to facilitate comparison of the total plant-nutrient contents, $N + P_2O_5$, of the saturated solutions in the different systems.

As shown in Figure 1, the 0° C isotherm over the pH range studied comprises four branches representing solutions saturated with the salt pairs $(NH_4)_2HPO_4$ + $(NH_4)_4P_2O_7 \cdot H_2O$, $(NH_4)_2HPO_4$ + $(NH_4)_3HP_2O_7 \cdot H_2O$, $NH_4H_2PO_4$ + $(NH_4)_3HP_2O_7 \cdot H_2O$, and $NH_4H_2PO_4$ + $(NH_4)_2H_2P_2O_7 \cdot H_2O$. These branches have slopes and contours that resemble those of the 0° C isotherms of the three ternary systems and the quinary system. At any ratio $N{:}P_2O_5$, the total fertilizer nutrient contents, $N + P_2O_5$, of the saturated solutions in the system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O are significantly higher than those of solutions that are saturated with only ammonium orthophosphate or ammonium pyrophosphate, but are significantly lower than those of solutions saturated with ammonium ortho-, pyro-, and tripolyphosphates, particularly in the range of weight ratios $N{:}P_2O_5$ of 0.25–0.30 (about pH 5–6).

Properties of the three invariant solutions determined in the system NH_3–H_3PO_4–$H_4P_2O_7$–H_2O are listed in Table I. The invariant solution saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_3HP_2O_7 \cdot H_2O$ has a pH of 5.93, a value very near that (5.75) of the invariant solution of the quinary system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_5P_3O_{10} \cdot 2H_2O$, and that (5.82) of the invariant solution of the ternary system NH_3–H_3PO_4–H_2O saturated with $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$. The maximum nutrient contents of the two multicomponent systems are those of the invariant solutions in which both mono- and diammonium orthophosphate are among the saturating solids.

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Solubility of PuF_3 in Molten 2 LiF-BeF_2

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The solubility of PuF_3 in molten 2 LiF-BeF_2 was determined over the temperature range of 500–660° C. The results can be expressed by the least-squares equation: $\log_{10} S(\text{mol \% } PuF_3) = 3.2305 - 3096/T(°K)$. The solid phase present at equilibrium was probably pure PuF_3.

Oak Ridge National Laboratory has been engaged in the development of molten salt reactors in which the fissile material (^{235}U, ^{233}U, or ^{239}Pu) is dissolved in a molten fluoride solvent. The solvent 2 LiF-BeF_2 has been of particular interest because it was used both as the coolant and the flush salt in the Molten-Salt Reactor Experiment (MSRE) and had a composition close to that of the MSRE fuel carrier salt (*4*). In addition, Baes (*1*) used 2 LiF-BeF_2 as the reference composition in correlating thermodynamic data obtained with molten LiF-BeF_2 solutions. Barton (*2*) has measured the solubility of PuF_3 in several LiF-BeF_2 solutions ranging in BeF_2 concentration from 29 to 48 mol %. We measured the solubility of PuF_3 in molten 2 LiF-BeF_2 over the temperature range of 500–660° C; our results are summarized in this paper.

EXPERIMENTAL

Materials Used. The 2 LiF-BeF_2 used in this work was prepared by J. H. Shaffer *et al.* of the ORNL Reactor Chemistry Division. In the technique used (*6*), the appropriate amounts of LiF and BeF_2 were first melted and, then, the resulting solution was treated at about 600° C with HF-H_2 (about 10-90 mol %) followed by pure H_2. This treatment removed oxide impurities and reduced dissolved contaminants such as iron, nickel, and chromium fluorides to their respective metals. The treated solution was transferred through a sintered nickel filter into a clean nickel vessel before it was allowed to freeze. The oxide content of the purified salt was negligible, whereas the chromium, nickel, and iron concentrations were about 15, 25, and 175 ppm, respectively (*5*).

The PuF_3 powder, supplied by the Los Alamos Scientific Laboratory, was part of the same batch used by Barton (*2*). It was practically free of metallic impurities except for about 0.1% ^{241}Am, and, based on optical microscopic examination (*2*), contained less than 1% of other compounds.

Procedure. The apparatus and general technique used have been described elsewhere (*3*). Initially, 100 grams of the 2 LiF-BeF_2, contained in a molybdenum crucible, was sparged at 600° C with HF-H_2 (50-50 mol %) for about 24 hours to ensure that oxide impurities had been removed. After hydrofluorination, the salt was sparged—first with pure hydrogen, then with pure argon. With the system at 595° C under an argon atmosphere, about 6.5 grams

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Table I. Solubility of PuF_3 in Molten 2 LiF-BeF_2

Sample	Temp, °C	Time at temp before sampling, hr	PuF_3 solubility, mol %
1	595	72	0.465
2	574	6[a]	0.387
3	540	19[a]	0.270
4	522	6[a]	0.224
5	502	19[a]	0.169
6	550	6[b]	0.253
7	590	19[b]	0.451
8	625	6[b]	0.659
9	657	19[b]	0.722

[a] Temperatures attained by progressive cooling of the system from original temperature of 595° C. [b] Temperatures attained by progressive warming of the system from 502° C.

