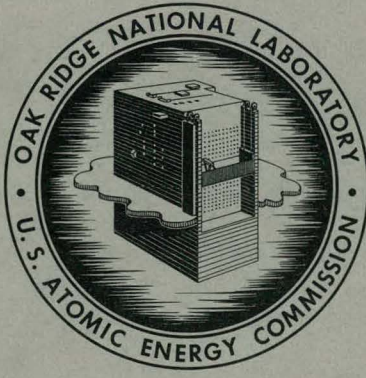ORNL-3594
UC-4 – Chemistry
TID-4500 (31st ed.)

MOLTEN-SALT SOLVENTS FOR FLUORIDE VOLATILITY PROCESSING OF ALUMINUM-MATRIX NUCLEAR FUEL ELEMENTS

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Contract No. W-7405-eng-26

Reactor Chemistry Division

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AUGUST 1964

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OF ALUMINUM-MATRIX NUCLEAR FUEL ELEMENTS

R. E. Thoma, B. J. Sturm, E. H. Guinn

ABSTRACT

The results of a search for molten-salt solvents for use in fluoride volatility processing of aluminum-matrix fuel elements are presented. The solubility of aluminum fluoride in various mixtures of fluorides was determined in order to estimate the feasibility and cost of processing methods. Sufficient data were accumulated to construct equilibrium phase diagrams of the solution systems, $LiF-NaF-AlF_3$, $LiF-KF-AlF_3$, $LiF-K_3AlF_6-MF_2$ (where MF_2 is CaF_2, SrF_2, or ZnF_2), and $KF-ZrF_4-AlF_3$. New and revised phase diagrams were determined for the limiting binary systems of the alkali fluorides with AlF_3 by use of a new visual method for determining the occurrence of liquidus transitions. This method provided several advantages not available in classical methods of obtaining liquidus data. For example, it was observed for the first time that immiscible liquids are formed at high temperatures in AlF_3-based systems. The temperatures at which such liquids form are, however, higher than is feasible for adoption in most current chemical technologies. Of the various materials evaluated as solvents for the volatility process, the greatest potential for application was displayed by the $KF-ZrF_4-AlF_3$ system. High solubility and good dissolution rates are afforded by the inexpensive solvent salt K_2ZrF_6. At operating temperatures, approximately 600°C, the AlF_3 capacity of the solvent is in excess of 25 mole %.

INTRODUCTION

Development of the fluoride volatility process is sought as a useful and effective alternative to conventional aqueous processing for recovery of uranium from spent nuclear fuels. The process depends on dissolving fuel elements in a suitable molten fluoride solvent by passage of HF gas followed by fluorination of the resulting melt to volatilize uranium as UF_6.[1] The UF_6 is purified by selective sorption on solid NaF or other

fluorides. Molten-salt fluoride volatility processing of nuclear fuels offers advantages not available with other chemical reprocessing methods: (1) the process is simple,[2] requiring only a hydrofluorination step and a fluorination step instead of the many steps--dejacketing, acid dissolution, precipitation, filtration,[3-5] etc.--characteristic of the usual aqueous procedures; (2) the uranium is recovered as UF_6, the form required for isotope separation,[6] and (3) disposal is made of essentially all fission products as water-insoluble solids. It is also one of the few methods that can be used for processing certain ceramic fuels.[7]

The process has been previously applied successfully to zirconium-matrix fuels.[1,8,9] Currently, it is considered for aluminum-matrix fuels because of their use in numerous reactors[10,11] and because of the need anticipated for processing large quantities of these fuels.

One of the most important aspects of volatility process development in adapting the process to a particular kind of fuel element is the selection of a suitable molten-salt solvent into which to pass the HF gas during dissolution. A preliminary survey of prospective AlF_3 solvents reported by Boles and Thoma[12] showed that a BeF_2-LiF solvent provides moderately good solubility for AlF_3, but, because of expense and toxicity, an alternative solvent system is preferred. They considered KF-ZrF_4 solvents to be of potential use. The preliminary data obtained at that time were too limited for a critical selection of optimal solvents for use in volatility processing. Accordingly, a more intensive search for solvents was initiated using newer methods which permit rapid accumulation of large numbers of liquid-solid transition data.

Desirable characteristics of the solvent for the process include the following:

1. Low cost.
2. Liquidus temperatures below 600°C.
3. Substantial solubility of AlF_3 at 500 to 600°C.
4. Low vapor pressure.
5. Low viscosity.
6. Noncorrosive with respect to the INOR-8 container.

In reprocessing aluminum-matrix fuel elements, the temperature must be kept below the melting point of aluminum (600°C)[13] to avoid forming liquid metal, which is corrosive to the container alloy, INOR-8. The susceptibility of INOR-8 to corrosion by liquid aluminum is offset by its excellent structural properties at high temperatures and its resistance to corrosion by fluorine and HF. It is desirable to prevent the maximum operating temperature from exceeding a limit of at least 50°C lower than the melting point of aluminum; consequently, 600°C has been tentatively chosen as the maximum temperature for the process. The economic feasibility of the process is highly dependent upon the cost of the solvent. Solvents in which the saturating concentrations for AlF_3 are as low as 8 mole % may be useful if the solvent costs less than 50 cents a pound. If, however, higher-priced solvent components are required in order to obtain the desirable solvent characteristics, the economic feasibility of the process may then require higher saturating concentrations of AlF_3.

Choice of Constituent Fluorides as AlF_3 Solvents

The choice of possible solvent constituents can be rapidly narrowed to one group: cheap fluorides which are stable in the presence of gaseous HF and fluorine. Cationic constituents should either have only one valence state as the fluoride, or both the lower fluoride, existing during dissolution, and the higher fluoride, formed during fluorination, should be noncorrosive, possess sufficiently low vapor pressure, and have suitable melting characteristics for use in the solvent.

Previous to the ORNL work on the volatility process there was little published information concerning the attack of aluminum metal by molten fluorides, and none regarding the relationship of HF or other dissolved oxidant gases to this attack. It is known that aluminum reacts with molten alkali metal fluorides and with molten cryolite to form free alkali metal and the appropriate fluoroaluminate.[14] The metal also reacts with molten K_2ThF_6, forming a Th-Al alloy and a potassium fluoroaluminate. Aluminum metal reacts with solid CeF_3 at 1000°C to form cerium metal and AlF_3. With K_2TiF_6, aluminum reacts to form K_2AlF_6, free titanium metal, and an opaque phase believed to be a complex of TiF_3.[15] Published free-energy values[16] favor the formation of TiF_3 by the reaction:

$$Al + 3TiF_4 \rightleftharpoons 3TiF_3 + AlF_3 \ .$$
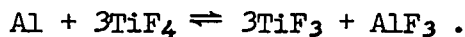
The free-energy values suggest that the alkali metal fluorides ThF_4, CeF_3, AlF_3, and TiF_4 may serve as potential solvent constituents. Molten SnF_2 and NH_4HF_2 both attack aluminum metal[17-19] but have disadvantages which preclude their use as potential volatility solvents. The former is very corrosive to structural metals;[20] the latter presents a vapor problem and decomposes during fluorination. Aluminum reacts vigorously when heated with fluorides of Ni, Co, Fe, or Os.[14] Aluminum reacts with molten alkali metal fluoroborates and fluorosilicates to form, respectively, aluminum boride and silicon or silicides. The use of fluoroborates and fluorosilicates in the volatility process presumably should be avoided because borides and silicides are so inert that they are likely to remain in the processing solvent in the form of an annoying sludge.

Relatively few fluorides possess the properties required for their use as major constituents of a solvent. Fluorides of nonmetals, semimetals, inert gases, and the platinum metals either have too high a vapor pressure or are too corrosive to be considered. (See Table 1 for boiling points.) These objections apply as well to fluorides of Cu, Mo, Ag, W, Au, Hg, Nb, Ta, V, Cr, Mn, Co, Tl, Pb, and Sn. Scarcity would eliminate consideration of most rare earths, all transuranium elements, also Sc, Y, Re, Hf, Tc, Fr, Ra, Ac, and Pa. Fluorides of Zn, Ga, In, and Cd do not qualify because their reduction by aluminum would form corrosive liquid metal. Uranium fluoride of natural isotopic composition is objectionable because its use would alter the isotopic composition of the fuel being processed. Thus the list of possible solvent constituents is therefore narrowed to the following fluorides:

LiF	BeF_2	AlF_3	TiF_4	FeF_2
NaF	MgF_2	LaF_3	ZrF_4	NiF_2
KF	CaF_2	CeF_3	ThF_4	
RbF	SrF_2			
CsF	BaF_2			

Most of the fluorides in this group are suitable only as minor constituents of the solvent for the following reasons:

1. RbF, CsF, LaF_3, and ThF_4 are moderately expensive.

2. FeF_2 and NiF_2 in high concentrations may present corrosion problems during fluorination.

3. MgF_2, CaF_2, SrF_2, BaF_2, and CeF_3 have very high melting points (see Table 1).

4. TiF_4 in high concentrations may exert somewhat excessive vapor pressure.

These compounds were, therefore, considered not as major solvent constituents but merely as possible additives for possibly depressing the liquidus of a promising solvent. The remaining six compounds--LiF, NaF, KF, BeF_2, AlF_3, and ZrF_4--were given the principal consideration as solvent components.

