AN INVESTIGATION OF ThF_4-FUSED SALT SOLUTIONS FOR HOMOGENEOUS BREEDER REACTORS

J. O. Blomeke

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Abstract

A consideration of the characteristics of fused salt-ThF_4 solutions suitable for use in homogeneous reactors is presented, together with a brief survey of the literature pertaining to such solutions and a summary of the experimental work accomplished.

Summary

Fused salt solutions containing thorium, primarily by virtue of their generally low vapor pressures, will probably assume a role of increasing importance as blanket and fuel solutions of high temperature power and breeder reactors. The literature offers little information on ThF_4 solutions with other salts and contains no reference to a specific solution which would be satisfactory for homogeneous reactor use. Experimental work has been initiated with a view to finding an acceptable ThF_4 solution. Binary systems of ThF_4 with LiF, MgF_2, PbF_2, AlF_3 and UF_4 have been investigated and some preliminary measurements have been made on the ternary, ThF_4-LiF-MgF_2, and the quaternary, ThF_4-LiF-MgF_2-NaF. To date, the mixtures found which are of most interest are a ThF_4-LiF binary eutectic containing 26 mole % ThF_4 and melting at 550°C, and a quaternary eutectic containing 20 mole % ThF_4, 62.3 mole % LiF, 12.7% NaF and 5% MgF_2, melting at 530°C. The concentration of Th in both of these mixtures is greater than 1000 g/liter and the ratios of the neutron capture cross section of Th-232 to the sum of the cross sections of the other constituents of the mixture are 73 in the case of the binary and 16 for the quaternary.

It is believed that a further reduction of the melting point of ThF_4 can be obtained in fluoride solutions meeting other requirements for reactor use and that the search for such solutions should be continued when the design and construction of homogeneous U-233 power-breeders comes nearer to actuality.

Introduction

Fused salt solutions for service as either reactor fuels or breeding blankets in high-temperature power or breeder reactors appear to combine many of the more desirable features of both aqueous media and liquid metal and alloy systems. They might be expected to possess the low vapor pressures characteristic of liquid metals and alloys while, at the same time, they might contain the high concentrations of fuel or breeding material expected of aqueous systems. Since the Chemical Technology Division is a group concerned primarily with the chemical processing of reactor product solutions, it was felt that some familiarity with fused salts and especially with problems likely to arise in their processing should be acquired.

A considerable effort has been underway for some time in the Materials Chemistry Division to find a UF_4-fused fluoride solution suitable for use as a fuel for the aircraft reactor of the ANP Project and a survey of the literature relative to this problem has been made.(1) Other work of this nature has been carried out at Battelle.(2) Relatively little experimental work has been done with ThF_4 in such solutions and so far as is known, no organized program of research on this subject is at present underway. Consequently, it was believed that a search for a fused fluoride solution containing Th which would be suitable for use in a U-233 breeder reactor would serve the double purpose of initiating studies along a line of great potential interest to the planning and design of future reactors and, at the same time, would serve as a starting point in the study of the chemical processing of fused salt systems in general.

Introduction (continued)

The experimental work covered by this report represents only the first step of a search for a thorium solution satisfactory for use in some future homogeneous reactor. Considerably more effort will probably be necessary before such a solution is found.

The remainder of this report is divided into three parts. The first part deals with the specifications for an acceptable thorium reactor solution; the second deals with the results of a literature survey made at one stage of the problem; and the last part is devoted to a description and discussion of the experimental work accomplished.

Thorium Reactor Solutions

Thorium-fused salt solutions could find use in either of two general applications in breeder reactors. One application is that in which the solution would be situated around and on the outside of the reactor core in the form of a so-called blanket; the second application might be in a self-moderated type of breeder in which the thorium would be present in the fuel solution together with U-233 and a moderator, e.g. beryllium.

