

*Part II*  
**MOLTEN-SALT REACTORS**

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## PREFACE

The Oak Ridge National Laboratory, under the sponsorship of the U. S. Atomic Energy Commission, has engaged in research on molten salts as materials for use in high-temperature reactors for a number of years. The technology developed by this work was incorporated in the Aircraft Reactor Experiment and made available for purposes of civilian application. This earlier technology and the new information found in the civilian power reactor effort is summarized in this part.

So many present and former members of the Laboratory staff have contributed directly or indirectly to the molten salt work that it should be regarded as a contribution from the entire Laboratory. The technical direction of the work was provided by A. M. Weinberg, R. C. Briant, W. H. Jordan, and S. J. Cromer. In addition to the contributors listed for the various chapters, the editor would like to acknowledge the efforts of the following people who are currently engaged in the work reported: R. G. Affel, J. C. Amos, C. J. Barton, C. C. Beusman, W. E. Browning, S. Cantor, D. O. Campbell, G. I. Cathers, B. H. Clampitt, J. A. Conlin, M. H. Cooper, J. L. Crowley, J. Y. Estabrook, H. A. Friedman, P. A. Gnadt, A. G. Grindell, H. W. Hoffman, H. Insley, S. Langer, R. E. MacPherson, R. E. Moore, G. J. Nettle, R. F. Newton, W. R. Osborn, F. E. Romie, C. F. Sales, J. H. Shaffer, G. P. Smith, N. V. Smith, P. G. Smith, W. L. Snapp, W. K. Stair, R. A. Strehlow, C. D. Susano, R. E. Thoma, D. B. Trauger, J. J. Tudor, W. T. Ward, G. M. Watson, J. C. White, and H. C. Young.

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## CHAPTER 11

### INTRODUCTION\*

The potential utility of a fluid-fueled reactor that can operate at a high temperature but with a low-pressure system has been recognized for a long time. Some years ago, R. C. Briant of the Oak Ridge National Laboratory suggested the use of the molten mixture of  $\text{UF}_4$  and  $\text{ThF}_4$ , together with the fluorides of the alkali metals and beryllium or zirconium, as the fluid fuel. Laboratory work with such mixtures led to the operation, in 1954, of an experimental reactor, which was designated the Aircraft Reactor Experiment (ARE).

Fluoride-salt mixtures suitable for use in power reactors have melting points in the temperature range 850 to 950°F and are sufficiently compatible with certain nickel-base alloys to assure long life for reactor components at temperatures up to 1300°F. Thus the natural, optimum operating temperature for a molten-salt-fueled reactor is such that the molten salt is a suitable heat source for a modern steam power plant. The principal advantages of the molten-salt system, other than high temperature, in comparison with one or more of the other fluid-fuel systems are (1) low-pressure operation, (2) stability of the liquid under radiation, (3) high solubility of uranium and thorium (as fluorides) in molten-salt mixtures, and (4) resistance to corrosion of the structural materials that does not depend on oxide or other film formation.

The molten-salt system has the usual benefits attributed to fluid-fuel systems. The principal advantages over solid-fuel-element systems are (1) a high negative temperature coefficient of reactivity, (2) a lack of radiation damage that can limit fuel burnup, (3) the possibility of continuous fission-product removal, (4) the avoidance of the expense of fabricating new fuel elements, and (5) the possibility of adding makeup fuel as needed, which precludes the need for providing excess reactivity. The high negative temperature coefficient and the lack of excess reactivity make possible a reactor, without control rods, which automatically adjusts its power in response to changes of the electrical load. The lack of excess reactivity also leads to a reactor that is not endangered by nuclear power excursions.

One of the attractive features of the molten-salt system is the variety of reactor types that can be considered to cover a range of applications. The present state of the technology suggests that homogeneous reactors which use a molten salt composed of  $\text{BeF}_2$  and either  $\text{Li}^7\text{F}$  or  $\text{NaF}$ , with  $\text{UF}_4$  for fuel and  $\text{ThF}_4$  for a fertile material, are most suitable for early construction.

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\*By H. G. MacPherson.