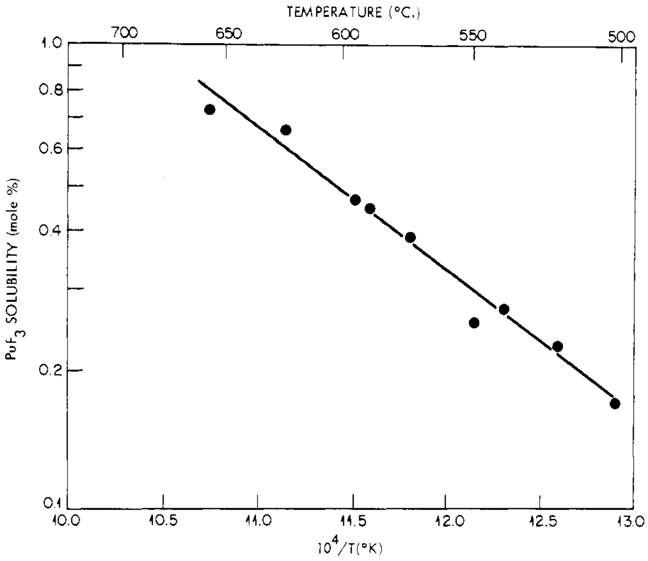

Figure 1. Solubility of PuF_3 in molten 2 LiF-BeF_2

of PuF_3 powder was added through a long-stemmed funnel. After the addition, a period of 3 days was allowed for the attainment of equilibrium before a sample of the liquid was taken. The temperature of the system was first decreased, in increments of about 20°, to 502° C and was then increased, in about 40° increments, to 657° C. The equilibration time at a given temperature was either 6 or 19 hr (Table I). A sample of the liquid phase was taken at each temperature, using stainless steel samplers (*3*) of the filter-stick type. The median pore size of the filter was 20 microns. The ^{241}Am concentration in each sample was determined by counting the incidence of the 0.06-MeV γ-rays on a 200-channel γ-ray spectrometer. The samples were then transferred to the Analytical Chemistry Division for plutonium analysis. In this analysis, each sample was initially dissolved in concentrated perchloric acid. Then the solution was fumed almost to dryness to remove fluoride, and the residue was dissolved in a known volume of 2-4*M* HNO_3. An aliquot of this solution was counted in an alpha spectrometer, and the ^{239}Pu concentration was determined by the alpha-pulse-height technique.

RESULTS

The values obtained for PuF_3 solubility are given in Table I and are plotted as a function of temperature in Figure 1. These data can be represented by the least-squares equation: $\log_{10} S$ (mol % PuF_3) = 3.2305 − 3096/T (°K). The standard deviation of log S is 0.026. The absence of a hysteretic effect in the plot of log S *vs.* $1/T$ (Figure 1) provides evidence that equilibrium was achieved at each temperature. The ^{241}Am analyses, along with material balance considerations, showed that the behavior of americium was almost identical to that of plutonium.

DISCUSSION

The PuF_3 solubilities obtained in this study are in excellent agreement with those interpolated from the results of Barton (*2*), who determined PuF_3 solubilities between 500 and 650° C in five lithium fluoride-beryllium fluoride solutions ranging in BeF_2 concentration from 29 to 48 mol %. In addition, the heat of solution of PuF_3 in 2 LiF-BeF_2 obtained in this investigation, 14.2 kcal/mole, is within the range obtained by Barton with the other solutions—*i.e.*, 12.0 to 16.8 kcal/mole. Over the range of conditions studied, Barton (*2*) found that the solid phase at equilibrium was pure crystalline PuF_3. Thus, the equilibrium solid phase in the present study was undoubtedly PuF_3, and the activity of PuF_3 in each saturated solution was unity. Activity coefficients for dissolved PuF_3 can be calculated from the solubility data, using the relationship $\gamma_{PuF_3} = 1/X_{PuF_3}$ in which X_{PuF} is the mole fraction of PuF_3 in the saturated solution. Our data, obtained with 2 LiF-BeF_2, yield $\log_{10}\gamma_{PuF_3} = -1.2305 + 3096/T$ (°K).

Both Ward *et al.* (*7*), who studied the solubility relationships among fission products in molten fluoride solutions, and Barton (*2*) found that, when a given molten solvent was saturated with two trivalent fluorides—*e.g.*, PuF_3 and CeF_3—the solid phase at equilibrium was a solid solution of the two trifluorides. The solubility of each solute in the molten solvent was dependent on the concentration of the solute in the solid solution and its solubility in the molten solvent in the absence of the other solute. The relationship is: $X_{(l)} = S^0 X_{(ss)}$, in which $X_{(l)}$ is the mole fraction of the solute in liquid solution, $X_{(ss)}$ is the mole fraction of the solute in solid solution, and S^0 is the solubility of the solute in the molten solvent when no other solute is present. If we assume that AmF_3 and PuF_3 formed solid solutions in our system, the solubility of AmF_3 in 2 LiF-BeF_2 would necessarily be about the same as that of PuF_3 since the AmF_3/PuF_3 mole ratios in the solid and liquid phases were found to be about equal.

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