With the assistance of R. B. Briggs of the Long Range Planning Group, several preliminary specifications, summarized in Table I, were proposed which could serve as a guide in the search for these thorium solutions. The four properties considered (cross section, Th composition, vapor pressure and melting point) do not represent either a complete or an inviolate list of the

Table I

General Requirements for Thorium Reactor Solutions

Characteristic	Blanket	Self Moderated Fuel
$\frac{\sigma_{Th\text{-}232}}{\Sigma \sigma_{other\ components}}$	≥ 10	$\gg 10$
Composition	$\geq$ 1000 g/L Th	Th = 1 atom U-233 = 0.02 atom Moderator = 100 atoms
Vapor Pressure	$<$ 760 mm at 500-800°C	$<$760 mm at 500-800°C
Melting Point	$\leq$300°C	$\leq$300°C

Thorium Reactor Solutions (continued)

specifications required; they are intended to give merely a rough picture of what, in the light of current thinking, would be desirable characteristics for an eventual thorium reactor solution to possess.

In both applications, the nuclear considerations are of paramount importance. If the specifications of Table I are accepted, it becomes apparent that one is limited to only a small number of fluorides having sufficiently low capture cross sections and favorable vapor pressures to enable them to be used in a reactor solution with thorium. These salts are listed with their neutron capture cross sections and melting points in Table II.

It is realized that of the compounds listed in Table II, ZrF_4 might prove unusable because of its tendency to sublime at temperatures of the order of several hundred degrees and BiF_3 might eventually prove troublesome because of difficulty in preventing the displacement of Bi^{+++} from the melt by many of the structural metals of which the container walls would normally be made. Other fluorides of slightly higher cross section than those listed in Table II might be considered for use but could, of course, be present only in relatively smaller concentrations.

A Literature Survey

A survey of the project and open literature was made to supplement the search made by Grimes and Hill.[1] Special emphasis was placed on phase studies of the particular salts listed in Table II. The results of this survey which

[redacted]

Table II

Cross Sections and Melting Points of Several Inorganic Fluorides

Compound	Melting Point °C	Barns**
BeF_2	800	0.03
Li^7F	845*	0.034
BiF_3	727	0.045
MgF_2	1263	0.08
PbF_2	813*	0.21
ZrF_4	872	0.22
AlF_3	1040	0.23
ThF_4	1080*	7

** The cross section of F in this table has been taken as 0.01 barns.

* The figures so marked are experimental determinations made as part of the present work.

A Literature Survey (continued)

were adjudged to be of the most interest to this problem are noted in Table III.

The ThF_4-KF and ThF_4-RbF reference was included in Table III despite the unfavorable nuclear characteristics of K and Rb because it represented the only specific reference to ThF_4 eutectic mixtures found in the literature. Zachariasen[11] has studied double salt formation in the systems NaF-ThF_4 and KF-ThF_4 by the X-ray diffraction method but he apparently did not investigate the complete phase diagrams of these systems. ThF_4 has also been found to form a very stable complex with Rb, having the formula, Rb_3ThF_7.[3]

Experimental

Apparatus

The equipment used for this work was the same as that used by other workers for thermal analysis studies of UF_4 salt mixtures.[12] In essence, it consisted of a 5-inch chromel-wound pot furnace capable of operation at temperatures up to 1100°C. The temperature of the furnace was controlled by means of a variable transformer connected in series with the A. C. supply. The salt mixtures were heated in graphite crucibles which fit into the furnace in such a manner that an atmosphere of N_2 could be maintained over the melt during heating and cooling periods. Temperatures were measured by means of a chromel-alumel thermocouple situated on the inside of a graphite stirrer which extended to the bottom of the crucible. The temperatures were measured and recorded by a Brown "Electronik" potentiometer and tests indicated that the temperatures

Table III

Some Published Phase Relationships of the Fluorides of Table II

System	Eutectic Composition Mole Percent	Eutectic Temp. °C	Reference
ThF_4-KF	17 ThF_4	664	(3)
	33 ThF_4	750	
	57 ThF_4	878	
	80 ThF_4	954	
ThF_4RbF	15 ThF_4	664	(3)
	37 ThF_4	762	
	80 ThF_4	1000	
LiF-AlF_3	14.5 AlF_3	706	(4)
	37 AlF_3	691	
LiF-AlF_3	36 AlF_3	710	(5)
LiF-MgF_2	33 MgF_2	742	(6)
LiF-MgF_2	53 MgF_2	718	(7)
LiF-BeF_2	52 BeF_2	360	(8)
LiF-MgF_2-NaF	10 MgF_2, 43 NaF	630	(6)
	29 MgF_2, 12 NaF	684	
MgF_2-BeF_2	Complete Miscibility		(9)
BiF_3-PbF_2	Complete Miscibility		(10)

so recorded were accurate to ± 5°C.

