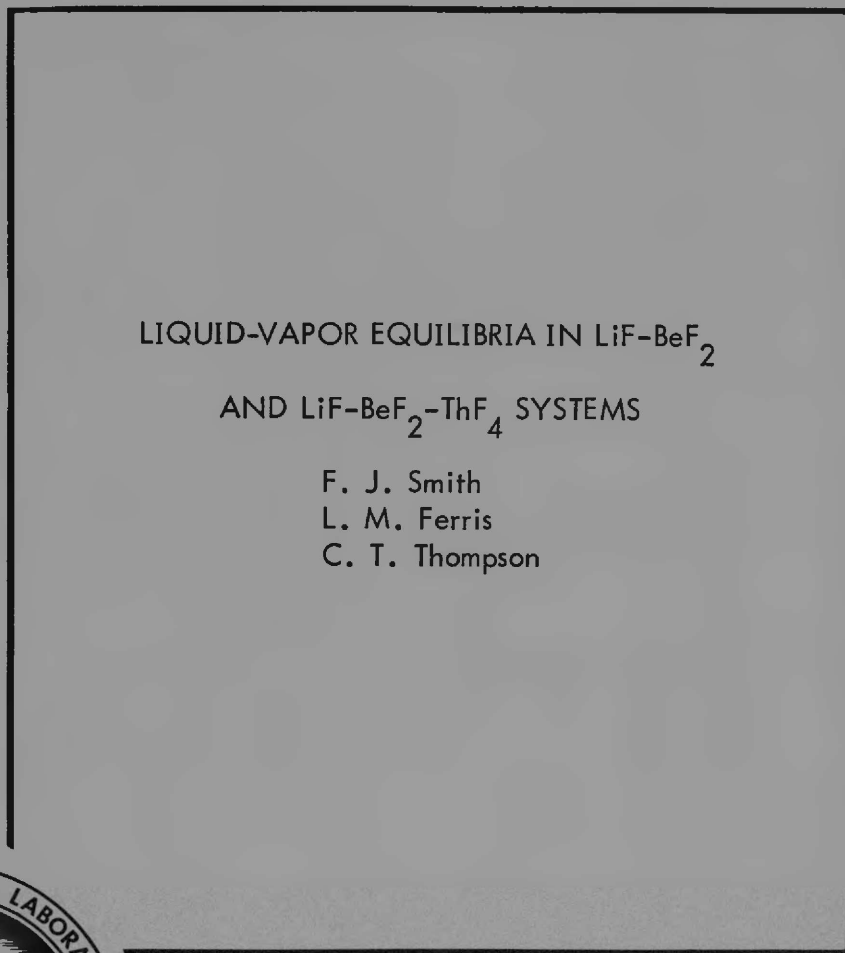


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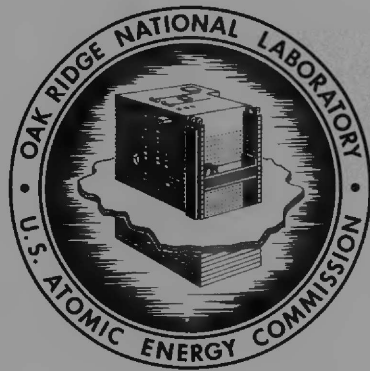
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UC-80 - Reactor Technology



LIQUID-VAPOR EQUILIBRIA IN  $\text{LiF}-\text{BeF}_2$   
AND  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$  SYSTEMS

F. J. Smith  
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CHEMICAL TECHNOLOGY DIVISION  
Chemical Development Section B

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LIQUID-VAPOR EQUILIBRIA IN LiF-BeF<sub>2</sub> AND LiF-BeF<sub>2</sub>-ThF<sub>4</sub> SYSTEMS

F. J. Smith, L. M. Ferris, and C. T. Thompson

## ABSTRACT

Liquid-vapor equilibrium data for several LiF-BeF<sub>2</sub> and LiF-BeF<sub>2</sub>-ThF<sub>4</sub> systems were obtained by the transpiration method over the temperature range of 900 to 1050°C. Relative volatilities, effective activity coefficients, and apparent partial pressures are tabulated for the major components, as well as for solutes such as UF<sub>4</sub>, ZrF<sub>4</sub>, CsF, RbF, and some rare-earth fluorides. The values are in reasonable agreement with those reported in the literature. Results of this study show that distillation may not be feasible as a primary separations method in the processing of single-fluid MSBR fuels.

## 1. INTRODUCTION

To be an efficient breeder, a molten-salt reactor must be close-coupled to a chemical processing facility to provide for the continuous removal of protactinium, fission products, and corrosion products from the system. The initial molten-salt breeder reactor (MSBR) concepts<sup>1,2</sup> were based on the use of two fluids: a fuel salt composed of LiF-BeF<sub>2</sub> (66-34 mole %) containing about 0.3 mole % UF<sub>4</sub>, and a blanket salt having the approximate composition LiF-BeF<sub>2</sub>-ThF<sub>4</sub> (73-2-25 mole %). Recently,<sup>3</sup> however, emphasis has been centered on a single-fluid MSBR that would utilize a salt such as LiF-BeF<sub>2</sub>-ThF<sub>4</sub>-UF<sub>4</sub> (72-16-12-0.3 mole %). Considerable effort was expended on the development of a fluorination-distillation method<sup>4-7</sup> for the processing of the fuel salt from a two-fluid MSBR. Fluorination was selected as the method for removing the uranium from the salt as UF<sub>6</sub>, and distillation was proposed as the means for separating the rare-earth fission products from the bulk of the LiF-BeF<sub>2</sub> carrier salt. Results of batch distillation experiments by Kelly<sup>8</sup> and experiments by Scott<sup>9</sup> in a simple closed vessel with a "cold finger" to collect the vapor sample indicated that the rare-earth separation factors were about 100. More recent experiments by Cantor,<sup>10</sup> who used the transpiration method, and by

