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SOLUBILITY AND STABILITY OF PuF_3 IN FUSED ALKALI FLUORIDE-BERYLLIUM FLUORIDE MIXTURES

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ABSTRACT

The solubility of PuF_3 in one $NaF-LiF-BeF_2$ mixture, three $NaF-BeF_2$ mixtures and four $LiF-BeF_2$ mixtures was determined at temperatures ranging from about 550 to 650°C. Solubility-composition diagrams for the binary systems at 565°C show that in the $LiF-BeF_2$ system a minimum solubility of 0.25 mole % PuF_3 occurs at about 63 mole % LiF while in the $NaF-BeF_2$ system the minimum solubility of 0.18 mole % PuF_3 occurs at approximately 57 mole % NaF. In both systems, the solubility increases rather slowly on adding BeF_2 to the composition exhibiting minimum solubility but increases quite rapidly on adding alkali fluoride to this composition. The highest solubility observed at 565°C was 1.2 mole % PuF_3 in the mixture $NaF-LiF-BeF_2$ (56.5-17.5-26 mole %). In fused $LiF-BeF_2-PuF_3$ mixtures, the only plutonium species observed with the help of a polarizing microscope was PuF_3 but another compound believed to have the formula $NaPuF_4$ was found in the fused $NaF-BeF_2-PuF_3$ mixture containing 64 mole % NaF and in the mixture resulting from the addition of PuF_3 to the ternary solvent composition. No evidence of disproportionation of PuF_3 was found in the course of the solubility studies.

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INTRODUCTION

An extensive series of studies conducted by W. R. Grimes and co-workers[1] in the Chemistry Division of Oak Ridge National Laboratory demonstrated that UF_4 can be dissolved in a number of fused fluoride solvents to provide fuel for fused salt reactors. The feasibility of the circulating fused salt reactor concept was established by the successful operation of the Aircraft Reactor Experiment.[2,3] The only fissionable species that have been considered for a fused fluoride burner reactor are $U^{235}F_4$ and $U^{235}F_3$ but the possibility of a ThF_4-$U^{233}F_4$ fused salt breeder reactor seems promising.[1] Some consideration has also been given to the use of $U^{235}Cl_4$ or $U^{235}Cl_3$ as the fissionable material in a fast neutron fused salt reactor.[1] Thermodynamic data[4] which indicate that PuF_3 is more stable than UF_3 and that PuF_4 is much more corrosive than UF_4 prompted the choice of PuF_3

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1. W. R. Grimes et al., Reactor Handbook, Vol. 2, Section 6, AECD-3646, May 1955.
2. A. M. Weinberg and R. C. Briant, "Molten Fluorides as Power Reactor Fuels," Nuclear Science and Engineering, 2, 797-803 (1957).
3. E. S. Bettis, W. B. Cottrell, E. R. Mann, J. L. Meem, and G. D. Whitman, "The Aircraft Reactor Experiment--Operation," Nuclear Science and Engineering, 2, 841-853 (1957).
4. Alvin Glassner, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K," ANL-5750.

as the plutonium-bearing species for the first experimental examination of the possibility of using Pu_{239} as the fissionable material in a fused fluoride power reactor (see Appendix A). It seems reasonable to expect that PuF_3 will not be more corrosive than UF_4 under proposed power reactor conditions but it is recognized that data to support this belief will not be easy to obtain. This report gives the results obtained to date of a preliminary investigation of one aspect of this problem, namely, the solubility and stability of PuF_3 in suitable fused salt solvents. Alkali fluoride-beryllium fluoride systems were used in these studies since they are the only solvents currently of interest in the fused salt power reactor program. The studies included determination of the effect of solvent composition and temperature on the solubility of PuF_3. The effect of addition of other fluorides on the solubility of PuF_3 in fused $LiF-BeF_2$ is being studied and will be reported at a later date.

EXPERIMENTAL

Equipment

Two glove boxes constructed for fused salt studies are shown in Figures 1 and 2. They are connected by an interchange chamber and constitute an extension of an inter-connected series of negative-pressure glove boxes used by personnel of the Isotopes Division, Oak Ridge National Laboratory, for handling plutonium isotopes separated by use of the calutron. The microscope glove box shown in Figure 1 has plywood back, bottom

and sides while the front and top are made of clear plastic material for maximum visibility. The eyepiece of a Zeiss polarizing microscope protrudes through an opening in the slanting front of the glove box which is sealed with an airtight bellows arrangement permitting vertical movement of the eye piece. The microscope support is constructed of transparent plastic material to facilitate observation of objects beneath the microscope which are illuminated with light from a bulb in the base of the microscope. The microscope glove box is a modification of one used at Los Alamos Scientific Laboratory for microscopic examination of highly toxic materials. The stainless steel glove box shown in Figure 2 is a modification of a muffle box built for plutonium isotope work. Some of the more interesting features of this glove box are: (1) A heating well consisting of a 1-1/2" length of 6" I.D. pipe welded around an opening in the bottom of the box and connected to an 8" length of 4" I.D. pipe closed at the bottom. The interior of the well is heated to a maximum of approximately 800°C by means of a 5" I.D. 2700-watt tube furnace mounted on a jack beneath the box so that it can be lowered to facilitate rapid cooling of the well. The box is kept cool by water flowing through a copper coil soldered to the bottom of the box around the well. (2) A discharge chute consisting of a 12" length of 4" I.D. pipe welded to the right side of the box at an angle of 60° from the vertical, loosely sealed on the inside of the box by a sliding door and tightly

sealed at the other end by a long plastic sock which is also used to encase materials removed from the box. This discharge arrangement is similar to that used on a number of glove boxes at Los Alamos Scientific Laboratory. (3) A small protrusion on the front of the box at the left side having a glass top over which a low-power long focal length (9X and 18X) binocular microscope and light is mounted for examination of objects inside the box. (4) Sodium fluoride traps (not visible in Figure 2) mounted inside of the box on the back wall, consisting of two 30" lengths of 3" I.D. copper tubing filled with 1/8" NaF pellets to remove HF from exhaust gases. The first one of the traps connected in series is heated to 100°C by means of a heating coil to prevent caking of the NaF through formation of HF-rich complexes, while the second trap is unheated in order to effect more complete removal of HF.

The pressure in the boxes is maintained 1/2 to 1" of water below that of the laboratory by means of an exhaust system. Air filtered through a CWS filter can be alternately supplied to the box from the room (50% RH), from an "Lectrodryer" (approximately 15% RH) or from a drying tower packed with Drierite (moisture content not determined). Bellows-type valves mounted on a panel below the front face of the box control admission of argon, 95% argon-5% hydrogen mixture, HF, and vacuum to apparatus within the box. The argon-hydrogen mixture was used to supply a reducing atmosphere over the melts instead of pure hydrogen because of safety considerations. The gas tanks and

vacuum pump are located outside of the laboratory.