These reactors can be either one or two region and, depending on the size of the reactor core and the thorium fluoride concentration, can cover a wide range of fuel inventories, breeding ratios, and fuel reprocessing schedules. The chief virtues of this class of molten-salt reactor are that the design is based on a well-developed technology and that the use of a simple fuel cycle contributes to reduced costs.

With further development, the same base salt, that is, the mixture of  $\text{BeF}_2$  and  $\text{Li}^7\text{F}$ , can be combined with a graphite moderator in a heterogeneous arrangement to provide a self-contained Th-U<sup>233</sup> system with a breeding ratio of one. The chief advantage of the molten-salt system over other liquid systems in pursuing this objective is that it is the only system in which a soluble thorium compound can be used, and thus the problem of slurry handling is avoided. The possibility of placing thorium in the core obviates the necessity of using graphite as a core-shell material.

Plutonium is being investigated as an alternate fuel for the molten-salt reactor. Although it is too early to describe a plutonium-fueled reactor in detail, it is highly probable that a suitable  $\text{PuF}_3$ -fueled reactor can be constructed and operated.

The high melting temperature of the fluoride salts is the principal difficulty in their use. Steps must be taken to preheat equipment and to keep the equipment above the melting point of the salt at all times. In addition, there is more parasitic neutron capture in the salts of the molten-salt reactor than there is in the heavy water of the heavy-water-moderated reactors, and thus the breeding ratios are lower. The poorer moderating ability of the salts requires larger critical masses for molten-salt reactors than for the aqueous systems. Finally, the molten-salt reactor shares with all fluid-fuel reactors the problems of certain containment of the fuel, the reliability of components, and the necessity for techniques of making repairs remotely. The low pressure of the molten-salt fuel system should be beneficial with regard to these engineering problems, but to evaluate them properly will require operating experience with experimental reactors.

## CHAPTER 12

### CHEMICAL ASPECTS OF MOLTEN-FLUORIDE-SALT REACTOR FUELS\*

The search for a liquid for use at high temperatures and low pressures in a fluid-fueled reactor led to the choice of either fluorides or chlorides because of the requirements of radiation stability and solubility of appreciable quantities of uranium and thorium. The chlorides (based on the  $\text{Cl}^{37}$  isotope) are most suitable for fast reactor use, but the low thermal-neutron absorption cross section of fluorine makes the fluorides a uniquely desirable choice for a high-temperature fluid-fueled reactor in the thermal or epithermal neutron region.

Since for most molten-salt reactors considered to date the required concentrations of  $\text{UF}_4$  and  $\text{ThF}_4$  have been moderately low, the molten-salt mixtures can be considered, to a first approximation, as base or solvent salt mixtures, to which the fissionable or fertile fluorides are added. For the fuel, the relatively small amounts of  $\text{UF}_4$  required make the corresponding binary or ternary mixtures of the diluents nearly controlling with regard to physical properties such as the melting point.

#### 12-1. CHOICE OF BASE OR SOLVENT SALTS

The temperature dependence of the corrosion of nickel-base alloys by fluoride salts is described in Chapter 13. From the data given there,  $1300^\circ\text{F}$  ( $704^\circ\text{C}$ ) is taken as an upper limit for the molten-salt-to-metal interface temperature. To provide some leeway for radiation heating of the metal walls and to provide a safety margin, the maximum bulk temperature of the molten-salt fuel at the design condition will probably not exceed  $1225^\circ\text{F}$ . In a circulating-fuel reactor, in which heat is extracted from the fuel in an external heat exchanger, the temperature difference between the inlet and outlet of the reactor will be at least  $100^\circ\text{F}$ . The provision of a margin of safety of  $100^\circ\text{F}$  between minimum operating temperature and melting point makes salts with melting points above  $1025^\circ\text{F}$  of little interest at present, and therefore this discussion is limited largely to salt mixtures having melting points no higher than  $1022^\circ\text{F}$  ( $550^\circ\text{C}$ ). One of the basic features desired in the molten-salt reactor is a low pressure in the fuel system, so only fluorides with a low vapor pressure at the peak operating temperature ( $\sim 700^\circ\text{C}$ ) are considered.

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\*By W. R. Grimes, D. R. Cuneo, F. F. Blankenship, G. W. Keilholtz, H. F. Poppendiek, and M. T. Robinson.