Materials

ThF_4

The thorium fluoride used was obtained from the Iowa State College. The thorium analyzed, gravimetrically, 75.1% and the fluoride, 25.5%. The theoretical Th content is 75.3%. A spectrographic analysis indicated the sample was essentially free of rare earths. The melting point of this ThF_4 was found by experiment to be 1080 ± 5°C. No reference could be found to a previous melting point determination for this compound.

AlF_3

The AlF_3 was prepared from a stock of Baker and Adamson $AlF_3 \cdot xH_2O$ by heating the hydrated material in an atmosphere of HF to about 600°C over a period of 3 to 5 hours. The vendor reported impurities in the $AlF_3 \cdot xH_2O$ amounting to less than 0.014%. The dehyrated product analyzed 32.5% Al and 67.9% F.(theoretical Al = 32.1%). The high volatility of AlF_3 in the neighborhood of 1000°C prevented an experimental determination of its melting point with the equipment on hand.

MgF_2

The MgF_2 used in this work was purchased from Eimer and Amend and was reported by them to be 99% pure. A spectrographic analysis indicated the major impurities to be Ca, Na, Cr, Fe and Ta.

PbF_2

The PbF_2 used was Baker and Adamson "Purified" material and was not

PbF_2 (continued)

analyzed chemically. The melting point was found experimentally to be 813 ± 5°C, which may be compared with a literature value of 822°C.[13]

LiF

The LiF was material purchased from the Maywood Chemical Works. No analysis of the LiF was carried out but an experimental determination of its melting point (845°C) agreed exactly with the most reliable value obtained from the literature.[14] On the basis of this agreement and its clean appearance, it is believed that this was material of high purity.

UF_4

The UF_4 used was obtained from K-25 through the ORNL SF Accountability Office.

Prior to their use in this work, all of the chemicals were dried by heating in an oven at 110-115°C for 24 hours and were stored in dessicators upon removal from the oven.

Results

ThF_4-LiF

The phase diagram for this system is given in Figure 1. A eutectic containing about 26 mole % ThF_4 is formed which melts at 550°C. Some difficulty was experienced in obtaining liquidus points from cooling curves of mixtures in the vicinity of the eutectic because of very pronounced supercooling. A compound with an incongruent melting point at about 925°C is formed at 75 mole % ThF_4.

ThF_4-MgF_2

The ThF_4-rich side of this system up to 60 mole % MgF_2 was investigated and the results are shown in Figure 2. Two eutectics were found which melted at 915° and 925°C corresponding to compositions of 25 mole % and 40 mole % ThF_4, respectively. A compound with a congruent melting point of 937° was indicated at 33 mole % MgF_2 and can be represented by the formula, $MgTh_2F_{10}$. The investigation of this binary system was not carried further than 60% MgF_2 because of the temperature limitations of the equipment but it seems probable that no further eutectics of immediate interest to this problem would be found at higher MgF_2 concentrations.

ThF_4-PbF_2

The proposed phase diagram for this system is given in Figure 3. Two eutectics were obtained, one at 35 mole % ThF_4, melting at 925° and a second at 62 mole % ThF_4 which melted at 880°C. Some indications of a third eutectic melting at about 760° and containing less than 2 mole % ThF_4 were obtained but its presence was not definitely established. Two compounds with congruent melting points at about 950° and 942°C were indicated, corresponding to the formulas $Pb_{17}Th_3F_{46}$ and $PbThF_6$, respectively. A third compound having an incongruent melting point of about 1045°C was indicated with a formula, $PbTh_9F_{38}$.

Measurements of this binary proved unsatisfactory in a sense because of a reduction of the Pb^{++} to elemental Pb by the graphite crucible and stirrer. This reduction was not observed to occur appreciably at temperatures less than 800° but became a greater problem with increasing temperature.

