THE BINARY AND TERNARY SYSTEMS FORMED BY CALCIUM FLUORIDE, LITHIUM FLUORIDE AND BERYLLIUM FLUORIDE: PHASE DIAGRAMS AND ELECTROLYTIC STUDIES

By

John L. Speirs

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1952

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ACKNOWLEDGMENT

The writer wishes to express his sincere appreciation of the patient guidance of Dr. Laurence L. Quill in all phases of the investigation.

Thanks are also due to Dr. Elmer Leininger for his helpful advice on analytical procedures.

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THESIS ABSTRACT

Production of elemental fluorine from calcium fluoride by a direct method involving electrolysis of fused fluoride mixtures was considered. A ternary mixture was required to obtain the lowering in the melting point of calcium fluoride essential to give the possibility of fluorine recovery after electrolytic evolution.

Lithium and beryllium fluorides were chosen from among the limited number of possible additives for the purpose. The binary system phase diagrams were determined for the component systems: calcium fluoride--lithium fluoride, calcium fluoride--beryllium fluoride and lithium fluoride--beryllium fluoride. For the latter system the results were compared with the conflicting reports of two earlier investigations. Methods of synthesis of two compounds occurring in these systems were discussed and X-ray examinations reported for calcium fluoberyllate, $CaBeF_4$, and lithium fluoberyllate, Li_2BeF_4.

The phase diagram of the ternary system calcium fluoride--lithium fluoride--beryllium fluoride was determined. A region of suitably low temperature was located in which, however, the calcium fluoride content was very small.

Electrolyses of mixtures in this composition region of the ternary system produced inconclusive results. Evolved fluorine reacted with the anode preventing any recovery of gaseous product. It was not possible to demonstrate the cathodic deposition of calcium and thus determine whether, effectively, calcium fluoride was being decomposed rather than one of the additive substances.

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INTRODUCTION

INTRODUCTION

The requirements of industry for fluorine and fluorinated products have been greatly stimulated in the last decade, particularly by the uranium isotope separation program. As an additional result of this interest, there has been a marked increase in the amount of research in this previously rather neglected field.

Despite the progress that has been made, the principle difficulty continues to be the rather expensive and difficult generation of elemental fluorine. The present method of production is an indirect one which involves two main steps. First, anhydrous hydrogen fluoride is prepared by the action of sulfuric acid on calcium fluoride. In the second step electrolytic decomposition of the hydrogen fluoride is accomplished at about 100°, using a mixture of potassium fluoride and hydrogen fluoride with the approximate composition $KF:2HF$.

The principal generation process therefore continues to be essentially only a modification, due to LeBeau and Damiens (94,95), of the classical Moissan method with which elemental fluorine was first isolated (113). The historical development of the process has been adequately described by Damiens (20). More recent information and practical production methods have been summarized in a collection of symposium reports (144) and by Simons _et_ _al_. (150).

A direct method for the production of fluorine, from its present natural source--calcium fluoride, might have considerable economic advantage. The extreme electronegative position of fluorine among the elements makes electrolysis the only practical method of liberation, no chemical process having ever been found capable of liberating the free element. Thermal methods of supplying the energy necessary for free fluorine evolution are unsatisfactory for one or the other of two reasons. Those compounds capable of evolving fluorine by heating to moderate temperature require fluorine for their preparation. Other compounds, preparable without the use of the free element, thermally liberate fluorine only at such high temperatures that attack on the container is prohibitive and no practical yield is obtained.

Historically, the direct electrolysis of calcium fluoride has received scant attention as a means of fluorine generation. Two of the earliest workers in fluorine chemistry, Fremy (49) and Gore (53) both probably accomplished the "liberation" of fluorine in this way, but neither was able to isolate the product. Fremy actually observed the evolution of gas from the anode in the electrolysis of fused calcium fluoride, but the experiment was quickly terminated by attack of liberated calcium metal on the platinum container. Had he been able to continue, the phenomenon of "metal fog" would undoubtedly have reduced the yield to practically nothing in a very short time.

