

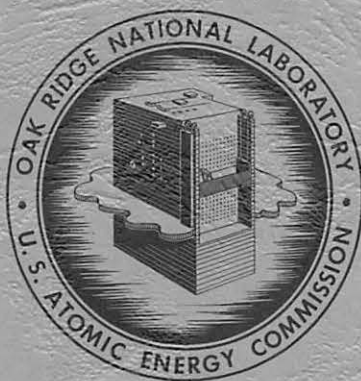
27
ORNL
MASTER COPY

ORNL-2719
Chemistry-General
TID-4500 (14th ed.)

PHASE EQUILIBRIA IN THE SYSTEMS

$\text{UF}_4\text{-ThF}_4$ AND $\text{LiF-UF}_4\text{-ThF}_4$

C. F. Weaver
R. E. Thoma
H. Insley
H. A. Friedman



OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

This document has been reviewed and is determined to be
APPROVED FOR PUBLIC RELEASE.

Name/Title: *Heera Layman / TID*

Date: *9-1-2015*

CONTENTS

Summary.....	1
Introduction.....	1
Materials, Methods, and Apparatus	2
General Discussion of the System $\text{LiF-UF}_4\text{-ThF}_4$ and the Limiting Binary Systems	2
The 20 Mole % LiF Join and the $\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss) Fractionation Paths	20
The $33\frac{1}{3}$ Mole % LiF Join and the $\text{LiF}\cdot 2\text{Th(U)F}_4$ (ss) Fractionation Paths	21
The 53.8 Mole % LiF Join and the $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) Fractionation Paths	21
The 75 Mole % LiF Join and the $3\text{LiF}\cdot \text{ThF}_4$ (ss) Fractionation Paths.....	21
Relations Between the Solid Solutions.....	31
Acknowledgments.....	34
Appendix	43

Contract No. W-7405-eng-26

REACTOR CHEMISTRY DIVISION

PHASE EQUILIBRIA IN THE SYSTEMS

$\text{UF}_4\text{-ThF}_4$ AND $\text{LiF-UF}_4\text{-ThF}_4$

C. F. Weaver
R. E. Thoma
H. Insley
H. A. Friedman

This document has been reviewed and is determined to be APPROVED FOR PUBLIC RELEASE.	
Name/Title:	<i>Leesa Layman / TIO</i>
Date:	<i>9-1-2015</i>

DATE ISSUED

AUG 17 1959

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

PHASE EQUILIBRIA IN THE SYSTEMS $\text{UF}_4\text{-ThF}_4$ AND $\text{LiF-UF}_4\text{-ThF}_4$

C. F. Weaver

R. E. Thoma

H. Insley

H. A. Friedman

SUMMARY

As part of a study of materials potentially useful as fluid fuels for high-temperature reactors, equilibrium diagrams for the condensed systems $\text{UF}_4\text{-ThF}_4$ and $\text{LiF-UF}_4\text{-ThF}_4$ have been determined. Both thermal analysis and quenching techniques were used, with phase identification accomplished by petrographic and x-ray diffraction analysis. A complete series of solid solutions without maximum or minimum is formed by UF_4 and ThF_4 . The system $\text{LiF-UF}_4\text{-ThF}_4$ contains no ternary compounds but does contain four ternary solid solutions. The compounds $\text{LiF}\cdot 4\text{ThF}_4$ and $\text{LiF}\cdot 4\text{UF}_4$ form a continuous series of solid solutions, as do the compounds $7\text{LiF}\cdot 6\text{ThF}_4$ and $7\text{LiF}\cdot 6\text{UF}_4$. A series of solid solutions exists having compositions at $33\frac{1}{3}$ mole % LiF between $\text{LiF}\cdot 2\text{ThF}_4$ and 23 mole % UF_4 . Another series of solid solutions exists having compositions at 75 mole % LiF between $3\text{LiF}\cdot \text{ThF}_4$ and 15.5 mole % UF_4 . Seven primary-phase fields appear in the system, those which are solid solutions being indicated by (ss): LiF , $4\text{LiF}\cdot \text{UF}_4$, $3\text{LiF}\cdot \text{Th}(\text{U})\text{F}_4$ (ss), $7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss), $\text{LiF}\cdot 2\text{Th}(\text{U})\text{F}_4$ (ss), $\text{LiF}\cdot 4\text{ThF}_4\text{-LiF}\cdot 4\text{UF}_4$ (ss), and $\text{UF}_4\text{-ThF}_4$ (ss). Phase relations were established from the liquidus to about 300°C . The three invariant points which occur are the following: peritectic, 19 mole % UF_4 , 18 mole % ThF_4 , 609°C ; peritectic, 20.5 mole % UF_4 , 7 mole % ThF_4 , 500°C ; and eutectic, 26.5 mole % UF_4 , 1.5 mole % ThF_4 , 488°C .

The solid phases taking part in the invariant reactions are the following: peritectic point at 609°C : $\text{LiF}\cdot 4\text{ThF}_4\text{-LiF}\cdot 4\text{UF}_4$ (ss) containing 28 mole % UF_4 , $\text{LiF}\cdot 2\text{Th}(\text{U})\text{F}_4$ containing 23 mole % UF_4 , and $7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ containing 23 mole % UF_4 ; peritectic point at 500°C : LiF , $7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss) containing 31 mole % UF_4 , and $3\text{LiF}\cdot \text{Th}(\text{U})\text{F}_4$ (ss) containing 15.5 mole % UF_4 ; eutectic point at 488°C : $4\text{LiF}\cdot \text{UF}_4$, LiF , and $7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss) containing 42.5 mole % UF_4 .

The refractive indices of the ternary solid solutions were determined as functions of composition and used for an optical analysis of the solid solutions when they occurred with other phases. This information made possible the

construction of tie lines, fractionation paths, and compatibility triangles for the three ternary invariant points.

INTRODUCTION

Several years ago, R. C. Briant of the Oak Ridge National Laboratory suggested the use of a molten mixture of UF_4 and ThF_4 together with fluorides of alkali metals and beryllium fluoride or zirconium fluoride as a potential fuel for a high-temperature, low-pressure nuclear reactor.¹ A systematic study at ORNL during the past several years has developed molten salt mixtures whose chemical and physical properties seem to suit them for use as fuels in U^{235} burner reactors,² in plutonium burner reactors, and in one-region U^{233} breeder reactors and as blankets in two-region U^{233} breeder reactors. Nuclear reactor designs have been proposed which would utilize mixtures of Li^7F , BeF_2 , ThF_4 , and UF_4 as fuels.³⁻⁵

Little is known concerning the phase relationships of the system $\text{LiF-BeF}_2\text{-UF}_4\text{-ThF}_4$ except that solid solutions involving LiF , UF_4 , and ThF_4 occur as primary and secondary phases at low UF_4 and ThF_4 concentrations. Phase diagrams of the limiting binary systems LiF-BeF_2 (ref 6), LiF-UF_4 (ref 7), and LiF-ThF_4 (ref 8)

¹A. M. Weinberg and R. C. Briant, *Nuclear Sci. and Eng.* 2, 797-803 (1957).

²E. S. Bettis et al., *Nuclear Sci. and Eng.* 2, 804-825 (1957).

³J. K. Davidson and W. L. Robb, *A Molten Salt Thorium Converter for Power Production*, KAPL-M-JKD-10 (1956).

⁴L. G. Alexander et al., "Conceptual Design of a Power Reactor," chap 17 of *Fluid Fuel Reactors*, Addison-Wesley, Reading, Mass., 1958.

⁵L. G. Alexander, "Nuclear Aspects of Molten-Salt Reactors," chap 14 of *Fluid Fuel Reactors*, Addison-Wesley, Reading, Mass., 1958.

⁶R. E. Thoma, *Phase Diagrams of Nuclear Reactor Materials*, ORNL-2548.

⁷C. J. Barton et al., *J. Am. Ceram. Soc.* 41(2), 63-69 (1958).

⁸R. E. Thoma et al., "Phase Equilibria in the Fused Salt Systems LiF-ThF_4 and NaF-ThF_4 ," *J. Phys. Chem.* (in press).

have been published. The systems $\text{BeF}_2\text{-UF}_4$ (ref 9) and $\text{LiF-BeF}_2\text{-UF}_4$ (ref 10) have been investigated at the Mound Laboratory. Results of phase equilibrium studies of the systems $\text{BeF}_2\text{-ThF}_4$ and $\text{LiF-BeF}_2\text{-ThF}_4$ will soon be reported by the authors. Preliminary diagrams of these systems are in the literature.^{11,12} The system $\text{BeF}_2\text{-UF}_4\text{-ThF}_4$ has not, to our knowledge, been investigated. The remaining systems, $\text{UF}_4\text{-ThF}_4$ and $\text{LiF-UF}_4\text{-ThF}_4$, are the subject of this report. Preliminary diagrams of these systems have been reported by the authors.^{12,13} As is to be expected from the known similarities in the parameters of the unit cells of ThF_4 and UF_4 (refs 14 and 15), a salient characteristic of the condensed systems $\text{UF}_4\text{-ThF}_4$ and $\text{LiF-UF}_4\text{-ThF}_4$ is the extensive formation of solid solutions.

MATERIALS, METHODS, AND APPARATUS

The lithium fluoride used in this investigation was reagent grade, obtained from Foote Mineral Company and from Maywood Chemical Works. The thorium tetrafluoride was obtained from Iowa State College and from National Lead Company. The uranium tetrafluoride was obtained from Mallinkrodt Chemical Works. No appreciable impurities were found in the uranium tetrafluoride or thorium tetrafluoride by spectrographic, x-ray diffraction, or microscopic analysis.

The phase equilibria data were obtained by thermal analysis of slowly cooled melts and by identifying the phases present in mixtures which had been equilibrated and quenched. Because uranium and thorium fluorides are easily converted

to oxides or oxyfluorides at elevated temperatures, it was necessary to remove small amounts of water and oxygen as completely as possible from the starting materials. To facilitate the removal of these substances, ammonium bifluoride was added to the mixtures of lithium fluoride, thorium fluoride, and uranium fluoride before initial heating in the thermal analysis experiments. While the mixtures were being heated the water was evaporated from the system. The oxides were converted by reaction with the ammonium bifluoride to products which have not yet been identified but which are likely to be ammonium fluometallates.^{16,17} Upon further heating, the "ammonium fluometallates" decomposed to form the metal fluorides. These same mixtures were later used in the quenching experiments.

The phases were identified by petrographic and x-ray diffraction techniques. These methods for characterizing phases, as well as a description of the apparatus used for preparing and annealing samples, were reported previously.^{7,8,18-21}

GENERAL DISCUSSION OF THE SYSTEM $\text{LiF-UF}_4\text{-ThF}_4$ AND THE LIMITING BINARY SYSTEMS

The phase diagram of the condensed ternary system $\text{LiF-UF}_4\text{-ThF}_4$ is shown in Fig. 1, and a photograph of a three-dimensional model²² of the system is shown in Fig. 2. The associated binary systems are shown in Figs. 3-5.

One metastable compound ($3\text{LiF}\cdot\text{UF}_4$) and three incongruently melting compounds ($4\text{LiF}\cdot\text{UF}_4$, $7\text{LiF}\cdot 6\text{UF}_4$, and $\text{LiF}\cdot 4\text{UF}_4$) are formed in the system LiF-UF_4 . Optical properties, except those of $3\text{LiF}\cdot\text{UF}_4$, and x-ray diffraction data for these

⁹J. F. Eichelberger, E. F. Joy, E. Orban, T. B. Rhinehammer, and P. A. Tucker, unpublished work.

¹⁰J. F. Eichelberger, D. E. Etter, C. R. Hudgens, L. V. Jones, T. B. Rhinehammer, P. A. Tucker, and L. J. Wittenberg, unpublished work.

¹¹W. R. Grimes *et al.*, "Chemical Aspects of Molten-Fluoride Reactor Fuels," chap 12 of *Fluid Fuel Reactors*, Addison-Wesley, Reading, Mass., 1958.

¹²"Supplement to 'Phase Diagrams for Ceramists'" (compiled by E. M. Levin and H. F. McMurdie), American Ceramics Society, Inc., Easton, Pa. (in press).

¹³R. E. Thoma *et al.*, *MSR Quar. Prog. Rep.* Jan 31, 1958, ORNL-2474, p 81.

¹⁴W. H. Zachariasen, *X-Ray Diffraction Studies of Miscellaneous Uranium Compounds*, MDDC-1152 (June 1946).

¹⁵J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium*, NNEs VIII-5, McGraw-Hill, New York, 1951.

¹⁶*MSR Quar. Prog. Rep.* April 30, 1959, ORNL-2723, p 93.

¹⁷B. J. Sturm, Oak Ridge National Laboratory, personal communication.

¹⁸C. J. Barton *et al.*, *J. Phys. Chem.* 62, 665 (1958).

¹⁹R. E. Thoma *et al.*, *J. Am. Ceram. Soc.* 42(1), 21-26 (1959).

²⁰H. A. Friedman, "Modifications of Quenching Techniques for Phase Equilibrium Studies," *J. Am. Ceram. Soc.* (in press).

²¹P. A. Tucker and E. F. Joy, *Am. Ceram. Soc. Bull.* 36(2), 52-54 (1957).

²²Model constructed by C. Johnson, summer participant at ORNL, 1958.

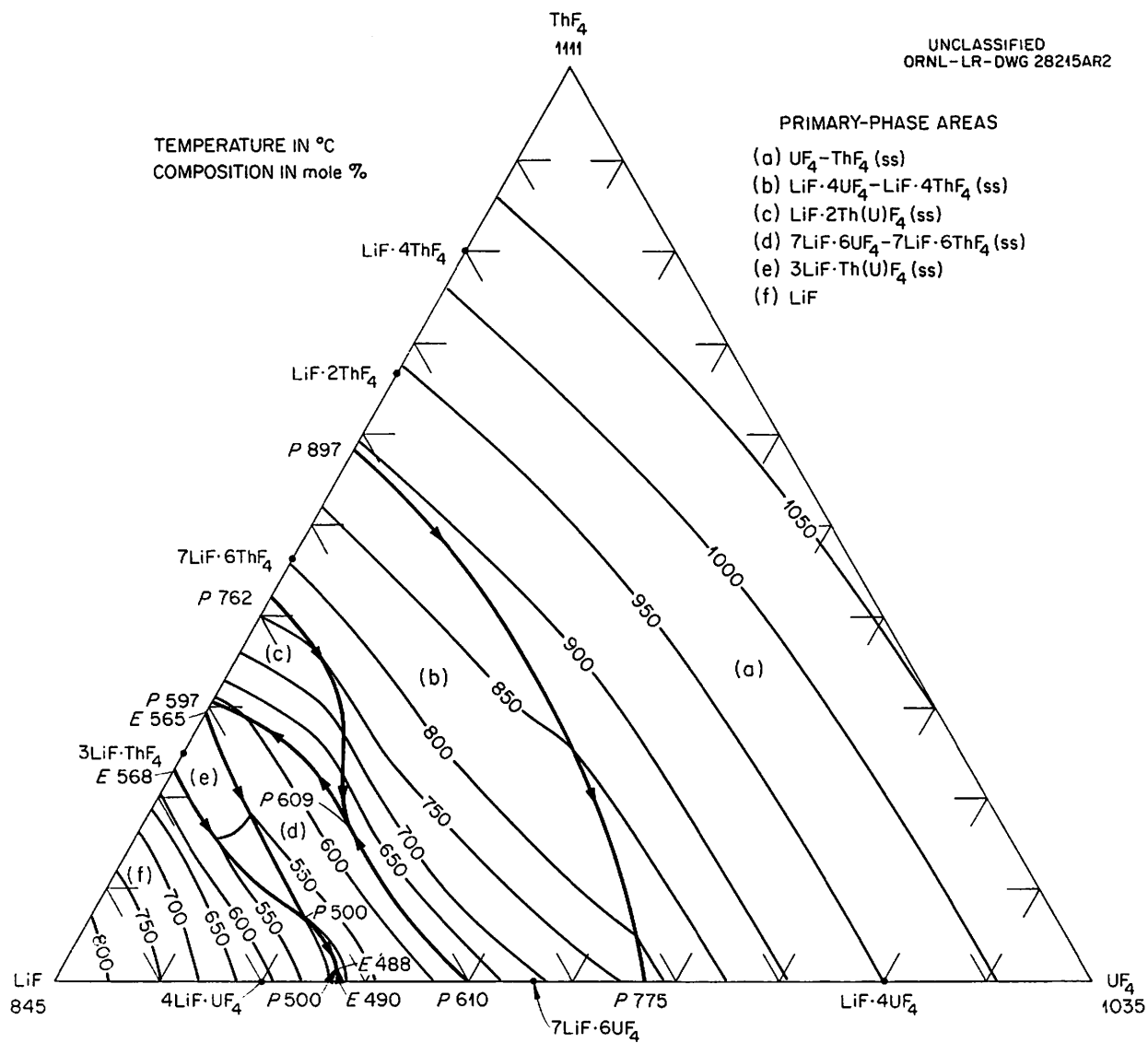


Fig. 1. The System $\text{LiF-UF}_4\text{-ThF}_4$.