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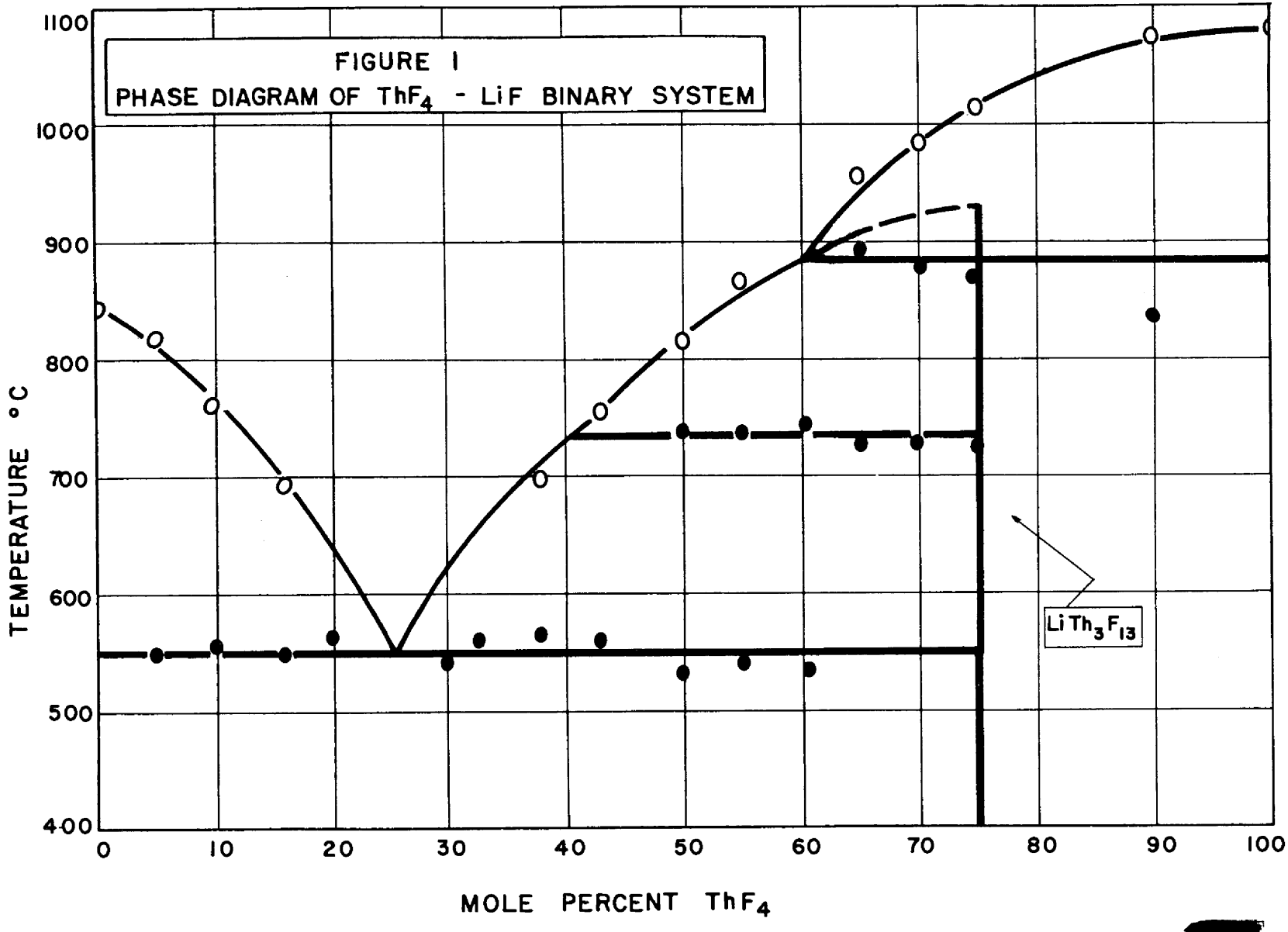
Drawing # 11461