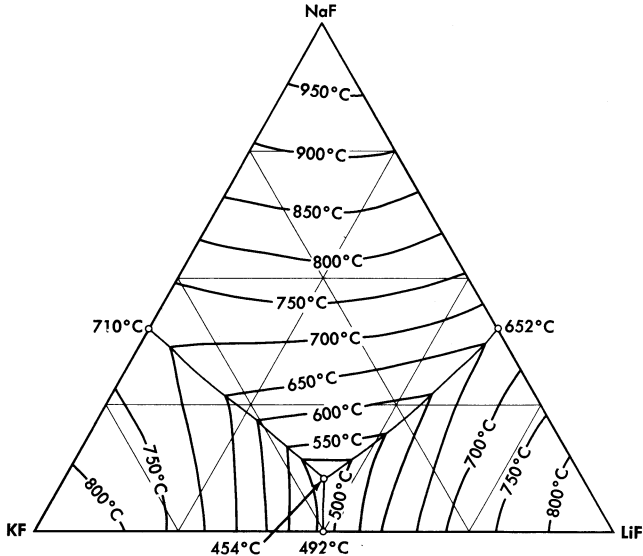


FIG. 12-1. The system LiF-NaF-KF [A. G. Bergman and E. P. Dergunov, *Compt. rend. acad. sci. U.R.S.S.*, 31, 754 (1941)].

Of the pure fluorides of molten-salt reactor interest, only  $\text{BeF}_2$  meets the melting-point requirement, and it is too viscous for use in the pure state. Thus only mixtures of two or more fluoride salts provide useful melting points and physical properties.

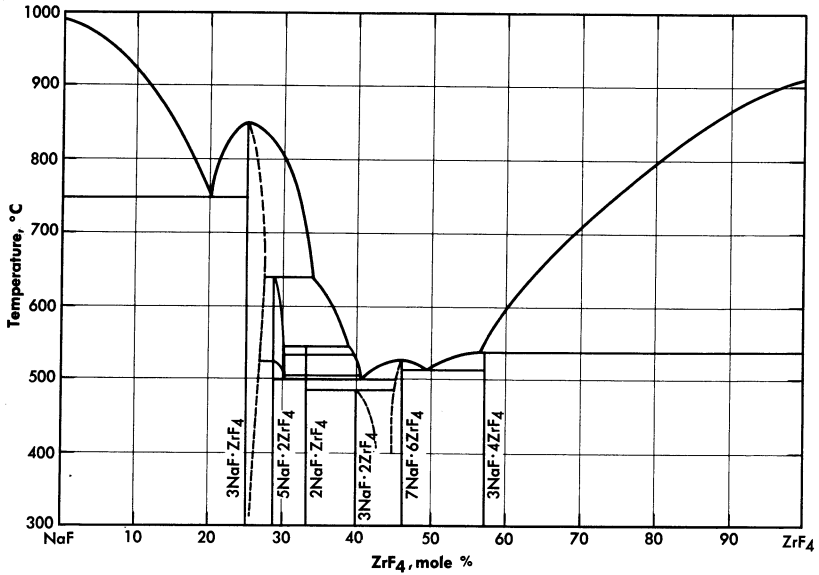
The alkali-metal fluorides and the fluorides of beryllium and zirconium have been given the most serious attention for reactor use. Lead and bismuth fluorides, which might otherwise be useful because of their low neutron absorption, have been eliminated because they are readily reduced to the metallic state by structural metals such as iron and chromium.

Binary mixtures of alkali fluorides that have sufficiently low melting points are an equimolar mixture of KF and LiF, which has a melting point of  $490^\circ\text{C}$ , and a mixture of 60 mole % RbF with 40 mole % LiF, which has a melting point of  $470^\circ\text{C}$ . Up to 10 mole %  $\text{UF}_4$  can be added to these alkali fluoride systems without increasing the melting point above the  $550^\circ\text{C}$  limit. A melting-point diagram for the ternary system LiF-NaF-KF, Fig. 12-1, indicates a eutectic with a lower melting point than the melting points of the simple binary LiF-KF system. This eutectic has interesting properties as a heat-transfer fluid for molten-salt reactor systems, and data on its physical properties are given in Tables 12-1 and 12-2. The KF-LiF and RbF-LiF binaries and their ternary systems with NaF are the only available systems of the alkali-metal fluorides alone which have