Materials

Plutonium trifluoride used in these studies was high-purity material supplied by Los Alamos Scientific Laboratory. Solvent mixtures were purified prior to being introduced into the glove box by treating fused mixtures with gaseous HF and H_2 at about 800°C and cooling under an inert atmosphere. The composition of some of the purified mixtures was modified either by addition of crystalline BeF_2 purified by the above-described procedure or by addition of Harshaw optical grade LiF.

Apparatus

A picture of the filtration apparatus used in this investigation is shown in Figure 3. This apparatus is a modification of that used earlier in these laboratories for solubility determinations,* the main change being a reduction in the diameter of the sample container in order to permit smaller charges to be used. The copper bellows permit the filter medium to be kept out of contact with the charge material prior to the actual filtration in order to minimize clogging of the filter medium. The apparatus shown in Figure 3 was assembled by heliarc welding in the Special Services Shop of the Y-12 Plant. An improved version of the apparatus used for the last few experiments performed was assembled in the Welding and Brazing Facility, ORNL,

* Designed by B. H. Clampitt, formerly a member of the Chemistry Division, Oak Ridge National Laboratory.

by brazing the top part together with gold-nickel alloy in a hydrogen atmosphere at about 1000°C. This procedure permitted use of thin-wall tubing for the thermocouple well and also effected removal of oxide film from the nickel surfaces.

The temperature of the melt surrounding the tip of the thermocouple well was measured and controlled by means of a platinum-platinum 10% rhodium thermocouple connected to a Brown proportional controller. It was recorded on a 300-1000°C recorder. A portable potentiometer provided an e.m.f. to keep the recorder on scale while the temperature was below 300°C and was also used to check the potential of the thermocouple junction. The recorder and potentiometer readings generally agreed within 2°C. The temperature near the center of the furnace heating coils was indicated on a Brown Protect-O-Vane controller.

The temperature of the heated NaF trap was measured and controlled by means of a chromel-alumel thermocouple, in a thermocouple well extending from the center of one end of the trap to a point near the middle, connected to a Brown Pyr-O-Vane controller.

Experimental Procedure

The filtration apparatus (Figure 3) was first connected to the gas tanks and vacuum pump through the manifold system below the stainless steel glove box (Figure 2) and vacuum tested at room temperature. After a vacuum of about 50 microns was obtained, the filter stick was removed and charge material consisting of 5.0 to 5.5 grams of solvent mixture and enough PuF_5

to give 6.0 grams total charge was transferred from plastic vials into the filter apparatus through a long-neck metal funnel. The ratio of solvent to PuF_3 was adjusted to provide at least twice the amount of PuF_3 that was expected to be dissolved. After the filter stick was replaced, the filter apparatus was re-connected and vacuum tested. It was then filled with argon-hydrogen mixture introduced through the filter stick, which was positioned so that its lower end was close to the fused salt mixture, providing reducing atmosphere to help keep the plutonium in the trivalent state. Argon-hydrogen mixture was used in preference to pure hydrogen because of safety considerations. Gaseous HF was mixed with the argon-hydrogen mixture before the temperature of the filter bottle reached 250°C in order to minimize hydrolysis resulting from adsorbed water on the surface of the fused salt and PuF_3 crystals or to reconvert any hydrolysis products to fluorides.

The filter bottle and contents were held at the desired filtration temperature $\pm$ 5°C for two hours with a slow flow of the mixed gases over the surface of the liquid and then filtration was effected by applying a vacuum to the filter stick and argon pressure of 3 to 6 lbs to the surface of the liquid while the bellows was compressed to bring the filter stick into contact with the liquid for a period of 5 to 10 minutes. The filtrate and residue were allowed to cool slowly to room temperature in an argon atmosphere. The filter stick was then removed

and cut into sections for removal of the filtrate. A new charge of solvent and PuF_3 was added to the residue from the previous filtration, a new filter stick was inserted in the apparatus and the above filtration procedure was repeated at a different temperature. After the required number of filtrations had been completed with each solvent composition, the filter bottle was cut open and the residue from the final filtration experiment was removed for examination and analysis.

A variation of the above-described procedure was used in filtration experiments with one solvent (71.3 LiF-28.7 BeF_2). Flexible hose connections were placed in the three gas lines leading to the filtration apparatus. This permitted the filter bottle to be withdrawn from the furnace at the conclusion of the filtration period while argon gas was still being pulled through the filter stick, causing the filter bottle and contents to cool quite rapidly (approximately 100° per minute between 600 and $300^{\circ}C$). This procedure eliminated any possibility of a portion of the filtrate running through the filter medium during the cooling period and it had the advantage of making the filtrate available for examination at room temperature about 30 minutes after the end of the filtration. It was also possible with this arrangement to agitate the contents of the filter bottle by moving the apparatus up and down. The principal disadvantages are the hazards associated with the handling of hot objects in the glove box and the extremely small crystal size of the

rapidly cooled mixtures which makes microscopic identification of crystals difficult.

Results

Table I gives the composition of solvent mixtures which were analyzed chemically. The first column shows the nominal or intended composition of the mixtures while the last column shows the composition calculated from analytical data. The composition of solvent mixtures not included in Table I was calculated.

Solubility data obtained with $LiF-BeF_2$ mixtures are given in Table II; $NaF-BeF_2$ solubility data are contained in Table III; and the solubility of PuF_3 in one $NaF-LiF-BeF_2$ mixture is shown in Table IV. The data are shown graphically in Figures 4 and 5, omitting doubtful results, as a plot of the log of the molar concentration of PuF_3 versus 1/T (^{o}K). Figure 6 shows solubility data at three temperatures as a function of solvent composition for $LiF-BeF_2$ mixtures while Figure 7 shows a similar plot for $NaF-BeF_2$ compositions. The data obtained with the ternary mixture (Table IV) were used to extend the data in Figure 7 by considering 56.5% NaF and 17.5% LiF as equivalent to 74 mole % NaF. A comparison of the two systems, using interpolated solubility values at 565°C is shown in Figure 8, again using data on the ternary system to extend the $NaF-BeF_2$ curve.

Dissolved portions of seven samples were examined spectrophotometrically for Pu^{+4} content. No Pu^{+4} was detected in any of the samples. The limit of detection varied from 0.2 to 3.0%,

Table I

Composition of Solvent Mixtures

Nominal Composition (mole %)	Na or Li (Wt. %)	Be (Wt. %)	Calculated Composition (mole %)
50 NaF-50 BeF_2	25.32	10.06*	49.7 NaF-50.3 BeF_2
57 NaF-43 BeF_2	29.14	8.64*	57.0 NaF-43.0 BeF_2
64 NaF-36 BeF_2	33.12	7.48*	63.4 NaF-36.6 BeF_2
66.7 LiF-33.3 BeF_2	14.47	8.80*	68.1 LiF-31.9 BeF_2
50 LiF-50 BeF_2	9.90	12.0	51.7 LiF-48.3 BeF_2
56 LiF-44 BeF_2	10.98	11.12*	56.3 LiF-43.7 BeF_2
56 NaF-16 LiF-28 BeF_2	30.86 Na 2.89 Li	5.98*	56.5 NaF-17.5 LiF-26.0 BeF_2

* Average of results obtained by two laboratories.