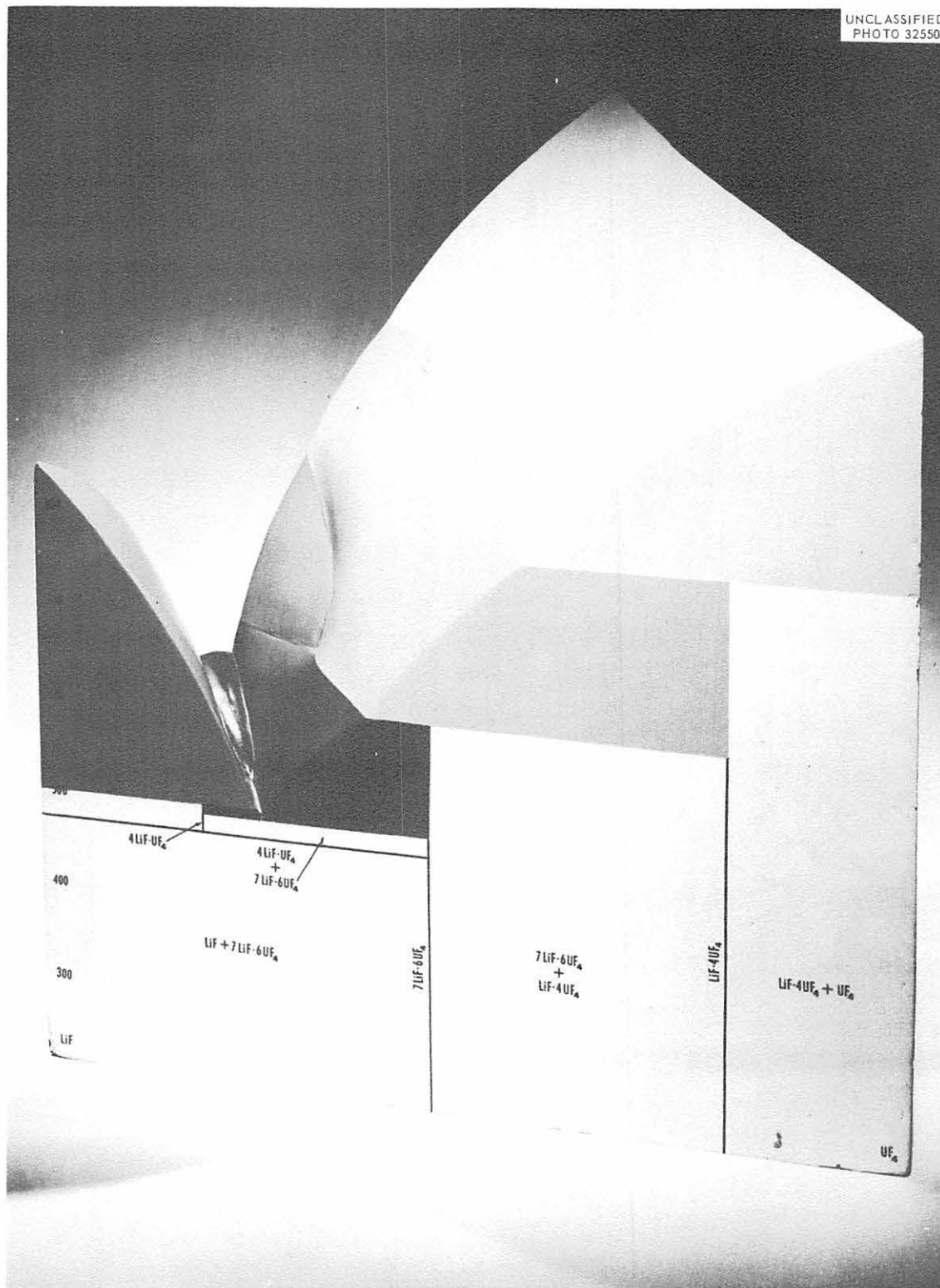


Fig. 2. Three-Dimensional Model of the System LiF-UF₄-ThF₄.

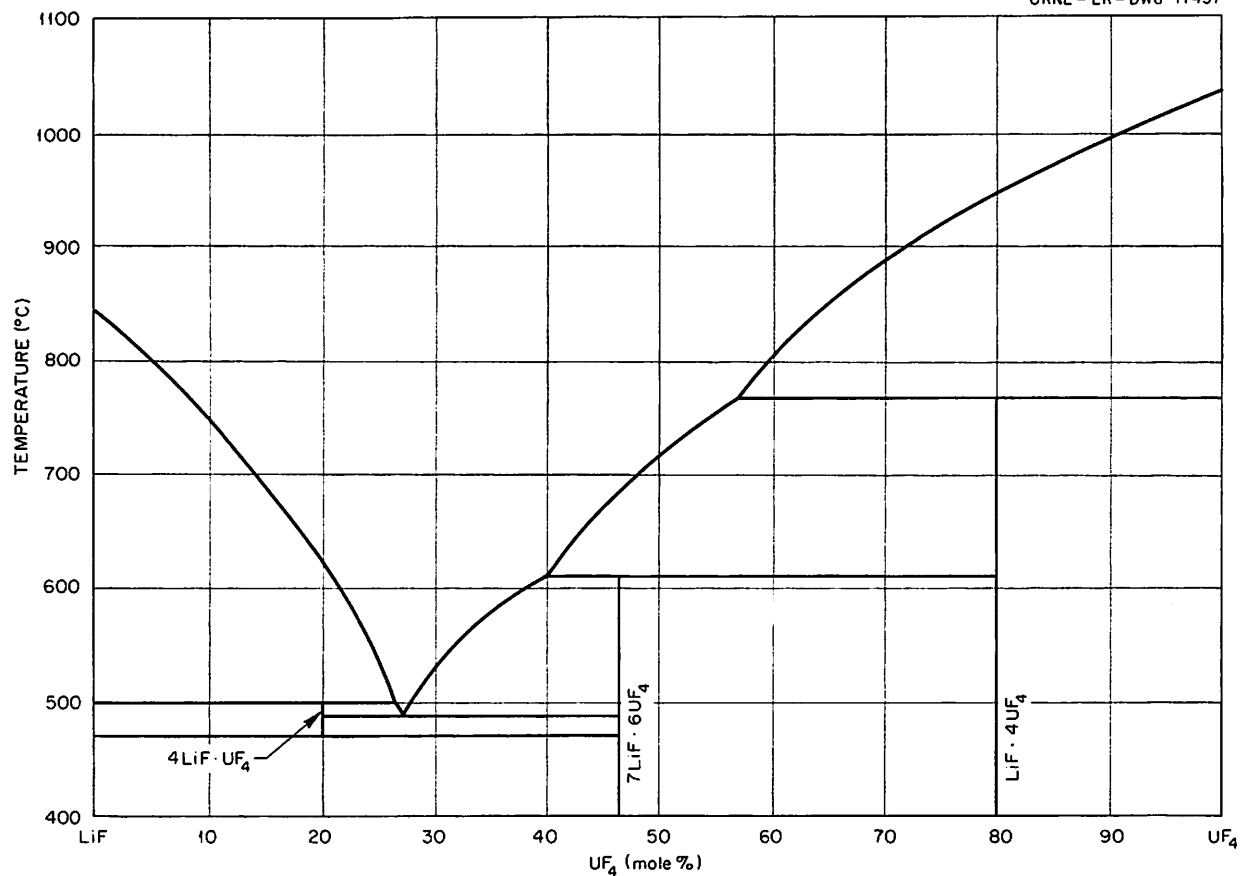


Fig. 3. The System $\text{LiF}-\text{UF}_4$.

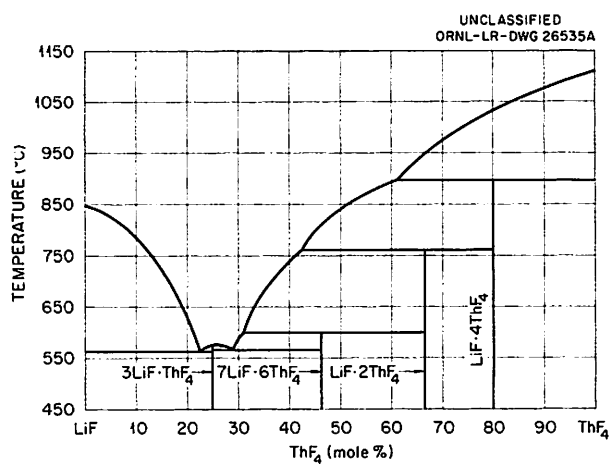


Fig. 4. The System $\text{LiF}-\text{ThF}_4$.

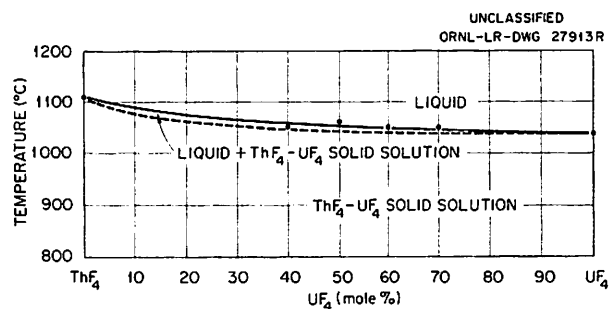


Fig. 5. The System ThF_4-UF_4 .

compounds are shown in Tables 1 and 2, respectively. The compound $4\text{LiF}\cdot\text{UF}_4$ has a lower limit of stability at 470°C . The compositions and temperatures of the three peritectic invariant points and the eutectic invariant point are (1) peritectic: 26 mole % UF_4 , 500°C ; (2) eutectic: 27 mole % UF_4 , 490°C ; (3) peritectic: 40 mole % UF_4 , 610°C ; (4) peritectic: 57 mole % UF_4 , 775°C .

One congruently melting compound ($3\text{LiF}\cdot\text{ThF}_4$) and three incongruently melting compounds ($7\text{LiF}\cdot 6\text{ThF}_4$, $\text{LiF}\cdot 2\text{ThF}_4$, and $\text{LiF}\cdot 4\text{ThF}_4$) are formed in the system $\text{LiF}\text{-ThF}_4$. Optical properties and x-ray diffraction data for these compounds are shown in Tables 1 and 2, respectively. The compositions and temperatures of the three peritectic and two eutectic invariant points and one congruent melting point are (1) eutectic: 23 mole % ThF_4 , 565°C ; (2) congruent melting point: 25 mole % ThF_4 , 573°C ; (3) eutectic: 29 mole % ThF_4 , 568°C ; (4) peritectic: 30.5 mole % ThF_4 , 597°C ; (5) peritectic: 42 mole % ThF_4 , 762°C ; (6) peritectic: 58 mole % ThF_4 , 897°C .

A complete series of solid solutions without maximum or minimum is formed in the system $\text{UF}_4\text{-ThF}_4$. The optical properties of these solid solutions are shown in Table 1 and Fig. 6. The

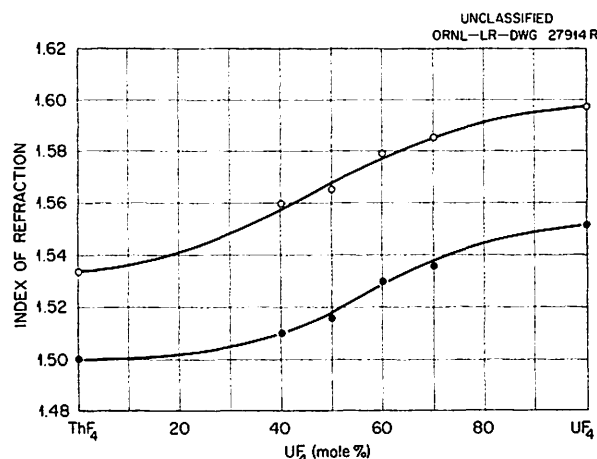


Fig. 6. Indices of Refraction vs Composition for $\text{ThF}_4\text{-UF}_4$ (ss).

Table 1. Optical Properties of $\text{LiF}\text{-UF}_4$, $\text{LiF}\text{-ThF}_4$, and $\text{UF}_4\text{-ThF}_4$ Solid Phases^a

Compound	Optical Character	Sign	Optic Angle	N_ω or N_α	N_ϵ or N_γ
$4\text{LiF}\cdot\text{UF}_4$	Biaxial	+	45°	1.460	1.472
$7\text{LiF}\cdot 6\text{UF}_4$	Uniaxial	-		1.554	1.551
$\text{LiF}\cdot 4\text{UF}_4$	Biaxial	-	10°	1.584	1.600
$3\text{LiF}\cdot\text{ThF}_4^b$	Biaxial	-	10°	1.480	1.488
$7\text{LiF}\cdot 6\text{ThF}_4$	Uniaxial	+		1.502	1.508
$\text{LiF}\cdot 2\text{ThF}_4$	Uniaxial	-		1.554	1.548
$\text{LiF}\cdot 4\text{ThF}_4^b$	Biaxial	-	10°	1.528	1.538
$\text{UF}_4\text{-ThF}_4$ (ss) ^c					
(70% UF_4)	Biaxial	-	60°	1.536	1.586
(60% UF_4)	Biaxial	-	60°	1.530	1.580
(50% UF_4)	Biaxial	-	60°	1.516	1.566
(40% UF_4)	Biaxial	-	60°	1.510	1.560

^a Data taken from R. E. Thoma *et al.*, "Phase Equilibria in the Fused Salt Systems $\text{LiF}\text{-ThF}_4$ and $\text{NaF}\text{-ThF}_4$," *J. Phys. Chem.* (in press); H. Insley *et al.*, *Optical Properties and X-Ray Diffraction Data for Some Inorganic Fluoride and Chloride Compounds*, ORNL-2192 (Oct. 23, 1956); and L. A. Harris, G. D. White, and R. E. Thoma, "Analysis of the Solid Phases in the System $\text{LiF}\text{-ThF}_4$," *J. Phys. Chem.* (in press).

^b This routinely observed biaxiality appears to be produced by strain in the $3\text{LiF}\cdot\text{ThF}_4$ and $\text{LiF}\cdot 4\text{ThF}_4$ crystals, inasmuch as the crystal type is tetragonal as determined by x-ray diffraction measurements.

^c Solid solution.