Hightower and McNeese,<sup>11</sup> who used an equilibrium still, demonstrated that distillation is possible and reported rare-earth separation factors of about 1000. Prior to the present study, no experiments were conducted with  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$  systems; hence, the applicability of distillation to the processing of single-fluid MSBR fuels could not be properly assessed.

This report summarizes the results of experiments in which the transpiration method of obtaining liquid-vapor equilibrium data was used in the temperature range of 900 to 1050°C. These experiments had three objectives: (1) to corroborate data obtained by the equilibrium still technique with two-fluid MSBR fuel salt, (2) to determine relative volatilities of other components of interest in two-fluid MSBR processing, and (3) to obtain sufficient data on  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$  systems to allow a preliminary evaluation of the applicability of distillation in the processing of single-fluid MSBR fuel.

Acknowledgments. — The authors are indebted to the following members of the ORNL Analytical Chemistry Division: the group of W. R. Laing for the colorimetric analyses for thorium and uranium; Marion Ferguson for the flame-photometric analyses for lithium and other alkali metals; and C. A. Pritchard for the emission-spectrographic analyses for beryllium, thorium, rare earths, and zirconium. Bulk quantities of  $\text{LiF}-\text{BeF}_2$  and  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$  of varying compositions were provided by the group of J. H. Shaffer of the ORNL Reactor Chemistry Division. We thank J. F. Land and C. E. Schilling for further purifying the small batches of salt used in the individual experiments.

## 2. EXPERIMENTAL

In using the transpiration method with molten salts, an inert (carrier) gas is passed over a molten salt (becoming saturated with the vapor in equilibrium with it), through a condenser where the salt vapors are deposited and collected, and, finally, through a Wet Test Meter where the total volume of inert gas used is determined. After the vapors have transpired for a known period of time at a given temperature,

the condenser is removed and the salt contained within is dissolved. Analyses of the solution, along with the pressure of the system and the volume of inert gas used, provide the information necessary for calculating apparent partial pressures of the components of the system.

The transpiration apparatus, shown schematically in Fig. 1, closely resembles that used by Sense *et al.*<sup>12</sup> and Cantor.<sup>13</sup> The basic components consisted of a 36-in.-long alumina tube contained in a 16-in.-long Marshall furnace. A nickel liner was placed inside the alumina tube to protect the alumina from corrosion by the fluoride vapors and to help "flatten" the temperature profile. The temperature profile of the Marshall furnace was adjusted by the use of shunts until the hottest region of the furnace was located exactly in the center and the maximum temperature variation (at 1000°C) over the length of the nickel boat (used to contain the salt sample) was 5°C. The furnace temperature was controlled by a Wheelco "Capacitrol" time-proportional controller and a Chromel-Alumel thermocouple. The temperatures of the melt and vapor were measured by means of Chromel-Alumel thermocouples and a Brown recorder.

Salt samples (about 100 g) of the desired composition were initially treated, in graphite containers, with HF-H<sub>2</sub> mixtures at 850 to 900°C to remove oxide impurities; residual HF and H<sub>2</sub> were stripped from the salt with high-purity argon. After being cooled to room temperature, each salt ingot was transferred (under argon) to the nickel boat, which was placed in the center of the Marshall furnace. The transpiration apparatus was heated (with argon flowing slowly) to the desired temperature. Then a condenser was inserted into the system, and transpired vapors were collected over a predetermined length of time.

Each condenser (made of 1/4-in.-diam nickel tubing) had a 1/32-in.-diam hole in the end that was in contact with the vapor phase above the salt sample. The carrier gas was high-purity argon that had been further purified by passage through a Molecular Sieve trap to remove water and through a heated (450°C) trap filled with metallic copper to remove oxygen. Removal and replacement of the condensers could be accomplished while the system remained at temperature; thus duplicate