Table II

Solubility of PuF_3 in $LiF-BeF_2$ Mixtures

Solvent Composition Mole % Li	Filtration Temperature (°C.)	Plutonium in Filtrate Wt. % Pu	Mole % PuF_3
51.7	463	1.02	0.16
"	549	2.44	0.38
"	599	2.96*	0.47*
"	654	5.76	0.93
56.3	494	1.04**	0.15
"	560	1.89**	0.28
"	602	3.15**	0.48
"	653	5.47**	0.86
"	550	1.98	0.30
"	599	2.04*	0.31*
"	649	6.24*	0.98*
65.4	532	1.15	0.16
"	600	1.78*	0.27*
"	643	4.30	0.63
71.3	546	4.00	0.56
"	597	5.90	0.85
"	650	8.48	1.26

* Doubtful result, excluded from Figure 4.

** Results obtained with a pre-fused mixture. Other results with this composition were obtained with mixtures prepared by mixing LiF, Li_2BeF_4 and PuF_3 in the filter bottle.

Table III

Solubility of PuF_3 in $NaF-BeF_2$ Mixtures

Solvent Composition Mole % NaF	Filtration Temperature (°C)	Plutonium in Filtrate Wt. % Pu	Plutonium in Filtrate Mole % PuF_3
49.7	552	1.18	0.22
"	600	1.73	0.33
"	600	1.79	0.34
"	651	2.72	0.52
57.0	538	1.17*	0.22*
"	552	1.63*	0.31*
"	600	1.35	0.26
"	600	1.26	0.24
"	609	1.26	0.24
"	650	1.48*	0.28*
"	652	2.21	0.42
"	706	3.40	0.66
63.4	550	1.54	0.29
"	598	2.43	0.46
"	600	2.00*	0.38*
"	650	4.40	0.85

* Doubtful result, excluded from Figure 5.

Table IV

Solubility of PuF_3 in $NaF-LiF-BeF_2$ (56.5-17.5-26 mole %)

Filtration Temperature (°C)	Plutonium in Filtrate Wt. % Pu	Mole % PuF_3
500	2.92	0.51
554	7.68	1.43
565	2.61*	0.46*
600	7.59	1.41
634	13.0	2.58
655	6.45*	1.18*

* Doubtful result, excluded from Figure 5.

depending upon the plutonium concentration in the samples and the size of the sample analyzed. Since these results, coupled with a careful examination of each sample by means of the petrographic microscope, demonstrated that all of the plutonium in these samples was in the trivalent form, other samples were analyzed chemically only for total plutonium content but microscopic examination of the samples continued. A summary of the petrographic observations made by R. A. Strehlow is contained in Appendix B.

Since Pu^{+4} produced by disproportionation of PuF_3 could have been reduced by hydrogen in the atmosphere above the melt or by the nickel walls of the container, it seemed advisable to look for other evidence of the absence of disproportionation of PuF_3. In similar studies with UF_3-containing melts, U metal resulting from disproportionation of UF_3 was found to have alloyed with the container wall. In order to determine whether a similar alloying effect occurred when PuF_3-containing melts were in contact with nickel, the bottom section of two welded nickel filter bottles (Figure 3) that had been in contact with such melts were scraped as clean as possible and analyzed for total plutonium content. One sample had contacted a mixture of NaF, BeF_2 and PuF_3 at 600°C for two hours while the other had contacted a similar mixture at temperatures varying from 550 to 650°C for approximately eight hours. The plutonium found in the two samples, amounting to 0.05 and 0.17 mg respectively, could

be accounted for by the trace of fused salt remaining on the nickel. No evidence of disproportionation of PuF_3 in fused alkali fluoride-beryllium fluoride melts under the conditions maintained in these solubility studies has been observed to date.

Discussion

Straight lines correlate the data in Figures 4 and 5 within the limits of reproducibility of the results. Changes in composition of the solvent mixtures seem to have little effect on the slope of the lines. It appears, therefore, that the heat of solution of PuF_3 in these solvents is essentially constant for the temperature and composition ranges studied.

The solubility-composition plots, Figures 6, 7, and 8, show that the solubility of PuF_3 in the melts goes through a minimum with a sharp increase on the alkali fluoride side and a gradual increase on the BeF_2 side of the minimum. This result is not unexpected since the BeF_2-PuF_3 eutectic probably contains a very low concentration of PuF_3 while the alkali fluoride-PuF_3 eutectics almost certainly contain a much higher PuF_3 concentration.

Inspection of Figure 8 and the phase diagrams of the binary systems LiF-BeF_2[5] and NaF-BeF_2[6] shows that a higher solubility

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5. D. M. Roy, R. Roy, and E. F. Osborn, J. Ceram. Soc. 37, 300 (1954); Novoselova, Simanov, and Yarembash, J. Phys. Chem. USSR, 26, 1244 (1952).
6. D. M. Roy, R. Roy, and E. F. Osborn, J. Ceram. Soc., 33, 85 (1950); Ibid, 36, 185 (1953); E. Thilo and H. Schröder, Z. physik. chem., 197, 41 (1951).

of PuF_3 at 565°C can be achieved in the $LiF-BeF_2$ system than in the $NaF-BeF_2$ system for solvent mixtures having the same liquidus temperature. For example, the $LiF-BeF_2$ mixture containing 69 mole % LiF which is liquid at 520°C, will dissolve about 0.50 mole % of PuF_3 at 565° while the comparable $NaF-BeF_2$ mixture melting at 520°C contains 62.5 mole % NaF and will hold 0.26 mole % PuF_3 in solution at 565°. If much more than 0.5 mole % PuF_3 is needed for a circulating fuel reactor having a minimum temperature of 565°, it may be necessary to resort to a ternary solvent in order to keep the liquidus temperature of the solvent at an acceptably low figure.

Approximation 25% of the filtration data recorded in Tables II, III, and IV (those results marked with asterisks) were excluded from Figures 4 and 5 and some of the points in these graphs do not lie very close to the lines. This scatter of data reflects to some extent the difficulty in obtaining equilibrium data with small amounts of fused salts. It was desirable to use small amounts of materials for these experiments because of neutron production in plutonium-beryllium fluoride melts. However, an analysis of factors having a possible influence on the results may be of help in evaluating the data. Low results could be due to failure to saturate the solvent because of inadequate equilibration time, absence of a means of agitation (see page 9), or lack of a sufficient amount of PuF_3 in the mixture. There are two fairly obvious explanations of high results. A temperature gradient is known to

exist in the heated zone occupied by the filter bottle during filtration experiments, with the temperature decreasing in going from the bottom to the top of the chamber. If the thermocouple junction was above the surface of the liquid in the filter bottle, the temperature indicated by the thermocouple was probably lower than that of the liquid. Some of the filter bottles used in these studies had thermocouple wells too short to reach the surface of the liquid and it is also possible that errors in the determination of the temperature of the melts resulted from the thermocouple being inadvertently pulled part way out of the thermocouple well. The other possibility is that a portion of the solvent or a low-melting ternary eutectic having a lower plutonium content than that of the original filtrate ran back through the filter after partial solidification of the filtrate occurred. (See Experimental Procedure, p. 7)

Confidence in plutonium values reported by the analytical laboratory was strengthened by having a number of samples reanalyzed under different sample designations. The results, shown in Appendix C, indicate that satisfactory reproducibility was obtained although the differences for some samples were greater than expected from the precision of the potentiometric plutonium determination. It is possible that some of the early samples which were ground but not sieved were not entirely homogeneous.