Table 2. X-Ray Diffraction Patterns for the Solid Phases Occurring in the Systems LiF-ThF₄ and LiF-UF₄*

3LiF·ThF ₄		7LiF·6ThF ₄		LiF·2ThF ₄		LiF·4ThF ₄		4LiF·UF ₄		3LiF·UF ₄		7LiF·6UF ₄		LiF·4UF ₄	
d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
6.42	100	6.07	15	7.97	5	8.34	3	5.67	20	4.98	20	6.61	6	7.02	8
4.46	100	5.91	20	6.37	10	7.76	3	5.46	25	4.80	15	5.97	20	6.33	12
4.37	100	5.36	90	3.96	100	6.51	5	5.13	70	4.41	100	5.82	15	6.07	5
3.62	85	5.25	15	3.57	65	5.80	25	4.93	100	4.34	100	5.24	90	5.73	25
3.09	55	4.95	30	3.25	5	4.62	5	4.55	45	3.98	15	5.15	10	4.98	8
2.866	70	4.85	20	3.21	5	4.33	70	4.44	100	3.91	8	4.65	10	4.70	25
2.768	30	4.75	100	2.97	20	3.88	100	4.23	7	3.60	80	4.37	13	4.25	90
2.542	25	4.01	85	2.822	25	3.60	60	3.82	40	3.40	10	3.95	55	3.88	20
2.327	10	3.92	15	2.675	7	3.25	10	3.55	30	3.14	25	3.85	13	3.78	100
2.189	20	3.74	15	2.528	10	2.92	25	3.03	50	3.07	50	3.68	20	3.52	90
2.104	65	3.55	65	2.388	5	2.822	25	2.89	25	2.84	80	3.49	75	3.16	8
2.071	25	3.44	10	2.123	85	2.603	10	2.866	30	2.771	30	3.33	90	3.13	8
2.036	40	3.39	70	2.053	30	2.398	10	2.747	50	2.529	35	3.15	70	3.06	12
1.959	30	3.29	60	2.001	65	2.137	25	2.468	40	2.169	15	3.07	10	2.84	40
1.933	60	3.03	100	1.787	7	2.053	35	2.398	20	2.083	75	2.99	95	2.771	55
1.877	25	2.814	25	1.701	10	2.040	10	2.221	40	2.055	35	2.771	30	2.542	8
1.771	25	2.747	25	1.689	5	2.018	10	2.167	75	1.943	50	2.707	30	2.350	10
1.743	30	2.578	20	1.603	5	2.005	30	2.074	20	1.913	25	2.542	25	2.310	10
1.701	35	2.430	10	1.519	5	1.937	20	2.025	20	1.861	30	2.350	13	2.226	8
1.661	10	2.392	10			1.820	20	1.872	20	1.751	25	2.286	25	2.000	10
1.618	10	2.302	20			1.778	3	1.836	25	1.723	25	2.264	13	2.088	35
1.547	35	2.137	20			1.725	5			1.685	25	2.184	10	2.016	60
1.520	35	2.018	5			1.719	5			1.662	8	2.097	30	1.991	50
		2.001	15			1.666	5			1.646	20	2.060	30	1.888	20
		1.892	55			1.605	5			1.599	8	2.047	75	1.819	8
		1.859	15			1.595	5					1.993	25	1.767	25
		1.804	15			1.563	5					1.972	20		
		1.680	15									1.947	25		
		1.653	20									1.924	15		
		1.600	20									1.909	30		
												1.854	45		
												1.825	20		
												1.773	20		
												1.757	25		
												1.709	15		
												1.680	15		
												1.625	15		
												1.579	25		
												1.562	8		

*Data taken from R. E. Thoma *et al.*, "Phase Equilibrium in the Fused Salt Systems LiF-ThF₄ and NaF-ThF₄," *J. Phys. Chem.* (in press); H. Insley *et al.*, *Optical Properties and X-Ray Diffraction Data for Some Inorganic Fluoride and Chloride Compounds*, ORNL-2192 (Oct. 23, 1956); L. A. Harris, G. D. White, and R. E. Thoma, "Analysis of the Solid Phases in the System LiF-ThF₄," *J. Phys. Chem.* (in press); and L. A. Harris, *Crystal Structures of 7:6 Type Compounds of Alkali Fluorides with Uranium Tetrafluoride*, ORNL CF-58-3-15 (March 6, 1958).

equilibrium phase diagram is based on the thermal analysis data shown in Table 3 and the results of quenching studies shown in Table 4.

The system LiF-UF₄-ThF₄ contains no ternary compounds but does contain four ternary solid solutions. The compounds LiF·4ThF₄-LiF·4UF₄ form a continuous series of solid solutions, as do the compounds 7LiF·6ThF₄-7LiF·6UF₄. A series of solid solutions exists having compositions at 33 $\frac{1}{3}$ mole % LiF between LiF·2ThF₄ and 23 mole % UF₄. Another series of solid solutions exists having compositions at 75% LiF between 3LiF·ThF₄ and 15.5 mole % UF₄. The

joins containing these solid solutions are described in detail in sections below.

Seven primary-phase fields appear in the system: LiF, 4LiF·UF₄, 3LiF·ThF₄ (ss), 7LiF·6ThF₄-7LiF·6UF₄ (ss), LiF·2ThF₄ (ss), LiF·4ThF₄-LiF·4UF₄ (ss), and ThF₄·UF₄ (ss). Phase relations were established from the liquidus to about 300°C. Three invariant points occur: peritectic: 20.5 mole % UF₄, 7 mole % ThF₄, 500°C; eutectic: 26.5 mole % UF₄, 1.5 mole % ThF₄, 488°C; peritectic: 19 mole % UF₄, 18 mole % ThF₄, 609°C. The reactions which take place at

Table 3. Thermal Analysis Data for the Systems $\text{UF}_4\text{-ThF}_4$ and $\text{LiF-ThF}_4\text{-UF}_4^*$

Interpretation Key

- l = liquidus
a = boundary between $\text{UF}_4\text{-ThF}_4$ (ss) and $\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss) primary-phase fields
b = $4\text{LiF}\cdot \text{UF}_4$ decomposition
c = boundary between $\text{LiF}\cdot 2\text{ThF}_4$ (ss) and $\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss) primary-phase fields
d = ternary eutectic
e = LiF , $3\text{LiF}\cdot \text{ThF}_4$ (ss), $7\text{LiF}\cdot 6\text{UF}_4\text{-7LiF}\cdot 6\text{ThF}_4$ (ss) peritectic
f = boundary between $3\text{LiF}\cdot \text{ThF}_4$ (ss) and $7\text{LiF}\cdot 6\text{UF}_4\text{-7LiF}\cdot 6\text{ThF}_4$ (ss) primary-phase fields
g = boundary between LiF and $7\text{LiF}\cdot 6\text{UF}_4\text{-7LiF}\cdot 6\text{ThF}_4$ (ss) primary-phase fields
h = liquid disappearance at f
i = $3\text{LiF}\cdot \text{ThF}_4$ (ss) exsolution
k = liquid disappearance at m
m = boundary between LiF and $3\text{LiF}\cdot \text{ThF}_4$ (ss) primary-phase fields
s = solidus

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
$\text{UF}_4\text{-ThF}_4^{**}$			$\text{LiF-ThF}_4\text{-UF}_4$		
70-30	1025		20-10-70	747	
	1023			750	
	1005		20-20-60	965	l
	985			951	l
60-40	1051	l		780	a
	1045	l		785	a
	1010		20-30-50	982	l
	993			941	l
50-50	955			825	a
	1085	l		817	a
	1080	l	20-40-40	805	a
	1050	l		795	a
	1035		20-50-30	915	
	1017			837	a
	1005			832	a
	990			825	a
40-60	985		20-60-20	835	a
	1040	l		832	a
	1035		20-70-10	855	a
	1022			860	a
	1005		$33\frac{1}{3}\text{-}33\frac{1}{3}\text{-}33\frac{1}{3}$	859	a
	990			846	a
	960			830	a
				815	a
$\text{LiF-ThF}_4\text{-UF}_4$				815	a
20-10-70	962	l	$33\frac{1}{3}\text{-}46\frac{2}{3}\text{-}20$	478	b
	960	l		430	

*In general, more than one thermal analysis was made for each nominal composition. All the thermal breaks are listed, but it is not intended to imply that they all occurred on a single cooling curve. The variation in temperatures associated with the same phenomenon is believed to be caused by supercooling effects.

**Each of these slowly cooled melts contained only one phase according to x-ray diffraction and petrographic analysis, indicating that there is no miscibility gap in the system $\text{UF}_4\text{-ThF}_4$.

Table 3 (continued)

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
33 $\frac{1}{3}$ -46 $\frac{2}{3}$ -20	320		40-30-30	823	
	300			470	b
33 $\frac{1}{3}$ -51 $\frac{2}{3}$ -15	890	a	40-40-20	458	b
	870	a		902	
	852	a		902	
33 $\frac{1}{3}$ -56 $\frac{2}{3}$ -10	961	l		861	l
	961	l		860	l
	875	a		590	
	875	a		588	
	665	c		467	b
	663	c	40-50-10	423	
	960	l		865	l
	956	l		860	l
	875	a		855	l
	875	a		675	c
	695	c		675	c
35-20-45	692	c	50-10-40	755	l
	895	l		755	l
	893	l		482	d
	805	a		480	d
	805	a		420	
	800	a	50-15-35	428	
	799	a		635	
	480	d		483	d
	423			482	d
	928	l		430	
35-45-20	928	l	50-25-25	803	l
	850	a		490	d
	850	a		490	d
	845	a		451	
	845	a		442	
	840	l	53.8-6.2-40	720	l
40-10-50	840	l		715	l
	777			482	d
	777			450	
	475	b	53.8-10-36.2	717	l
	445			717	l
	825	l		481	d
40-20-40	800		53.8-11.2-35	445	
	790			730	l
	782			625	
	467	b		490	d
	428			485	d
40-30-30	863	l	53.8-13.2-33	441	
	853	l		430	
	825			725	l

Table 3 (continued)

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
53.8-13.2-33	725	l	57-15-28	467	b
	487	d	57-21.5-21.5	717	l
	485	d		690	
	436			481	d
53.8-15-31.2	726	l		481	d
	718	l		458	
	485	d		458	
	455		57-26-17	708	l
53.8-18.2-28	740	l		707	l
	740	l		496	e
	485	d		495	e
	485	d		485	d
	446			485	d
53.8-23.1-23.1	773	l		427	
	770	l	57-28-15	733	l
	485	d		733	l
	437			500	e
53.8-30-16.2	766	l		499	e
	751	l		480	d
	498	e		480	d
	485	d		417	
	468	b	57-30-13	748	l
53.8-36.2-10	763	l		748	
	762	l		515	f
	517	f		514	f
	515	f		487	d
	447			485	d
57-4-39	666	l		422	
	663	l	57-32-11	750	
	550			750	
	535			687	l
	493	g		686	l
57-10-33	493	g		521	f
	488	d		521	f
	480	d	58-22-20	725	l
				725	l
				490	d
57-15-28	688	l		442	
	687	l	58-24-18	715	l
	491	d		715	l
	490	d		495	e
	470	b		480	d
	470	b		430	
	705	l	60-5-35	625	l
	705	l		620	l
	492	g		489	d
	487	d			
	483	d			

Table 3 (continued)

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
60-5-35	488	d	60-30-10	685	l
	450			670	
	445			665	
	435			527	f
60-10-30	655	l	60-35-5	525	f
	655	l		420	
	490	d		726	l
	489	d		718	l
	489	d	62-10-28	546	f
	475	b		546	f
	475	b		618	l
	465			615	l
60-15-25	462		62-20-18	545	
	670	l		535	
	670	l		492	g
	490	d		491	g
	489	d	62-28-10	485	d
	458			470	b
	451			650	l
	445			650	l
60-20-20	678	l	62-33-5	497	
	678	l		495	
	495	g		495	
	495	g		485	d
	490	d	64-24-12	485	d
	490	d		440	
	465	b		687	
	465	b		685	
	458		64-31-5	675	l
	445			665	l
60-22-18	445			587	
	685	l		525	f
	685	l	64-31-5	410	
	550	f		704	l
	495			703	l
	492			545	f
	485	d		543	f
	485	d	64-31-5	652	
60-25-15	467	b		625	
	710			533	f
	657	l		525	f
	657	l		525	f
	508	e		523	f
	483	d	64-31-5	673	l
60-30-10	470	b		669	l
	690	l		544	f

Table 3 (continued)

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
64-31-5	543	f	69-27-4	540	f
	525		69-29-2	612	
66-24-10	622			611	
	620			558	f
	567	l		557	f
	528	f	70-10-20	495	f
	523	h		495	f
	517	h		487	d
66-29-5	640	l		485	d
	640	l		477	b
	536	f		462	b
	535	f	70-20-10	544	f
	530	h		540	f
	525	h		524	h
67-26-7	615			521	h
	615			520	h
	547	f		520	h
	542	f		430	
68-17-15	592	l		415	
	592	l	70-24-6	575	l
	543	f		575	l
	530	f		549	f
	512	h		540	f
	511	h	70.5-12.5-17	500	e
	487	i		500	e
	487	i		475	b
	430			475	b
68-24-8	610			455	
	607			450	
	540	l		442	
	536	l		441	
	530	f		400	
	520	f	70.5-17-12.5	525	f
	500	e		520	f
69-4-27	490	g		515	h
	487	g		511	h
	480	d		511	h
	478	d		475	b
	472	b		471	b
	467	b		442	
	445			439	
	425		71-1-28	507	l
	420			489	d
69-27-4	604	l		475	b
	600	l		545	
	549	f	71-2-27	484	d

Table 3 (continued)

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
71-2-27	475	b	72-8-20	516	l
	475	b		508	l
	448			508	l
71-5-24	488	d		492	d
	485	d		490	d
	485	d		450	
	483	d	72-10-18	560	
	452			500	e
	442			475	b
	440			428	
71-24-5	435		72-11-17	512	l
	560	l		501	e
	558	l		500	e
	545	h		461	b
	544	h		456	
71.5-1-27.5	535	h	72-12-16	517	l
	484	d		515	l
	484	d		508	l
	470	b		489	d
	455			485	d
71.5-2-26.5	504			441	
	487	d		428	
	475	b	72-18-10	530	l
	467	b		527	l
	451			472	b
72-1-27	762			425	
	469	b	72.5-1-26.5	480	d
	467	b		475	d
	463	b		467	b
72-2-26	475	b		467	b
	475	b		450	
	450		73-2-25	485	d
	430			476	b
72-3-25	658			475	b
	484	d		433	
	475	b	73-11-16	517	l
	462	b		511	f
	444			500	e
72-4-24	428			484	d
	504			482	d
	490	d		469	b
	487	d		460	b
72-6-22	445		73-12-15	514	l
	487	d		503	e
	482	d		477	
	480	d		477	

Table 3 (continued)

Composition (mole %)	Temperature (°C)	Interpretation	Composition (mole %)	Temperature (°C)	Interpretation
73-12-15	460		75-15-10	535	l
	439			525	m
	415			525	m
	412		75-20-5	555	l
73-15-12	517	l		555	l
	515	l		550	l
	510	f	75-23-2	803	
	507	f		563	l
	505	e		532	s
	390		77-15-8	645	
74-20-6	535	f		546	l
	535	f		545	l
74-24-2	555	f		540	k
	553	f		538	k
	465	j	77-19-4	575	
	460	i		575	
75-5-20	535			550	l
	528	l		550	l
	526	l	80-10-10	538	k
	489	d		755	
	487	d		748	
	445			493	j
75-10-15	431			490	i
	535	l		428	
	527	l	80-15-5	625	l
	512	k		625	l
	507	k		541	k
	442			541	k
75-12-13	432			430	
	524	l		420	
75-15-10	521	l		415	
	740				

Table 4. Thermal-Gradient Quenching Results for the $\text{ThF}_4\text{-UF}_4$ Liquidus and the $\text{LiF-ThF}_4\text{-UF}_4$ Liquidus^a

Composition (mole %)	Liquidus Temperature (°C)	Primary Phase
$\text{UF}_4\text{-ThF}_4$		
40-60	1053 ± 4	$\text{UF}_4\text{-ThF}_4$ (ss) ^b
50-50	1062 ± 3	$\text{UF}_4\text{-ThF}_4$ (ss)
60-40	1053 ± 4	$\text{UF}_4\text{-ThF}_4$ (ss)
70-30	1053 ± 4	$\text{UF}_4\text{-ThF}_4$ (ss)
$\text{UF}_4\text{-ThF}_4\text{-LiF}$		
2-23-75	572 ± 3	$3\text{LiF}\cdot\text{ThF}_4$ (ss)
2-24-74	562 ± 3	$3\text{LiF}\cdot\text{ThF}_4$ (ss)
2-29-69	594 ± 3	$7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
4-19-77	567 ± 3	LiF
4-27-69	598 ± 6	$7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
5-15-80	615 ± 3	LiF
5-19-76	562 ± 2	$3\text{LiF}\cdot\text{ThF}_4$ (ss)
5-20-75	562 ± 3	$3\text{LiF}\cdot\text{ThF}_4$ (ss)
5-24-71	565 ± 3	$7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
22-6-72	504 ± 4	LiF
23.1-23.1-53.8	744 ± 3	$\text{LiF}\cdot 4\text{ThF}_4\text{-LiF}\cdot 4\text{UF}_4$ (ss)
24-4-72	495 ± 2	$\text{LiF} + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
25-2-73	491 ± 2	$\text{LiF} + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
25-3-72	495 ± 2	$\text{LiF} + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
25-25-50	806 ± 3	$\text{LiF}\cdot 4\text{ThF}_4\text{-LiF}\cdot 4\text{UF}_4$ (ss)
26-2-72	496 ± 2	$\text{LiF} + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss) ^c
26.5-1-72.5	495 ± 2	$4\text{LiF}\cdot\text{UF}_4 + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
26.5-2-71.5	504 ± 2	$4\text{LiF}\cdot\text{UF}_4 + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
27-1-72	491 ± 2	$4\text{LiF}\cdot\text{UF}_4 + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
27-2-71	495 ± 2	$\text{LiF} + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
27.5-1-71.5	495 ± 2	$4\text{LiF}\cdot\text{UF}_4 + 7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
28-1-71	508 ± 2	$7\text{LiF}\cdot 6\text{ThF}_4\text{-}7\text{LiF}\cdot 6\text{UF}_4$ (ss)
28-10-62	615 ± 3	$\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss)
28-18.2-53.8	729 ± 3	$\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss)
30-10-60	633 ± 2	$\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss)
30-30-40	859 ± 1	$\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss)
30-50-20	968 ± 4	$\text{UF}_4\text{-ThF}_4$ (ss)