Subsequent to the work of these two investigators, there is no published record of any further attempt to obtain fluorine directly by the electrolysis of calcium fluoride, or of its mixtures with other compounds. The original objective of this dissertation was to investigate the possibility of such a method and to determine at the same time if it was reasonably practical.

The development of a practical method must overcome two major difficulties. The primary difficulty is the high melting point of calcium fluoride, approximately 1418° C., which makes it necessary that suitable additives be found which will permit lowering of the melting point to a practical temperature range. Such additives must meet a criterion imposed by the secondary difficulty, namely that fluorine is the most electronegative element and that calcium ranks high among the electropositive metals. For a practical process, such additives should be substantially unaffected by the electrolysis, or the main purpose would be defeated, even though fluorine were evolved.

As further discussed, in later sections, other difficulties must be overcome, but primarily the study involved the choice of suitable additives and the resultant temperature-composition investigation to determine the phase diagram. The additives chosen were lithium fluoride and beryllium fluoride for reasons to be more fully discussed. At this point, however, it may be noted that the choice of additives with respect to metal cations is very limited, and with respect to simple anions there is no choice. Since the addition of lithium fluoride alone would not be expected to produce sufficient lowering, another component was needed. The beryllium fluoride was intended to furnish this additional lowering, but functioning as a complex anion rather than as a simply additive component.

Subsequent to the work on the phase diagrams of the binary and ternary systems, and other problems which were suggested during the investigation, attention was directed toward the original problem of fluorine generation. Crude comparative conductance measurements and small scale electrolyses were carried out on mixtures in the ternary system to determine the practicality of the method for the generation and recovery of fluorine from calcium fluoride.

GENERAL AND THEORETICAL

GENERAL AND THEORETICAL

Sources of Fluorine and Methods of Production

Fluorine has been obtained in the past from its only abundant concentrated source, the mineral fluorspar. Deposits of this natural form of calcium fluoride are of relatively high purity, or may be beneficiated readily to obtain a satisfactory grade of material. The steel industry's demand for use as a flux formerly was the largest application, but since 1939 an enormous increase has occurred in the demand for the best grades of fluorspar for hydrofluoric acid preparation. The primary cause of this increase was the use of hydrofluoric acid by the petroleum industry in "alkylation" processes for aviation gas production. A secondary factor was the use of hydrofluoric acid, fluorine and fluorinated organic compounds in the uranium isotope separation program.

As these chemical applications have grown it has become apparent that the "abundance" of the supply of fluorspar was only apparent and that the concentrated ore deposits are rapidly being depleted, leaving only marginal and low grade deposits in reserve. The prospective exhaustion of the economic deposits in a matter of years, rather than decades, has stimulated development of a new source.

The largest potential source suggested (62) is the phosphate rock processing industry. Although fluorine is present as only a minor constituent (approximately 3.5%) in phosphate rock, the huge tonnages handled annually make available a large potential supply of fluorine, principally in the form of hydrogen fluoride waste gases. The toxicity of fluorine in both fertilizers and cattle food supplements make it essential to remove it in large part during the manufacturing process. As a waste gas, hydrogen fluoride is a serious atmospheric pollutant. The combination of circumstances would seem to indicate that in the near future there will be a substantial contribution of fluorine from this source, in addition to the current partial recovery in the form of fluosilicates. Recovery in the form of a very pure grade of calcium fluoride has been described (69,10), which requires only simple equipment and a cheap raw material, limestone.

The direct demand created by the manufacture of fluorine and fluorinated organic compounds is still small. The properties of fluorocarbons are so unusual, particularly with respect to stability, that it might reasonably be expected that their commercialization would be quite rapid. One item, the cost of fluorine generation and handling, has been the principal deterrent. In general the highly fluorinated compounds have only been effectively prepared by the use of fluorine "carriers", i.e. higher inorganic fluorides such as CoF_3, and AgF_2, which require the use of elemental fluorine in their preparation. A brief examination of the most important fluorine production system will indicate the inherent reasons for the high cost.