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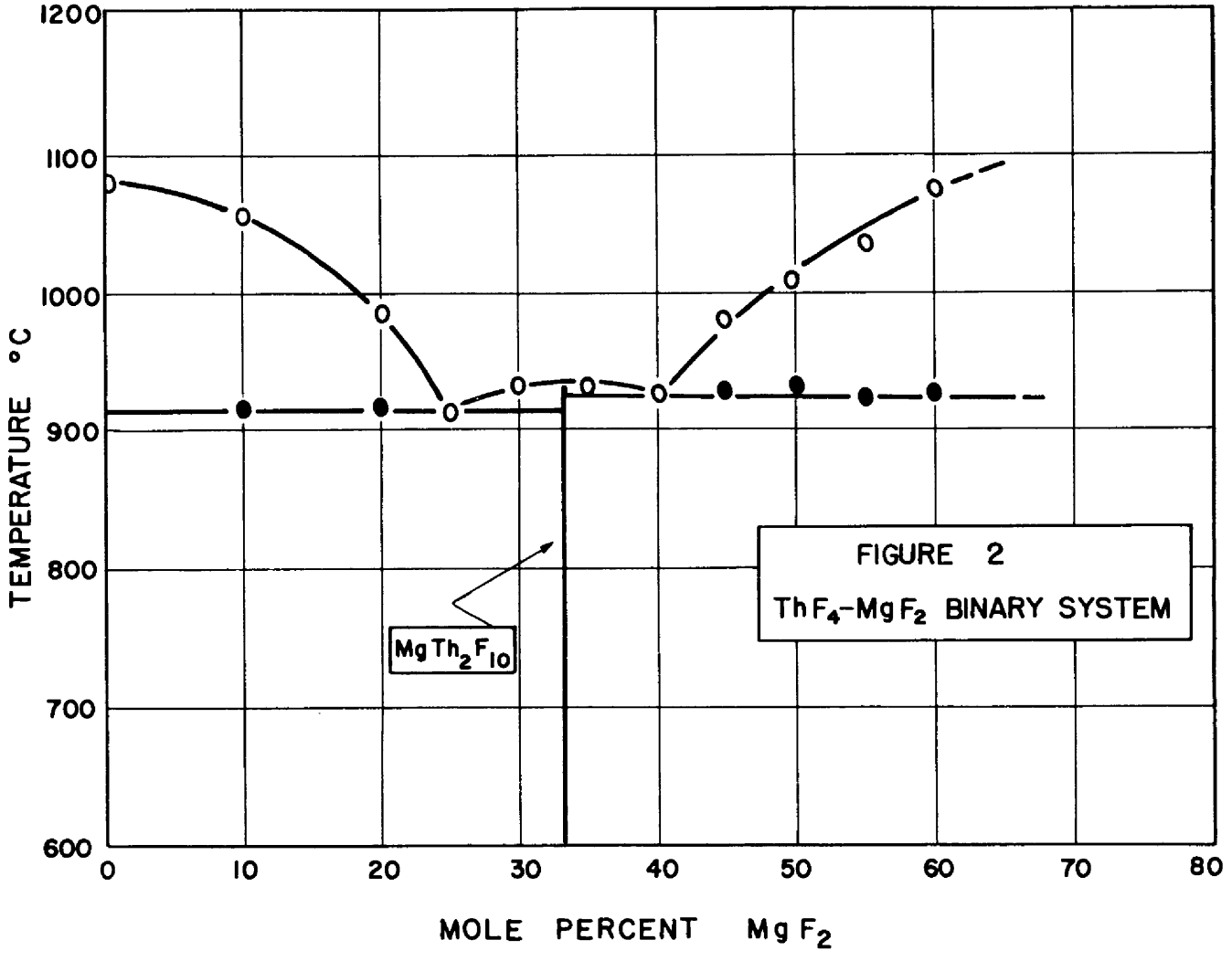