TABLE 12-1  
MELTING POINTS, HEAT CAPACITIES, AND EQUATIONS FOR DENSITY  
AND VISCOSITY OF TYPICAL MOLTEN FLUORIDES

Composition, mole %	Melting point, °C	Liquid density, g/cc $\rho = A - BT(°C)$		Heat capacity at 700°C, cal/gram	Viscosity, centipoise		
		A	B		$\eta = Ae^{B/T(°K)}$		At 600°C
					A	B	
LiF-BeF <sub>2</sub> (69-31)	505	2.16	40	0.65	0.118	3624	7.5
LiF-BeF <sub>2</sub> (50-50)	350	2.46	40	0.67	0.0189	6174	22.2
NaF-BeF <sub>2</sub> (57-43)	360	2.27	37	0.52	0.0346	5164	12.8
NaF-ZrF <sub>4</sub> (50-50)	510	3.79	93	0.28	0.0709	4168	8.4
LiF-NaF-KF (46.5-11.5-42)	454	2.53	73	0.45	0.0400	4170	4.75
LiF-NaF-BeF <sub>2</sub> (35-27-38)	338	2.22	41	0.59	0.0338	4738	7.8

FIG. 12-2. The system NaF-ZrF<sub>4</sub>.

low melting points at low uranium concentrations. They would have utility as special purpose reactor fuel solvents if no mixtures with better properties were available.

TABLE 12-2

## THERMAL CONDUCTIVITY OF TYPICAL FLUORIDE MIXTURES

Composition, mole %	Thermal conductivity, Btu/(hr)(ft)(°F)	
	Solid	Liquid
LiF-NaF-KF (46.5-11.5-42)	2.7	2.6
NaF-BeF <sub>2</sub> (57-43)		2.4

Mixtures with melting points in the range of interest may be obtained over relatively wide limits of concentration if ZrF<sub>4</sub> or BeF<sub>2</sub> is a component of the system. Phase relationships in the NaF-ZrF<sub>4</sub> system are shown in Fig. 12-2. There is a broad region of low-melting-point compositions that have between 40 and 55 mole % ZrF<sub>4</sub>.

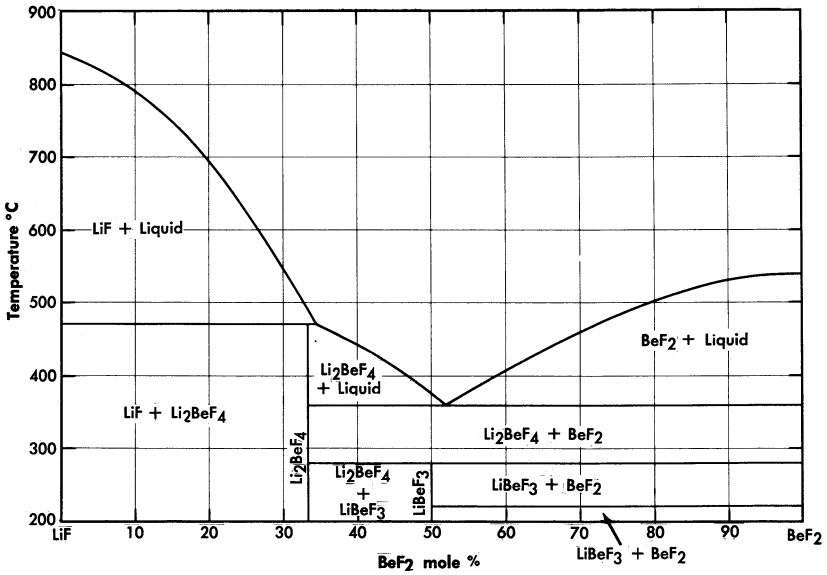


FIG. 12-3. The system LiF-BeF<sub>2</sub>.