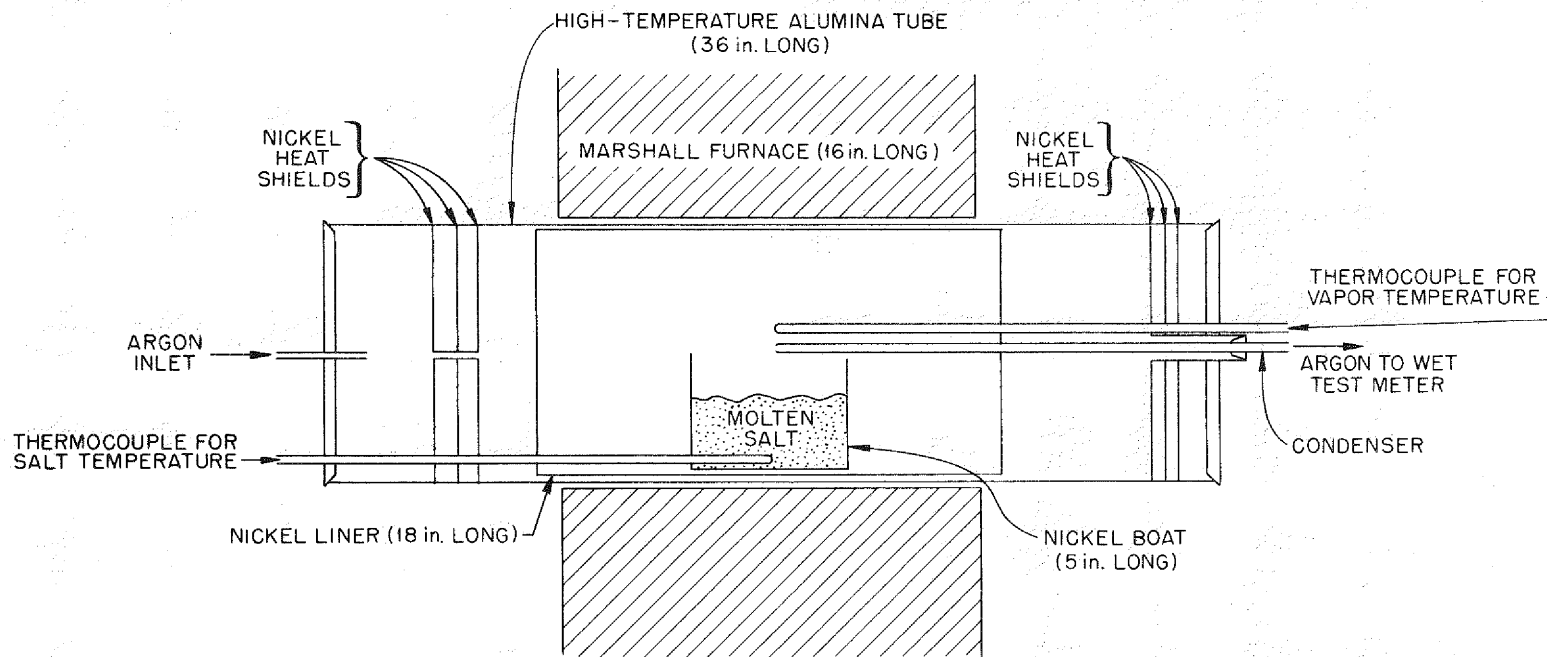


Fig. 1. Cross Section of Transpiration Apparatus Used to Determine Relative Volatilities in Molten Salt Systems.

samples at a given temperature and/or a series of samples at different temperatures could be obtained using a single batch of salt. After a condenser was removed, its exterior was polished to remove surface contamination. The condenser was then cut into sections, and the salt contained within was recovered by leaching the sections with 1 N H<sub>2</sub>SO<sub>4</sub>. Aliquots of the leachate were submitted for the desired analyses.

Apparent partial pressures were calculated from the following expression:

$$P_A = \frac{N_A P}{N_A + N_B + \dots + N_n + M} ,$$

where

$P_A$  = the apparent partial pressure of species A,

$P$  = the total pressure of the vaporized salt and carrier gas,

$N_A$  = total moles of species A collected in the condenser, and

$M$  = total moles of carrier gas passed through the system.

This expression was derived by assuming that the behavior of each gas was ideal and that Dalton's law of partial pressures was applicable.

The transpiration method gives no direct information about the molecular formulas of the vapor species or about the total vapor pressure of the system. Therefore, it was assumed that each species existed as the monomer in the vapor phase. In using this method, the gas flow rate must be carefully controlled. If it is too high (i.e., greater than the rate at which evaporation occurs at the liquid surface), the carrier gas will not become saturated with vapor and the measured value of the vapor pressure will be low. If it is too low, thermal diffusion effects in the vapor phase will make the calculated value of  $P_A$  too large. For the experimental apparatus described above, the measured vapor pressure of a typical salt was found to be independent of the argon flow rate in the range of 15 to 50 cc (STP)/min. Therefore, no correction was needed for diffusion or kinetic effects. Under the conditions used, no change in the composition of the liquid phase was detected during the course of an experiment.

### 3. RESULTS

#### 3.1 Systems of Interest in Processing Two-Fluid MSBR Fuel

Data obtained for LiF-BeF<sub>2</sub> and LiF-BeF<sub>2</sub>-metal fluoride systems are given in Table 1. In the absence of any information regarding complex molecules in the vapor phase, the partial pressures of LiF, BeF<sub>2</sub>, and solute fluorides were calculated by assuming that only monomers existed in the vapor. In each experiment, the apparent partial pressures, P<sub>A</sub>, could be described adequately by the linear expression

$$\log P_A \text{ (mm of Hg)} = a - b/T(^{\circ}\text{K}) ,$$

in which a and b were constants over the temperature range investigated, 900 to 1050°C. Typical plots of log P vs 1/T are shown in Figs. 2 and 3.