The large, modern fluorine cells, operating at about 100° C. on a mixture having the approximate composition KF:2HF, have been improved to a point of reliability far removed from the laboratory cells of the past. However despite high efficiencies and cell currents of 2000 to 3000 amperes at densities of approximately 75-100 amp./sq.ft., the production rates are only approximately 3 to 5 pounds per hour on quite sizable units. A comparison may be made with the chlorine-caustic industry where a tremendous investment in electrical equipment, cells and buildings is required to obtain tonnage production. The high cost of fluorine generation is understandable when the raw material costs (brine vs. anhydrous hydrogen fluoride), corrosion difficulties and difficulties of product shipment are compared.

The electrochemical field has but one solution to the problem of low unit production, namely to increase the current. In the higher temperature fused salt melts it is customary to use current densities as large as 1,000 amps./sq.ft., with cell currents of 50,000 amperes, and a consequent increase in unit output.

The absence of data on any attempts at the direct production of fluorine by electrolysis of the fused raw material, calcium fluoride, prompted this approach to the problem. The possibility was present that the obvious difficulties might be solved, with some possible gain in efficiency because of the cheaper raw material and possible higher unit production rate.

As another approach to this problem, the process patented by Simons (152), should be mentioned. Essentially the generation and handling of fluorine is minimized by the addition to the KF:2HF melt of the organic material which is to be fluorinated. Upon application of the current it is claimed that fluorination occurs without actual generation of fluorine. Regardless of the correctness of the claim the process is being commercially developed and will undoubtedly be a more satisfactory method for the production of some materials. Problems such as insolubility of reactants, "fragmentation" of molecules, and production of difficultly separable mixtures will probably restrict its application to many products.

Theoretical and Practical Problems of Fused Salt Electrolysis

Certain difficulties peculiar to this particular case and others which are inherent for most high temperature fused salt electrolyses should be mentioned. The temperature of the melt from the standpoint of fluorine reactivity, the "anode" effect, and problems of metal recovery at the cathode, including "metal fog" formation must be considered. Also the problem of relative decomposition potentials is of controlling importance.

At the start of this work it was judged that no calcium fluoride mixture melting higher than 600° would have any chance of evolving fluorine since no metallic cathode material was known capable of withstanding molecular fluorine at higher temperatures. The evolution of fluorine in atomic form at the electrode surface would be expected to be even more actively corrosive, so that to be practical a considerably lower temperature would probably be necessary. These considerations affected the choice of components to be added to the calcium fluoride to reduce its normal melting point of approximately 1418° C. Occasionally non-metallic conductors have been used as electrodes, but this possibility was not investigated as such a substance would have to be a fluoride, to be free from fluorine attack, and would probably be itself soluble in the melt.

In order to produce the lowering of temperature essential to possible recovery of fluorine evolved from the electrolysis of calcium fluoride, choice of added substances must be restricted to those which are not themselves decomposed by the electrolysis. This restriction greatly limits the possibilities, particularly since the fluoride ion is the only simple anion additive which is compatible with this requirement, all other simple anions being more readily oxidizable. No report to the contrary is on record, nor would it be expected since any evolved fluorine would be capable of oxidizing reduced forms, such as other anions, because of its extreme position as the most electronegative element.

With respect to possible cation additives meeting the above requirement, that is those more difficultly reducible than the Ca^{+2} ion, it must be admitted that the present state of the art does not permit a very systematic or scientific decision on the matter. The literature on the subject is relatively meager, a condition which is understandable from a consideration of the historical development. Successful applications of fused salt methods have been few and in general have been restricted to a few companies that have not been noted for their liberality in publication of research results. Academic interest in the subject has been low and largely confined to a few German investigators.