Acknowledgments

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Appendix A

Thermodynamic Calculations for Reactions at 1000°K.

Reaction	ΔF for Reaction as written (k Cal)	ΔF per Gm. Atom of F, k Cal
$4UF_3 \rightarrow 3UF_4 + U^o$	+ 12	+ 1.0
$4PuF_3 \rightarrow 3PuF_4 + Pu^o$	+ 214	+ 18
$2UF_4 + Cr^o \rightarrow 2UF_3 + CrF_2$	+ 31	+ 3.9
$2UF_3 + 3Cr^o \rightarrow 2U^o + 3CrF_2$	+ 120	+ 20
$2PuF_4 + Cr^o \rightarrow 2PuF_3 + CrF_2$	- 80	- 10
$2PuF_3 + 3Cr^o \rightarrow 2Pu^o + 3CrF_2$	+ 194	+ 32

Appendix B

R. A. Strehlow

Optical Properties of Fluoride Mixtures Containing PuF_3

Petrographic examinations were carried out on filtrates and residues obtained in the study with a principal objective of identifying the plutonium containing phase. All of the slide preparations for the work were made in a glove-port plexiglas box (Figure 1) in which was mounted a polarizing microscope. The optical character of the various plutonium compounds permitted distinction to be made from the crystals of the various solidified solvents. The solvents generally contained one or more of the compounds: Li_2BeF_4,[1] Na_2BeF_4,[2] $NaBeF_3$,[2] $LiBeF_3$[1] and BeF_2[1]. All of these compounds have refractive indices of less than 1.4.

Inasmuch as the plutonium phases had much higher refractive indices an initial observation was made of the growth form of all phases of higher index by examining the crushed specimen in an oil with a refractive index of about 1.35. Under these conditions all phases of appreciably higher index appear quite heavily bordered and are easily located in the microscope field. Observation of the color and birefringence of the phase indicated which of the possible compounds con-

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1. D. M. Roy, R. Roy and E. F. Osborn, J. Ceram. Soc. 37, 300 (1954)
2. D. M. Roy, R. Roy and E. F. Osborn, J. Ceram. Soc. 33, 85 (1950).

taining plutonium was present: Pu(III) fluorides are blue and Pu(IV) fluorides tan. (No PuF_4 was observed in the filtrates or residues in this study.) The maximum birefringence of PuF_3 observed in this study is about 0.003. The interference color (observed with crossed polarizing discs) is approximately that of the crystal observed in "white" light, pale blue. The compound $NaPuF_4$ appears reddish blue and has a maximum birefringence of about 0.02. The optical properties of these compounds are compared in Table B-1 with those of some Ce^{+3}, U^{+3}, and U^{+4} compounds.

The Pu(III) ion is about the same size as the Ce(III) and U(III) ions and differs from them in its polarizability which is, of course, shown by the differences in refractive indices.

The most common growth form of PuF_3 as crystallized from the solvents used in the study was that of thin sheets which could be observed with their maximum birefringence only when they existed as platy inclusions in the solvent crystals. Under these conditions they exhibited their maximum birefringence and parallel extinction. No compound was found which could be considered a $LiF-PuF_3$ binary compound in $LiF-BeF_2-PuF_3$ melts and no change in the refractive index of PuF_3 was seen which would indicate solid solution of LiF in the PuF_3.

The growth form of the PuF_3 is strongly dependent on the

Table B-1

Refractive Indices and Optical Character of Some Plutonium, Cerium, and Uranium Fluorides

	η_ϵ	η_ω	Description
PuF_3	1.683	1.685	Uniaxial (-); blue*
UF_3	~2		Isotropic; red
CeF_3	1.607	1.613	Uniaxial (-); colorless

	η_α	η_γ	Description
PuF_4	1.577 pink	1.629 green-brown	$2\nu = -65^\circ$
UF_4	1.550 blue-green	1.594 green-brown	$2\nu = -57^\circ$

	η_ω	η_ϵ	Description
$NaUF_4$	1.552	1.564	Uniaxial (+)
$NaPuF_4$	1.534	1.552	Uniaxial (+) (length slow)
$NaCeF_4$	1.494	1.512	Uniaxial (+)

* The sign of PuF_3 as observed in this work does not agree with that listed by E. Staritsky and A. L. Truitt in "The Actinide Elements," NNES, IV-14A, McGraw-Hill Book Co.

cooling rate and is described in Table B-2.

Table B-2

The Effect of Extremes in Cooling Rates

On Appearance of PuF_3 in $LiF-BeF_2$ Mixtures

Rate	Appearance
Rapid	Asterisms <5μ across frequently imbedded in glassed solvent. Occasional identifiable crystals near 3-8μ in diameter.
Slow	Large plates (>50μ across, 5μ thick) giving the uniaxial (-) interference figure; solvent well crystallized.

A sample prepared by mixing $LiF-NaF-PuF_3$ (50-33.3-16.7 mole %) was examined petrographically after fusing. A large amount of a plutonium containing phase, LiF crystals, and NaF-LiF eutectic aggregates were observed. Since the plutonium compound was found only in mixtures containing sodium fluoride and since the optical properties were similar to those for the known compounds $NaCeF_4$ and $NaUF_4$, this plutonium compound was designated as $NaPuF_4$.

It is interesting to note that $NaPuF_4$ was observed as the sole plutonium containing phase in the filtrate from the mixture $NaF-LiF-BeF_2$ (56.5-17.5-26 mole %). Some $NaPuF_4$ was seen in the residue from the mixture containing 64 mole % NaF but not in the filtrate. This indicates that the isotherms as shown in Figure 7 probably cross the $NaPuF_4-PuF_3$ primary phase field

boundary at a relative composition of very near 64-36 mole NaF per mole BeF_2. PuF_3 was observed in both filtrates and residues of other NaF content.

A comparison was made of transmission spectra by means of a Leitz pupillary spectroscope. The principal difference between $NaPuF_4$ and PuF_3 is an absorption band between 6500 Å and 6650 Å for PuF_3 which exists at 6660 Å to 6800 Å for $NaPuF_4$. For the PuF_3 there is also more transmission between 5200 Å and 6000 Å which presumably accounts for the difference in color between $NaPuF_4$ and PuF_3.