Other workers have expressed their vapor-liquid equilibrium data in terms of relative volatility, which is defined by:

$$\alpha_{AB} = \frac{y_A/y_B}{x_A/x_B} ,$$

where  $\alpha_{AB}$  is the relative volatility of component A with respect to component B, y is the mole fraction of the designated component in the vapor phase, and x is the mole fraction in the liquid phase. The relative volatilities of BeF<sub>2</sub> (with respect to LiF) obtained in our experiments with LiF-BeF<sub>2</sub> binary systems are in reasonable agreement with those reported by Cantor,<sup>10,14</sup> who also used the transpiration method. For example, Cantor obtained values of 4.28 for LiF-BeF<sub>2</sub> (85-15 mole %) at 1000°C and 3.75 for LiF-BeF<sub>2</sub> (90-10 mole %); the corresponding values from the present study were about 3.8 and 3.77 (Table 1). Our value obtained with LiF-BeF<sub>2</sub> (90-10 mole %) is somewhat lower than the average value of 4.71 reported by Hightower and McNeese,<sup>11</sup> who used an equilibrium still method, and is higher than our values obtained when the salt contained small amounts of RbF, CsF, ZrF<sub>4</sub> (Table 1). This scatter in values is not surprising, however, because small variations in the composition of the liquid and/or vapor cause large changes in the relative volatility value. For

Table 1. Apparent Partial Pressures, Relative Volatilities, and Effective Activity Coefficients in LiF-BeF<sub>2</sub>-Metal Fluoride Systems

Salt Composition (mole %)			Species	Apparent Partial Pressure,* log P (mm) = a - b/T (°K)		Effective Activity Coefficient at 1000°C	Relative Volatility, With Respect to LiF, at 1000°C
LiF	BeF <sub>2</sub>	Third Component		a	b		
86	14		LiF	8.497	11,055	1.60	
			BeF <sub>2</sub>	7.983	10,665	4.42 × 10 <sup>-2</sup>	3.82
90	10		LiF	7.604	10,070	1.30	
			BeF <sub>2</sub>	8.707	11,884	3.55 × 10 <sup>-2</sup>	3.77
95	5		LiF	8.804	11,505	1.30	
			BeF <sub>2</sub>	11.510	15,303	4.33 × 10 <sup>-2</sup>	4.60
90	10	UF <sub>4</sub> : 0.02	LiF	9.481	12,386	1.33	
			BeF <sub>2</sub>	9.339	12,411	5.96 × 10 <sup>-2</sup>	6.19
			UF <sub>4</sub>	4.361	12,481	7.36 × 10 <sup>-3</sup>	2.9 × 10 <sup>-2</sup>
89.6	9.9	UF <sub>4</sub> : 0.5	LiF	8.384	10,987	1.34	
			BeF <sub>2</sub>	7.421	10,112	4.65 × 10 <sup>-2</sup>	4.78
			UF <sub>4</sub>	6.686	13,443	1.09 × 10 <sup>-2</sup>	4.2 × 10 <sup>-2</sup>
86.4	9.6	UF <sub>4</sub> : 4.0	LiF	10.790	13,992	1.55	
			BeF <sub>2</sub>	10.177	13,726	3.84 × 10 <sup>-2</sup>	3.42
			UF <sub>4</sub>	10.272	16,786	1.25 × 10 <sup>-2</sup>	4.2 × 10 <sup>-2</sup>
90	10	RbF: 0.09	LiF	8.286	10,811	1.47	
			BeF <sub>2</sub>	6.596	10,552	3.11 × 10 <sup>-2</sup>	2.93
			RbF	5.187	8,907	2.19	24.7
89.9	10	CsF: 0.03	LiF	9.654	13,459	1.99	
			BeF <sub>2</sub>	8.310	11,313	4.07 × 10 <sup>-2</sup>	2.82
			CsF	0.819	3,375	1.17	95.1
90	10	ZrF <sub>4</sub> : 0.083	LiF	7.915	10,358	1.41	
			BeF <sub>2</sub>	7.167	10,070	2.83 × 10 <sup>-2</sup>	2.77
			ZrF <sub>4</sub>	13.095	20,382	3.05 × 10 <sup>-4</sup>	2.19

\*Temperature range: 900 to 1050°C. It was assumed that LiF, BeF<sub>2</sub>, and the solute fluorides existed only as monomers in the vapor.

