Relative Volatilities of Fluorides of Ce, La, Pr, Nd, Sm, Eu, Ba, Sr, Y, and Zr in Molten Mixtures of LiF and LiF–BeF$_2$ at 1000°C

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The relative volatilities, with respect to LiF, of the fluorides of Ce, La, Pr, Nd, Sm, Eu, Ba, Sr, Y, and Zr were measured in molten mixtures of LiF and LiF–BeF$_2$, using small recirculating equilibrium stills operating at 1000°C and 0.5–1.5 mm Hg. In the LiF–BeF$_2$ system, the relative volatilities for CeF$_3$, LaF$_3$, NdF$_3$, SmF$_3$, BaF$_2$, SrF$_2$, and YF$_3$ were less than 5×10^{-4} and the values for PrF$_3$ and EuF$_3$ were 1.9×10^{-3} and 1.1×10^{-3}, respectively. The relative volatility of ZrF$_4$ varied from 0.114 to 1.4 as the liquid-phase mole fraction ranged from 1.6×10^{-5} to 10^{-2}. The relative volatility of BeF$_2$ was 4.64.

One version of the molten-salt breeder reactor (MSBR) is fueled with an LiF–BeF$_2$–^{233}UF$_4$ mixture that circulates continuously through the reactor core, where fission occurs, and through a heat exchanger where most of the fission energy is removed. A close-coupled processing facility for removing fission products, corrosion products, and fissile materials from this fused fluoride mixture will be an integral part of the reactor system.

During one step of a proposed method for processing the fuel stream, LiF and BeF$_2$ are separated from less volatile rare-earth and alkaline-earth fission product fluorides by low-pressure distillation. Evaluation of the distillation process and design of the distillation equipment require the knowledge of the relative volatility of each fission product fluoride with respect to LiF, the least volatile major component in the salt. Relative volatility is defined as

$$\alpha_{i\text{-LiF}} \equiv \frac{y_i/x_i}{y_{\text{LiF}}/x_{\text{LiF}}} \tag{1}$$

where y_i and y_{LiF} are vapor-phase mole fractions of component i and LiF, respectively, and x_i and x_{LiF} are liquid-phase mole fractions of component i and LiF, respectively.

This report summarizes measurements of the relative volatilities, with respect to LiF, of fluorides of Ce, La, Pr, Nd, Sm, Eu, Ba, Sr, Y, Zr, and Be at 1000°C in molten mixtures of LiF and of 89.5 mol % LiF–10.5 mol % BeF$_2$. The latter composition is of interest since the equilibrium vapor (66 mol % LiF–34 mol % BeF$_2$) has a composition equal to that of a proposed reactor fuel carrier salt.

EXPERIMENTAL

The rare earths and yttrium were obtained from commercial sources as oxides with a minimum purity of 99.9% and were converted to the trifluorides by fusion with ammonium bifluoride as described by Thoma et al. (7). The LiF, SrF$_2$, and ZrF$_4$ were chemically pure (CP grade) materials, also obtained commercially. Bulk quantities of 66 mol % LiF–34 mol % BeF$_2$ (2LiF·BeF$_2$) were supplied by the ORNL Reactor Chemistry Division. The commercially supplied fluorides contained 0.3–1.0 wt % oxygen, the LiF–BeF$_2$ mixture contained less than 0.5 wt % oxygen, and 0.1 wt % oxygen was present in the fluorides prepared by ammonium bifluoride fusion. The low concentrations of oxides indicated by these oxygen analyses could not have caused significant errors in the relative volatility measurements.

Because of the extremely low rare-earth trifluoride concentrations (about 20 ppm), condensate samples weighing greater than 1 gram were required for analysis. For this reason, the vapor-liquid equilibrium data were obtained using small recirculated equilibrium stills of the type shown schematically in Figure 1. The vaporizing section was a 16-in. length of 1$^1/_2$-in.-diam sched 40 nickel pipe. The condensing section was made from 1-in.-diam sched 40 nickel pipe wrapped with cooling coils made from $^1/_4$-in. nickel tubing. Condensate was collected at the bottom of the condenser in a trap. The composition of the salt initially charged to the still was appropriately chosen, based on preliminary experiments in this series, to be such that about 5 grams of condensate having the composition 66 mol % LiF–34 mol % BeF$_2$ (the composition of the reactor fuel carrier salt) could be collected in this trap. The condensate flowed over a weir before returning to the vaporizing section.