Collected information on the subject of fused salt electrolysis is non-existent in English texts, other than as a brief survey of the field in very short chapters. In German, two modern publications are available, one technical in nature edited by Engelhardt (40), the other a theoretical approach by Drossbach (27), based on a collection of the van Laar thermodynamic papers on the subject. Information contained in the former work with respect to exact values of decomposition potentials is probably worthless in the light of Drossbach's criticisms (28), except as a general indication of the approximate order of decomposition potentials.

In brief, these criticisms concerned failure to obtain equilibrium conditions, to isolate anode and cathode products from each other, and failure to identify actual electrode products. The only extensive survey made on the subject (118), has been widely criticized (135) (29), and the values shown to be impossible from a thermodynamic viewpoint, and incompatible with the results of other investigators. While it might be thought that any thorough study would be made in such a way as to obviate the above criticisms, the practical difficulties with respect to isolation of the products by means of suitable diaphragms are such that only a very few studies have been made which are free of such defects in experimental technique. These have largely been confined to low temperature studies of tractable salts, with low corrosive properties, in glass and porcelain apparatus (99) (30).

With respect to data on operating cells naturally no very informative data on relative decomposition potentials is obtained, since such cells normally operate at considerable overvoltages which are dependent upon a multiplicity of variables.

The collected information given by Engelhardt (40), was however valuable for its quite complete review of published work on all phases of fused salt electrolysis. It constituted a large source of "negative" information, that is on the subject of additives which could not be expected to work satisfactorily with calcium fluoride. This circumstance arose from the fact that, at one time or another, calcium fluoride has been applied as an additive to mixtures intended for the deposition of almost all metals suited to electrolytic preparation.

While the thermodynamic approach to the problem of decomposition potential, as exemplified by the van Laar theory (27), will require much more data to permit general applicability, it is mentioned here as it represents the only systematic approach which has shown itself capable of producing data in agreement with careful experimental work.

Essentially the theory deals with the behaviour of solutions as affected by the "intermolecular" forces exerted by the components. In the absence of suitable quantitative theories of the liquid state and forces of interaction, van Laar used a description of the temperature-volume dependence in terms of the van der Waals equation of state. He proposed suitable additive values of the constants a_k and b_k (the constants at the critical points) for a large number of the chemical elements as elements and in "molecular" (non-ionic) compounds, and for a few elements in ionic compounds.

Very complex expressions are then developed for the molar thermodynamic potentials of substances in binary mixtures, the constants of which may be evaluated from a knowledge of such information as the partial molal volumes and heats of fusion (at the temperature in question), which may be obtained from differential heat of solution measurements. Another approach involving the use of molar thermodynamic potentials for prediction of melting point lowering in mixtures may be reversed to obtain approximate values of the molecular interaction constants of the equation from the experimental data on melting point curves of mixtures.

Such expressions, when developed for higher than binary systems, become extremely cumbersome and the approximate forms are limited to dilute solutions with small values of melting point lowering. Excellent correlations are given by Drossbach (31) for the decomposition potentials of some alkali metal halides, but the lack of sufficient thermal data generally restricts the application of the theory and it did not facilitate a theoretical approach in this work.

Several other simplified theoretical treatments and a number of empirical contributions have been made with respect to decomposition potentials in fused salt electrolysis. Among the former may be mentioned the work of Newman and Brown (119), Drossbach (32), and Thomson (168). Essentially their work was based on the Gibbs-Helmholtz relation, $E = -\Delta F/nF$, for the reaction Metal salt $\longrightarrow$ elements, with in general some attempt to apply the proper value of ΔF (i.e. at the particular temperature involved) and with correction of the ΔF value in the case where a secondary reaction occurred at the electrode.