Appendix C

Analysis of Re-submitted Samples

Original Sample	% Pu	Re-Check	% Pu
A5	1.36	G2	1.33
B5	1.41	E8-C9	1.15-1.22
A7	2.16	G3	2.25
B3	1.37	G6	1.60
D6	1.77	G7	1.68
B7	1.82	H3	1.74
E7	2.88	H8	3.03

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Fig. 1

Pu

-1.22

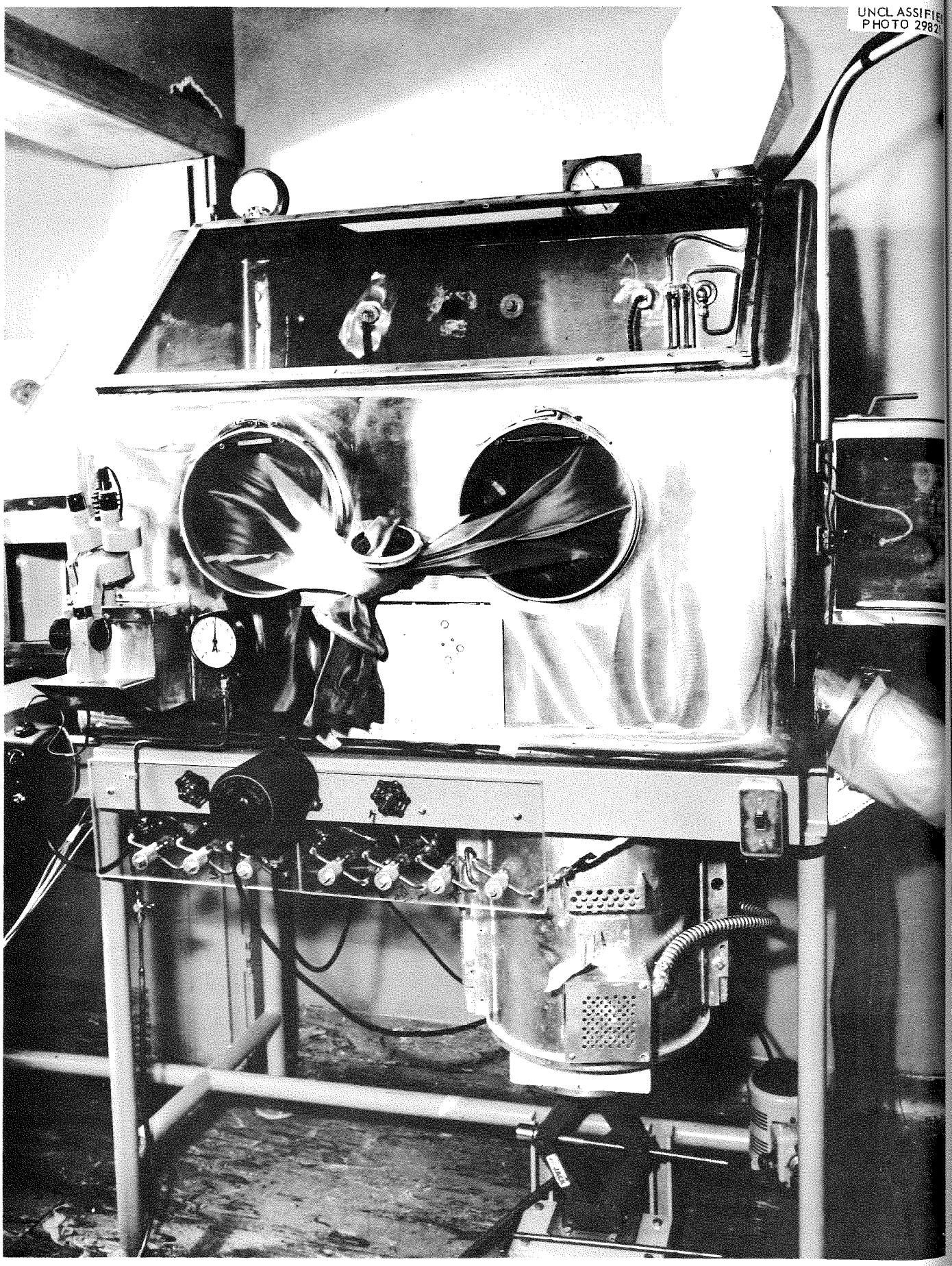
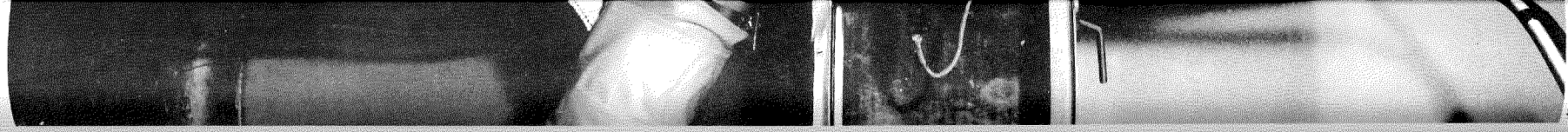


Fig. 2



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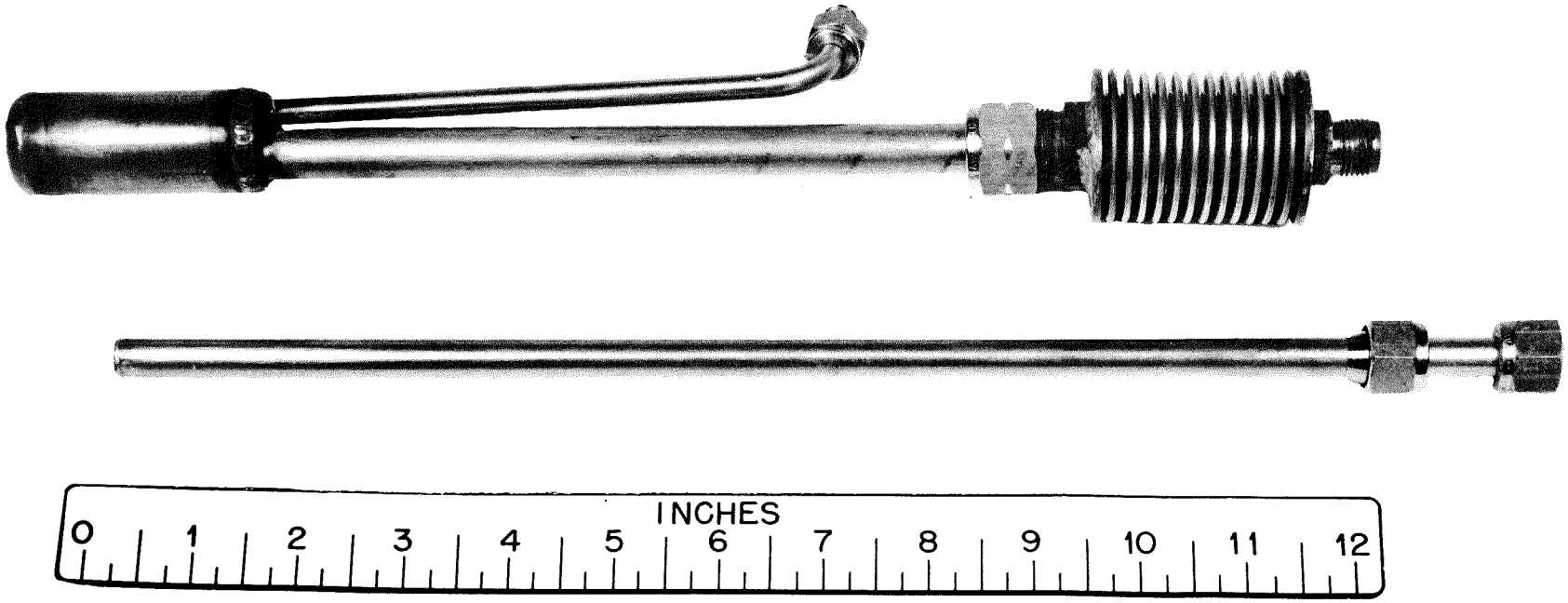