Table 4 (continued)

Composition (mole %)	Liquidus Temperature (°C)	Primary Phase
$\text{UF}_4\text{-ThF}_4\text{-LiF}$		
31.2-15-53.8	736 ± 3	$\text{LiF} \cdot 4\text{UF}_4\text{-LiF} \cdot 4\text{ThF}_4$ (ss)
33-10-57	687 ± 3	$\text{LiF} \cdot 4\text{UF}_4\text{-LiF} \cdot 4\text{ThF}_4$ (ss)
33-13.2-53.8	723 ± 3	$\text{LiF} \cdot 4\text{UF}_4\text{-LiF} \cdot 4\text{ThF}_4$ (ss)
5-26-69	581 ± 2	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$
5-29-66	645 ± 3	$\text{LiF} \cdot 2\text{ThF}_4$ (ss)
5-31-64	667 ± 3	$\text{LiF} \cdot 2\text{ThF}_4$ (ss)
5-33-62	704 ± 3	$\text{LiF} \cdot 2\text{ThF}_4$ (ss)
5-35-60	714 ± 3	$\text{LiF} \cdot 2\text{ThF}_4$ (ss)
6-24-70	555 ± 2	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
7-26-67	612 ± 5	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
8-15-77	548 ± 3	$\text{LiF} + 3\text{LiF} \cdot \text{ThF}_4$ (ss)
10-10-80	649 ± 3	LiF
10-15-75	547 ± 3	$3\text{LiF} \cdot \text{ThF}_4$ (ss)
10-16-74	555 ± 2	$3\text{LiF} \cdot \text{ThF}_4$ (ss)
10-18-72	544 ± 2	$3\text{LiF} \cdot \text{ThF}_4$ (ss) + $7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
10-20-70	577 ± 9	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
10-24-66	596 ± 3	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
10-26-64	600 ± 3	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
10-36.2-53.8	770 ± 3	$\text{LiF} \cdot 4\text{ThF}_4\text{-LiF} \cdot 4\text{UF}_4$ (ss)
	772 ± 2	$\text{LiF} \cdot 4\text{ThF}_4\text{-LiF} \cdot 4\text{UF}_4$ (ss)
10-50-40	880 ± 2	$\text{LiF} \cdot 4\text{ThF}_4\text{-LiF} \cdot 4\text{UF}_4$ (ss)
10-70-20	1013 ± 6	$\text{UF}_4\text{-ThF}_4$ (ss)
12-15-73	533 ± 3	$3\text{LiF} \cdot \text{ThF}_4$ (ss)
12.5-17-70.5	565 ± 3	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
13-12-75	528 ± 3	$3\text{LiF} \cdot \text{ThF}_4$ (ss)
15-12-73	523 ± 2	$\text{LiF} + 3\text{LiF} \cdot \text{ThF}_4$ (ss)
	528 ± 3	$\text{LiF} + 3\text{LiF} \cdot \text{ThF}_4$ (ss)
15-17-68	587 ± 2	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
16-11-73	519 ± 2	$3\text{LiF} \cdot \text{ThF}_4$ (ss)
16-12-72	528 ± 3	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)
16.2-30-63.8	777 ± 3	$\text{LiF} \cdot 4\text{ThF}_4\text{-LiF} \cdot 4\text{UF}_4$ (ss)
17-11-72	532 ± 2	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss) + $3\text{LiF} \cdot \text{ThF}_4$ (ss)
17-12.5-70.5	547 ± 3	$7\text{LiF} \cdot 6\text{ThF}_4\text{-}7\text{LiF} \cdot 6\text{UF}_4$ (ss)

Table 4 (continued)

Composition (mole %)	Liquidus Temperature (°C)	Primary Phase
UF ₄ -ThF ₄ -LiF		
18-10-72	511 ± 2	3LiF·ThF ₄ (ss)
18-18-64	612 ± 4	7LiF·6ThF ₄ -7LiF·6UF ₄ (ss)
18-20-62	634 ± 4	LiF·2ThF ₄ (ss) ^c
18-22-60	680 ± 3	LiF·4ThF ₄ -LiF·4UF ₄ (ss)
20-8-72	508 ± 2	3LiF·ThF ₄ (ss) ^c
20-20-60	637 ± 2	LiF·4ThF ₄ -LiF·4UF ₄ (ss)
20-40-40	862 ± 3	LiF·4ThF ₄ -LiF·4UF ₄ (ss)
20-45-35	892 ± 2	UF ₄ -ThF ₄ (ss)
20-60-20	1011 ± 3	UF ₄ -ThF ₄ (ss)
21.5-21.5-57	736 ± 2	LiF·4ThF ₄ -LiF·4UF ₄ (ss)
35-5-60	630 ± 3	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
35-11.2-53.8	729 ± 3	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
35-15-50	780 ± 3	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
39-4-57	625 ± 2	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
40-6.2-53.8	717 ± 3	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
40-10-50	767 ± 4	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
40-20-40	829 ± 4	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
40-40-20	972 ± 3	UF ₄ -ThF ₄ (ss)
50-10-40	808 ± 3	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
50-30-20	968 ± 4	UF ₄ -ThF ₄ (ss)
60-20-20	960 ± 2	UF ₄ -ThF ₄ (ss)
70-10-20	963 ± 3	UF ₄ -ThF ₄ (ss)

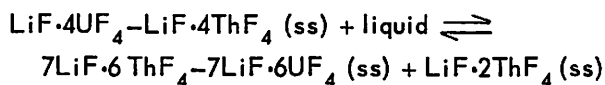
^aThe uncertainty in temperatures in this table indicates the temperature differences between the quenched samples.

^bSolid solution.

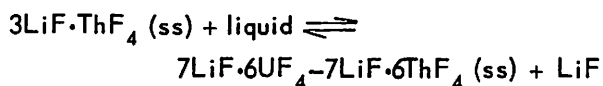
^cMost of the phases were identified by optical microscopy; in addition, this phase was identified by x-ray diffraction.

these invariant points are the following:

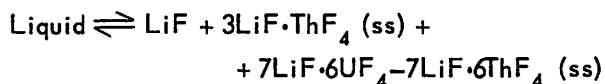
The peritectic at 609°C ·



The peritectic at 500°C



The eutectic at 488°C



The equilibrium phase diagram in Fig. 1 is based on the thermal analysis data shown in Table 3 and the results of quenching studies shown in Table 4 and in the appendix. The results of quenching experiments, excluding liquidus

temperature and compositions, which aid in locating the invariant points and in describing the invariant reactions are shown in Table 5. The peritectic or eutectic nature of the invariant reactions is further confirmed by the construction of compatibility triangles and observing the position of these triangles relative to their invariant points.

Because this system contains several series of extensive ternary solid solutions, it cannot be completely described without knowledge of the composition of the crystalline phase or phases at equilibrium at any temperature and composition. (The phrase "ternary solid solution" as used in this report implies that the solid solution composition lies within the system $\text{LiF}\text{-}\text{UF}_4\text{-ThF}_4$.

Table 5. Invariant-Point Data^a for the System $\text{LiF}\text{-ThF}_4\text{-UF}_4$

Quench Composition (mole %)		Temperature ^b (°C)	Phases ^c Above Temperature	Phases ^c Below Temperature
ThF_4	UF_4			
6	22	495 ± 2	Liquid + LiF	Liquid + LiF + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)
		492 ± 2	Liquid + LiF + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)	$\text{LiF}^d + 7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) ^d
8	20	502 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) ^d	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)
		498 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)	$\text{LiF} + 3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)
10	18	502 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss)	$\text{LiF} + 3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)
		489 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)	$\text{LiF} + 3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)
11	16	510 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss)	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)
		506 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss)	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + LiF [inclusions in $3\text{LiF}\cdot \text{ThF}_4$ (ss)]
		496 ± 3	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + LiF [inclusions in $3\text{LiF}\cdot \text{ThF}_4$ (ss)]	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + LiF
		492 ± 2	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + LiF	$3\text{LiF}\cdot \text{ThF}_4$ (ss) + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + LiF
11	17	501 ± 3	Liquid + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss)	Liquid + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + LiF
		497 ± 3	Liquid + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + LiF	$7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + LiF
12	15	511 ± 3	Liquid + $3\text{LiF}\cdot \text{ThF}_4$ (ss)	Liquid + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss)
		502 ± 3	Liquid + $7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss)	$7\text{LiF}\cdot 6\text{UF}_4\text{-}7\text{LiF}\cdot 6\text{ThF}_4$ (ss) + $3\text{LiF}\cdot \text{ThF}_4$ (ss) + LiF

Table 5 (continued)

Quench Composition (mole %)		Temperature ^b (°C)	Phases ^c Above Temperature	Phases ^c Below Temperature
ThF ₄	UF ₄			
12	16	523 ± 2	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
		504 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
1	26.5	490 ± 3	Liquid + 4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
1	27	487 ± 2	Liquid + 4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
1	27.5	485 ± 3	4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
1	28	490 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	4LiF·UF ₄ + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF(?) + liquid(?)
		485 ± 3	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 4LiF·UF ₄ + LiF(?) + liquid(?)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 4LiF·UF ₄ + LiF
24	18	640 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d	Liquid + LiF·2ThF ₄ (ss) ^d
		615 ± 4	Liquid + LiF·2ThF ₄ (ss) ^d	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^d
22	20	615 ± 4	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^d

^aFor liquidus data near invariant points see Table 4.

^bThe uncertainty in temperatures indicates the temperature differences between the quenched samples.

^cOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."

^dMost of the phases were identified by optical microscopy. In addition, this phase was identified by x-ray diffraction.

Each of the solid solutions in this system, however, may be formed from mixtures of two end members and in this sense form a binary series.) In general, in any series of complete solid solution the physical properties (e.g., density, optical properties, x-ray diffraction patterns, etc.) of the individual members show a continuous change between those of the end members. Hence a determination of refractive indices of a number of samples of known compositions in the solid solution series provides a method of establishing in the ternary system tie lines between the composition of crystals in this solid solution series

with the liquid with which it is in equilibrium. In the case of the system LiF-ThF₄-UF₄ the determination of refractive indices of the members of each of the four ternary solid solution series present provides a particularly good method of establishing tie lines, because the refractive indices of the end members of each series are so different that a good degree of precision can be obtained.

Once the tie lines are established for a primary-phase area, the fractionation paths may be drawn. Fractionation paths in four of the primary-phase areas of system LiF-UF₄-ThF₄ are shown in

Fig. 7. The compounds LiF and $4\text{LiF}\cdot\text{UF}_4$ do not form solid solutions. Consequently, the tie lines, equilibrium paths, and fractionation paths for their primary-phase areas can be drawn directly from Fig. 1, and the case is trivial. The fractionation paths for the $\text{UF}_4\text{-ThF}_4$ (ss) primary-phase area cannot be drawn from Fig. 1. From Fig. 6 it can be seen that the indices of refraction for $\text{UF}_4\text{-ThF}_4$ (ss) do not always change rapidly enough with respect to composition to allow a high degree of precision in tie-line determinations. Consequently, no attempt was made to determine the fractionation paths in this primary-phase area.

THE 20 MOLE % LiF JOIN AND THE $\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss) FRACTIONATION PATHS

A diagram of the 20 mole % LiF join is shown in Fig. 8 and is based on the thermal analysis data in Table 3 and the results of quenching studies in Tables 4, 6, and 7. The join contains the $\text{LiF}\cdot 4\text{UF}_4\text{-LiF}\cdot 4\text{ThF}_4$ (ss) series, whose members are green, are biaxial negative, and have optic angles of approximately 10° . The indices of refraction of these solid solutions shown in Fig. 9 and Table 8 vary almost linearly with UF_4 concentration.

UNCLASSIFIED
ORNL-LR-DWG 35505R

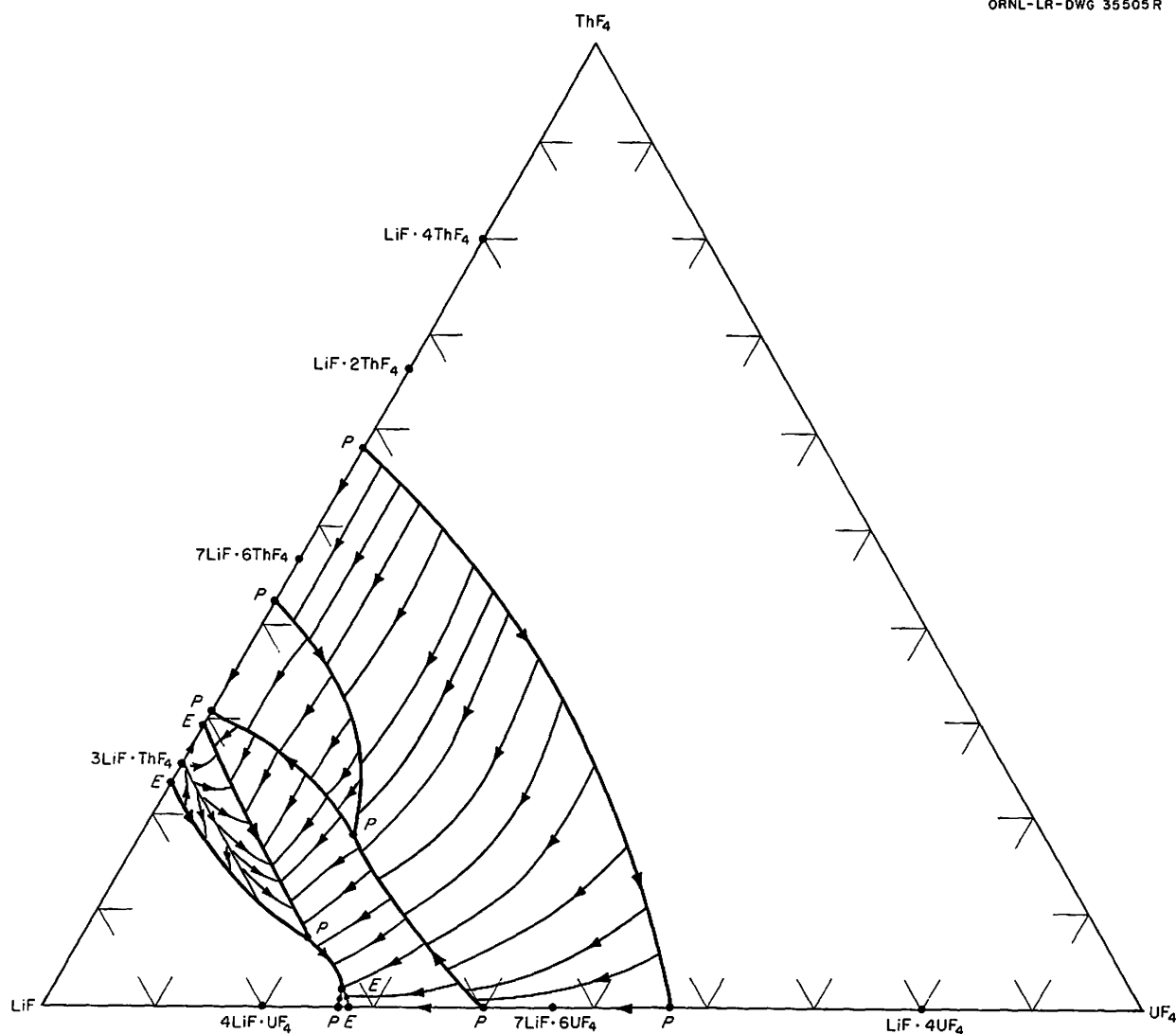


Fig. 7. Fractionation Paths.