Such simplified approaches naturally fail to take into account the possible change in environment which occurs when one salt is dissolved in another. To assume lack of interaction and complete dissociation into independent ions or molecules is hardly compatible with the evidence for strong association of the components which follows from a consideration of the large differences between the melting and boiling points of fused salts.

Of the empirical relations the only reference specifically pertaining to alkali and alkaline earth halides is that of Balce (5), claiming fair agreement for a relationship between the change in volume per unit volume (on formation of the salt from the elements) and the decomposition potential and heat of formation.

Certain problems which are peculiarly important in fused salt electrolyses essentially involve the isolation of the cathode and anode products so that recombination and consequent efficiency losses may be prevented. Temperature, density and solubility factors must be taken into consideration.

In general adherent deposits of metal on the cathode are not obtainable under conditions where the local temperature of the bath is so low that the metal does not initially form a molten mass. Thus bath temperatures below this melting point tend to form loose powdery deposits which may become mechanically suspended in the melt so that transfer to the vicinity of the anode becomes possible. In cases where the liquid metal density is less than that of the fused salt, a common procedure is to recover the metal in the form of a "carrot" by gradually raising a water cooled cathode from the melt. Operation at high current density will produce sufficient local heating of the melt so that a floating puddle of the metal will be present, which solidifies in an adherent manner on the rising cathode (9) (127).

Another method of attack on the problem is the use of a liquid metallic cathode which may be the deposited metal itself provided the density relationship permits it to remain on the bottom of the cell. An example of this would be the process used in aluminum manufacture in which the product is collected on the bottom of the cell and tapped off at periodic intervals. A modification of this system is the deposition of a metal (less dense than the melt) on a liquid cathode composed of a more dense metal with which it may then form an alloy having a density sufficient to hold it on the bottom of the cell.

Such a system will be further considered in connection with its effect on decomposition potentials, but it should be mentioned at this point that such a method presents difficulty because of rapid saturation of the surface of the cathode by deposited metal. Diffusion rates in such alloys are very slow and means must be provided to produce fresh surfaces for deposition in order to obtain satisfactory operation (114).

On the other extreme, high temperatures, or temperatures much in excess of the melting point of the cathodically deposited metal, cause another serious difficulty, commonly referred to as "metal fog". Under such circumstances solutions (19), or dispersions of metal may be produced in the melt which have been described as colloidal, probably because of the variety of colors obtained, in analogy with such aqueous colloidal dispersions as gold sols (100,6). Alkaline earth metals are quite subject to this behavior in halide melts.

While at first this effect was attributed to vaporization and condensation of the deposited metal (101,102), subsequent preparation of so-called "sub-halide" compounds such as "CaCl" (174,107) lead to the belief that such ions as Ca^{+1} were produced at the cathode by primary or secondary reduction processes (33). More recent studies on the effects of electron excesses and deficiencies in solids and particularly a thorough study made by Cubiciotti (18) of the calcium-calcium chloride system lead to the belief that "double ions" such as Ca_2^{++} are formed.

Regardless of the particular reduced form of the metal present, it is clear that the problem of isolation of cathode product from the anode becomes most difficult and very poor or zero efficiencies may be expected under such circumstances.

One of the serious problems in the electrolysis of fused salts, the "anode effect", has been speculated upon and discussed by numerous investigators (48,165,115,34). This phenomenon, particularly noted with fluoride melts, is exhibited as a sudden rise in cell resistance accompanied by an apparent failure of the melt to wet the anode. Even though the current then falls sharply, the common practice of arranging cells in a series circuit imposes higher voltage on the faulty anode-melt interface. This probably aggravates the source of difficulty by causing further localized heating of a film of gas believed to be effectively insulating the anode.