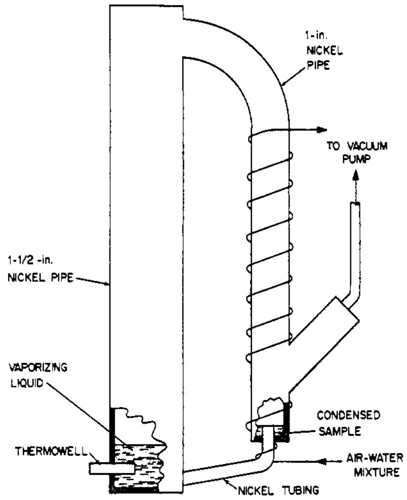

Figure 1. Equilibrium still used for relative volatility measurements in molten salt systems

The 90-gram salt charge for an experiment was prepared by melting LiF, 2LiF·BeF$_2$, and the fluorides of interest in a graphite-lined crucible under an argon atmosphere. Sufficient quantities of the components were used to yield a mixture having the desired composition. The melted mixture was sparged with argon for approximately $^1/_2$ hr at 800–850°C and was then allowed to solidify; the resulting salt ingot was subsequently loaded into the still. With this procedure, there was little danger of transferring finely divided salt into the condensate trap (which would have resulted in a substantial error in relative volatility). The threaded cap on the still was then back-welded to produce a leak-tight system, the condenser section of the still was insulated, and the still was suspended

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in a furnace. After being leak-checked, the system was repeatedly evacuated and brought to a pressure of 1 atm with argon to remove all oxygen from the system. The pressure was then decreased to the desired value, the still temperature was increased to 1000°C, and the condenser temperature was set at a value slightly above the temperature of the condensate liquidus. During runs with fluorides dissolved in LiF, the operating pressure was 0.5 mm Hg and the condenser outlet temperature was 855–75°C; during runs with the LiF–BeF_2 mixture, the pressure was 1.5 mm Hg and the condenser outlet temperature was 675–700°C.

After each experiment had been continued for approximately 30 hr, the system was cooled to room temperature and the still was cut open so that the material in the still pot and condensate trap could be sampled. Calculations indicated that steady-state conditions would have been achieved in about 22 hr (*4*). The samples were then analyzed for all components used in the experiment. Analyses for the rare earths, alkaline earths, beryllium, and zirconium were made using emission spectroscopy, and the analyses for lithium were done by flame photometry.

Since beryllium compounds are toxic when inhaled or ingested, special precautions were taken during runs using BeF_2 to protect the operating personnel from exposure to this material.

RESULTS

Relative volatilities, with respect to LiF, were measured for YF_3, BaF_2, SrF_2, BeF_2, ZrF_4, and six rare-earth fluorides in an LiF–BeF_2 system. The results are given in Table I. The measurements were made at 1000°C and 1.5 mm Hg in a ternary liquid having an LiF–BeF_2 molar ratio of approximately 8.5. The mole fractions of the rare-earth fluorides in the still pot were either 0.025 or 0.05, the mole fractions of the alkaline earths were about 0.01, and the mole fraction of ZrF_4 varied from 1.6×10^{-5} to 0.01. It should be noted that the relative volatilities of the fluorides of the rare earths (with the exception of Pr and Eu), Ba, Sr, and Y were lower than 5×10^{-4}. Praseodymium and europium had relative volatilities of 1.9×10^{-3} and 1.1×10^{-3}, respectively. The relative volatility of ZrF_4 varied between 0.114 and 1.4 as the ZrF_4 concentration was increased from 0.000016 mole fraction to 0.01 mole fraction. The average volatility of BeF_2 was 4.64.

The liquid-phase mole fractions of all components except ZrF_4 were varied over only small ranges, and data scatter obscured any correlation of relative volatilities with liquid-phase compositions. The observed variation of the relative volatility of ZrF_4 over the concentration range studied is consistent with the known variation of the ZrF_4 activity coefficient over a range of ZrF_4 concentrations in other LiF–BeF_2 systems at lower temperatures (*5*). Smith et al. (*6*) reported the relative volatility of ZrF_4 at 1000°C to be 2.19 in a study made with a ZrF_4 mole fraction of 8.3×10^{-4} in a 90–10 mol % mixture of LiF–BeF_2.