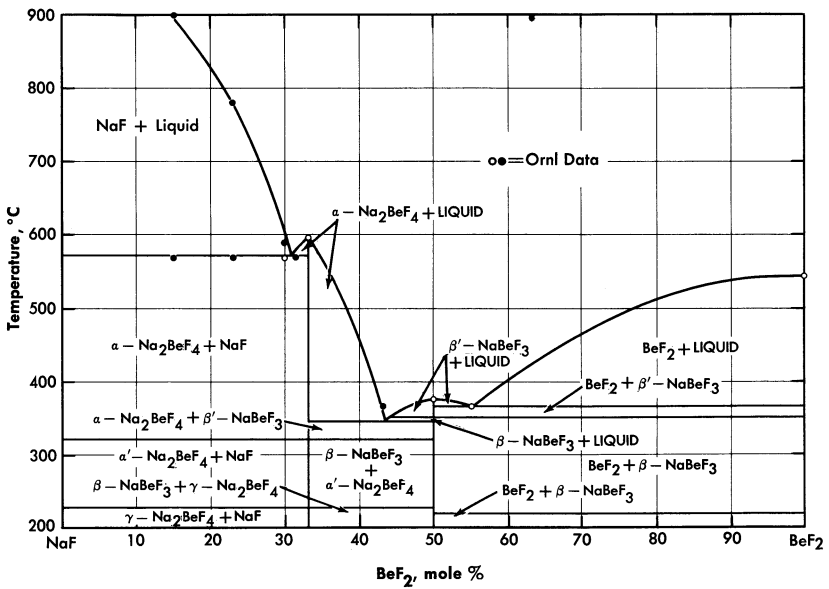


FIG. 12-4. The system NaF-BeF<sub>2</sub>.

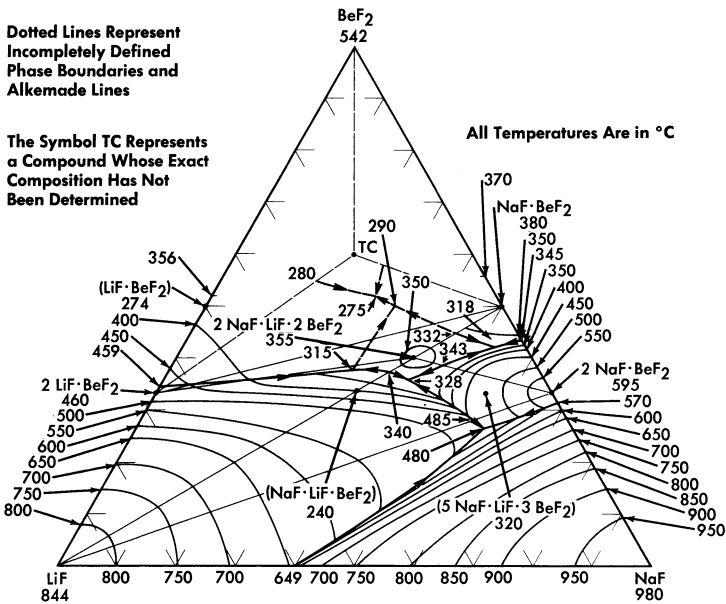


FIG. 12-5. The system LiF-NaF-BeF<sub>2</sub>.

The lowest melting binary systems are those containing BeF<sub>2</sub> and LiF or NaF. Since BeF<sub>2</sub> offers the best cross section of all the useful diluents, fuels based on these binary systems are likely to be of highest interest in thermal reactor designs.

The binary system LiF-BeF<sub>2</sub> has melting points below 500°C over the concentration range from 33 to 80 mole % BeF<sub>2</sub>. The presently accepted LiF-BeF<sub>2</sub> system diagram presented in Fig. 12-3 differs substantially from previously published diagrams [1-3]. It is characterized by a single eutectic between BeF<sub>2</sub> and 2LiF · BeF<sub>2</sub> that freezes at 356°C and contains 52 mole % BeF<sub>2</sub>. The compound 2LiF · BeF<sub>2</sub> melts incongruently to LiF and liquid at 460°C; LiF · BeF<sub>2</sub> is formed by the reaction of solid BeF<sub>2</sub> and solid 2LiF · BeF<sub>2</sub> below 274°C.

The diagram of the NaF-BeF<sub>2</sub> system (Fig. 12-4) is similar to that of the LiF-BeF<sub>2</sub> system. The ternary system combining both NaF and LiF with BeF<sub>2</sub>, shown in Fig. 12-5, offers a wide variety of low-melting compositions. Some of these are potentially useful as low-melting heat-transfer liquids, as well as for reactor fuels.