Survey of Potential Solvent Systems

Except for BeF_2, which is too viscous, none of the promising fluoride constituents individually has the necessary low melting point (below 600°C) to be used directly as the solvent (see Table 1). A number of binary mixtures of these fluorides do, however, form adequately low melting eutectics (see Table 2). The only AlF_3 binary system which provides sufficiently low melting mixtures for possible use in the process is the KF-AlF_3 system; its capacity for additional AlF_3 at the process temperature is, however, limited to about 5 mole %, too low for process use.

In order to find low-melting solvent systems suitable for the process, phase relationships were studied in the ternary systems formed by dissolving AlF_3 in a molten binary solvent. Little concern was given to more complex solvent systems because the study of polycomponent systems delineating the phase reactions occurring as AlF_3 dissolves in such solvents is too involved to permit adequate characterization in a reasonable length of time. In addition, the probability of diagnosing the cause of off-performance difficulties in engineering tests by identification of crystallized solids is remote for multicomponent salt systems unless detailed investigation of the phase behavior has been made. Accordingly, when a fourth component was considered, it was usually only as a minor addition to a promising ternary system, e.g., A-B-AlF_3, included in order to lower the liquidus temperatures enough to meet process requirements. Although the fluoride volatility process is intended for reprocessing

fuels containing both uranium and aluminum, consideration was given only to the solubility of the resulting AlF_3 in evaluating a solvent. The uranium content of these fuels, generally less than 1 at. %, yields too low a UF_4 concentration in the solvent to affect the liquidus temperature significantly.

PROCEDURES

The initial phase studies[12,21] of the solvent systems were performed primarily by classical procedures which proved to be generally inadequate for systems containing AlF_3. Because AlF_3 and alkali metal fluoroalumi- nates are frequently not microscopically distinguishable from each other, these systems were not amenable to studies employing the quenching tech- nique. Also, the thermal change at the liquidus temperature was often too small to be readily detected by thermal analysis. Even when a thermal change was detected, its interpretation, without visual observation or accompanying quench data, was equivocal.

Most of these difficulties were overcome by melting the mixtures in an inert-atmosphere glove box (Figs. 1 and 2) and observing phase changes through a window. Liquidus temperatures were determined accurately (usu- ally ± 2°C) by noting the temperature at which the first crystals were observed in a cooling melt. The melts were stirred manually to prevent supercooling and to ensure uniformity of composition and temperature. Usually about a mole of salt contained in a hydrogen-fired, polished nickel crucible was used for the study. Intense illumination was provided by a Zirconarc photomicrographic lamp (Fish-Schurman Corporation, New York). The light from this instrument overrides the near infrared background radiation from the melt to temperatures of about 1200°C and thus facili- tates determination of liquidus under conditions where other methods would be difficult or impossible. Atmosphere control was obtained by evacuating the glove box to 30 μ and refilling with helium purified by passage through activated charcoal cooled with liquid nitrogen. The procedure is rapid. As many as sixteen compositions in a given system can be studied in an 8-hr period by sequential additions of preweighed specimens. Since the

melt may be observed as phase changes occur, the apparatus is also useful
for obtaining interpretable thermal analysis data. To ensure accuracy,
the temperature recorder was periodically standardized against LiF melt-
ing at 848 ± 1°C.[22-24]

The precision of temperature measurements obtainable in routine use
of Chromel-Alumel thermocouples is generally believed to be ±5°C. Occa-
sional calibrations with pure salts have shown that the accuracy of thermal
transition temperatures reported here is within the ±5°C precision limits.
Correspondingly, the accuracy of visual transition data reported here is
within ±3°C.

A similar visual procedure called "visual polythermal method" has
been used by Russian investigators,[25] but their procedure seems inferior
to that used here in that it apparently does not permit (1) agitation of
the observed melt, (2) addition of salt during the run to alter the com-
position, or (3) use of vacuum to control the atmosphere.

A sharp increase in viscosity is often displayed by molten salts as
they cool to temperatures approaching the liquidus. This effect was noted
in most of the systems discussed in this report and was useful in signal-
ing the onset of crystallization. Such a sharp change in viscosity has
been observed also by Velyukov and Sipriya[26] for Na_3AlF_6 and Li_3AlF_6 and
by Ellis[27] for $ZnCl_2$. A sharp change in the electrical conductance at
phase-trnasition temperatures was also noted. Preliminary measurement of
electrical conductance using an ohmmeter (Model 630, Triplett Electrical
Instrument Company, Bluffton, Ohio) indicated that it may also provide a
procedure useful for studying AlF_3 systems.

MATERIALS

Purity of the fluorides used in the phase studies was very important.
The molten-salt systems were studied primarily by a visual procedure which,
in determination of a liquidus temperature, depended on the appearance of
precipitate, often in such a form that it clouded the melt. Accordingly,
any impurity which clouded the melt interfered with the study. Because
they reacted to form very sparingly soluble phases, hydroxides and water

vapor proved to be especially objectionable and in some cases initially very difficult to remove or avoid in the preparation of these fluorides. Hydroxides and moisture were additionally objectionable because they attacked the metal container, contaminating the melt with highly colored nickel ion. Often such melts gave rise to irreproducible liquidus temperatures due, presumably, to a progressive increase in oxide concentration as the hydroxide reacted.

Three methods were found to be useful for preparing fluorides of low oxygen content:

1. Vacuum sublimation: Applicable to purifying commercial AlF_3 and ZrF_4, as the corresponding oxides have extremely low volatility. ZrF_4 was obtained with as little as 250 ppm oxygen using the apparatus shown in Fig. 3.

2. Vacuum distillation after precipitation of oxide: Applicable to KF. The vapor pressure of KOH at 850 to 1000°C is high enough to preclude reduction of oxygen impurity to less than 1200 to 1500 ppm by distillation. However, in molten potassium fluoride, KOH reacts with various metal fluorides to precipitate metal oxides as follows:

$$2MF_x + xKOH \rightarrow 2MO_{x/2}\downarrow + xHF\uparrow\ xKF\ ,$$
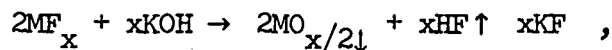
and purification of KF is possible by vacuum distillation from the remaining molten mixture. The use of FeF_2 and FeF_3 to precipitate oxide produced crystals of KF which contained 900 ppm oxygen; the use of 2.3 mole % UF_4 gave a product containing only 500 ppm.

3. Ammonium bifluoride fusion: Fusion of alkali metal fluorides with hydrated AlF_3 in the presence of molten NH_4HF_2 proved to be useful for preparing Li_3AlF_6, Na_3AlF_6, K_3AlF_6, $KAlF_4$, and Cs_3AlF_6. Slow cooling of the melts to promote crystal growth and selection of the better-crystallized portion served to provide additional purification. Fusion of NH_4HF_2 with hydrated AlF_3 formed $(NH_4)_3AlF_6$. Its thermal decomposition at 600°C in a helium stream yielded anhydrous AlF_3 which was comparable in purity to the sublimed product. Alkaline earth fluorides were also purified by NH_4HF_2 treatment.