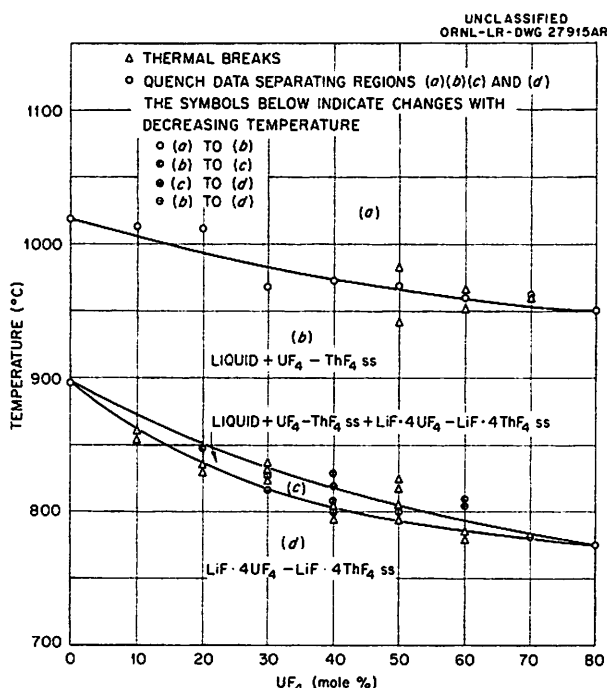


Fig. 8. The Join $\text{LiF} \cdot 4\text{UF}_4$ – $\text{LiF} \cdot 4\text{ThF}_4$.

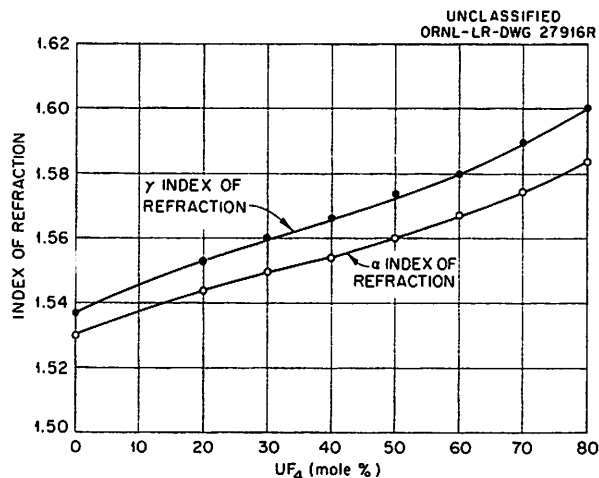


Fig. 9. Indices of Refraction vs Composition for $\text{LiF} \cdot 4\text{UF}_4$ – $\text{LiF} \cdot 4\text{ThF}_4$ (ss).

The fractionation paths for the $\text{LiF} \cdot 4\text{UF}_4$ – $\text{LiF} \cdot 4\text{ThF}_4$ (ss) primary-phase area shown in Fig. 7 are based on the tie-line data in Table 7. They tend to parallel the system LiF – ThF_4 over most of the $\text{LiF} \cdot 4\text{UF}_4$ – $\text{LiF} \cdot 4\text{ThF}_4$ (ss) primary-phase area, and they change from this pattern only at the higher UF_4 concentrations.

THE $33\frac{1}{3}$ MOLE % LiF JOIN AND THE $\text{LiF} \cdot 2\text{Th}(\text{U})\text{F}_4$ (ss) FRACTIONATION PATHS

A diagram of the $33\frac{1}{3}$ mole % LiF join is shown in Fig. 10 and is based on the thermal analysis data in Table 3 and the results of quenching studies in Tables 4, 9, and 10. The join contains the $\text{LiF} \cdot 2\text{Th}(\text{U})\text{F}_4$ (ss) series, whose members are green and are uniaxial negative. The indices of refraction of these solid solutions shown in Fig. 11 and Table 11 vary linearly with UF_4 concentration. The maximum extent of $\text{LiF} \cdot 2\text{Th}(\text{U})\text{F}_4$ (ss) at the solidus is 23 mole % UF_4 .

The fractionation paths for $\text{LiF} \cdot 2\text{Th}(\text{U})\text{F}_4$ (ss) primary-phase area shown in Fig. 7 are based on the tie-line data in Table 10. The fractionation paths tend to parallel the system LiF – ThF_4 over the entire primary-phase area.

THE 53.8 MOLE % LiF JOIN AND THE $7\text{LiF} \cdot 6\text{UF}_4$ – $7\text{LiF} \cdot 6\text{ThF}_4$ (ss) FRACTIONATION PATHS

A diagram of the 53.8 mole % LiF join is shown in Fig. 12 and is based on thermal analysis data in Table 3 and the results of quenching studies in Tables 4, 12, and 13. The join contains the $7\text{LiF} \cdot 6\text{UF}_4$ – $7\text{LiF} \cdot 6\text{ThF}_4$ (ss) series, whose members are green and are uniaxial. Their indices of refraction, shown in Fig. 13 and Table 14, vary linearly with UF_4 concentration. There should be one composition which is practically isotropic, since the ordinary and extraordinary indices of refraction cross. Actually there is a range of compositions in the midportion of the series which have a birefringence too low to be observed.

The fractionation paths for the $7\text{LiF} \cdot 6\text{ThF}_4$ – $7\text{LiF} \cdot 6\text{UF}_4$ primary-phase area shown in Fig. 7 are based on the tie-line data in Table 13. They parallel the system LiF – ThF_4 over most of the $7\text{LiF} \cdot 6\text{UF}_4$ – $7\text{LiF} \cdot 6\text{ThF}_4$ primary-phase area and change from this pattern only at the higher UF_4 concentrations.

THE 75 MOLE % LiF JOIN AND THE $3\text{LiF} \cdot \text{ThF}_4$ (ss) FRACTIONATION PATHS

A diagram of the 75 mole % LiF join is shown in Fig. 14 and is based on the thermal analysis data in Table 3 and the results of quenching

Table 6. Thermal-Gradient Quenching Data for 20 Mole % LiF Join^a

UF ₄ Content (mole %)	Temperature ^b (°C)	Phases ^c Above Temperature	Phases ^c Below Temperature
20	849 ± 3	Liquid + UF ₄ -ThF ₄ (ss) ^d	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d + UF ₄ -ThF ₄ (ss) ^d
30	827 ± 3	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) + UF ₄ -ThF ₄ (ss)
	816 ± 6	Liquid + UF ₄ -ThF ₄ (ss) + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
40	830 ± 3	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) + UF ₄ -ThF ₄ (ss)
	820 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) + UF ₄ -ThF ₄ (ss)	LiF·4UF ₄ -LiF·4ThF ₄ (ss)
	809 ± 5	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + UF ₄ -ThF ₄ (ss) + LiF·4UF ₄ -LiF·4ThF ₄ (ss)
	800 ± 5	Liquid + UF ₄ -ThF ₄ (ss) ^d + LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d	LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d
50	800 ± 4	Liquid + UF ₄ -ThF ₄ (ss) ^d	Liquid + UF ₄ -ThF ₄ (ss) + LiF·4UF ₄ -LiF·4ThF ₄ (ss)
60	811 ± 4	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + UF ₄ -ThF ₄ (ss) + LiF·4UF ₄ -LiF·4ThF ₄ (ss)
	805 ± 4	Liquid + UF ₄ -ThF ₄ (ss) + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d
70	782 ± 2	Liquid + UF ₄ -ThF ₄ (ss)	LiF·4UF ₄ -LiF·4ThF ₄ (ss)

^aSee Table 4 for liquidus values.^bThe uncertainty in temperatures in this table indicates the temperature differences between the quenched samples.^cOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."^dMost of the phases were identified by optical microscopy; this phase was also identified by x-ray diffraction.

Table 7. Tie-Line Data for $\text{LiF} \cdot 4\text{UF}_4$ – $\text{LiF} \cdot 4\text{ThF}_4$ (ss) Primary-Phase Area

Quench Composition (mole %)		Temperature Range (°C)	Index of Refraction, n_γ	Solid Solution Composition (mole % UF_4)
UF_4	ThF_4			
5	$61\frac{2}{3}$	729–801	1.541	5
10	36.2	695–765	1.548	13
10	50	753–879	1.544	8
10	$56\frac{2}{3}$	708–801	1.546	10
13	30	690–700	1.550	15.5
15	28	683–700	1.550	15.5
15	$51\frac{2}{3}$	670–735	1.548	13
16.2	30	648–651	1.556	24.5
		646–763	1.554	21.5
17	26	663–700	1.552	18.5
18	24	643–658	1.554	21.5
20	20	635	1.558	28
20	22	619–658	1.556	24.5
20	40	860	1.548	13
		741	1.552	18
20	45	877	1.550	15.5
		734	1.554	20
20	$46\frac{2}{3}$	635–735	1.552	18
21.5	21.5	613–736	1.559	29
23.1	23.1	614	1.562	34
		620–641	1.562	34
		646	1.560	31
		686–742	1.558	28
		621–661	1.560	31
25	15	708	1.564	38
		656	1.566	41
		613	1.568	44
		651	1.564	38
		618	1.566	41
		617–635	1.564	38
25	25	804	1.558	28
		693	1.560	31
28	10	613	1.568	44
28	18.2	707	1.562	34
		700	1.562	34
		610	1.565	40
30	10	613–629	1.570	47
30	30	843	1.552	18
31.2	15	611–641	1.569	45.5
		678	1.569	45.5
		734	1.565	40
		607	1.571	48
33	10	607–684	1.574	53

Table 7 (continued)

Quench Composition (mole %)		Temperature Range (°C)	Index of Refraction, N_γ	Solid Solution Composition (mole % UF_4)
UF_4	ThF_4			
33	13.2	720	1.574	53
		610	1.572	50
$33\frac{1}{3}$	$33\frac{1}{3}$	792-860	1.560	31
35	5	623-629	1.582	63
		612-623	1.582	63
35	11.2	726	1.574	53
		610	1.576	55
35	15	763-777	1.568	44
		756	1.570	47
		693-731	1.572	50
36.2	10	641	1.575	54
		608	1.578	58
		626-674	1.578	58
39	4	614-623	1.590	71
40	6.2	714	1.580	60
		610	1.584	65
40	10	731	1.576	55
		693	1.579	59
40	20	846	1.568	44
		741	1.570	47
45	20	855	1.572	50
		734	1.574	53
50	10	781-805	1.578	58

Table 8. Refractive Indices for $\text{LiF} \cdot 4\text{UF}_4$ - $\text{LiF} \cdot 4\text{ThF}_4$ (ss)

UF_4 Content (mole %)	Refractive Indices	
	N_a	N_γ
20	1.544	1.553
30	1.550	1.560
40	1.554	1.565
50	1.560	1.574
60	1.567	1.580
70	1.574	1.590

- (a) $\text{UF}_4 - \text{ThF}_4$ ss + LIQUID
(b) $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ + LIQUID
(c) $\text{UF}_4 - \text{ThF}_4$ ss + LIQUID + $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ ss
(d) $\text{LiF} \cdot 2\text{ThF}_4$ ss + LIQUID + $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ ss
(e) $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ ss + LIQUID + $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ ss
(f) $\text{LiF} \cdot 2\text{ThF}_4$ ss
(g) $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ ss + $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ ss
(h) $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ ss + $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ ss + $\text{LiF} \cdot 2\text{ThF}_4$ ss

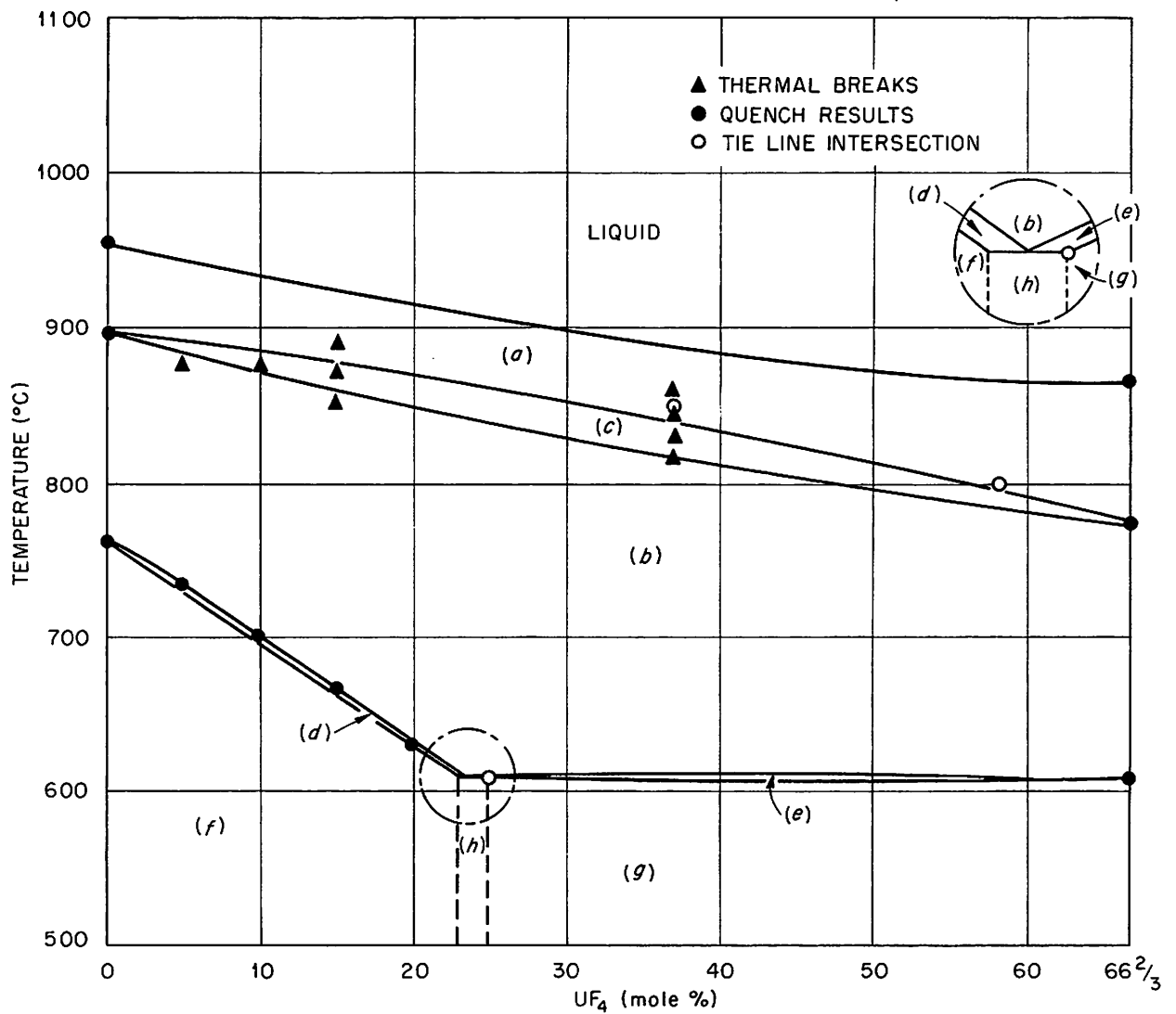


Fig. 10. The $33\frac{1}{3}$ Mole % LiF Section.

Table 9. Quench Data for LiF·2ThF₄ (ss)

UF ₄ Content (mole %)	Temperature ^a (°C)	Phases Above ^b Temperature	Phases Below ^b Temperature
5	723 ± 4	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss) ^c	LiF·2ThF ₄ (ss) ^c
10	700 ± 4	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss) ^c	LiF·2ThF ₄ (ss) ^c
15	667 ± 4	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss) ^c	LiF·2ThF ₄ (ss) ^{c,d}
20	632 ± 4	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss) ^c	LiF·2ThF ₄ (ss) ^{c,d}

^aThe uncertainty in temperatures indicates the temperature differences between the quenched samples.

^bOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."

^cMost of the phases were identified by optical microscopy; this phase was also identified by x-ray diffraction.

^dThis continues down to at least 578°C.