The difficulty probably normally arises from a depletion of the concentration of the component normally oxidized at the anode so that the wrong constituent commences to deposit, for example, fluorine which in the case of carbon anodes may then react to form fluorocarbons such as tetrafluoromethane which insulate the anode. In the normal case, the remedy is usually found in restoration of the proper composition of the melt and reduction of applied potential. However in the case of a cell intended for fluorine deposition the first remedy is not available and some difficulty might be anticipated if evolved fluorine reacted with the carbon anodes. The effect has been observed on metallic electrodes as well, where the remedy has usually been to decrease the current density or to replenish the bath constituent which acts to depolarize the anode.

In contrast to this behaviour, the usual KF:2HF type of low temperature fluorine cells give best results when the anode is not wetted by the electrolyte. At temperatures below 100° and with higher hydrogen fluoride contents the anodes are wetted, become swollen, and disintegrate, apparently as a result of the formation of the compound $(CF)_x$. (151).

Relative Decomposition Potentials and Choice of Components

As will be seen, the data on fused salt decomposition potentials present numerous contradictions and uncertainties. It may be helpful, therefore, to consider the relatively well established data for gaseous ionization and aqueous electrode potentials for pertinent cations, before discussing their behaviour in fused salts.

From inspection of the following table it may be observed that there is no simple relationship between the ionization potentials of gaseous atoms and their single electrode potentials in aqueous solution, as the heats of hydration of the gaseous ions may exert a compensating effect (92). Thus the easily ionizable Cs atom has the same value of aqueous electrode potential as the more difficultly ionizable Li because of the large contribution of the heat of hydration of the Li^+ ion to the over-all reaction.

Element	Ionization Potential of Gaseous Atom, volts	Heat of Hydration of Gaseous Ions, Kcal.	Electrode Potential for reaction in aqueous solution $M \rightarrow M^+_{aq.} + e^-$, volts	Ionic Radius of Metal, cm.x 10^{-8}
Li	5.36	123.	3.02	0.60
Na	5.12	97.	2.71	0.95
K	4.32	77.	2.92	1.33
Rb	4.16	70.	2.99	1.48
Cs	3.87	63.	3.02	1.69

Somewhat the same effect must be present in fused salt media, since for example potassium salts may be used as additives in lithium production, as a mixture of equal parts of LiCl and KCl will deposit predominately lithium on electrolysis (60). In view of this apparent reversal of the positions in aqueous solutions, it might be concluded that either the highly hydrated lithium ion is relatively more solvated in fused mixtures or that the more poorly hydrated potassium ion is relatively even less solvated in fused mixtures.

A similar relationship exists for Group II metals, as noted in the following table, except that the effect of hydration is even more important. (93)

With Group III metals, the even higher ionization potentials are so counteracted by larger heats of hydration that, in general, the net effect causes the electrode potentials of metals in all three groups to lie largely in the range of 2 to 3 volts.

Similarly the indications are that in fused salt electrolysis the relative single electrode potentials of the metals (as judged by relative

Element	Ionization of Gaseous 1st. e^-, volts	Potential Atom, 2nd e^-, volts	Heat of Hydration of Gaseous Ions, Kcal.	Electrode Potential for reaction in aqueous solution $M \rightarrow M^{++} + 2e^-$, volts	Ionic Radius of Metal, cm.x 10^{-8}
Be	9.28	18.1	--	1.70	0.31
Mg	7.61	14.96	460.	2.34	0.65
Ca	6.09	11.82	395.	2.87	0.99
Sr	5.67	10.98	355.	2.89	1.13
Ba	5.19	9.95	305.	2.90	1.35

decomposition potentials of their compounds) likewise lie within an approximately similar voltage range. Relative positions in the electromotive series are, however, somewhat shifted and the types of anions present in mixtures appear to exert more of an effect, apart from cases where stable complex formation would be expected.

From the above considerations it would seem to be apparent that interaction between species present in fused salt mixtures must be taken into account in any theoretical approach to the problem of prediction of decomposition potentials. In all probability such interaction is as controlling in fused salts as in aqueous solutions. The very high conductance shown by fused salts, which has commonly been assumed to be due to nearly complete ionization of the components, is no certain indication of the fact as it is possible that other modes of effective electron transfer may be present.