RESULTS AND DISCUSSION

In the search for high-capacity solvent systems for use in the fluoride volatility process, equilibrium solubility data for aluminum fluoride in seven fluoride systems were obtained. The systems examined included $LiF-KF-AlF_3$, $K_3AlF_6-LiF-CaF_2$, $K_3AlF_6-LiF-SrF_2$, $K_3AlF_6-LiF-ZnF_2$, $LiF-NaF-AlF_3$, $NaF-KF-AlF_3$, and $KF-ZrF_4-AlF_3$. The phase diagrams constructed from the data obtained in these examinations show that only one of these systems, $KF-ZrF_4-AlF_3$, can be expected to have practical application as a solvent. New data were obtained for the limiting binary systems $LiF-AlF_3$, $NaF-AlF_3$, $KF-AlF_3$, and $KF-ZrF_4$. New phase diagrams of each of these systems are shown in Figs. 8 to 11. Experimental data for the systems reported here were collected simultaneously for several systems, thus making it possible to curtail the efforts on any one system as the development in another system showed promise.

AlF_3 Melting Point

Previously reported experimental values for the melting point of AlF_3 range from 986[12] to 1040°C.[28] All of our visual observation data indicate that these values are low and that the melting point is higher than the reported sublimation temperature, 1270°C,[29] though not as high (1920°C) as was regarded by Steunenberg and Vogel.[30] Because high liquidus temperatures and vapor pressures prevented visual study of mixtures containing over 56 mole % AlF_3, too little data were obtained to permit a good extrapolation of its melting point. Since AlF_3 is of similar structure to CrF_3[31] and of comparable size relationship,[32] we surmise that its equilibrium melting point at 1 atm is close to that for CrF_3, 1404°C.

Systems Based on LiF-KF

Mixtures of the lightest alkali fluorides, LiF, NaF, and KF, are not so low melting as those obtainable with RbF or CsF; the cost of these latter two materials, however, precludes their economic use in process development. The binary mixture of the cheaper fluorides which affords the lowest-melting

solvent is the equimolar LiF-KF eutectic mixture which melts at 500°C (see Fig. 4). The phase diagram of the system LiF-KF-AlF$_3$, constructed on the basis of the data shown in Table 3, is given in Fig. 5. Invariant equilibria are listed in Table 4. The diagram shows clearly that LiF-KF mixtures cannot provide useful solvents because of the extent to which the primary phase fields of the high-melting compounds K$_3$AlF$_6$ and K$_2$LiAlF$_6$ approach the limiting binary system LiF-AlF$_3$. The ternary system is comprised of the subsystems KF-LiF-K$_3$AlF$_6$, K$_3$AlF$_6$-Li$_3$AlF$_6$-LiF, and K$_3$AlF$_6$-Li$_3$AlF$_3$. Both of the composition sections K$_3$AlF$_6$-Li$_3$AlF$_6$ and K$_3$AlF$_6$-LiF are apparently quasi-binary. The minimum liquidus temperature along the composition section K$_3$AlF$_6$-LiF is 720°C; along the section K$_3$AlF$_6$-Li$_3$AlF$_6$ it is 645°C. The high liquidus profile for the system LiF-KF-AlF$_3$ excludes LiF-KF mixtures from possible use as a solvent. The possibility that the liquidus for some inexpensive four-component combinations might be significantly lower than for LiF-KF-AlF$_3$ gave impetus to an investigation of the effect of the additives CaF$_2$, SrF$_2$, and ZnF$_2$. Accordingly, an investigation was made of the extent to which some of the Group II fluorides depressed the ternary liquidus. Results of these experiments are given in Tables 5 to 7. The minor benefits of adding these components to the ternary mixtures were insufficient to suggest that extensive investigation of the multicomponent systems was practical.

At AlF$_3$ concentrations above 50 mole % in the LiF-KF-AlF$_3$ system we observed immiscible liquids. Their phase relationships are not yet adequately explained; either two true (i.e., isotropic) liquids or one true liquid and one liquid crystalline phase (mesophase[33,34]) could be present.

The System LiF-NaF-AlF$_3$

An examination was made of the liquidus surface of the LiF-NaF-AlF$_3$ system at AlF$_3$ concentrations between 0 and 35 mole %. As in the LiF-KF-AlF$_3$ system, the composition area at which liquidus temperatures are below 600°C is much too small for the system to be of practical value in the volatility process. The phase diagram, shown in Fig. 6, is dominated by the cryolite phase Na$_3$AlF$_6$, which crystallizes from LiF-NaF-AlF$_3$ liquids as a high-melting phase for much of the lower AlF$_3$ part of the system. Data obtained for the system are given in Table 8.

The System NaF-KF-AlF$_3$

Preliminary investigation of the system NaF-KF-AlF$_3$ made by Barton et al.[35] indicated that aluminum fluoride solubility was negligible in NaF-KF mixtures except at temperatures above the NaF-KF eutectic. This inference was corroborated by additional experiments conducted as part of the present investigation.

The System KF-ZrF$_4$-AlF$_3$

Binary systems of the alkali fluorides with ZrF$_4$ afford low-melting solvent mixtures for the heavy-metal fluorides UF$_4$ and ThF$_4$ and can be expected to provide useful solvents for AlF$_3$ as well. Other solvents would be preferred because of the high cost of ZrF$_4$ and because of the volatility of ZrF$_4$-rich liquids at high temperatures. Nevertheless, the liquidus temperatures at concentrations of 35 to 45 mole % ZrF$_4$ in the KF-ZrF$_4$ system and the availability of K$_2$ZrF$_6$ as an inexpensive reagent suggested the use of the reagent in the preliminary evaluation of the aluminum solvent systems.[12] The experimental data obtained in this investigation are shown in Table 9. The phase diagram of the system is shown in Fig. 7. Crystallization reactions within the system KF-ZrF$_4$-AlF$_3$ have been characterized in detail except for those involving AlF$_3$ and ZrF$_4$. Both of these components are high melting and volatile. Their phase reactions are extremely difficult to examine at high temperatures because of this volatility and their low heat of fusion, which preclude most dynamic methods for obtaining phase data. Their crystallization reactions in the ternary mixtures suggest that the only interaction occurring between them at high temperatures is the formation of a eutectic. For these reasons, we have omitted investigation of the limiting binary system AlF$_3$-ZrF$_4$. At 600°C, the maximum acceptable temperature for the process, a solvent, KF-ZrF$_4$ (63-37 mole %), was found to have 15 mole % AlF$_3$ capacity. Liquidus temperatures in the binary system KF-ZrF$_4$ exclude the use of solvents richer in KF. It can be seen from the phase diagram of the system KF-ZrF$_4$-AlF$_3$ (Fig. 7), constructed in this study, that by a single addition of KF after partial dissolution of the fuel element the solubility of AlF$_3$ is increased from 15 to 26 mole %.

Two immiscible liquids or a liquid and a liquid crystalline phase were found in the KF-AlF$_3$ binary system above 53 mole % AlF$_3$ at 980°C. The two-liquid region apparently extends into the KF-AlF$_3$-ZrF$_4$ ternary system but not to compositions currently of interest as volatility solvents.

CONCLUSIONS

The results of the investigations reported here together with the results of dissolution rate and corrosion rate tests made by Chemical Technology Division personnel indicate conclusively that the system KF-ZrF$_4$-AlF$_3$ is uniquely applicable for reprocessing aluminum-matrix reactor fuels. They also show that the essential criteria necessarily imposed in selecting a solvent system, i.e., maximum equilibrium solubility, maximum rates of dissolution, minimal rates of container vessel corrosion, and minimum solvent costs, are not met (competitively) by any of the other systems considered in preliminary or current studies. Accordingly, more complete data have been obtained for the system KF-ZrF$_4$-AlF$_3$ than for any of the other systems reported here. It was observed for the first time that immiscible liquids are formed at high temperatures in AlF$_3$-based systems. The temperatures at which such liquids form are, however, higher than is feasible for adoption in most current chemical technologies.

On evaluating the merits of possible AlF$_3$ solvent mixtures with respect to phase, corrosion, and cost data, the binary mixture KF-ZrF$_4$ (63-37 mole %) was found to satisfy best the composite criteria. On the basis of this evaluation, this mixture is recommended by Reactor Chemistry and Chemical Technology Division personnel as the most satisfactory solvent for dissolution of aluminum-based materials in the fluoride volatility process.