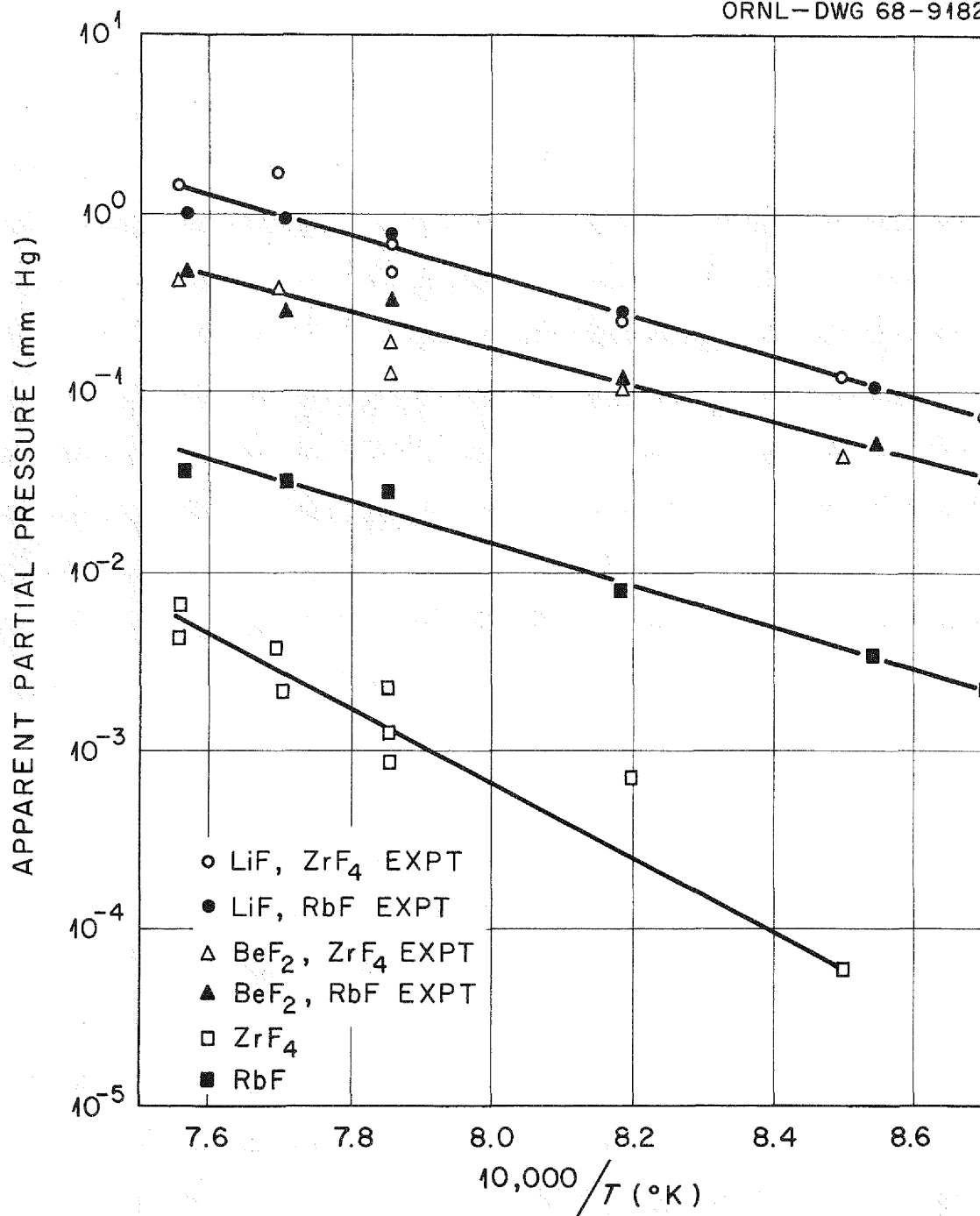


Fig. 2. Apparent Partial Pressure-Temperature Curves for the Systems LiF-BeF<sub>2</sub>-RbF (90-10.0-0.09 mole %) and LiF-BeF<sub>2</sub>-ZrF<sub>4</sub> (90-10.0-0.083 mole %).