Table I. Relative Volatilities of YF_3, BaF_2, SrF_2, ZrF_4, BeF_2, and Six Rare-Earth Trifluorides, with Respect to LiF, at 1000°C

Compound	Relative volatility in LiF–BeF_2 system[a]	Relative volatility in LiF[b]
CeF_3	$1.8 \times 10^{-4} \pm (1.5 \times 10^{-4})$	4.2×10^{-4}[c]
LaF_3	1.4×10^{-4}[c]	$5.9 \times 10^{-4} \pm (3.1 \times 10^{-4})$
NdF_3	$3.8 \times 10^{-5} \pm (1.8 \times 10^{-5})$	$5.3 \times 10^{-4} \pm (3 \times 10^{-4})$
PrF_3	$1.9 \times 10^{-3} \pm (0.6 \times 10^{-3})$	6.3×10^{-4}[c]
SmF_3	$8.4 \times 10^{-5} \pm (4 \times 10^{-5})$	$4.5 \times 10^{-4} \pm (1.8 \times 10^{-4})$
EuF_3	1.1×10^{-3}[c]	...
YF_3	3.4×10^{-5}[c]	...
BaF_2	1.1×10^{-4}[c]	...
SrF_2	5.0×10^{-5}[c]	...
ZrF_4	$0.114\ (x_{ZrF_4} = 1.6 \times 10^{-5})$	...
	$0.76\ (x_{ZrF_4} = 3.0 \times 10^{-4})$	...
	$1.4\ (x_{ZrF_4} = 0.01)$	...
BeF_2	$4.64 \pm (0.46)$	...

[a] Pressure was 1.5 mm Hg; $x_{LiF}/x_{BeF_2} = 8.5$; the mole fraction of the rare-earth trifluorides was either 0.025 or 0.05, and that of the alkaline-earth fluorides was 0.01. [b] Pressure was 0.5 mm Hg; mole fractions of rare-earth trifluorides ranged from 0.0006 to 0.06. [c] Based on a single determination.

The relative volatility of BeF_2 measured in this study was in the same range as that reported by Smith et al. (*6*) for LiF–BeF_2–UF_4, and LiF–BeF_2 systems containing low concentrations of RbF, CsF, and ZrF_4. Their results were in the range 2.82–6.19 (av value = 3.9) and showed no apparent correlation with system composition. A value of 3.6 for the relative volatility of BeF_2 in 88 mol % LiF–12 mol % BeF_2 has also been reported (*1*). Small errors in sample analyses could easily account for this variation in relative volatility values.

Relative volatilities with respect to LiF were measured for five rare-earth trifluorides (see Table I) in a binary mixture consisting of a rare-earth fluoride and LiF. These measurements were made at 1000°C and 0.5 mm Hg using mixtures having rare-earth fluoride concentrations of 0.6–6 mol %. Except for PrF_3, the relative volatilities for the rare-earth fluorides in this system were slightly higher than those measured in the LiF–BeF_2 system.

The relative volatilities for the rare-earth trifluorides measured in the experiments and summarized in Table I were substantially lower than values obtained in previous measurements. Relative volatilities of 0.01–0.05 have been reported for six rare-earth trifluorides in LiF in the temperature range 900–1050°C (*3*). Cantor (*2*) reported data obtained by use of a transpiration method which indicated relative volatilities of 1.4×10^{-3} and 1.1×10^{-3} for LaF_3 at 1000° and 1028°C, respectively. Because the relative volatilities of the rare-earth fluorides as determined in the experiments reported here differed significantly from these earlier measurements, the following factors, which might have introduced systematic error into the measurements, were analyzed (*4*): (1) nonuniform concentrations in the still pot liquid, (2) unequal diffusion rates of vaporized materials between the vaporization surface and the condensation surface, (3) holdup of condensate on the condenser walls and erratic flow into the condensate trap, and (4) inaccuracies in the chemical analyses. Estimated errors from these sources showed that the measured relative volatilities could be in error by no more than a factor of 5 and were more likely within a factor of 2 of the true values.

The relative volatility values presented in Table I show that almost complete recovery of the LiF and BeF_2 should be possible in a continuous still equivalent to a single equilibrium stage. For example, a relative volatility of 0.0005 for a rare-earth fluoride would allow recovery of 99.5% of the LiF and a greater fraction of the BeF_2 with the simultaneous vaporization of only 8.6% of the rare-earth fluoride.

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