Table 1. Fluoride Transition Temperature and Free Energy
of Formation

Compound	Melting Point[a] (°C)	Boiling Point[b,c] (°C)	$-\Delta F_f$, 298°K (kcal/mole)[c]
HF	-83.36	19.46	64.7
LiF	848.0[a]	1681.0	138.8
BeF$_2$	545.0[a]	1159.0	207.5
BF$_3$	-128.7[a]	-99.9	269.5
CF$_4$			151.9
NaF	996.0[a]	1704.0	129.0
MgF$_2$	1263.0[a]	2260.0	250.8
AlF$_3$		1273.0[d]	306.0
SiF$_4$	-90.3[a]	-95.5	360.0
PF$_5$	-93.8	-84.6	
KF	857.0[a]	1502.0	127.4
CaF$_2$	1418.0[a]	2500.0	
ScF$_3$			350.0
TiF$_4$		283.1	350.0
VF$_3$	1406.0[e]	~1400.0	254.0
VF$_5$	19.5	48.3	
CrF$_2$			172.0
CrF$_3$	1404.0[f]		250.0
CrF$_5$	~150.0	~150.0	327.0
MnF$_2$	930.0		180.0
MnF$_3$			223.0
FeF$_2$	950.0[g]	1800.0	158.0
FeF$_3$	1300.0[g]	~1300.0[g]	219.0
CoF$_2$	~1200.0	~1725.0	147.0
CoF$_3$			174.0
NiF$_2$		1677.0	147.0
CuF$_2$			118.0
ZnF$_2$	872.0	1500.0	164.0
GaF$_3$			239.0
GeF$_4$			271.0

Table 1. (continued)

Compound	Melting Point[a] (°C)	Boiling Point[b,c] (°C)	$-\Delta F_f$, 298°K (kcal/mole)[c]
AsF_3	-6.0	58	189.0
SeF_6	-34.6	-45.9	221.8
RbF	798.0[a]	1408.0	125.7
SrF_2	1400.0	2410.0	276.7
YF_3			380.0
ZrF_4	910.0[g]	~900.0[g]	424.0
NbF_5	78.9	233.3	320.0
MoF_6	17.5	35.0	383.0
RnF_5			279.0
PdF_3			105.0
AgF	435.0		44.3
CdF_2	1110.0	1748.0	153.3
InF_3			234.0
SnF_2	215.0[g]	850.0[g]	147.0
SnF_4			237.0
SbF_3	290.0	376.0	200.0
SbF_5	8.3	142.7	286.5
TeF_6	-37.8	38.9	292.0
CsF	682.0[a]	1251.0	124.5
BaF_2	1290.0	2260.0	274.0
LaF_3			403.0
CeF_3	1460.0[a]		398.0
HfF_4			413.0
TaF_5	95.1	229.2	339.0
WF_6	8.2	17.0	
ReF_6	18.8	47.6	258.0
OsF_6	34.4	47.3	199.0
PtF_2			72.0
AuF_3			84.0
HgF_2	645.0	647.0	83.0

Table 1. (continued)

Compound	Melting Point[a] (°C)	Boiling Point[b,c] (°C)	$-\Delta F_f$, 298°K (kcal/mole)[c]
TlF	327.0	655.0	60.0
TlF$_3$			159.0
PbF$_2$	824.0[c]		146.6
BiF$_3$	850.0		200.0
BiF$_5$	151.4	230.0	
ThF$_4$	1100.0	1680.0	454.0
UF$_4$	1036.0	1417.0	421.5

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[c]A. Glassner, The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750 (1957).

[d]Sublimation point.

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[g]Unreported melting points based on work at ORNL, sometimes only an approximate value based on preliminary experiments.

Table 2. Binary Fluoride Systems of Potential Use as Process Solvents

Eutectic Temperature ($^\circ$C)	Components	Concentration of Second Component (mole %)	Reference
706	LiF-AlF$_3$	14.5	a,b
689	LiF-AlF$_3$	32.5	a,b
685	NaF-AlF$_3$	46	a,b
570	KF-AlF$_3$	40	a,b
370	BeF$_2$-AlF$_3$	22	c
652	LiF-NaF	40	a,d
492	LiF-KF	50	a,d
710	NaF-KF	60	a,d
355	LiF-BeF$_2$	52	a,d,e
365	NaF-BeF$_2$	55	a,d
340	NaF-BeF$_2$	43	a,d
323	KF-BeF$_2$	72.5	d,e
330	KF-BeF$_2$	59	d,e
507	LiF-ZrF$_4$	49	d,e
500	NaF-ZrF$_4$	40.5	d,e
430[f]	KF-ZrF$_4$	42[f]	d,e
720	Na$_3$AlF$_6$-Li$_3$AlF$_6$	60	a
936	Na$_3$AlF$_6$-K$_3$AlF$_6$	39	b

[a]E. M. Levin et al., Phase Diagrams for Ceramists, Am. Ceram. Soc. 1956.

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[c]R. L. Boles and R. E. Thoma, Volatility Process Phase Studies - A Survey of Molten Fluoride Solvent Mixtures Suitable for Dissolution of AlF$_3$, ORNL TM-400 (Oct. 22, 1962); the binary eutectic composition and temperature were not actually determined but were estimated from preliminary data in the LiF-BeF$_2$-AlF$_3$ ternary system.

[d]R. E. Thoma, ed., Phase Diagrams of Nuclear Reactor Materials, ORNL-2548 (Nov. 6, 1959).

[e]Levin, op. cit., Part II, 1959.

[f]Values are based on current work.

Table 3. LiF-KF-AlF₃ Liquid-Solid Transition Data

Composition (mole %)			Liquidus Temperature (°C)			Second Crystallization Temperature (°C) (Thermal Analysis)	Solidus Temperature (°C)	
LiF	KF	AlF₃	Visual Observation	Thermal Analysis	Electrical Conductivity		Thermal Analysis	Electrical Conductivity
100.0			848	848			848	
88.5		11.5	779					
86.0		14.0	725		735			711
80.0		20.0	765.5	766				
75.2		24.8	784.5	785				
75.0		25.0	772	771	787			771
71.6		28.4	775	775			699	
66.7		33.3	735	734	738		708	711
63.2		36.8	745		772			706
62.5		37.5	728					
60.9		39.1	730.5					
60.0		40.0	770	770	775			
58.8		41.2	747	747			710	
57.2		42.8	812	812	824			
57.1		42.9	786					
55.6		44.4	802	802			709	
52.7		47.3	860					
50.0		50.0	1035					
	75.0	25.0	996	995			995	

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Table 3. (continued)

Composition (mole %)			Liquidus Temperature (°C)			Second Crystallization Temperature (°C) (Thermal Analysis)	Solidus Temperature (°C)	
LiF	KF	AlF₃	Visual Observation	Thermal Analysis	Electrical Conductivity		Thermal Analysis	Electrical Conductivity
	57.2	42.8	670				559	
	54.6	45.4	569				565	
	50.0	50.0	642				575	
	42.8	57.2	710					
5.9	70.6	23.5	971				714	
11.1	66.7	22.2	951					
20.0	60.0	20.0	917					
27.3	54.5	18.2	889					
33.3	50.0	16.7	865					
41.7	43.7	14.6	839.5					
45.5	40.9	13.5	821					
50.0	37.5	12.5	800					
55.6	33.3	11.1	769				718	
62.5	28.1	9.4	727					
64.1	26.9	9.0	722.5	722			722	
71.4	21.5	7.1	749.5				718	
83.4	12.5	4.1	791					
67.5	7.5	25.0	731.5	730			647	
61.4	13.6	25.0	690					
56.25	18.75	25.0	649.5				649	

Table 3. (continued)

Composition (mole %)			Liquidus Temperature (°C)			Second Crystallization Temperature (°C) (Thermal Analysis)	Solidus Temperature (°C)	
LiF	KF	AlF$_3$	Visual Observation	Thermal Analysis	Electrical Conductivity		Thermal Analysis	Electrical Conductivity
50.0	25.0	25.0	696				645	
45.0	30.0	25.0	727					
40.9	34.1	25.0	749	749			645	
37.5	37.5	25.0	767	762			645	
30.0	45.0	25.0	802				778	
25.0	50.0	25.0	843				779	
33.3	16.7	50.0	976					
25.0	25.0	50.0	893					
20.0	30.0	50.0	858					
16.7	33.3	50.0	824					
	100.0		854	852			852	
15.0	40.0	45.0	593	589			567	
14.3	38.0	47.7	623	622		587	565	
13.0	34.8	52.2	970			593	564	
12.0	32.0	56.0	1098			592	563	
15.4	30.8	53.8	1043			597	561	
21.4	28.6	50.0	813	805		605		
26.7	26.7	46.6	690	685				
25.0	25.0	50.0	858			608	560	

Table 4. Invariant Equilibria in the System $LiF-KF-AlF_3$

Composition (mole %)			Temperature ($^\circ$C)	Type of Equilibrium
LiF	KF	AlF_3		
50.0	50.0		492	Eutectic
	93.0	7.0	850	Eutectic
	56.0	44.0	560	Eutectic
	50.4	49.6	575	Peritectic
85.5		14.5	711	Eutectic
64.0		36.0	710	Eutectic
53.0		47.0	890	Peritectic (?)
56.0	19.0	25.0	648	Eutectic[a]
33.0	42.0	25.0	778.5	Peritectic[a]
28.1	62.5	9.4	722.5	Eutectic[b]
6.0	48.0	46.0	500	Eutectic
45.5	53.0	1.5	490	Eutectic

[a]In subsystem $K_3AlF_6-Li_3AlF_6$.