In approaching the problem of the selection of suitable additives, not decomposed under conditions where calcium is deposited, the literature was surveyed with respect to reports of experimental and commercial operating results on mixtures containing calcium ions, with most emphasis on fluoride melts containing calcium fluoride. For purposes of a general introduction of the topic, the widely criticized data of Neumann and Richter (118) is partially reproduced in the following table. It is emphasized that these values are probably not even relatively correct, but they are illustrative of the effects produced by phenomena such as metal fogs, reactions of anode gas with the anode, and the acceleration of such side reactions by increase in temperature. The first mentioned substance of a mixture is the one which the investigators believed they were decomposing.

Inspection of the table indicates a number of apparent peculiarities. The decomposition potentials of fluorides are probably all in the wrong relationships to the chlorides, i.e. the former should be the higher, but because of depolarization effects and reactions with the anode an effective undervoltage is operating to reduce the decomposition potential. The negative temperature effect is so extreme that it would appear that with but little more elevation of temperature the compounds would decompose spontaneously, an effect which is hardly realizable in practice.

The general observation that alkali metals are high, alkaline earth metals slightly lower, and Group III metals still lower in the single potential for metal deposition is substantially correct as judged by other results. The exact order and voltage separations between elements is not as indicated, according to the results of other investigators working with a more limited series of compounds and mixtures.

QUESTIONABLE VALUES OF DECOMPOSITION POTENTIAL OF NEUMANN AND RICHTER

Compound or Mixture	Decomp. Potential Volts	at Temp. °C.	Decomp. Potential Volts	at Temp. °C.
LiF (+ 15% KCl)	1.26	787	0.94	872
NaF (+ KCl)	0.96	827	0.77	872
KF	1.30	782	0.92	872
BeF_2 (+ KCl)	0.70	737	0.42	836
MgF_2 (+ KCl)	0.43	738	0.16	805
CaF_2 (+ KCl)	0.74	783	0.38	872
SrF_2 (+ KCl)	0.91	783	0.55	872
BaF_2 (+ KCl)	0.99	783	0.63	872
AlF_3 (+ KF + KCl)	0.53	783	0.32	855
LiCl	2.59	647	2.47	737
NaCl (+ 50 mole % KCl)	2.75	714	2.51	872
KCl (+ 50 mole % NaCl)	2.90	714	2.66	872
CsCl	3.28	647	3.14	737
RbCl	2.93	763	2.80	872
$BeCl_2$	1.47	737	1.38	827
$MgCl_2$	2.23	783	2.16	881
$CaCl_2$	2.82	638	2.72	773
$BaCl_2$	3.06	647	2.99	745
$AlCl_3$	1.49	640	1.37	746
$CeCl_3$	2.10	738	1.83	882
$LaCl_3$	1.65	783	1.50	863
$NdCl_3$	1.55	800	1.45	854
$PrCl_3$	1.45	737	1.02	872

In order to somewhat limit the field of this discussion, it may be said that the possible choice of suitable additives is essentially limited to periodic Groups Ia, IIa, IIIa and possibly IVa. Subsequent elements and transition series elements of b-sub-groups either form quite volatile fluorides or the metals have relatively low potentials required for deposition, so that they are inapplicable for the present purpose. Indeed the latter as a rule constitute a very troublesome class of impurities in melts intended for the preparation of the Groups Ia, IIa and IIIa metals for two reasons. Not only do they tend to deposit as impurities, but they may take part in a series of parasitic oxidation and reduction reactions within the cell, to the extent that yields may approach zero, because of their ability to assume different oxidation states (23) (24) (41,35).

The possibility of deposition of calcium from a solution in one of the volatile fluorides was considered initially, but the reactivity of the halogen fluorides, boron trifluoride, and others is so great that no calcium metal yield might be expected. Thus far calcium fluoride is known to be soluble in only one of the volatile fluorides, boron trifluoride, with formation of a compound $CaF_2{:}BF_3$, which decomposes on moderate heating (175).