FIGURE 2

ThF_4-MgF_2 BINARY SYSTEM

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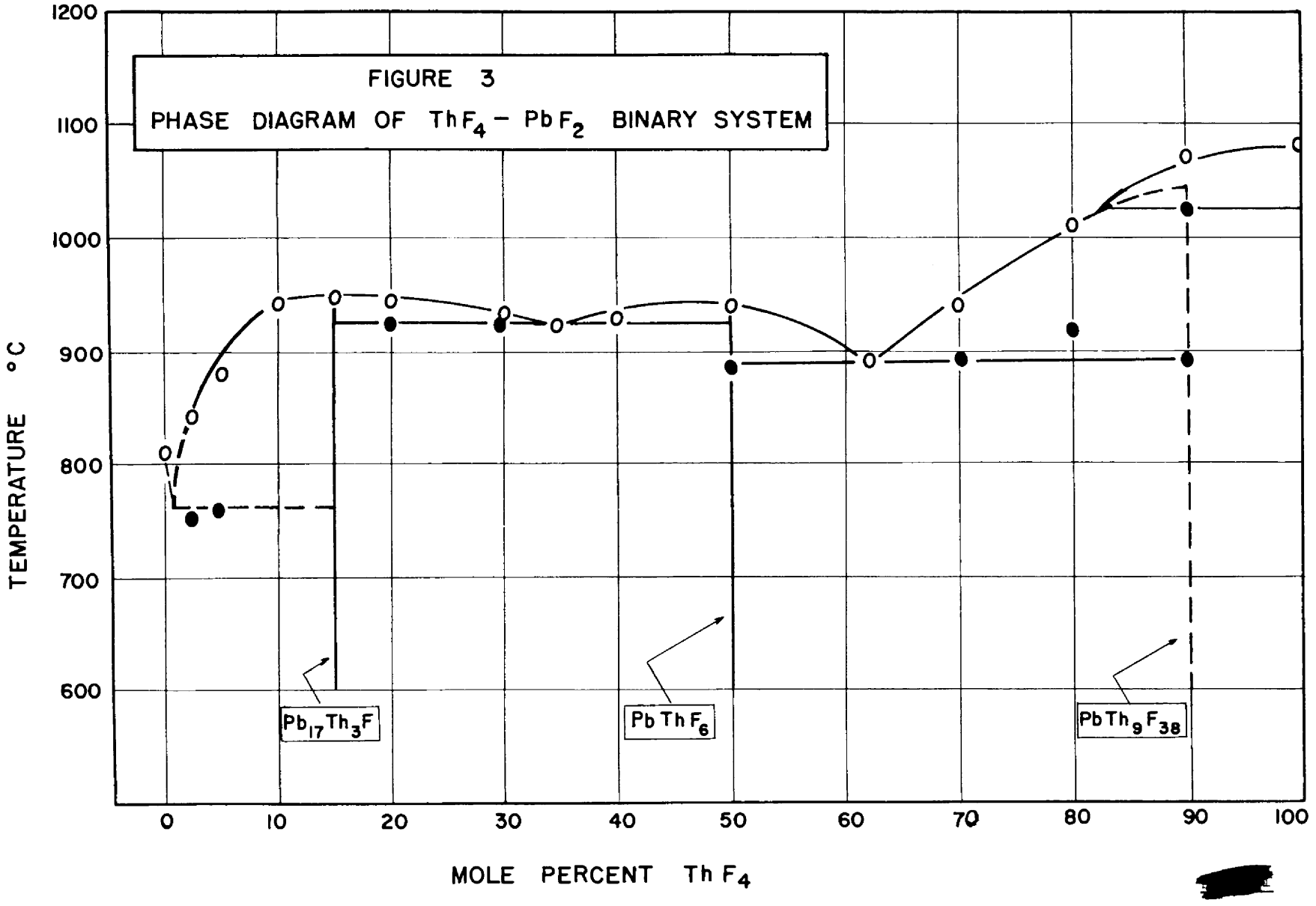

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ThF_4-AlF_3

Considerable effort was expended on this system with only moderate success. The AlF_3 sublimed at temperatures from 900 to 1100°C to such an extent that reliable results could not be obtained with mixtures containing more than 20 mole % AlF_3. A reproducible eutectic halt was obtained at about 950°C in the cooling curves of this binary system but the composition of the eutectic mixture could not be determined. It is estimated that it lay somewhere in the vicinity of 25 mole % AlF_3.

ThF_4-UF_4

The isomorphism of ThF_4 and UF_4[17] would lead one to expect them to be miscible in both the solid and liquid states. Although supercooling prevented the accurate determination by thermal analysis of a phase diagram for this system, indications were that liquidus and solidus curves existed which exhibited neither a maximum nor minimum point. X-ray analyses of several of the solidified melts showed that solid solutions were formed.