[b]In subsystem K_3AlF_6-LiF.

Table 5. K_3AlF_6-LiF-CaF_2 Liquid-Solid Transition Data

Composition (mole %)			Visually Determined Liquidus	Thermal Analysis Data		
K_3AlF_6	LiF	CaF_2		Liquidus	Second Crystallization Temp.	Solidus
100.0			993.5	992		992
80.0		20.0	971.5	969		
66.7		33.3	955	950		937
57.2		42.8	973			944
50.0		50.0	1011			945
40.0	20.0	40.0	959.5		905	
33.3	33.3	33.3	908		875	682
28.6	42.8	28.6	869.5		858	682
25.0	50.0	25.0	839.5			
20.0	40.0	40.0	961			
18.2	36.4	45.4	996.5			
13.3	53.3	33.3	912			
11.7	58.9	29.4	876		850	
8.7	69.6	21.7		781	697	688
8.0	64.0	28.0		848	695	688
7.6	61.6	30.8		870	695	
18.9	54.1	27.0	827.5		715	680
16.3	60.5	23.2	799.5			
14.3	65.3	20.4	779		759	675
12.7	69.1	18.2	761			
10.8	73.8	15.4	730.5		714	680
9.3	77.4	13.3	719		710	680
24.1	69.0	6.9	831		720	
22.6	64.5	12.9	830.5		714	680
21.2	60.6	18.2	826			
20.0	57.2	22.8	825		712	675

Table 6. K_3AlF_6-SrF_2 Liquid-Solid Transition Data

Composition (mole %)			Visually Determined Liquidus	Thermal Analysis Data		
K_3AlF_6	LiF	SrF_2		Liquidus	Second Crystallization Temp.	Solidus
	50.0	50.0	1048			757
	60.0	40.0	970	967		
	66.7	33.3	913			
	75.0	25.0	832			
	80.0	20.0	774			
	83.3	16.7	780	778		767
7.7	76.9	15.4	739		703	692
14.3	71.4	14.3	776		705	698
20.0	66.7	13.3	829			
25.0	62.5	12.5	853	848	703	695
66.7	16.7	16.7	965.5	964		
50.0	25.0	25.0	939		930	686
40.0	30.0	30.0	930		918	690
33.3	33.3	33.3		935	903	690

Table 7. K_3AlF_6-LiF-ZnF_2 Liquid-Solid Transition Data

| Composition (mole %) | | | Visually Determined Liquidus | Thermal Analysis Data | | |
K_3AlF_6	LiF	ZnF_2		Liquidus	Second Crystal-lization Temp.	Solidus
12.2	87.8		722.5	722		722
11.8	84.0	4.2	720	720	655	
11.3	80.6	8.1	713	712	663	
10.9	77.5	11.6	705	705	668	
10.4	74.6	14.9	701	701	670	
9.7	69.4	20.8	690	689	670	
9.0	65.0	26.0	675	675	668	563
8.5	61.0	30.5	668	668		562
8.0	57.5	34.5		673		562
7.5	54.4	38.1		666		
7.0	50.0	43.0		667		

Table 8. LiF-NaF-AlF₃ Liquid-Solid Transition Data

| Composition (mole %) | | | Visually Determined Liquidus | Thermal Analysis Data | | |
LiF	NaF	AlF$_3$		Liquidus	Second Crystallization Temp.	Solidus
	75.0	25.0	1007			1005
	55.6	44.4	720			692
	50.0	50.0	853			
	47.7	52.3	1030			
	45.4	54.6	1083			
8.3	41.7	50.0	858		674	
15.4	38.4	46.2	729		660	599
21.4	35.8	42.8	693		645	600
26.7	33.3	40.0	662		638	601
35.3	29.4	35.3	636		627	603
11.1	66.7	22.2	954	785		
20.0	60.0	20.0	919	744		692
27.3	54.5	18.2	882	697		694
33.3	50.0	16.7	849	722		694

Table 9. The System $KF-AlF_3-ZrF_4$

Composition (mole %)			Visually Determined Liquidus	Thermal Analysis Data[a]		
KF	AlF_3	ZrF_4		Liquidus	Second Crystal- lization Temp.	Solidus
75.0		25.0	920 ± 4	920		920
75.0		25.0	935.5 ± 4	932		932
50.0		50.0	604 ± 4	600		448[b],480
45.4		54.6	580 ± 6	580		440
40.0		60.0	573 ± 4			
33.3		66.7	650 ± 4			
25.0		75.0	760 ± 4			
50.0	50.0		648 ± 3			
44.4	44.4	11.1	975 ± 3		540	
40.0	40.0	20.0	1030 ± 4		520	408
33.3	33.3	33.3	>1030 ± 4		585,442	410
66.7	22.2	11.1	890 ± 3		499	480
70.0	10.0	20.0	920 ± 3	915		
72.7	9.1	18.2	938 ± 3	934		
72.7	9.1	18.2	942 ± 3	934		
76.9	7.7	15.4	932 ± 3			
71.4	14.3	14.3	934 ± 3			
66.7	13.3	20.0	847 ± 3			482
62.5	12.5	25.0	570 ± 4			
62.5	20.8	16.7	649 ± 4		505	485
53.6	17.9	28.6	721 ± 4			
46.9	15.6	37.5	743 ± 4	743		
41.7	13.9	44.4	821 ± 4	818	582	438
37.5	12.5	50.0	869 ± 5	858	575	428
34.1	11.4	54.5	>1000 ± 5			

[a] Precision limits on thermal transition data are approximately ± 5°.

[b] Metastable transition.

Table 10. Invariant Equilibria in the System $KF-AlF_3-ZrF_4$ [a]

Composition (mole %)			Temperature (^{o}C)	Type of Equilibrium
KF	AlF₃	ZrF₄		
86.0		14.0	765	Eutectic
63.0		36.0	590	Peritectic
60.0		40.0	445	Peritectic
58.0		42.0	430	Eutectic
45.0		55.0	440	Eutectic
63.0	15.0	22.0	490	Eutectic
~55.0	~5.0	~40.0	400	Eutectic

[a] $KF-AlF_3$ invariant equilibria are given in Table 4.