TABLE 12-3  
MELTING POINTS, HEAT CAPACITIES, AND EQUATIONS FOR DENSITY  
AND VISCOSITY OF FUEL BEARING SALTS

Composition, mole %	Melting point, °C	Liquid density, g/cc $\rho = A - BT(^{\circ}\text{C})$		Heat capacity at 700°C, cal/gram	Viscosity, centipoise		
		A	B		$\eta = Ae^B/T(^{\circ}\text{K})$	At 600°C	
						A	B
LiF-BeF <sub>2</sub> -UF <sub>4</sub> (67-30.5-2.5)	464	2.38	40	0.57			8.4
NaF-BeF <sub>2</sub> -UF <sub>4</sub> (55.5-42-2.5)	400	2.50	43	0.46			10.5
NaF-ZrF <sub>4</sub> -UF <sub>4</sub> (50-46-4)	520	3.93	93	0.26	0.0981	3895	8.5

TABLE 12-4  
THERMAL CONDUCTIVITY OF TYPICAL FLUORIDE FUELS

Composition, mole %	Thermal conductivity, Btu/(hr)(ft)(°F)	
	Solid	Liquid
LiF-NaF-KF-UF <sub>4</sub> (44.5-10.9-43.5-1.1)	2.0	2.3
NaF-ZrF <sub>4</sub> -UF <sub>4</sub> (50-46-4)	0.5	1.3
NaF-ZrF <sub>4</sub> -UF <sub>4</sub> (53.5-40-6.5)		1.2
NaF-KF-UF <sub>4</sub> (46.5-26-27.5)		0.5

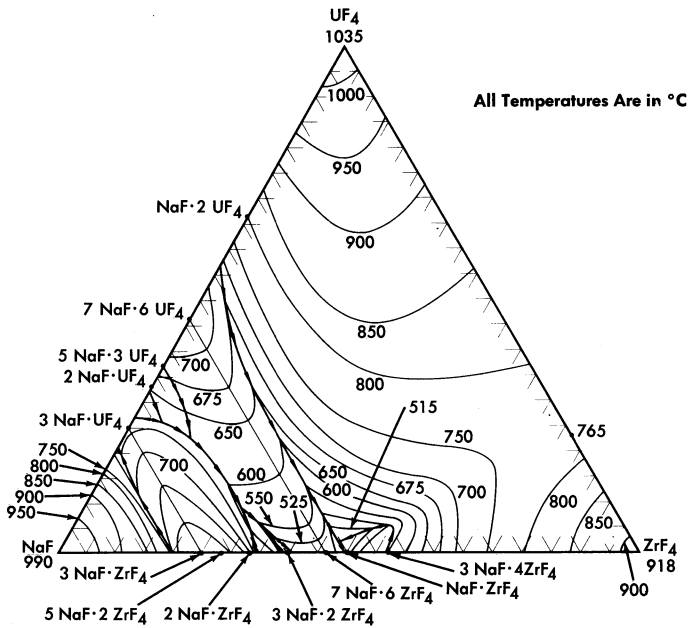
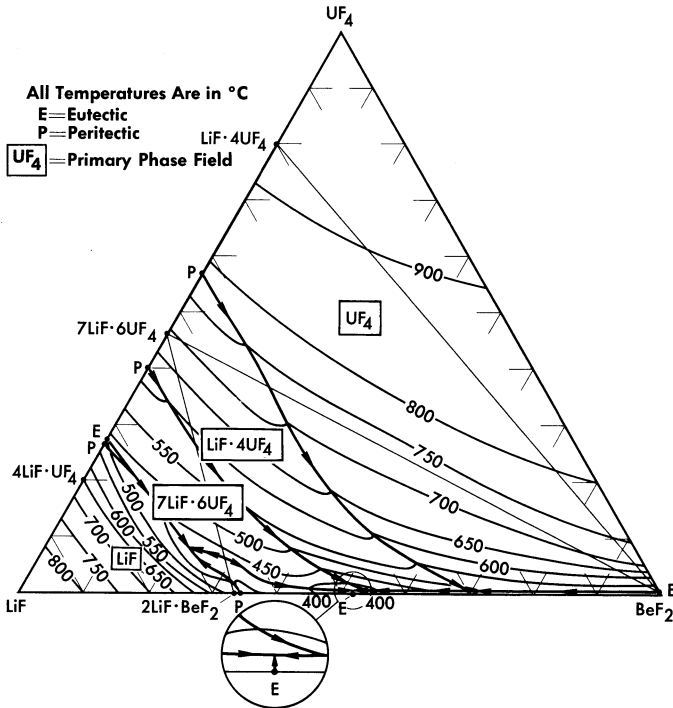
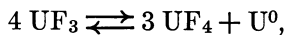