Table 10. Tie-Line Data for LiF·2ThF₄ (ss) Primary-Phase Area

Quench Composition (mole %)		Temperature Range (°C)	Index of Refraction, <i>N</i> _ω	Solid Solution Composition (mole % UF ₄)
UF ₄	ThF ₄			
5	29	618	1.556	5
5	31	644	1.556	5
5	33	658–670	1.556	5
5	35	698	1.556	5
10	36.2	611–665	1.560	15
		633–695	1.560	15
11	32	615–700	1.557	7.5
13	30	615–687	1.560	15
15	25	619–658	1.559	12.5
15	28	620–678	1.561	17.5
17	28	620–657	1.560	15
18	20	616–630	1.563	23
		618–634	1.563	23
18	22	618–624	1.564	23
		618–630	1.564	23
18	24	619–637	1.562	20

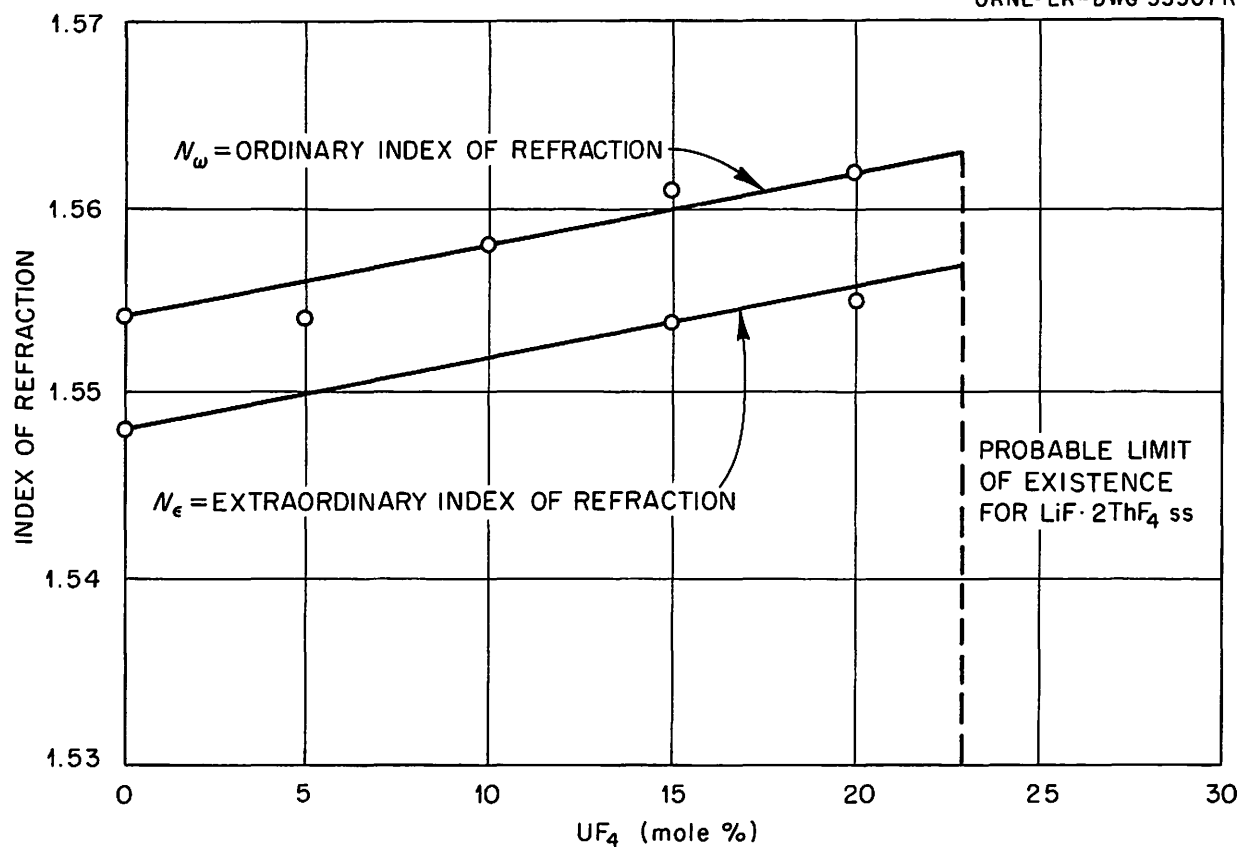


Fig. 11. Indices of Refraction vs Composition for $LiF \cdot 2Th(U)F_4$ (ss).

Table 11. Refractive Index Data for $LiF \cdot 2ThF_4$ (ss)

UF_4 Content (mole %)	Refractive Indices	
	N_ω	N_ϵ
5	1.554	
10	1.558	
15	1.561	1.554
20	1.562	1.555

- (a) $\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4 \text{ ss} + \text{LIQUID}$
 (b) $\text{LiF} \cdot 2\text{ThF}_4 \text{ ss} + \text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4 \text{ ss} + \text{LIQUID}$
 (c) $\text{LiF} \cdot 2\text{ThF}_4 \text{ ss} + \text{LIQUID}$
 (d) $\text{LiF} \cdot 2\text{ThF}_4 \text{ ss} + 7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4 \text{ ss} + \text{LIQUID}$
 (e) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4 \text{ ss} + \text{LIQUID}$
 (f) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4 \text{ ss}$

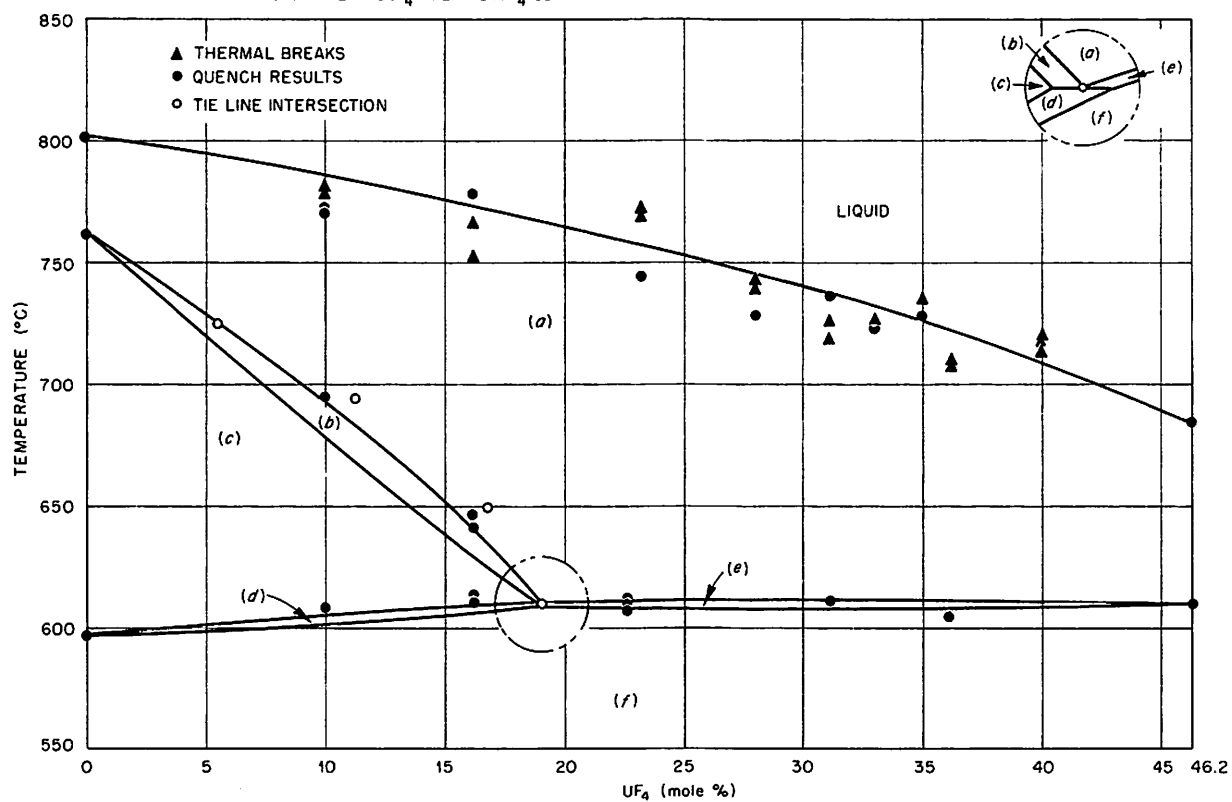


Fig. 12. The Join $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$.

Table 12. Thermal-Gradient Quenching Data for the 53.8 Mole % LiF Join^a

UF ₄ Content (mole %)	Temperature ^b (°C)	Phases ^c Above Temperature	Phases ^c Below Temperature
10	695 ± 5	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss)
	608 ± 3	Liquid + LiF·2ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
16.2	646 ± 2	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^d	Liquid + LiF·2ThF ₄ (ss) ^d
	642 ± 4	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss)
	612 ± 3	Liquid + LiF·2ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^d
	611 ± 4	Liquid + LiF·2ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
23.1	612 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
	611 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
	607 ± 2	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
31.2	611 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
36.2	642 ± 4	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss)

^aSee Table 4 for liquidus values.^bThe uncertainty in temperatures indicates the temperature differences between the quenched samples.^cOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."^dMost of the phases were identified by optical microscopy; this phase was also identified by x-ray diffraction.

Table 13. Tie-Line Data for $7\text{LiF} \cdot 6\text{UF}_4$ – $7\text{LiF} \cdot 6\text{ThF}_4$ (ss) Primary-Phase Area

Quench Composition (mole %)		Temperature Range (°C)	Index of Refraction, N_ω	Solid Solution Composition (mole % UF_4)
UF_4	ThF_4			
2	29	586–591	1.508	5.5
4	27	558–592	1.510	7
5	24	558–563	1.510	7
5	29	557–605	1.512	9
5	31	599	1.512	9
5	33	584–599	1.512	9
5	35	601	1.512	9
6	24	553	1.512	9
7	26	550–607	1.510	7
10	20	546–568	1.516	12.5
10	24	576–593	1.516	12.5
10	26	597	1.515	12
12.5	17	536–562	1.524	19.5
13	30	578–610	1.518	14.5
15	17	585	1.520	16
15	25	532–606	1.519	15
15	28	578–610	1.520	16
16	12	525	1.524	19.5
17	12.5	521–547	1.525	20.5
17	26	578–610	1.522	18
18	18	554–608	1.520	16
18	20	601–612	1.522	18
		554–608	1.522	18
18	22	521	1.524	19.5
		607	1.522	18
		608	1.522	18
18	24	532–612	1.522	18
20	20	520–620	1.526	21.5
20	22	612	1.524	19.5
		532	1.526	21.5
21.5	21.5	596–607	1.526	21.5
25	15	528–609	1.532	26.5
		601	1.534	28.5
		510–612	1.532	26.5
26.5	2	497	1.548	41
27	2	493	1.550	42.5
28	1	497	1.550	42.5
28	10	608	1.534	28.5
		544	1.536	30
30	10	609	1.536	30
		528	1.538	32
33	10	596–601	1.540	34
35	5	528–604	1.544	37.5
		606	1.544	37.5
		510	1.546	39
39	4	553–609	1.547	40

Table 14. Optical Properties for
7LiF·6UF₄-7LiF·6ThF₄ (ss)

UF ₄ Content (mole %)	Index of Refraction, N_{ω}	Birefringence
10	1.514	0.003
16.2	1.522	Low
23.1	1.528	Very low
	1.529	Very low
	1.530	Very low
31.2	1.538	Very low
36.2	1.540	Low
	1.542	Low

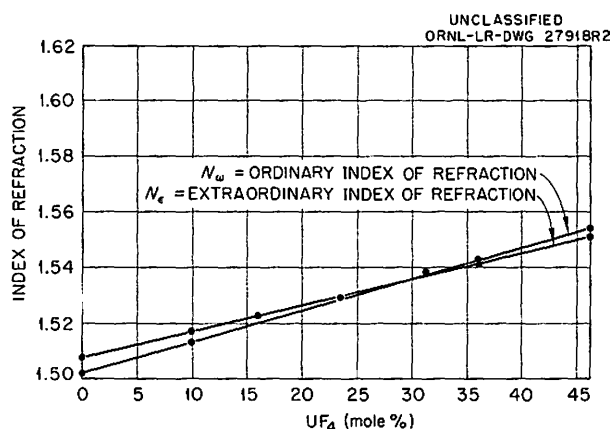


Fig. 13. Indices of Refraction vs Composition for
7LiF·6ThF₄-7LiF·6UF₄ (ss).

studies in Tables 4, 15, and 16. The join contains the 3LiF·ThF₄ (ss) series, whose members are green, biaxial negative, and have optic angles of approximately 10°. The indices of refraction of these solid solutions shown in Fig. 15 and Table 17 vary linearly with UF₄ concentration. The maximum extent of 3LiF·Th(U)F₄ (ss) is 15.5 mole % UF₄.

The fractionation paths for 3LiF·Th(U)F₄ (ss) primary-phase area shown in Fig. 7 are based on the tie-line data in Table 16.

RELATIONS BETWEEN THE SOLID SOLUTIONS Compatibility Triangles

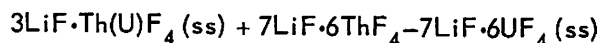
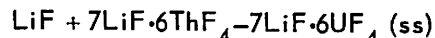
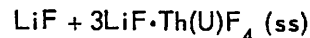
Since the composition of each of the phases in equilibrium at each of the invariant points has been determined, this information can be used to construct the compatibility triangles associated with the invariant points. Figure 16 shows these triangles and is based on the tie-line data in Table 18.

The position of the invariant-point compositions relative to their compatibility triangles indicates that the invariant points at 609, 500, and 488°C are peritectic, peritectic, and eutectic, respectively. These conclusions are in agreement with those in the section "General Discussion of the System LiF-UF₄-ThF₄ and the Limiting Binary Systems," this report.

The direction of decreasing temperature along the boundary line between the primary-phase areas of 7LiF·6UF₄-7LiF·6ThF₄ (ss) and LiF·4UF₄-LiF·4ThF₄ (ss) is difficult to determine because the temperature variation along this boundary line is less than 5°C. The relative directions of the tie lines from the 609°C invariant point to the corners of the associated compatibility triangle (Fig. 16) indicate, however, that this boundary temperature decreases in the direction of the ternary invariant composition.

Subsolidus Two-Phase Regions

For a point representing a specified composition in any two-phase subsolidus region in the system LiF-UF₄-ThF₄, the tie line connecting the compositions of the two phases in equilibrium at that point must be a straight line passing through the point. This fact provides a method for checking the accuracy of the refractive index curves (Figs. 8, 11, 13, and 15) of the ternary solid solutions. Tie-line data are given in Table 19 for the following regions:



The ends of these tie lines and the corresponding points of nominal composition are shown (Fig. 17) to be nearly colinear.