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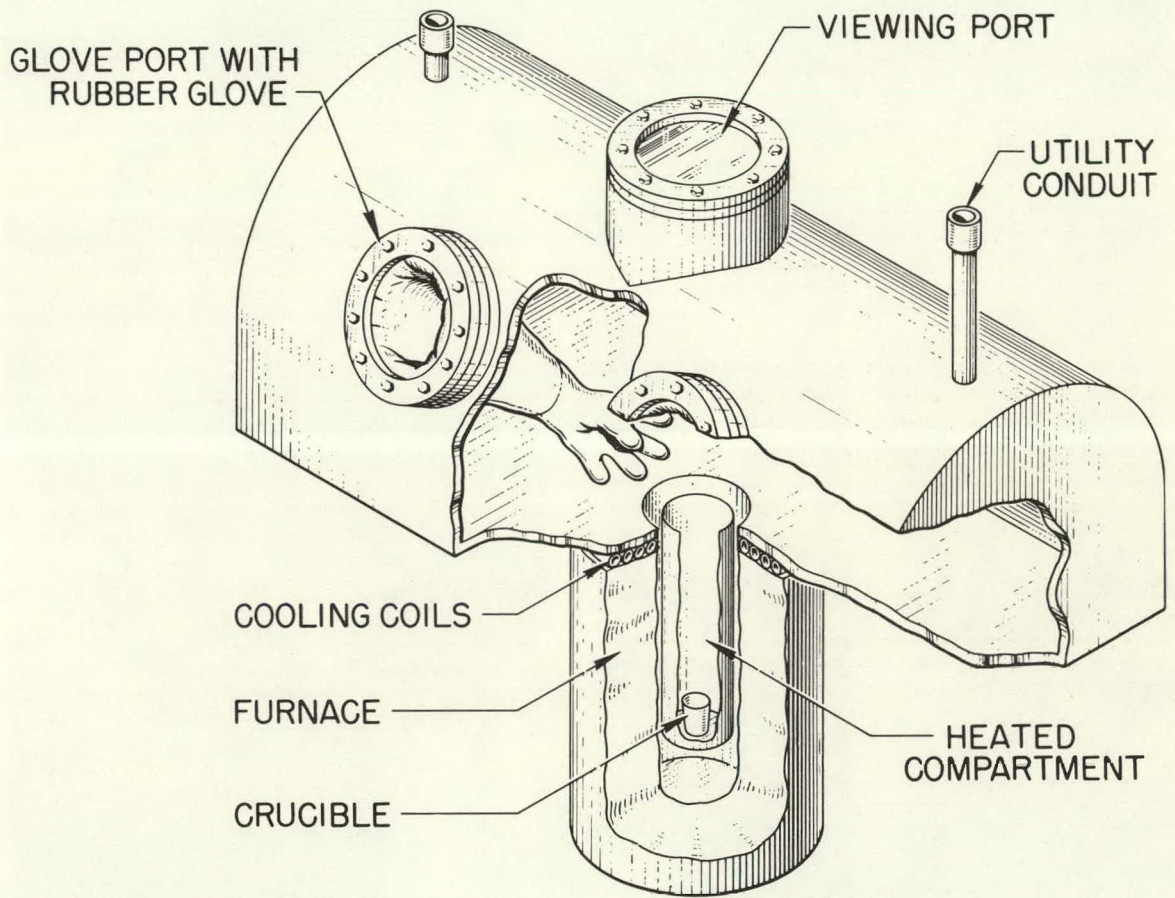
Fig. 1.   Schematic Drawing of Apparatus for Visual Studies.
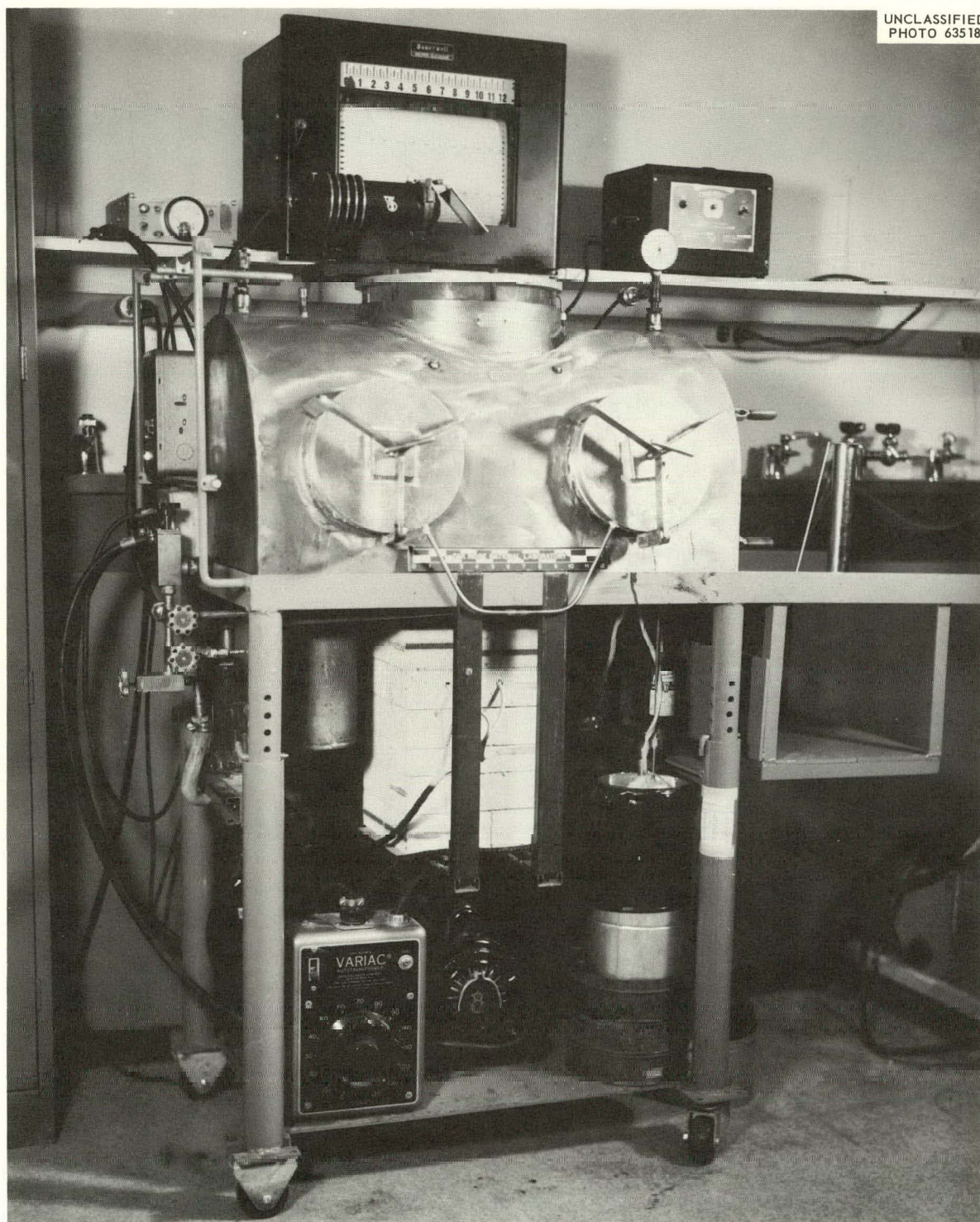
Fig. 2.   Visual Study Apparatus with Accessories.