Fig. 3

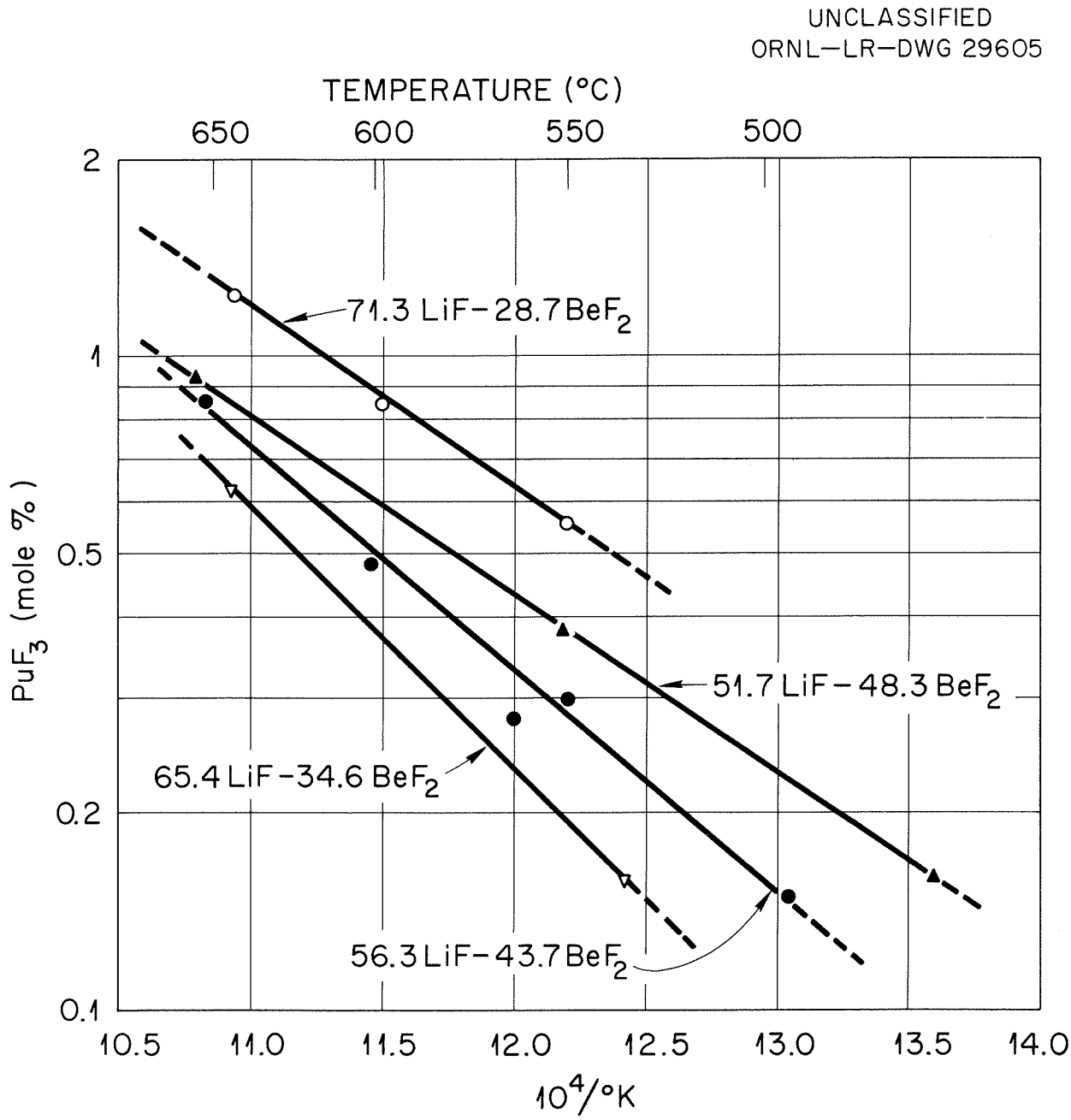

Fig. 4. Solubility of PuF_3 as a Function of Temperature for $LiF-BeF_2$ Solvents.