- (a) LIQUID + $3\text{LiF} \cdot \text{ThF}_4$ ss
- (b) LiF + LIQUID
- (c) LiF + $3\text{LiF} \cdot \text{ThF}_4$ ss + LIQUID
- (d) LiF + $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$ ss + LIQUID
- (e) $4\text{LiF} \cdot \text{UF}_4$ + LIQUID + LiF
- (f) $4\text{LiF} \cdot \text{UF}_4$ + LIQUID
- (g) $4\text{LiF} \cdot \text{UF}_4$ + $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$ ss + LIQUID
- (h) $3\text{LiF} \cdot \text{ThF}_4$ ss
- (i) $3\text{LiF} \cdot \text{ThF}_4$ ss + $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$ ss + LiF
- (j) LiF + $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$ ss
- (k) LiF + $4\text{LiF} \cdot \text{UF}_4$ + $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$ ss
- (l) $4\text{LiF} \cdot \text{UF}_4$ + $7\text{LiF} \cdot 6\text{ThF}_4 - 7\text{LiF} \cdot 6\text{UF}_4$ ss

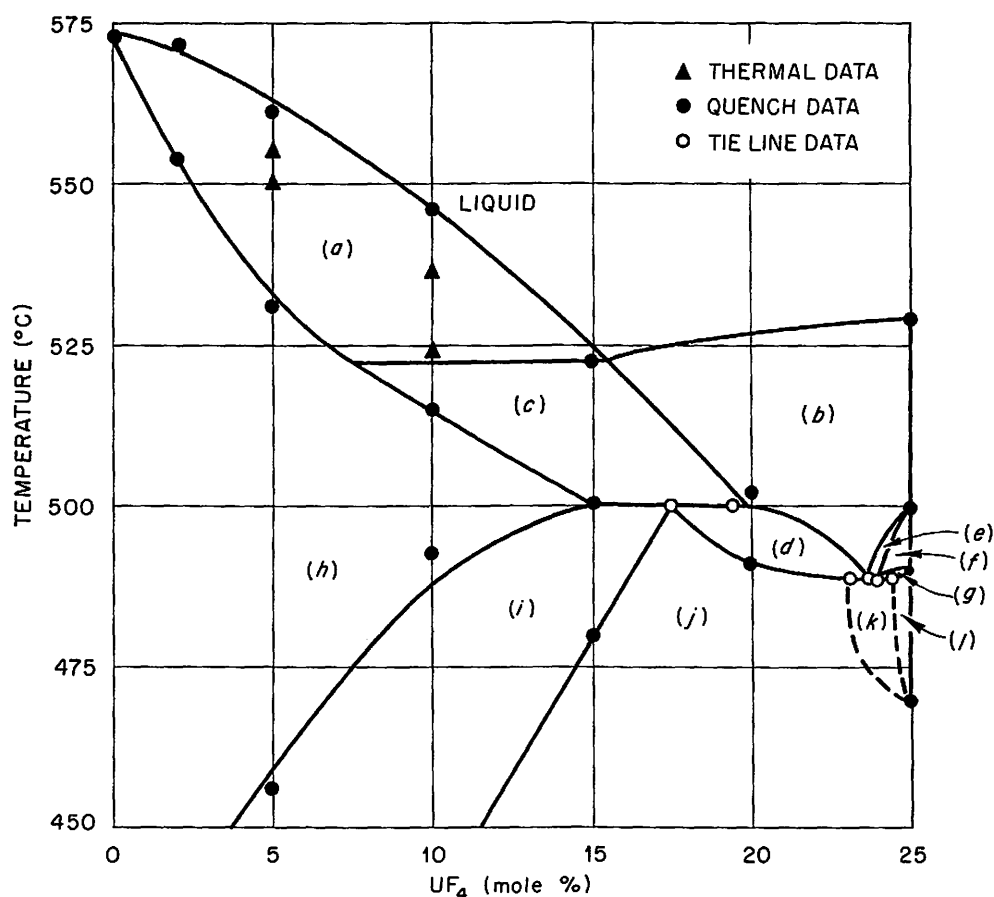


Fig. 14. The 75 Mole % LiF Section.

Table 15. Thermal-Gradient Quenching Data for the 75 Mole % LiF Join^a

UF ₄ Content (mole %)	Temperature ^b (°C)	Phases ^c Above Temperature	Phases ^c Below Temperature
2	554 ± 4	Liquid + 3LiF•ThF ₄ (ss)	3LiF•ThF ₄ (ss)
5	533 ± 3	Liquid + 3LiF•ThF ₄ (ss)	3LiF•ThF ₄ (ss)
	460 ± 2 ^d	3LiF•ThF ₄ (ss) ^e	3LiF•ThF ₄ ^e + 7LiF•6UF ₄ - 7LiF•6ThF ₄ (ss) ^e
10	515 ± 10	Liquid + 3LiF•ThF ₄ (ss)	3LiF•ThF ₄ (ss)
	493 ± 5	3LiF•ThF ₄ (ss) ^e	3LiF•ThF ₄ (ss) ^e + LiF + 7LiF•6UF ₄ - 7LiF•6ThF ₄ (ss)
13	506 ± 3	Liquid + 3LiF•ThF ₄ (ss)	3LiF•ThF ₄ (ss)
	491 ± 3	3LiF•ThF ₄ (ss) ^e	3LiF•ThF ₄ (ss) ^e + LiF + 7LiF•6UF ₄ -7LiF•6ThF ₄ (ss) ^e
15	500 ± 3	Liquid (traces) + LiF (traces) + 3LiF•6ThF ₄ (ss) ^e	LiF + 3LiF•ThF ₄ (ss) + 7LiF•6UF ₄ - 7LiF•6ThF ₄ (ss)
	480 ± 2	LiF + 3LiF•ThF ₄ (ss) ^e + 7LiF•6UF ₄ - 7LiF•6ThF ₄ (ss) ^e	LiF + 7LiF•6UF ₄ -7LiF•6ThF ₄ (ss) ^e
20	503 ± 5	Liquid + LiF	Liquid + LiF + 7LiF•6UF ₄ - 7LiF•6ThF ₄ (ss) ^e
	491 ± 2	Liquid + LiF + 7LiF•6UF ₄ - 7LiF•6ThF ₄ (ss)	LiF + 7LiF•6UF ₄ -7LiF•6ThF ₄ (ss) ^e

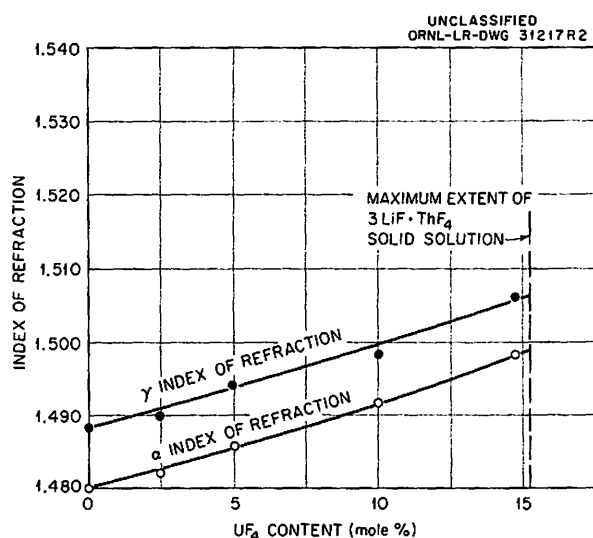
^aSee Table 4 for liquidus values.^bThe uncertainty in temperatures indicates the temperature differences between the quenched samples.^cOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."^dThis exsolution was observed by using x-ray diffraction technique only.^eMost of the phases were identified by optical microscopy; this phase was also identified by x-ray diffraction.

Table 16. Tie-Line Data for $3\text{LiF} \cdot \text{ThF}_4$ (ss) Primary-Phase Area

Quench Composition (mole %)		Temperature Range (°C)	Index of Refraction, N_γ	Solid Solution Composition (mole % UF_4)
UF_4	ThF_4			
2	24	559	1.490	2.0
5	19	560	1.490	2
10	16	535	1.496	6.5
12	15	530	1.495	6.0
15	12	514-525	1.500	10.0
16	11	513	1.500	10.0
18	10	504-510	1.500	10.0
20	8	504	1.503	12.5

Table 17. Refractive Indices for $3\text{LiF} \cdot \text{ThF}_4$ (ss)

UF_4 Content (mole %)	Refractive Indices	
	N_α	N_γ
2	1.482	1.490
5	1.486	1.494
10	1.492	1.498
13	1.496	1.503
15	1.498	1.507

Fig. 15. Indices of Refraction vs Composition for $3\text{LiF} \cdot \text{ThF}_4$ (ss).

Isothermal Sections

The equilibrium-phase behavior of a ternary system involving solid solutions can be clearly and unambiguously described only by an extensive series of isothermal sections. An abbreviated series of such sections for the system $\text{LiF}-\text{UF}_4-\text{ThF}_4$ is presented in Figs. 18 through 21. These

show the polyphase equilibria for all compositions at the temperatures specified.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of T. N. McVay, who was responsible for all the refractive index measurements in the system UF_4-ThF_4 and a portion of the petrographic phase identification in the system $\text{LiF}-\text{UF}_4-\text{ThF}_4$. In addition we are especially grateful to R. F. Newton, F. F. Blankenship, and J. E. Ricci for helpful advice concerning many phases of the investigation.

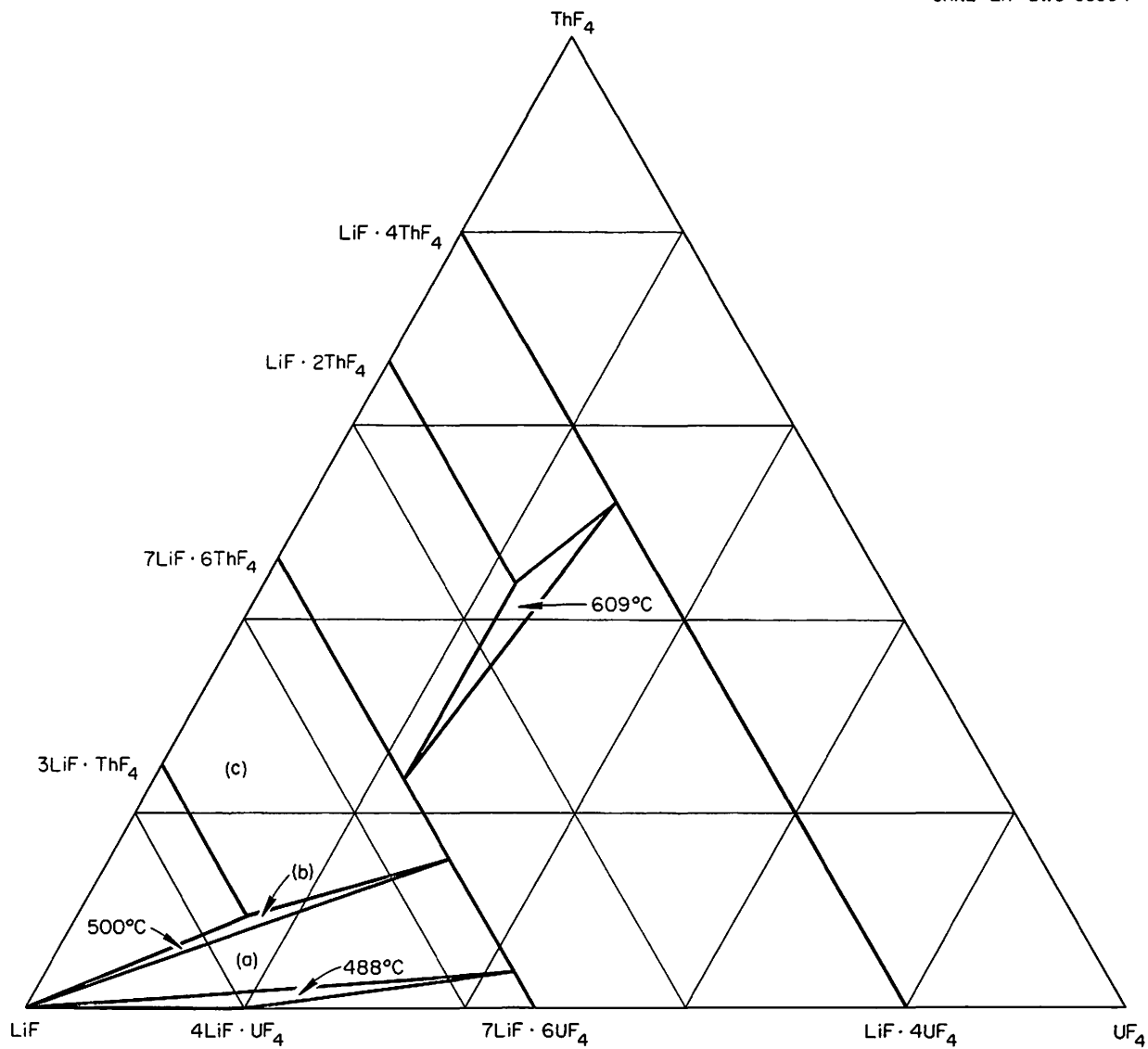


Fig. 16. Compatibility Triangles in the System $\text{LiF-UF}_4\text{-ThF}_4$.

Table 18. Compatibility Triangle Data

Quench Composition (mole %)		Phases Present*	Refractive Indices of Solid Solution		Composition of Solid Solution (mole % UF_4)
UF_4	ThF_4		N_ω	N_γ	
27	1	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss) $4\text{LiF} \cdot \text{UF}_4$ LiF	1.550		42.5
28	1	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss) $4\text{LiF} \cdot \text{UF}_4$ LiF	1.550		42.5
26.5	1	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss) $4\text{LiF} \cdot \text{UF}_4$ LiF	1.550		42.5
27	2	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss) $4\text{LiF} \cdot \text{UF}_4$ LiF	1.550		42.5
15	10	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)** $3\text{LiF} \cdot \text{ThF}_4$ (ss)** LiF	1.538	1.506 1.506	32 15
17	11	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss) $3\text{LiF} \cdot \text{ThF}_4$ (ss) LiF	1.536	1.504	30 13.5
20	8	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)** $3\text{LiF} \cdot \text{ThF}_4$ (ss)** LiF	1.537	1.504	31 13.5
18	10	$7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss) $3\text{LiF} \cdot \text{ThF}_4$ (ss) LiF	1.536	1.504	30 13.5
18	22	$\text{LiF} \cdot 4\text{UF}_4 - \text{LiF} \cdot 4\text{ThF}_4$ (ss) $\text{LiF} \cdot 2\text{ThF}_4$ (ss)** $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)**	1.564 1.524	1.558	28 23 23

*Only phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."

**Most of the phases were identified by optical microscopy; this phase was also identified by x-ray diffraction.

Table 19. Subsolidus Two-Phase Regions

Quench Composition (mole %)		Phases Present*	Refractive Indices of Solid Solution		Composition of Solid Solution (mole % UF_4)
UF_4	ThF_4		N_γ	N_ω	
4	19	LiF $3\text{LiF} \cdot \text{ThF}_4$ (ss)**	1.493		4
5	15	LiF $3\text{LiF} \cdot \text{ThF}_4$ (ss)**	1.495		6.5
8	15	LiF $3\text{LiF} \cdot \text{ThF}_4$ (ss)**	1.498		9
10	10	LiF $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)**		1.528	22
15	10	LiF $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)		1.524	28
20	5	LiF** $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)**		1.542	36
22	6	LiF** $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)**		1.542	35.5
24	4	LiF** $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)**		1.546	39.5
25	3	LiF $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)		1.548	41
26.5	2	LiF $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)		1.548	41
4	27	$3\text{LiF} \cdot \text{ThF}_4$ (ss)** $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)**	1.490	1.510	2 7
5	24	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.492	1.512	3 9
5	29	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.490	1.512	2 9
10	16	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.498	1.528	8 23.5
6	24	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.494	1.514	5 10
10	18	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.498	1.526	8 21.5
10	20	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.496	1.522	6.5 18
12	15	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.500	1.530	10 25
12.5	17	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.496	1.528	6.5 23.5
17	12.5	$3\text{LiF} \cdot \text{ThF}_4$ (ss) $7\text{LiF} \cdot 6\text{UF}_4 - 7\text{LiF} \cdot 6\text{ThF}_4$ (ss)	1.504	1.532	13 26.5

*Only phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."