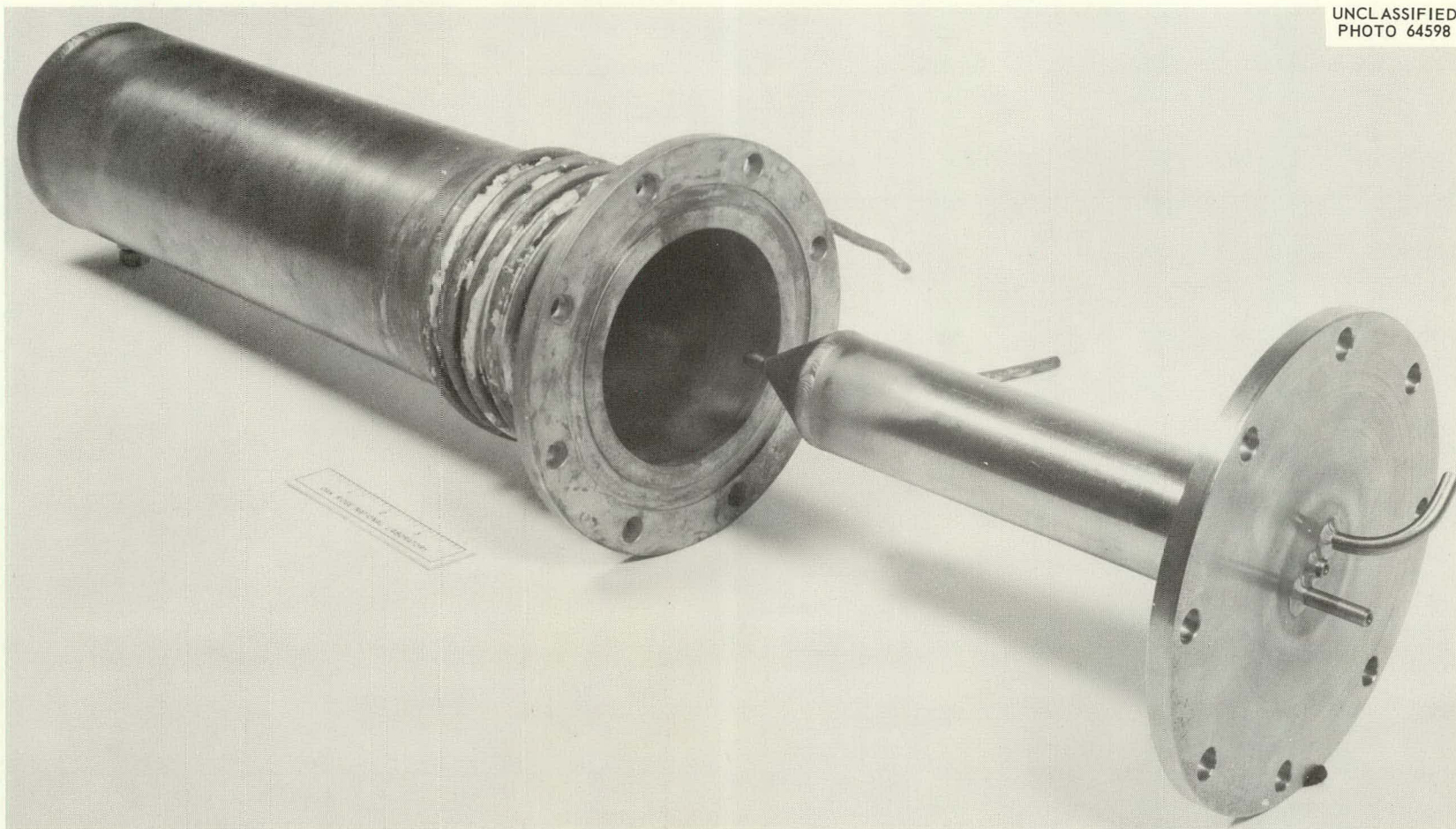
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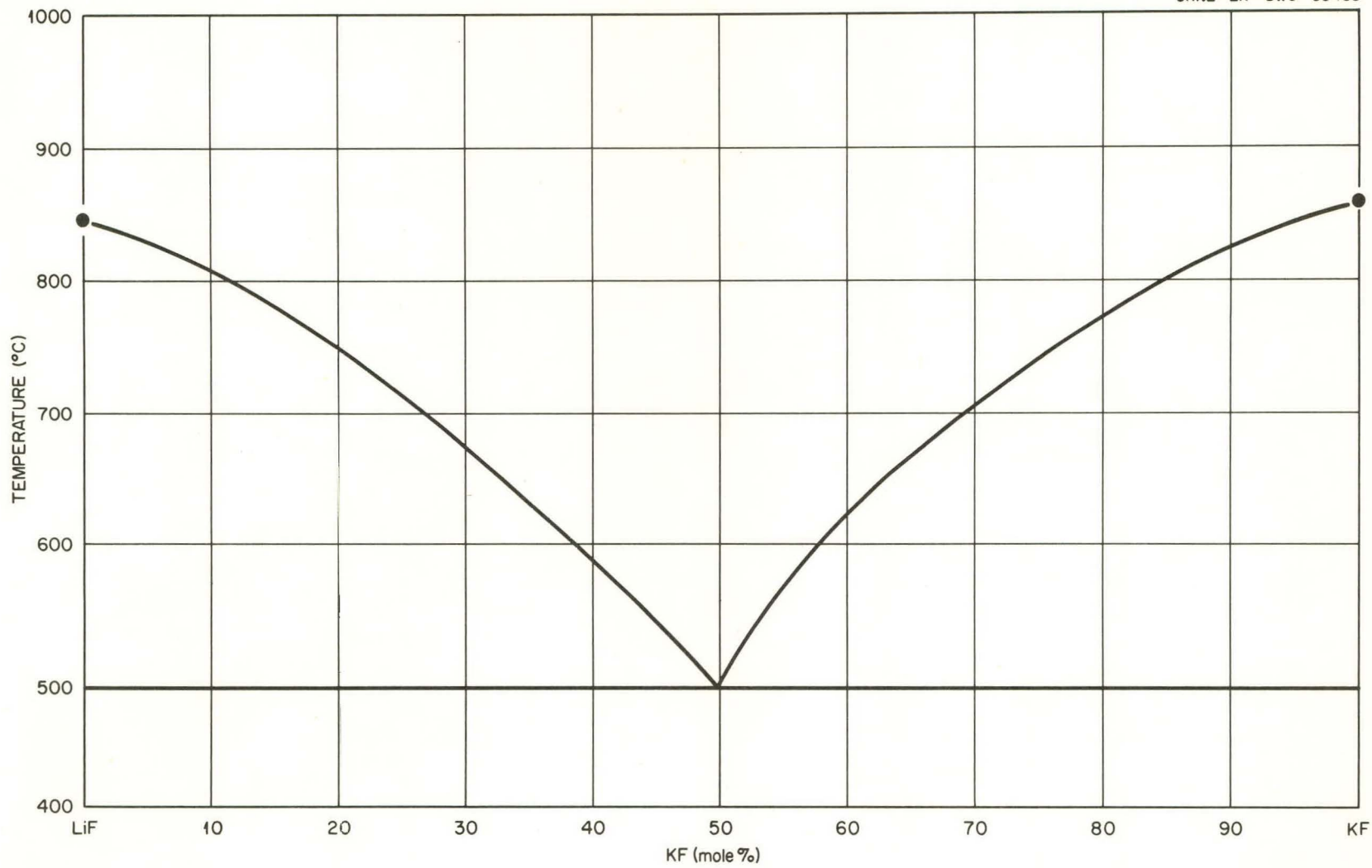
Fig. 4.   The System LiF-KF.
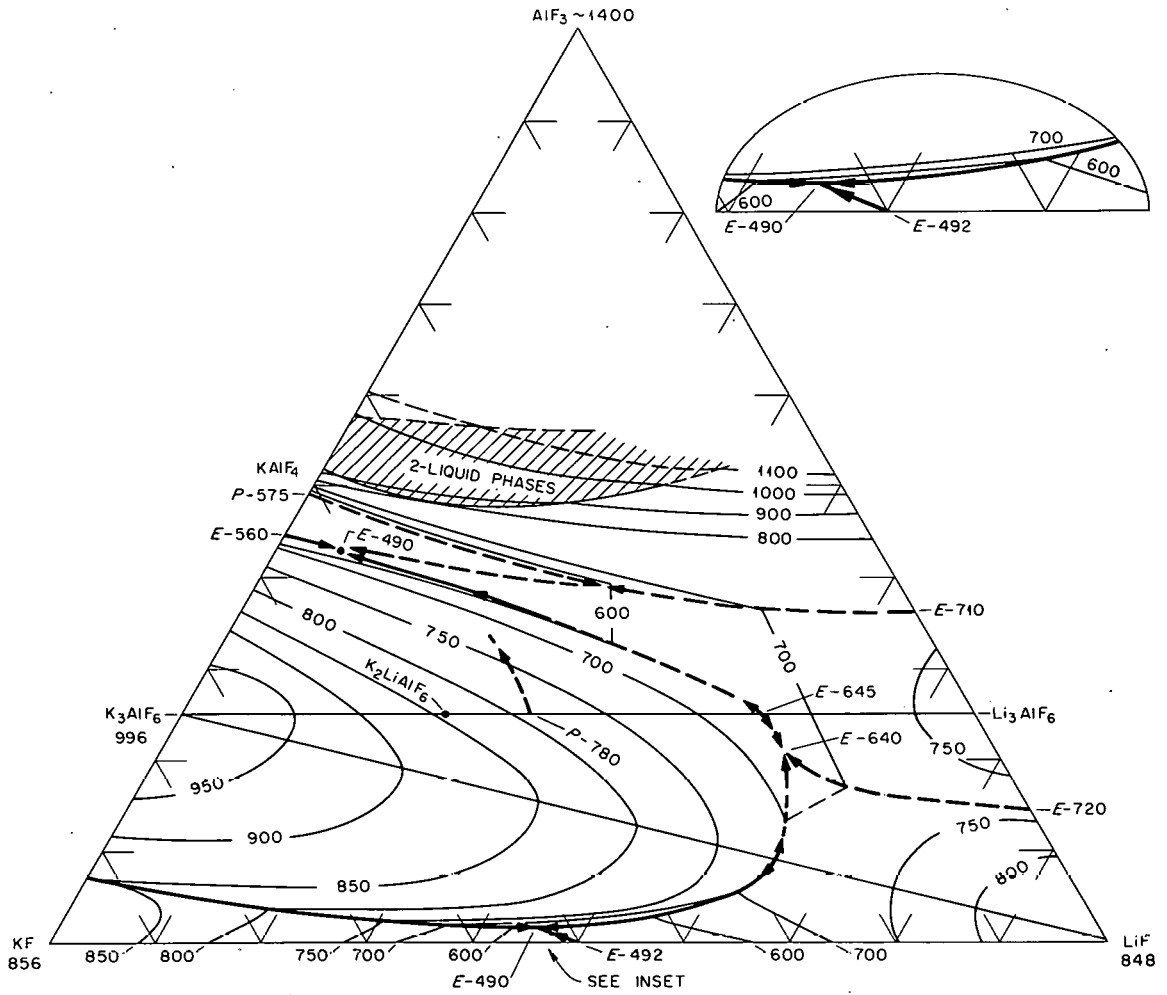