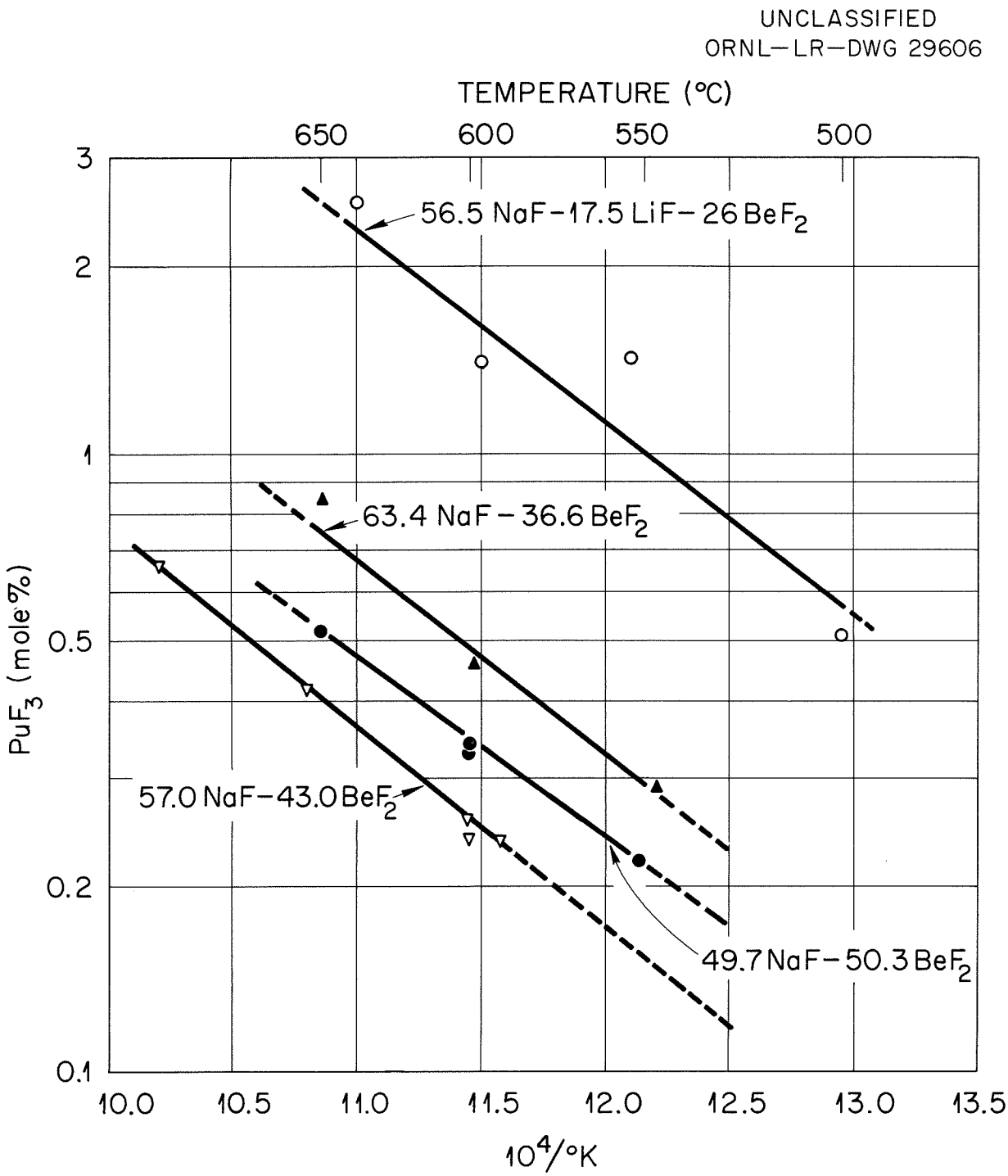

Fig. 5. Solubility of PuF_3 as a Function of Temperature for $NaF-BeF_2$ and $NaF-LiF-BeF_2$ Solvents.

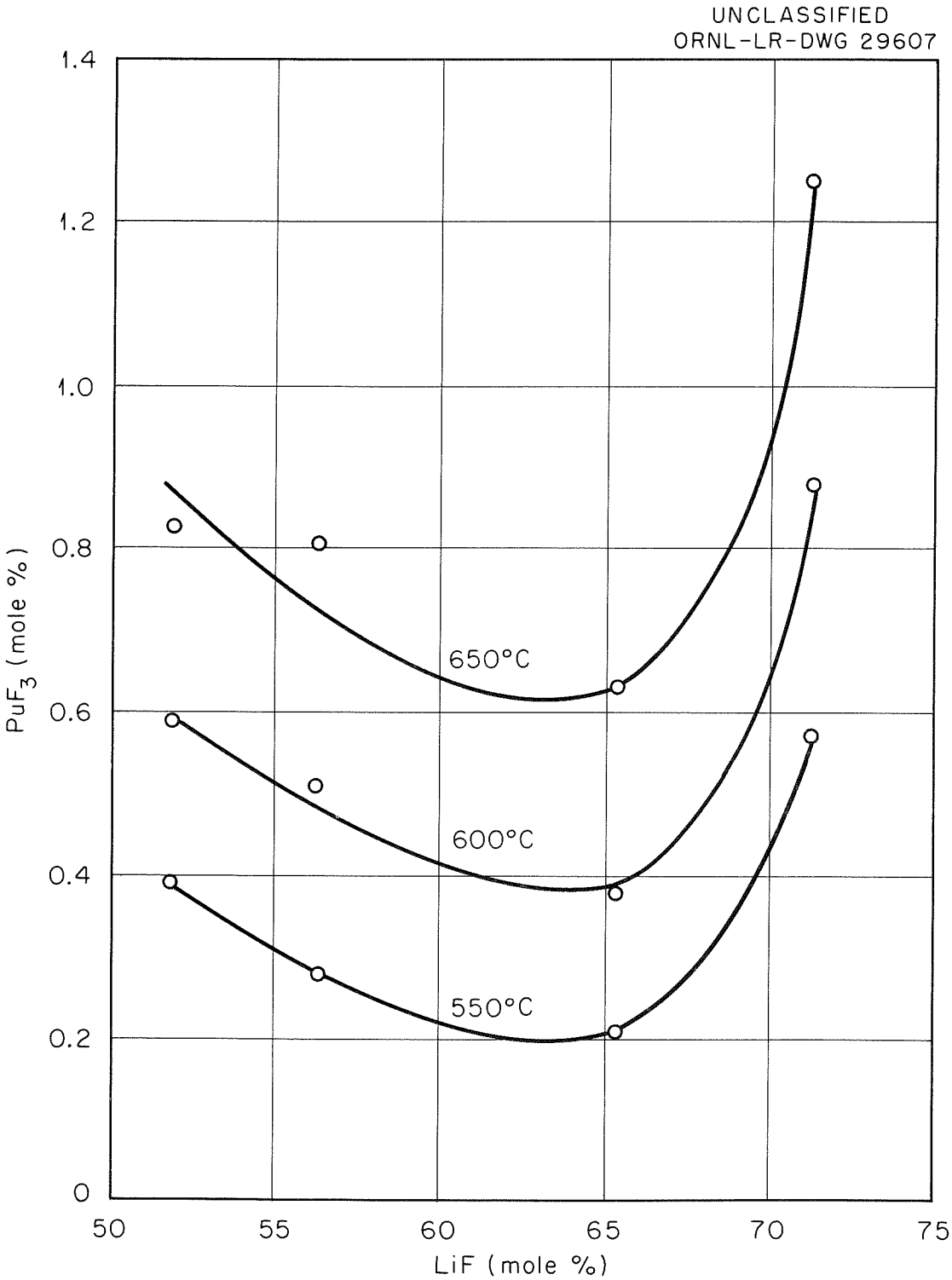

Fig. 6. Solubility of PuF_3 as a Function of Solvent Composition for $LiF-BeF_2$ Mixtures.