FIG. 12-6. The system NaF-ZrF<sub>4</sub>-UF<sub>4</sub>.

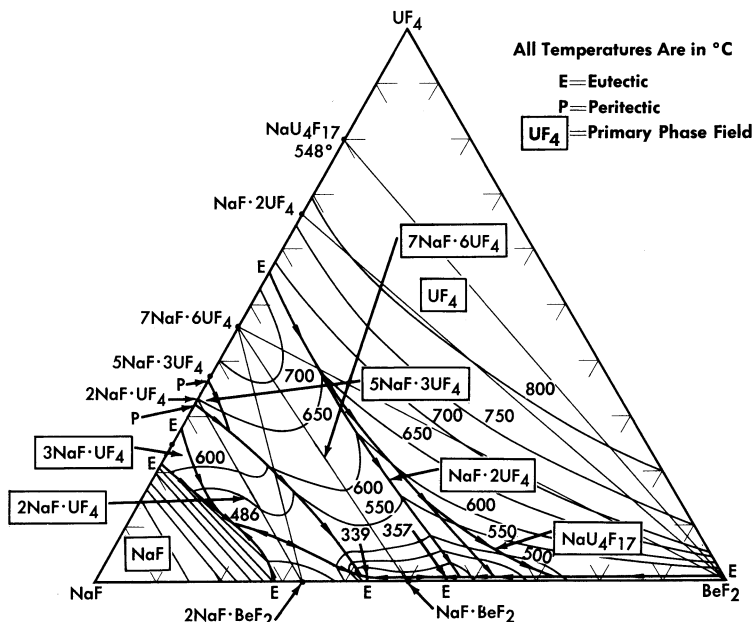
FIG. 12-7. The system LiF-BeF<sub>2</sub>-UF<sub>4</sub>.

## 12-2. FUEL AND BLANKET SOLUTIONS

**12-2.1 Choice of uranium fluoride.** Uranium hexafluoride is a highly volatile compound, and it is obviously unsuitable as a component of a liquid for use at high temperatures. The compound UO<sub>2</sub>F<sub>2</sub>, which is relatively nonvolatile, is a strong oxidant that would be very difficult to contain. Fluorides of pentavalent uranium (UF<sub>5</sub>, U<sub>2</sub>F<sub>9</sub>, etc.) are not thermally stable [4] and would be prohibitively strong oxidants even if they could be stabilized in solution. Uranium trifluoride, when pure and under an inert atmosphere, is stable even at temperatures above 1000°C [4,5]; however, it is not so stable in molten fluoride solutions [6]. It disproportionates appreciably in such media by the reaction



at temperatures below 800°C. Small amounts of UF<sub>3</sub> are permissible in the presence of relatively large concentrations of UF<sub>4</sub> and may be beneficial insofar as corrosion is concerned. It is necessary, however, to use UF<sub>4</sub> as the major uraniumiferous compound in the fuel.

FIG. 12-8. The system  $\text{NaF}-\text{BeF}_2-\text{UF}_4$ .