**Most of the phases were identified by optical microscopy; this phase was also identified by x-ray diffraction.

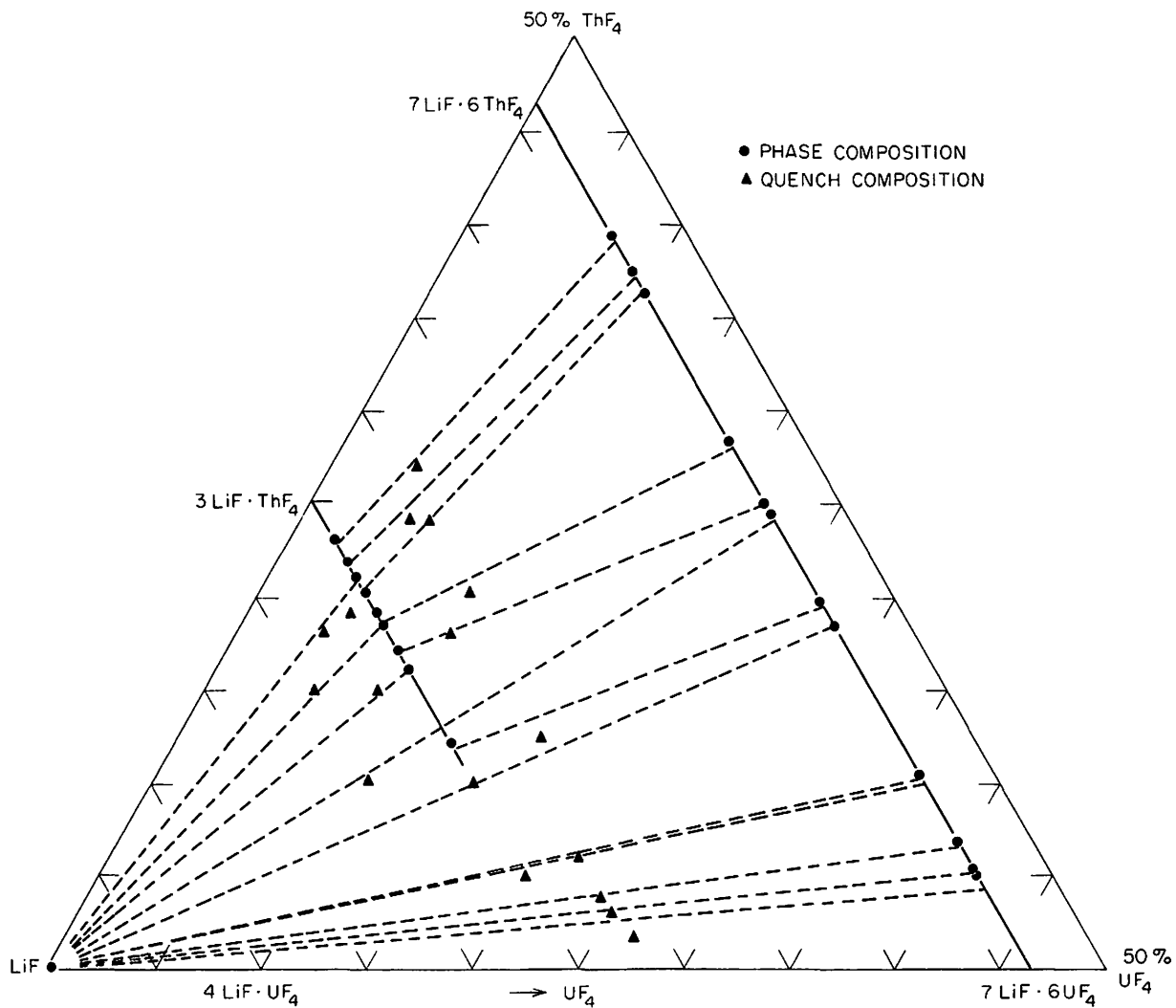


Fig. 17. Subsolidus Tie Lines.

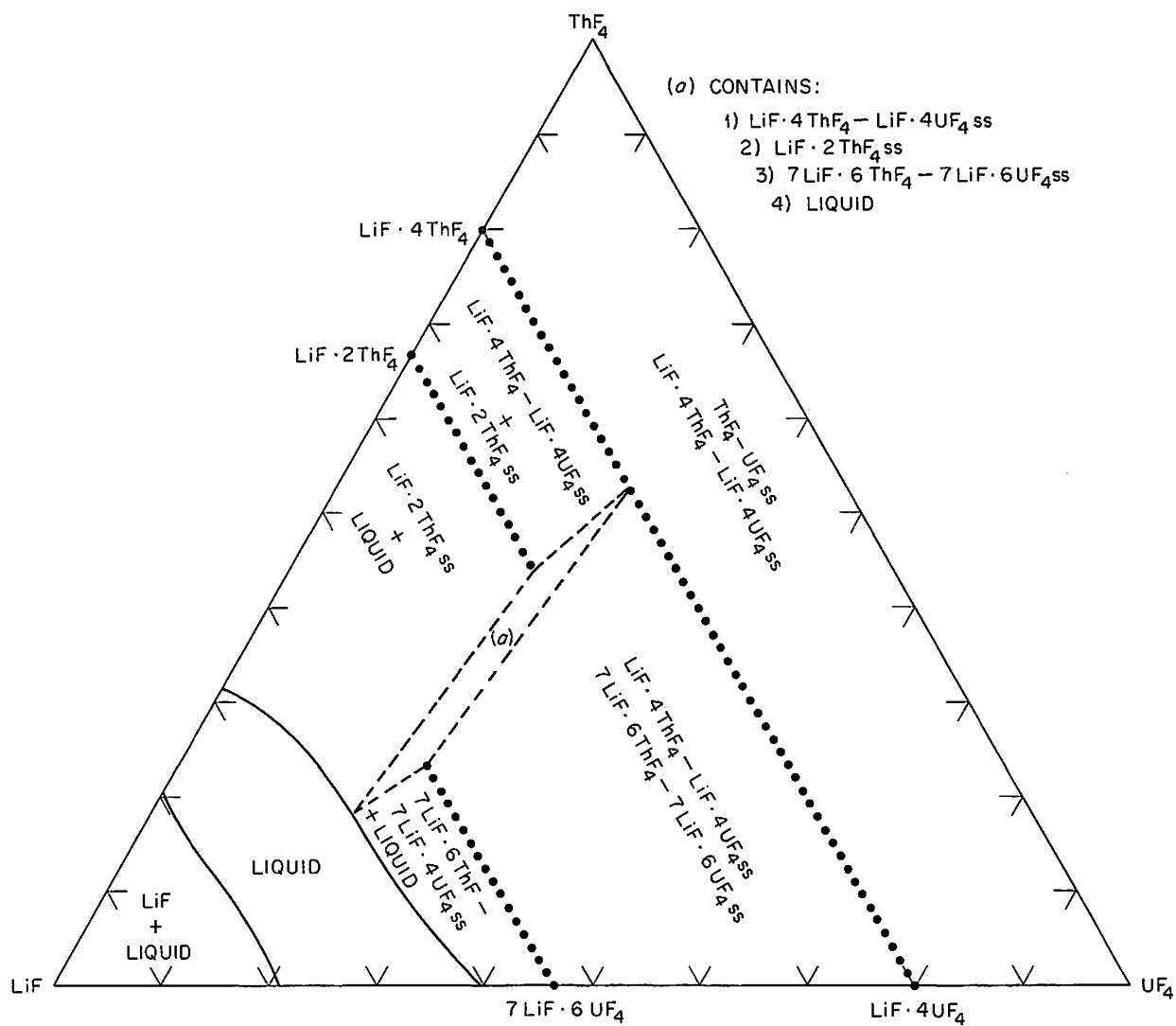


Fig. 18. 609°C Isothermal Section.



2

41



Appendix

MISCELLANEOUS THERMAL-GRADIENT QUENCHING RESULTS FOR THE SYSTEM LiF-UF₄-ThF₄

Composition (mole %)		Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
UF ₄	ThF ₄			
2	24	522 ± 4	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
2	29	563 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
3	19	561 ± 3	Liquid + LiF	Liquid + LiF + 3LiF·ThF ₄ (ss)
4	19	532 ± 7	Liquid + LiF + 3LiF·ThF ₄ (ss)	LiF + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^c
4	27	555 ± 4	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	LiF + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		548 ± 4	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
5	15	556 ± 4	Liquid + LiF	Liquid + LiF + 3LiF·ThF ₄ (ss)
		540 ± 3	Liquid + LiF + 3LiF·ThF ₄ (ss)	LiF + 3LiF·ThF ₄ (ss) ^c
		462 ± 3	LiF + 3LiF·ThF ₄ (ss)	LiF + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
5	19	558 ± 2	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + LiF
5	24	555 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		549 ± 3	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
5	26	558 ± 2	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		546 ± 2	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
5	29	615 ± 3	Liquid + LiF·2ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		605 ± 3	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		557 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
		547 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
5	31	609 ± 4	Liquid + LiF·2ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		602 ± 3	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)

Appendix (continued)

Composition (mole %)		Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
UF ₄	ThF ₄			
5	33	605 ± 3	Liquid + LiF·2ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		599 ± 3	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
5	35	605 ± 4	Liquid + LiF·2ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
6	24	551 ± 3	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		541 ± 3	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
7	26	547 ± 3	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
8	15	517 ± 3	Liquid + LiF + 3LiF·ThF ₄ (ss)	LiF + 3LiF·ThF ₄ (ss)
		480 ± 2	LiF + 3LiF·ThF ₄ (ss) ^c	LiF + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
10	10	528 ± 3	LiF + liquid	Liquid + LiF + 3LiF·ThF ₄ (ss)
		488 ± 3	Liquid + LiF + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c + LiF ^c + 3LiF·ThF ₄ (ss) ^c
		464 ± 3	LiF ^c + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss) ^c	LiF ^c + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c
10	16	533 ± 2	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
10	18	513 ± 2	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
10	20	543 ± 3	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		538 ± 2	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
10	70	889 ± 4	Liquid + UF ₄ –ThF ₄ (ss)	LiF·4UF ₄ –LiF·4ThF ₄ (ss)
11	32	612 ± 3	Liquid + LiF·2ThF ₄ (ss) ^c	Liquid + LiF·2ThF ₄ (ss) ^c + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss) ^c
		607 ± 3	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
12	15	525 ± 2	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		505 ± 2	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
12.5	17	532 ± 4	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)

Appendix (continued)

Composition (mole %)		Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
UF ₄	ThF ₄			
12.5	17	514 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
13	30	688 ± 2	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss) ^c	Liquid + LiF·2ThF ₄ (ss) ^c
		612 ± 3	Liquid + LiF·2ThF ₄ (ss) ^c	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^c
15	12	511 ± 3	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
15	25	612 ± 4	Liquid + LiF·2ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		529 ± 4	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
15	28	680 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss)
		617 ± 3	Liquid + LiF·2ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		612 ± 3	Liquid + LiF·2ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^c
16	11	510 ± 2	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		501 ± 8	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
		492 ± 2	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF	3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
16	12	523 ± 2	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
17	11	499 ± 5	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	LiF + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
17	12.5	519 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
		507 ± 3	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)
		490 ± 3	7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss)	3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) + LiF
17	26	660 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) ^c
		617 ± 3	Liquid + LiF·2ThF ₄ (ss) ^c	Liquid + LiF·2ThF ₄ (ss) ^c + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^c
		612 ± 4	Liquid + LiF·2ThF ₄ (ss) ^c + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^c	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
18	10	502 ± 2	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss) ^c

Appendix (continued)

Composition (mole %)		Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
UF ₄	ThF ₄			
18	10	489 ± 2	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + 3LiF·ThF ₄ (ss) + LiF
18	20	637 ± 3	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss) ^c	Liquid + LiF·2ThF ₄ (ss)
		615 ± 4	Liquid + LiF·2ThF ₄ (ss) ^c	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
		612 ± 4	Liquid + LiF·2ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
18	22	634 ± 4	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss)
		626 ± 3	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + LiF·2ThF ₄ (ss) ^c
		612 ± 3	Liquid + LiF·2ThF ₄ (ss) ^c	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c
		612 ± 4	Liquid + LiF·2ThF ₄ (ss) ^c	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c
20	8	502 ± 2	Liquid + 3LiF·ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		498 ± 2	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	LiF + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
20	20	620 ± 3	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c
		517 ± 2	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)	Liquid + 3LiF·ThF ₄ (ss) + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
20	45	883 ± 2	Liquid + UF ₄ ·ThF ₄ (ss)	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)
21.5	21.5	610 ± 3	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c
22	6	495 ± 2	LiF + liquid	LiF + liquid + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		487 ± 2	LiF + liquid + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss) ^c	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c + LiF ^c
24	4	488 ± 2	7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) + LiF + liquid	LiF + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
25	2	487 ± 2	Liquid + LiF + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	LiF + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
25	3	491 ± 3	Liquid + LiF + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	LiF + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
25	15	615 ± 3	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
		613 ± 2	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
		607 ± 6	Liquid + LiF·4UF ₄ –LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)
26	2	489 ± 2	Liquid + LiF + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss) ^c	LiF + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss) ^c
26.5	2	495 ± 2	Liquid + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)	Liquid + LiF + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)
		490 ± 3	Liquid + LiF + 7LiF·6UF ₄ – 7LiF·6ThF ₄ (ss)	LiF + 7LiF·6UF ₄ –7LiF·6ThF ₄ (ss)

Appendix (continued)

Composition (mole %)		Temperature ^a (°C)	Phases ^b Above Temperature	Phases ^b Below Temperature
UF ₄	ThF ₄			
28	10	610 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
30	10	611 ± 2	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
30	50	827 ± 5	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + UF ₄ -ThF ₄ (ss) + LiF·4UF ₄ - LiF·4ThF ₄ (ss)
33	10	604 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
33 $\frac{1}{3}$	33 $\frac{1}{3}$	862 ± 2	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)
39	4	612 ± 3	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)	Liquid + 7LiF·6UF ₄ -7LiF·6ThF ₄ (ss)
45	20	859 ± 3	Liquid + UF ₄ -ThF ₄ (ss)	Liquid + LiF·4UF ₄ -LiF·4ThF ₄ (ss)

^aThe uncertainty in temperatures indicates the temperature differences between the quenched samples.

^bOnly phases found in major quantity are given. Minor quantities of other phases resulting from lack of complete reaction between solids or from trace amounts of oxide impurities are not noted. Glasses or poorly formed crystals assumed to have been produced during rapid cooling of liquid were found in those samples for which the observed phase is indicated as "liquid."

^cMost of the phases were identified by optical microscopy; in addition, this phase was identified by x-ray diffraction.

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
- 4-5. Central Research Library
6. Reactor Experimental Engineering Library
- 7-26. Laboratory Records Department
27. Laboratory Records, ORNL, R.C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34. S. C. Lind
35. M. L. Nelson
36. C. P. Keim
37. J. H. Frye, Jr.
38. R. S. Livingston
39. H. G. MacPherson
40. F. L. Culler
41. A. H. Snell
42. A. Hollaender
43. M. T. Kelley
44. K. Z. Morgan
45. C. F. Weaver
46. A. S. Householder
47. C. S. Harrill
48. C. E. Winters
49. H. E. Seagren
50. D. Phillips
51. F. C. VonderLage
52. D. S. Billington
53. J. A. Lane
54. M. J. Skinner
55. W. H. Jordan
56. G. E. Boyd
57. C. J. Barton
58. J. P. Blakely
59. M. Blander
60. F. F. Blankenship
61. C. M. Blood
62. S. Cantor
63. R. B. Evans
64. H. A. Friedman
65. R. A. Gilbert
66. W. R. Grimes
67. H. Insley
68. F. Kertesz
69. S. Langer
70. R. E. Meadows
71. R. E. Moore
72. G. J. Nessel
73. R. F. Newton
74. L. G. Overholser
75. J. D. Redman
76. J. H. Shaffer
77. R. J. Sheil
78. N. V. Smith
79. R. A. Strehlow
80. B. J. Sturm
81. W. T. Ward
- 82-91. R. E. Thoma
92. G. M. Watson
93. M. A. Bredig
94. S. Datz
95. R. E. Minturn
96. A. S. Dworkin
97. G. P. Smith
98. M. T. Robinson
99. A. J. Miller
100. L. G. Alexander
101. R. R. Dickison
102. G. W. Keilholtz
103. W. D. Manly
104. A. P. Fraas
105. L. A. Mann
106. F. R. Bruce
107. E. S. Bettis
108. R. P. Milford
109. R. A. Charpie
110. W. K. Ergen
111. R. B. Lindauer
112. J. C. White
113. A. S. Meyer
114. W. F. Vaughan
115. D. E. Ferguson
116. R. E. Blanco
117. J. T. Long
118. G. I. Cathers
119. W. H. Carr, Jr.
120. H. E. Goeller
121. H. F. McDuffie
122. W. L. Marshall

123. J. S. Gill
 124. L. O. Gilpatrick
 125. C. F. Baes
 126. B. A. Soldano
 127. W. E. Browning
 128. M. J. Kelly
 129. J. O. Blomeke
 130. G. C. Williams

131. P. M. Reyling
 132. J. Ricci (consultant)
 133. C. E. Larson (consultant)
 134. P. H. Emmett (consultant)
 135. H. Eyring (consultant)
 136. G. T. Seaborg (consultant)
 137. ORNL - Y-12 Technical Library
 Document Reference Section

EXTERNAL DISTRIBUTION

138. Division of Research and Development, AEC, ORO
 139. Oak Ridge Institute of Nuclear Studies
 140-142. University of Cincinnati (1 copy each to H. S. Green, J. W. Sausville, and T. B. Cameron)

138. Division of Research and Development, AEC, ORO
 139. Oak Ridge Institute of Nuclear Studies
 140-142. University of Cincinnati (1 copy each to H. S. Green, J. W. Sausville, and T. B. Cameron)
 143. E. F. Osborn, Pennsylvania State University
 144. G. W. Morey, 5806 Bradley Blvd., Bethesda, Md.
 145-631. Distribution as shown in TID-4500 (14th ed.) under Chemistry-General category