl_4$ and $HfCl_4$ in the melt are different, the tetrachloride composition ($ZrCl_4$ + $HfCl_4$) in the melt system changes in the different total pressure measurement runs, even though the overall (vapor + liquid) composition of the tetrachloride in the different total pressure runs is fixed at 66.0 mol %. The composition of the tetrachlorides in the melt at 343° and 369°C are also shown in Figure 3 and in Table IV. The composition of the tetrachloride in the melt changes from 65.55 to 65.30 mol % at 369°C and from 65.72 to 65.55 mol % at 343°C over the entire range of $ZrCl_4$ and $HfCl_4$ composition.

The comparison of the total pressures shown on Figure 3 was not made at a fixed composition of tetrachlorides in the melt; therefore, the calculated values (using Raoult's law) do not lie on a straight line. The experimental data as shown deviate positively from the ideal curve to a certain extent. Despite this deviation of the data, the assumption of a Raoult's law-type behavior (salt-free basis) seems reasonable for calculations related to the design of a distillation column for the separation of $HfCl_4$ from $ZrCl_4$.

In the separation of $HfCl_4$ from $ZrCl_4$ via distillation of a fused salt mixture, a far greater number of plates will be required in the stripping section than in the rectifying section when one desires to obtain bottom and top products for use in nuclear reactors, i.e., zirconium metal containing less than 100 ppm of hafnium (bottom product) and hafnium metal containing 1% zirconium (top product). Since the vast majority of the stages lie at the low $HfCl_4$ concentration end of the equilibrium diagram, the application of Raoult's law for the construction of the equilibrium diagram would be reasonable, even though the experimental total pressure data deviated slightly from the calculated data (by use of Raoult's law) at higher concentrations of $HfCl_4$ (where relatively few plates are required).

It was not determined whether complex species of zirconium and hafnium compounds existed in the melt solution. However, if complex species of zirconium and hafnium compounds did form, it is believed that their behavior would be similar; thus, the difference in the stabilities of zirconium and hafnium species in the melt would be small, and their effect on the total pressure would be insignificant. Since the experimental total pressures agree with the calculated ones within a few percent, one may conclude that $ZrCl_4$ and $HfCl_4$ form a near ideal solution in the salt on a salt-free basis.

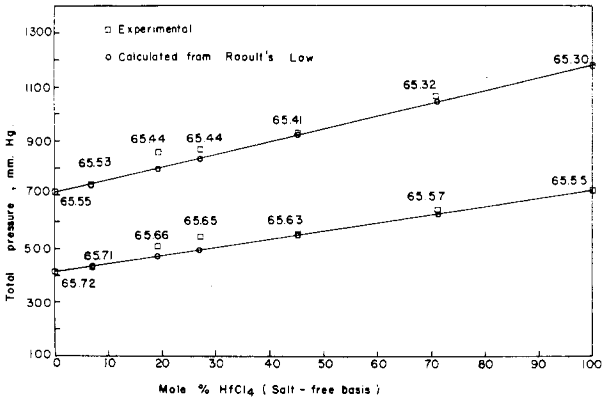

Figure 3. Total pressure of $ZrCl_4$ and $HfCl_4$ at 343° and 369°C in system of 34 mol % NaCl and KCl(8:29*M*)–66.0 mol % $ZrCl_4$ and $HfCl_4$

Table IV. Experimental and Calculated Total Pressures at 343° and 369°C

System: 34.0 mol % NaCl and KCl(8:29M)–66.0 mol % $ZrCl_4$ and $HfCl_4$

Total press expt no.	Temp, °C	Exptl total press, mm Hg	Compn of tet. in melt, mol %	$ZrCl_4$ and $HfCl_4$ vp at melt compn		Calcd total press, mm Hg
				$ZrCl_4$	$HfCl_4$	
1	343	552	65.63	408	713	546
	369	928	65.41	699	1185	919
2	343	511	65.66	408	714	467
	369	858	65.44	700	1187	793
3	343	528	65.65	408	713	491
	369	872	65.44	700	1180	832
4	343	640	65.57	406	715	623
	369	1064	65.32	695	1205	1040
5	343	427	65.71	410		431
	369	737	65.53	704		738
[a]	343		65.72	414	718	
	369		65.55	711	1175	
[b]	343		65.55			
	369		65.30			

[a] NaCl-KCl(8:29M)-$ZrCl_4$ system. [b] NaCl-KCl(8:29M)-$HfCl_4$ system.