**12-2.2 Combination of  $\text{UF}_4$  with base salts.** The fuel for the Aircraft Reactor Experiment (Chapter 16) was a mixture of  $\text{UF}_4$  with the  $\text{NaF}-\text{ZrF}_4$  base salt. The ternary diagram for this system is shown in Fig. 12-6. The compounds  $\text{ZrF}_4$  and  $\text{UF}_4$  have very similar unit cell parameters [4] and are isomorphous. They form a continuous series of solid solutions with a minimum melting point of  $765^\circ\text{C}$  for the solution containing 23 mole %  $\text{UF}_4$ . This minimum is responsible for a broad shallow trough which penetrates the ternary diagram to about the 45 mole %  $\text{NaF}$  composition. A continuous series of solid solutions without a maximum or a minimum exists between  $\alpha\text{-}3\text{NaF}\cdot\text{UF}_4$  and  $3\text{NaF}\cdot\text{ZrF}_4$ ; in this solution series the temperature drops sharply with decreasing  $\text{ZrF}_4$  concentration. A continuous solid-solution series without a maximum or a minimum also exists between the isomorphous congruent compounds  $7\text{NaF}\cdot 6\text{UF}_4$  and  $7\text{NaF}\cdot 6\text{ZrF}_4$ ; the liquidus decreases with increasing  $\text{ZrF}_4$  content. These two solid solutions share a boundary curve over a considerable composition range. The predominance of the primary phase fields of the three solid solutions presumably accounts for the complete absence of a ternary eutectic in this complex system. The liquidus surface over the area below 8 mole %  $\text{UF}_4$  and between 60 and 40 mole %  $\text{NaF}$  is relatively flat. All fuel compositions within this region have acceptable melting points. Minor



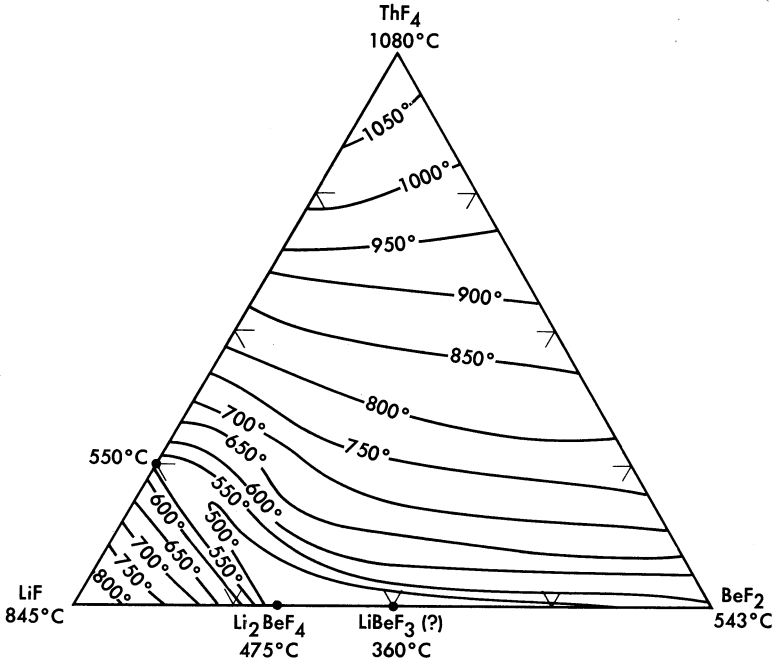


FIG. 12-9. The system LiF-BeF<sub>2</sub>-ThF<sub>4</sub>.

advantages in physical and thermal properties accrue from choosing mixtures with minimum ZrF<sub>4</sub> content in this composition range. Typical physical and thermal properties are given in Tables 12-3 and 12-4.

The nuclear studies in Chapter 14 indicate that the combination of BeF<sub>2</sub> with NaF or with LiF (provided the separated Li<sup>7</sup> isotope can be used) are more suitable as reactor fuels. The diagram of Fig. 12-7 reveals that melting temperatures below 500°C can be obtained over wide composition ranges in the three-component system LiF-BeF<sub>2</sub>-UF<sub>4</sub>. The lack of a low-melting eutectic in the NaF-UF<sub>4</sub> binary system is responsible for melting points below 500°C being available over a considerably smaller concentration interval in the NaF-BeF<sub>2</sub>-UF<sub>4</sub> system (Fig. 12-8) than in its LiF-BeF<sub>2</sub>-UF<sub>4</sub> counterpart.

The four-component system LiF-NaF-BeF<sub>2</sub>-UF<sub>4</sub> has not been completely diagrammed. It is obvious, however, from examination of Fig. 12-5 that the ternary solvent LiF-NaF-BeF<sub>2</sub> offers a wide variety of low-melting compositions; it has been established that considerable quantities (up to at least 10 mole %) of UF<sub>4</sub> can be added to this ternary system without elevation of the melting point to above 500°C.