ThF_4-LiF-MgF_2

This was the only ternary system investigated to any appreciable extent and it was studied in only an exploratory manner. An indication of a ternary eutectic of high ThF_4 content melting at 690° was obtained but since this temperature was greatly in excess of the desired melting point, no formal attempt was made to establish the composition.

ThF_4-LiF-NaF-MgF_2

A reference found in the literaature to the NaF-LiF-MgF_2 eutectics[3]

ThF_4-LiF-NaF-MgF_2 (continued)

seemed worthy of further investigation, especially the secondary eutectic containing only 12% NaF. Experiments were carried out which consisted, at first, of adding ThF_4 to the 29% MgF_2, 12% NaF, 59% LiF eutectic mixture and finally, of changing the concentrations of the other components empirically. In this way, a quaternary eutectic was obtained which melted at 530°C. The approximate composition of this eutectic, expressed in mole percentages was:

20.0%	ThF_4
62.3	LiF
12.7	NaF
5.0	MgF_2

UF_4-LiF-NaF-MgF_2

Proceeding along the same lines as described above for the case of the ThF_4 quaternary mixture, a eutectic was found in this system which melted at about 460°C. Its approximate composition was:

25.0%	UF_4
58.2	LiF
11.8	NaF
5.0	MgF_2

Discussion

Of the systems studied, two eutectic mixtures stand out in the respect that their melting points are both more than 100° under the next lowest melting mixture found. The eutectics referred to are the ThF_4-LiF binary eutectic, containing 26 mole % ThF_4 and melting at 550° and the ThF_4-LiF-NaF-MgF_2 quaternary, containing 20 mole % ThF_4 and melting at 530°C. The concentration of Th

[redacted]

Discussion (continued)

in these eutectics corresponds to about 2000 g/L in the binary and 1500 g/L in the quaternary. The neutron capture cross section ratios (Table I) are 73 and 16, respectively and the vapor pressures at 800°C were, by observation, much less than 760 mm. On the other hand, the melting points are still considerably higher than the 300°C taken as the maximum desirable melting point.

The ThF_4-PbF_2, ThF_4-MgF_2 and ThF_4-AlF_3 binary systems show no eutectic of sufficiently low melting point to be of immediate interest to this problem. Their principle value lies in the contribution they would make to a study of ternary systems containing these components. From the same viewpoint, binary systems of ThF_4 with BeF_2, BiF_3 and ZrF_4 should be investigated.

The UF_4-LiF-NaF-MgF_2 quaternary eutectic is similar in both melting point and uranium concentration to a UF_4-LiF-NaF ternary eutectic reported previously as being under consideration as a fuel for the ANP reactor.[15] Although indications are that the unavailability of Li^7 isotope will preclude, for the time being, the use of a LiF constituted fuel in this reactor, it should be pointed out that, other factors being equal, the better neutron economy of this quaternary would likely make it more acceptable than the ternary eutectic.

The similarity between the diagram found for the ThF_4-LiF system and that obtained by Grimes, et. al.[12] for UF_4-LiF is rather remarkable. A UF_4-LiF eutectic melting at 480°C was found at about 26 mole % UF_4 and likewise a compound, LiU_3F_{13}, with an incongruent melting point was obtained. The same investigators[16] have found a eutectic in the UF_4-PbF_2 system at 62 mole % UF_4

[redacted]

Discussion (continued)

which melts at about 730° and have obtained a diagram for the UF_4-PbF_2 system which conforms in most principle respects to the character of the diagram presented in Figure 3. No attempt was made to rigorously define the extent of the similarity between ThF_4 and UF_4 systems but from indications obtained in this investigation, a close coordination between the work done on these two general systems should be maintained.

From the results obtained thus far in this work, the possibility seems rather remote that a mixture meeting all the specifications set for this problem will be found. On the other hand, there appears to be a very real likelihood that mixtures which come nearer meeting them than anything so far found can be obtained and such mixtures might eventually prove as satisfactory for reactor use as the "ideal" one considered here. The work done to date can be considered as no more than a start on such a search and whenever the importance of this problem is adjudged more immediate, a thorough and more nearly complete solution to the problem should be allowed.

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