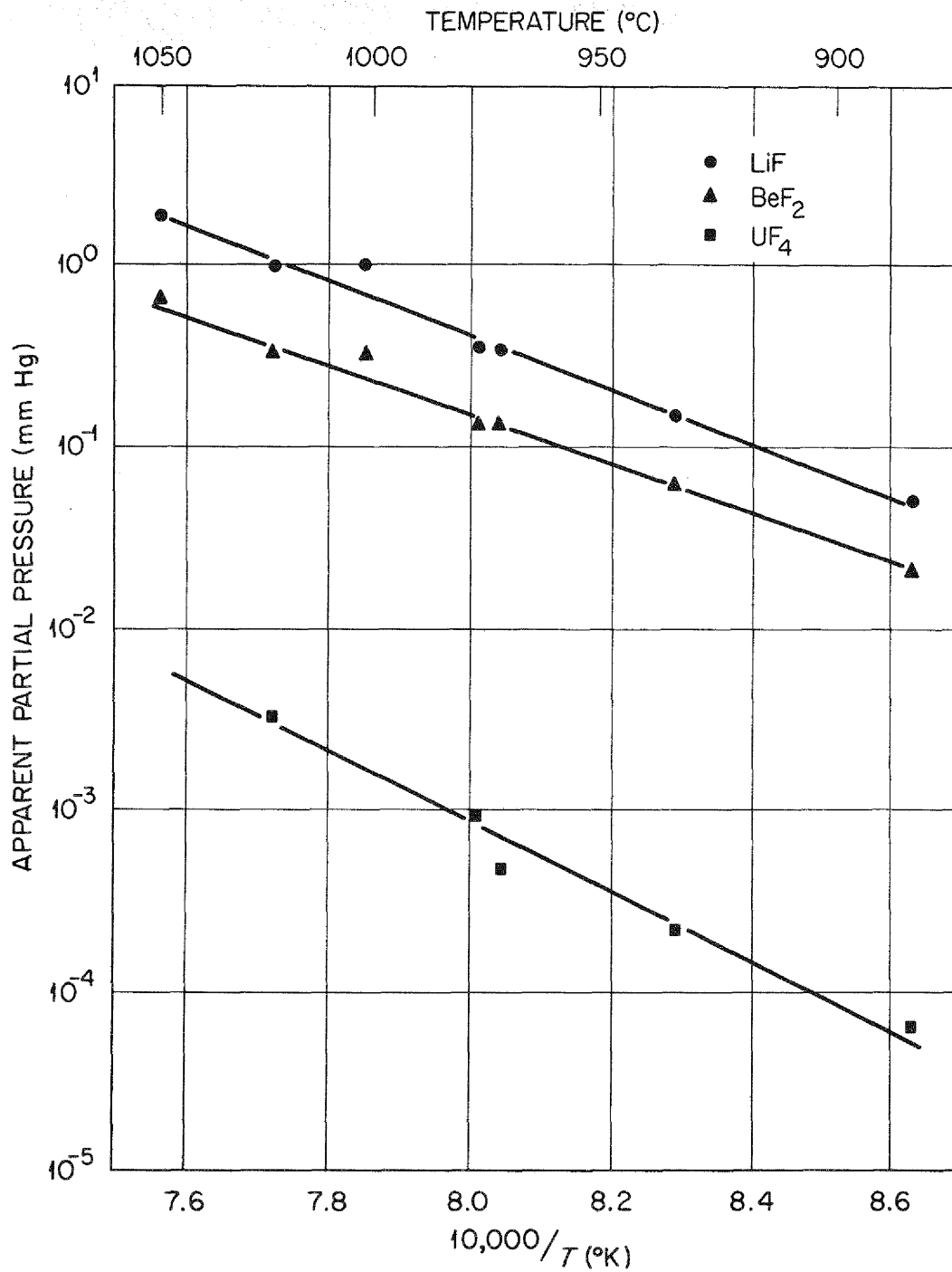


Fig. 3. Apparent Partial Pressure-Temperature Curves for the System  $\text{LiF}-\text{BeF}_2-\text{UF}_4$  (86.4-9.6-4.0 mole %).

example, it has been reported<sup>11</sup> that LiF-BeF<sub>2</sub> (66-34 mole %) is the vapor in equilibrium with LiF-BeF<sub>2</sub> (90-10 mole %) at 1000°C. This gives a value for the relative volatility of BeF<sub>2</sub>:

$$\alpha = \frac{34/66}{10/90} = 4.64 .$$

Another source<sup>13</sup> has reported that the composition of the vapor in equilibrium with LiF-BeF<sub>2</sub> (88-12 mole %) is LiF-BeF<sub>2</sub> (67-33 mole %), corresponding to

$$\alpha = \frac{33/67}{12/88} = 3.6 .$$

Our partial pressure data for LiF-BeF<sub>2</sub> systems are incompatible with some of the total pressure data presented by Cantor.<sup>13</sup> He has reported the total pressure of LiF-BeF<sub>2</sub> (90-10 mole %) to be 1.8 mm Hg at 1000°C. For the same system at 1000°C, we obtained the approximate values  $P_{\text{LiF}} = 0.55$  and  $P_{\text{BeF}_2} = 0.23$  mm Hg, corresponding to a total pressure of 0.78 mm Hg (assuming that no dissociation or association occurred in the vapor phase). The total pressure calculated from our transpiration data should have been higher than the actual total pressure because association in the vapor phase undoubtedly occurs. Association in the vapors above pure LiF has been noted,<sup>15</sup> and complexation has been observed (by mass spectrometry) in the vapors above LiF-BeF<sub>2</sub> solutions.<sup>16</sup>

Effective activity coefficients,  $\gamma_A$ , were calculated for each component of the LiF-BeF<sub>2</sub> systems (Table 1). The activity coefficient for component A is given by:

$$\gamma_A = \frac{P_A}{X_A P_A^{\circ}} ,$$

where  $X_A$  is the mole fraction of A in the solution,  $P_A$  is the apparent partial pressure of A, and  $P_A^{\circ}$  is the vapor pressure of pure A. The activity coefficients obtained for BeF<sub>2</sub> are in good agreement with those reported by Kelly,<sup>8</sup> who used distillation data and assumed the activity for LiF to be unity. Hightower and McNeese<sup>11</sup> noted that the relative volatilities obtained experimentally for several rare earths were

very close to those calculated by assuming ideal solution behavior (Raoult's law;  $\gamma = 1$ ). The results of the study presented in this report show that RbF and CsF also behave almost ideally; their activity coefficients are near unity (Table 1). Uranium tetrafluoride and  $ZrF_4$ , on the other hand, do not behave ideally in solution; activity coefficients for these solutes were only  $10^{-4}$  to  $10^{-2}$  (Table 1). The vapor pressures, at  $1000^\circ C$ , of the pure fluorides of interest are given in the following table:

<u>Component</u>	<u>Vapor Pressure at <math>1000^\circ C</math> (mm Hg)</u>	<u>Reference</u>
LiF	0.47	17
BeF <sub>2</sub>	65.	18
ZrF <sub>4</sub>	4770	19
UF <sub>4</sub>	2.44	20
RbF	7.8	17
CsF	76	17
ThF <sub>4</sub>	0.0668	21

### 3.2 Systems of Interest in Processing Single-Fluid MSBR Fuels

Liquid-vapor equilibrium studies of several LiF-BeF<sub>2</sub>-ThF<sub>4</sub> systems have been made to determine the feasibility of using certain distillation steps in the processing of single-fluid MSBR fuels. The data are summarized in Table 2. A typical partial-pressure--temperature plot is shown in Fig. 4. The partial pressures and the predicted total pressures were calculated assuming that only monomers existed in the vapor. Corrections for association in the vapor (known to occur in the vapor above pure LiF and LiF-BeF<sub>2</sub> systems) would cause both the calculated partial pressures and the predicted total pressures to be lower.