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Vapor-Liquid Equilibria in Mixtures of *o*-Methyl-cyclohexanol and *o*-Methyl-cyclohexyl Acetate from 50–296 mm Hg

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Vapor-liquid equilibrium data were measured for mixtures of *o*-methyl-cyclohexanol and *o*-methyl-cyclohexyl acetate over the pressure range 50–296 mm Hg. Vapor-pressure data for the pure components were also determined.

In a previous paper (*2*), we described an apparatus suitable for determination of vapor-liquid equilibrium of thermally sensitive materials. This paper reports the results of measurements on the system *o*-methyl-cyclohexanol–*o*-methyl-cyclohexyl acetate.

Experimental

The acetate was obtained from Laporte Industries Limited, and the alcohol from B.D.H. Ltd., UK. Each of the components was actually a mixture of cis and trans isomers. The properties of the isomers are, however, so similar that no attempt was made to separate them. Other impurities were removed by fractionation at 50 mm Hg in a 3-ft laboratory column packed with Fenske helices. The distillates were dried using a molecular sieve and contained less than 0.01 wt % of water. The refractive indices of the components are given in Table I, where they are compared with the literature values (*1*) for the cis and trans isomers. The flow still that was used in this investigation has been described previously (*2*). No changes in operational procedure were made.

The compositions of the liquid and condensed vapor samples obtained from the flow still were determined using a Perkin-Elmer Model 900 gas-liquid chromatograph. The 2-meter column contained Chromosorb W coated with Silicone fluid MS550 + Bentone 34. The system was calibrated with samples of accurately known composition. The precision of the analysis was 0.2 mol %. Under the conditions used for analysis, separate peaks corresponding to the cis and trans isomers were not detected. The compositions quoted later for both the alcohol and acetate are calculated without regard to the existence of geometric isomers.

Results

The boiling points of the pure components determined at different pressures, together with the fitted constants of the Antoine equation (*3*), are given in Table II. The root-mean-square deviations of the measured boiling-point temperatures are 0.16° for the alcohol and 0.23°C for the acetate. The still pressures could be controlled and measured to ±0.1 mm Hg.

The equilibrium vapor and liquid compositions for the binary mixture and boiling points at a series of pressures are given in Table III. Figure 1 is a plot of $y_1 - x_1$ against x_1, and the average deviation in the vapor mole

Table I. Refractive Indices (Na D-line) for *o*-Methyl-cyclohexanol and *o*-Methyl-cyclohexyl Acetate at 25°C

	This work, mixture of isomers	Arnold et al. (*1*)	
		Cis isomer	Trans isomer
o-Methyl-cyclohexanol	1.4613	1.4620	1.4596
o-Methyl-cyclohexyl acetate	1.4365	1.4376	1.4353

Table II. Boiling-Point Temperatures and Antoine Constants for *o*-Methyl-cyclohexanol and *o*-Methyl-cyclohexyl Acetate

o-Methyl-cyclohexanol		*o*-Methyl-cyclohexyl Acetate	
P, mm Hg	*t*, °C	*P*, mm Hg	*t*, °C
396.6	144.6	750.0	183.5
297.6	135.5	297.5	150.8
198.7	124.8	270.8	147.8
100.0	106.6	190.6	136.8
50.0	91.6	100.0	118.5
11.2	63.5	52.9	101.9
3.95	47.3	50.0	100.5
2.82	42.4	21.5	81.9
2.15	38.9	9.7	64.9

Antoine constants

$A = 6.8542$	$A = 7.4600$
$B = 1293.3$	$B = 1860.4$
$C = 159.41$	$C = 222.28$

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