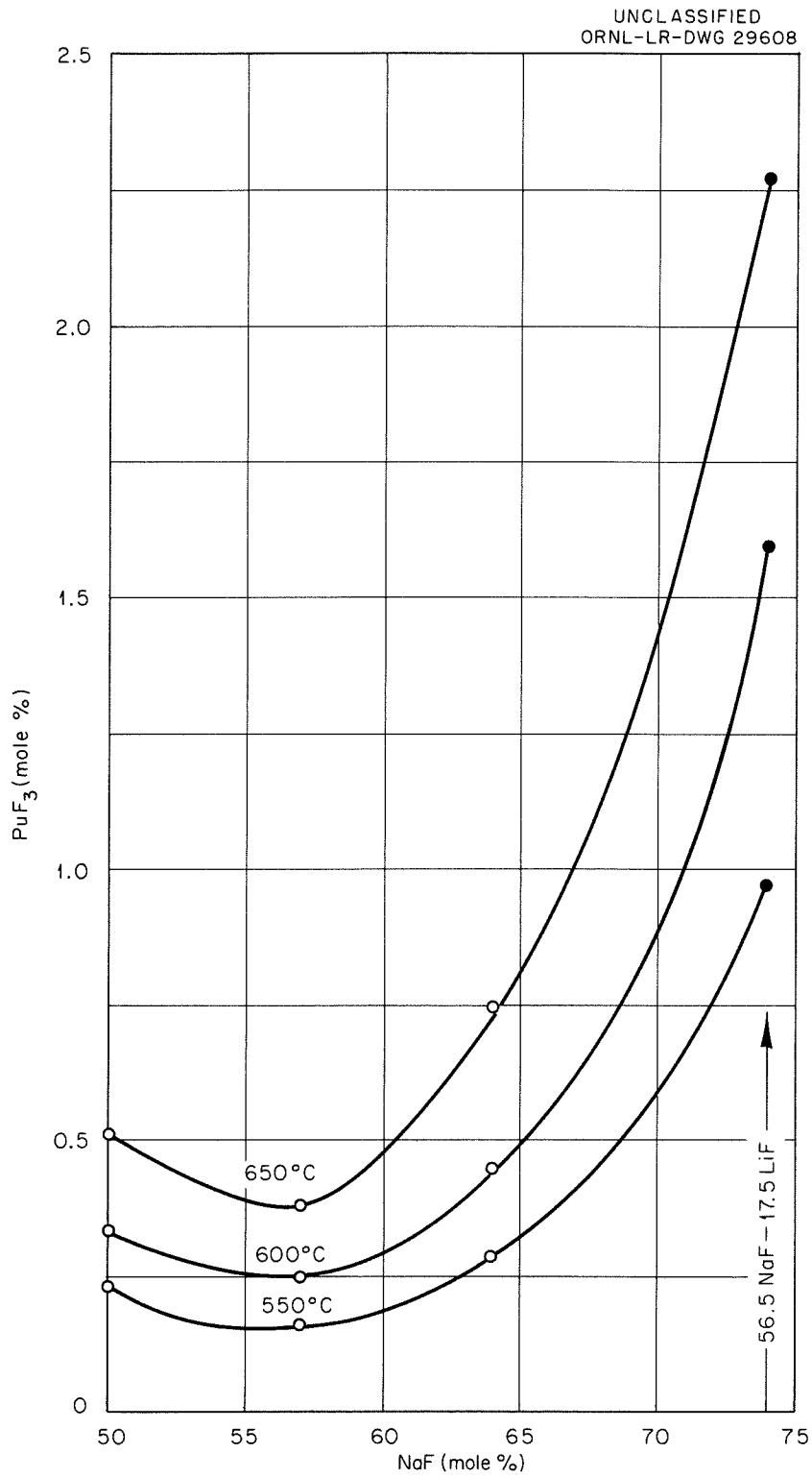

Fig. 7. Solubility of PuF_3 as a Function of Solvent Composition for $NaF-BeF_2$ Mixtures.

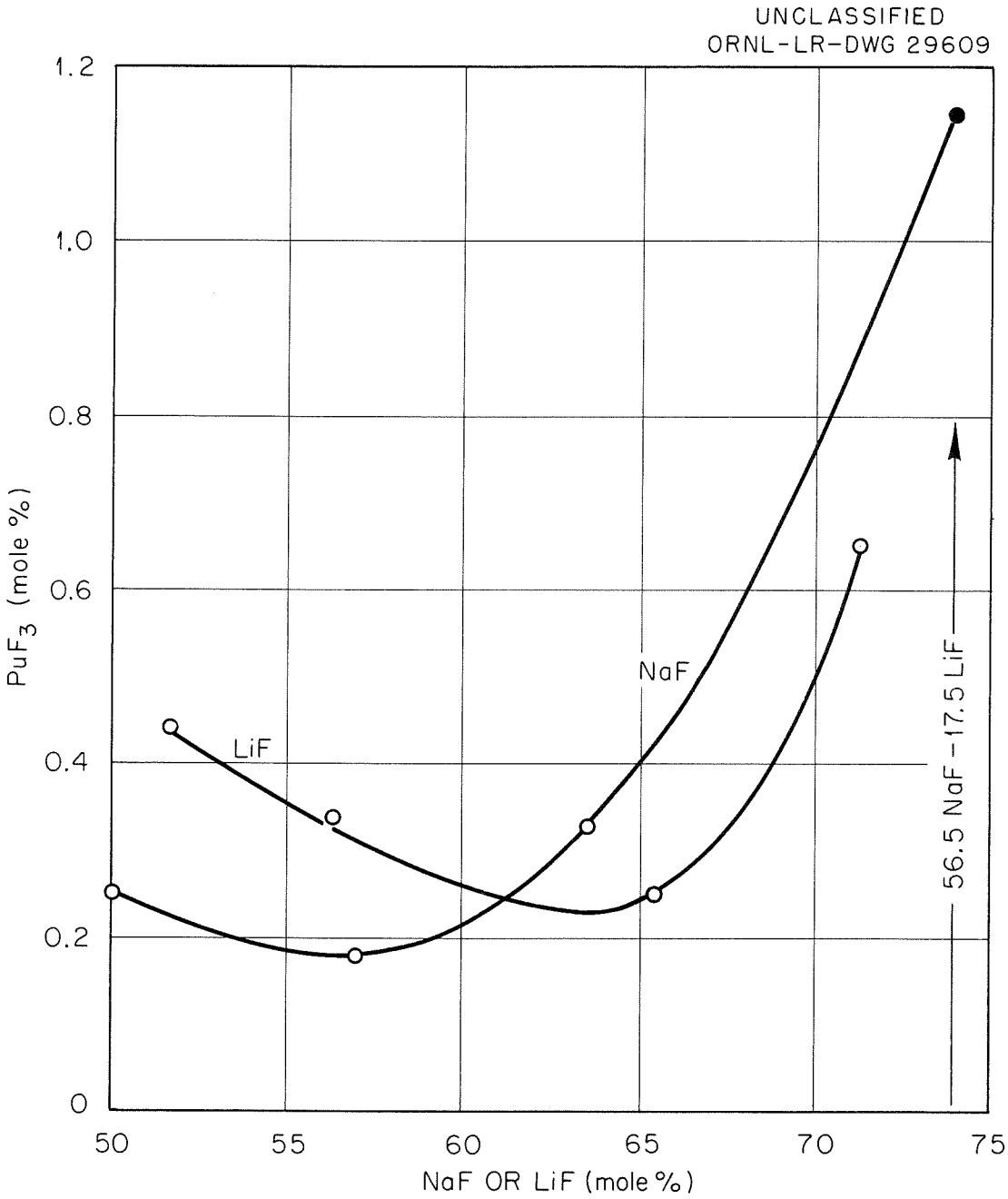

Fig. 8. Solubility of PuF_3 in $LiF-BeF_2$ and $NaF-BeF_2$ at 565°C.

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