In addition to the systems shown in Table 2, a limited amount of data was obtained with LiF-BeF<sub>2</sub>-ThF<sub>4</sub>-solute fluoride systems. Results obtained for the system LiF-BeF<sub>2</sub>-ThF<sub>4</sub>-LaF<sub>3</sub> (36.6-1.0-59.6-2.8 mole %) gave the following relative



Table 2. Apparent Partial Pressures, Relative Volatilities, and Effective Activity Coefficients in LiF-BeF<sub>2</sub>-ThF<sub>4</sub> Systems

Salt Composition (mole %)			Vapor Composition at 1000°C (mole %)			Species	Apparent Partial Pressure <sup>a</sup> log P(mm) = A - B/T		Effective Activity Coefficient at 1000°C	Relative Volatility at 1000°C	Predicted Total Pressure <sup>b</sup> at 1000°C (mm Hg)
LiF	BeF <sub>2</sub>	ThF <sub>4</sub>	LiF	BeF <sub>2</sub>	ThF <sub>4</sub>		A	B			
68	20	12	29	71	0.07	LiF	7.806	10,070	2.44	-	2.7
						BeF <sub>2</sub>	9.194	11,349	0.146	8.27	
						ThF <sub>4</sub>	c	c	~0.25	~0.014	
70.5	7.5	22	36.7	63.1	0.2	LiF	8.510	11,352	1.19	-	1.1
						BeF <sub>2</sub>	7.801	10,112	0.14	16.2	
						ThF <sub>4</sub>	4.360	8,935	0.15	0.018	
75.4	3.6	21	43.2	55.6	1.1	LiF	8.548	10,112	0.98	-	0.81
						BeF <sub>2</sub>	7.480	9,984	0.19	27.1	
						ThF <sub>4</sub>	2.879	6,233	0.61	0.088	
53.5	1.5	45	16.5	81.5	2.1	LiF	8.446	12,285	0.25	-	0.38
						BeF <sub>2</sub>	d	d	~0.32	~177	
						ThF <sub>4</sub>	10.575	16,146	0.27	0.15	
45	0.06	55	75.1	12	12.7	LiF	8.611	11,826	0.23	-	0.06
						BeF <sub>2</sub>	d	d	~0.20	~120	
						ThF <sub>4</sub>	10.314	16,459	0.23	0.14	
34	1.0	65	9.9	85.2	4.8	LiF	10.314	12,129	0.13	-	0.21
						BeF <sub>2</sub>	d	d	~0.28	~293	
						ThF <sub>4</sub>	11.539	17,232	0.24	0.26	

<sup>a</sup>Temperature range: 950 to 1050°C. It was assumed that no association occurred in the vapor.

<sup>b</sup>Calculated on the assumption that no association occurred in the vapor. Association, which undoubtedly occurs, would make the actual total pressure less than the value predicted here.

<sup>c</sup>The scatter in data points was too great for determination of these values.

<sup>d</sup>The BeF<sub>2</sub> concentration in the liquid phase decreased too rapidly to allow determination of these values.