Fig. 5. The System KF-LiF-AlF₃.
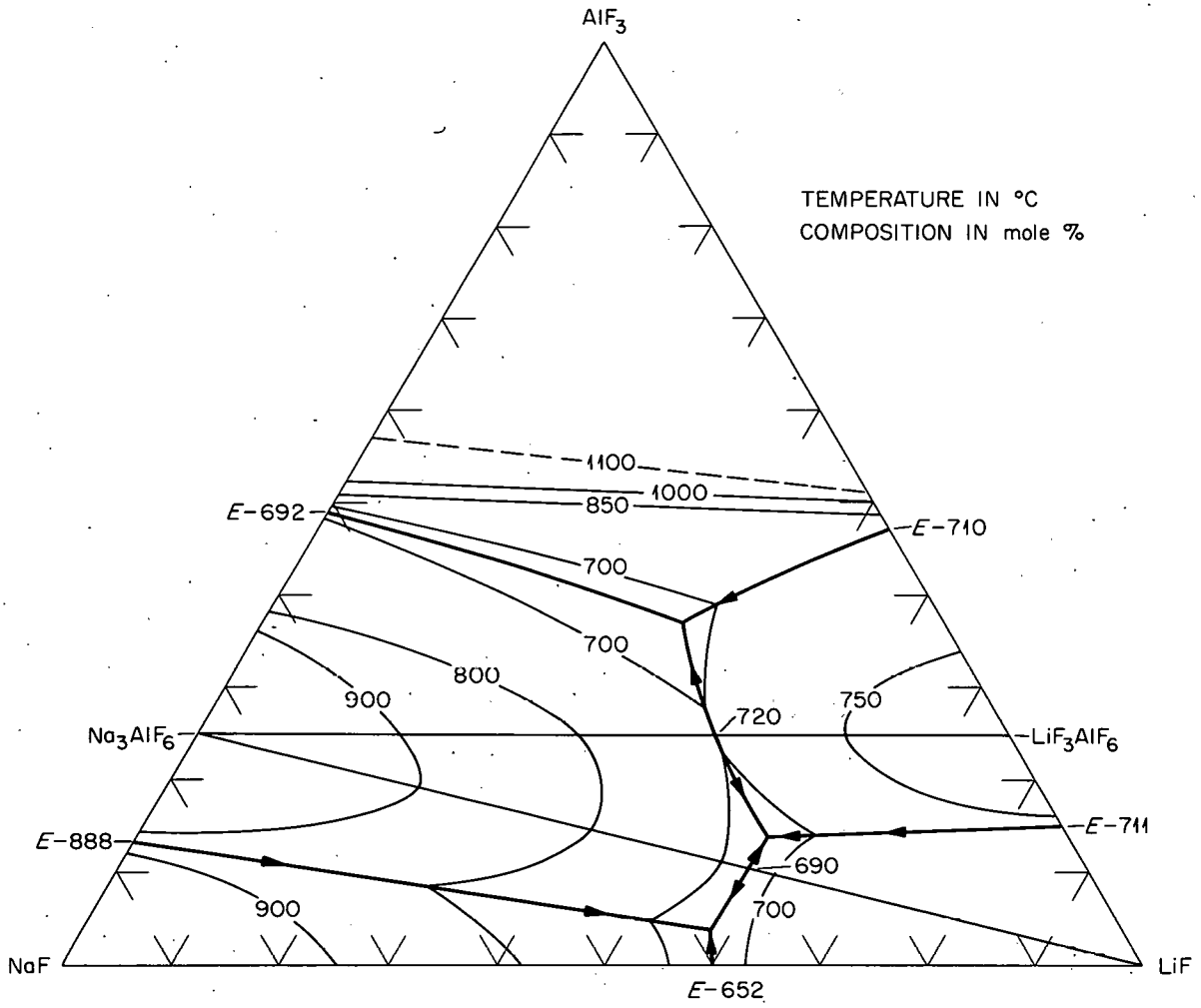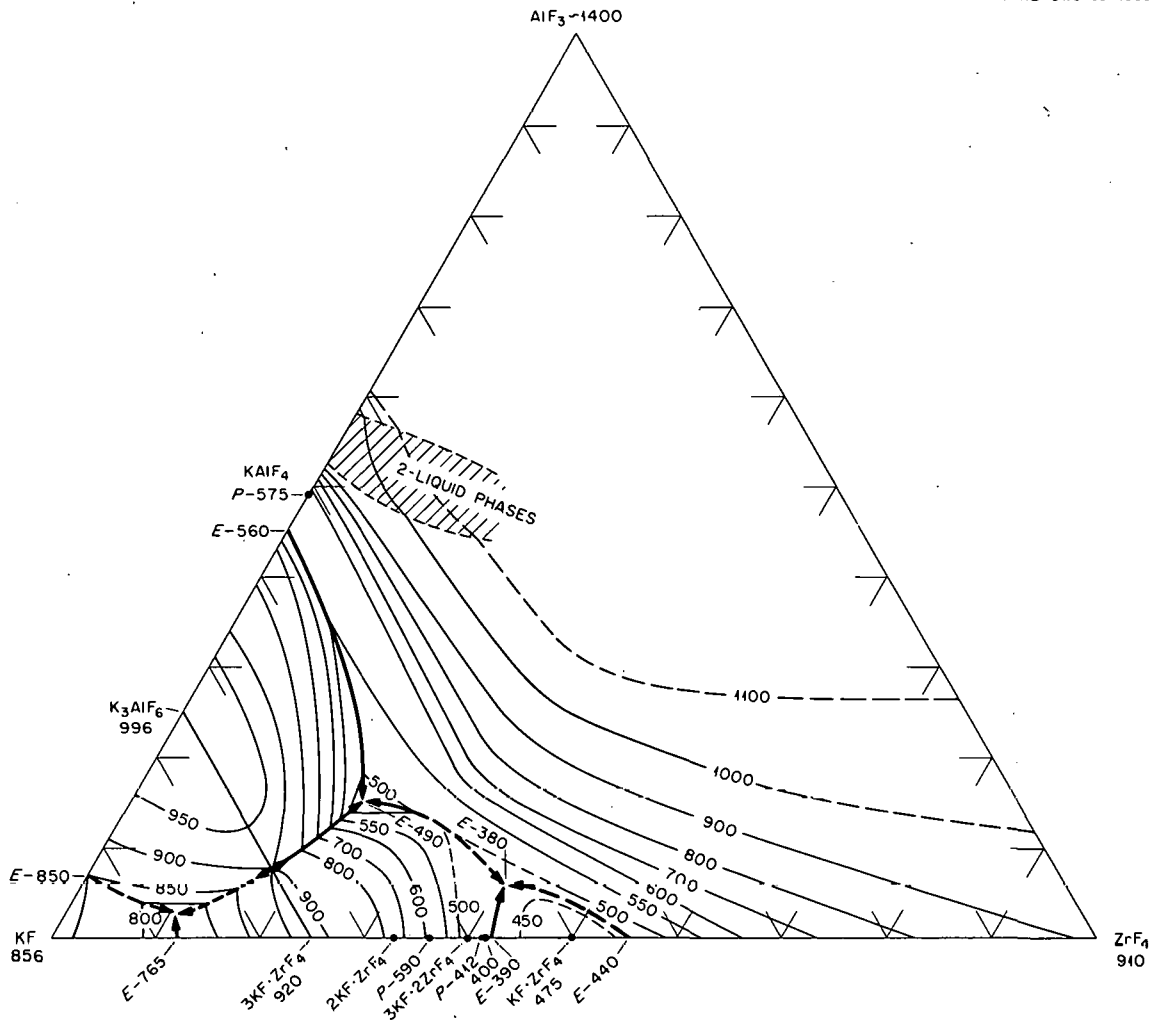
Fig. 6.   The System LiF-NaF-AlF₃.

Fig. 7.   The System KF-ZrF$_4$-AlF$_3$.

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