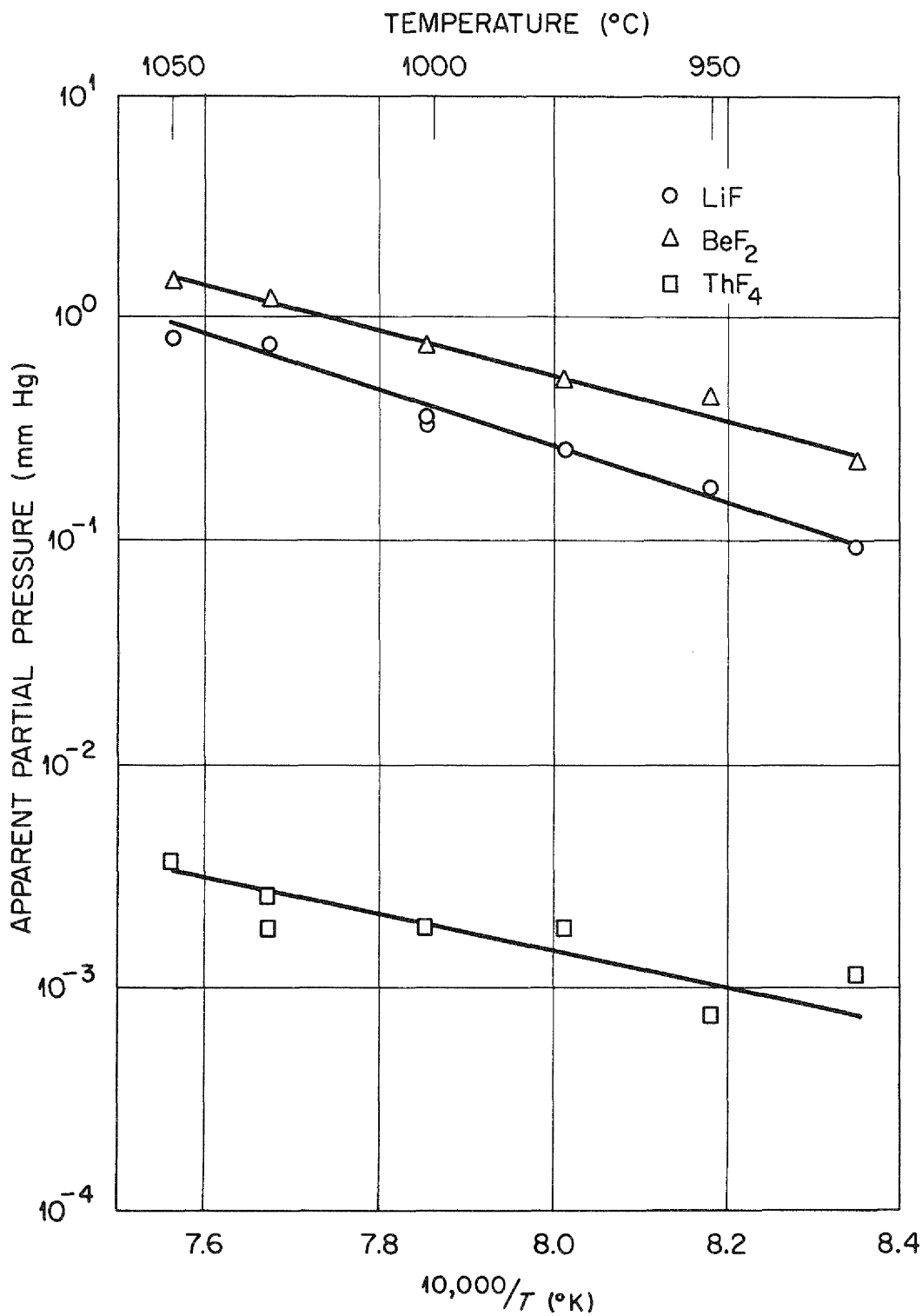


Fig. 4. Apparent Partial Pressure-Temperature Curves for the System LiF-BeF<sub>2</sub>-ThF<sub>4</sub> (70.5-7.5-22 mole %).

volatilities (with respect to LiF) at 1000°C:  $\text{BeF}_2$ , 37;  $\text{ThF}_4$ , 0.25; and  $\text{LaF}_3$ ,  $1.5 \times 10^{-3}$ . Data for the system  $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{CsF}-\text{RbF}$  (33.0-0.66-63.1-1.36-1.98 mole %) yielded relative volatilities of about 100, 0.65, 3.7, and 1.0 for  $\text{BeF}_2$ ,  $\text{ThF}_4$ ,  $\text{CsF}$ , and  $\text{RbF}$ , respectively, at 1000°C. The total pressure predicted for this system at 1000°C is less than 0.05 mm Hg. In contrast to the observation made with  $\text{LiF}-\text{BeF}_2$  systems, the behavior of  $\text{CsF}$  and  $\text{RbF}$  was far from ideal. The effective activity coefficients for these two solutes were  $3 \times 10^{-3}$  and  $8 \times 10^{-3}$ , respectively. This marked departure from ideality is probably due to complexation of the alkali-metal fluorides with  $\text{ThF}_4$ . (Note that the  $\text{ThF}_4/\text{LiF}$  mole ratio in this salt was rather high.) In another experiment at 1000°C with  $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{CsF}-\text{RbF}$  (68-20-12-0.13-0.08 mole %), a salt having a much lower  $\text{ThF}_4/\text{LiF}$  mole ratio, both  $\text{CsF}$  and  $\text{RbF}$  behaved much more ideally; the effective activity coefficients were 1.6 and 17, respectively. The corresponding relative volatilities (with respect to LiF) were 107 and 119. Data from a run with  $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{EuF}_3$  (42.4-0.06-51.8-5.8 mole %) yielded a relative volatility of about  $9 \times 10^{-3}$  for  $\text{EuF}_3$  at 1000°C.

#### 4. CONCLUSIONS

Measurements made with three different  $\text{LiF}-\text{BeF}_2$  solutions indicated that a melt having the approximate composition  $\text{LiF}-\text{BeF}_2$  (90-10 mole %) will, at 1000°C, be in equilibrium with vapor having the composition  $\text{LiF}-\text{BeF}_2$  (66-34 mole %). The latter composition is that desired for the fuel salt for a two-fluid MSBR. The results of this study show that recovery of the  $\text{UF}_4$  and most of the  $\text{LiF}$  and  $\text{BeF}_2$  from the fuel salt of a two-fluid MSBR, leaving fission products such as the rare earths in the still-pot bottoms, is not possible in a single-stage distillation system because the volatility of the  $\text{UF}_4$  is too low. The fluorides of the fission products cesium, zirconium, and rubidium have high relative volatilities, and would therefore concentrate in the distillate with the  $\text{LiF}$  and  $\text{BeF}_2$ . Although the relative volatilities of the various components are different, a complicated multistage distillation system would be required to effect the desired separations. Thus, these results support the

original conclusion<sup>4</sup> that distillation is best applied to the processing of two-fluid MSBR fuel salt after the uranium has been removed by fluorination.

The few results obtained with  $\text{LiF}-\text{BeF}_2-\text{ThF}_4$  systems showed that the volatilities of both the rare-earth fluorides and  $\text{ThF}_4$  are low, even at  $1000^\circ\text{C}$ . It is possible that the rare-earth-thorium separation required in the processing of single-fluid MSBR fuels could be achieved by distillation; however, the results of this work indicate that the temperature required to achieve adequate distillation rates would have to be at least  $1200^\circ\text{C}$ . Thus, determination of relative volatilities for the rare-earth fluorides and  $\text{ThF}_4$  at temperatures above  $1000^\circ\text{C}$  will be required in order to assess the feasibility of utilizing distillation in the processing of single-fluid MSBR fuels.

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