In the following table, the melting point data for fluorides of the Groups Ia to IVa elements have been tabulated in order that the possibilities on choice of additives may be noted. Some liquid and gaseous substances have been included for completeness. Likewise any available values for certain elements such as rubidium, cesium, scandium, yttrium, lanthanum and hafnium have been shown although their scarcity prohibited their consideration as practical additives.

As may be seen, the data for Groups I and II is reasonably complete although the values may not be well established in all cases. About two-thirds of these values are given erroneously in current handbooks and some of the remainder have not been checked by modern workers. With respect to Groups III and IV, data is incomplete and somewhat contradictory. This may have been the result of no effort, or in part it is probably due to the fact that these compounds may sublime instead of melting. Thus in Group III, possibilities of dimerization exist which may lead to sublimation.

MELTING POINT DATA FOR FLUORIDES OF THE ELEMENTS OF GROUPS Ia, IIa, IIIa and IVa

Compd.	M. Pt., °C.	Reference	Compd.	M. Pt., °C.	Reference
HF	-83		BF_3	-127	
LiF	845	(143)	AlF_3	1272	(11)
NaF	992	(79)	ScF_3	(1227)	(11)
KF	857	(79)	YF_3	(1387)	(11)
RbF	775	(11)	LaF_3	(1427)	(11)
CsF	682	(11)			
BeF_2	800?	(See note)	CF_4	-183	(11)
MgF_2	1263	(79)	SiF_4	-90	(11)
CaF_2	1418	(116)	TiF_4	B.Pt. 284	(11)
SrF_2	1400	(11)	ZrF_4	(Subl. 927)	(11)
BaF_2	1353	(11)	HfF_4	(Subl. 927)	(11)
RaF_2	(1427)	(11)	ThF_4	1027	(11)

Note: BeF_2 is polymeric and this value is only an approximate softening point.

Values in parentheses are uncertain or estimated values.

From the above information it would appear that Group IIIa and IVa fluorides would probably not be successful additives as such because of instability, with the exception of AlF_3. If however they were complexed by the formation in the melt of fluo-anions, such as fluo-titanates and fluo-zirconates, it would be expected that they would be stable. Of these elements, aluminum, zirconium and possibly titanium might be serviceable in the form of complex anions. Because of the experimental data available on aluminum production from complex fluoride melts, it was decided that complex fluorides of these two groups would probably have too low a decomposition potential for the complexed metal (42,12).

The thermal reduction studies on some of these metals lead to similar conclusions (39). Thus Marden and Rich (104) reduced potassium fluo-zirconate with aluminum, Ruff and Brintzinger (136) reduced zirconium oxide with a mixture of calcium and sodium and de Boer and Fast (22) reduced the oxide with magnesium and sodium. While such studies are not conclusive with respect to relative electropositivity, they generally indicate a lower decomposition potential than that of calcium or an instability with respect to it as the metal.

Of the Group Ia and IIa metals, rubidium and cesium were ruled out as impractical, even for small scale test work, because of cost considerations. Their relatively low gaseous ionization potentials would indicate their possibly high position in the electro-positivity series in fused salts as well as in aqueous solutions. However, the slight information available (145,146,147) would indicate that cesium is lower than barium (and probably calcium) in fused salt deposition potential.

The remaining possibilities, Li, Na and K in Group I and Be, Mg, Ca, Sr and Ba in Group II were considered with respect to their order of deposition, particularly from fluoride melts. Three of these may be excluded from consideration for the following reasons.

Magnesium definitely ranks lower than calcium in deposition potential from a consideration of the widespread use of calcium fluoride as an additive to melts used for magnesium production. Concentrations of calcium fluoride up to 20% by weight are reached before the magnesium product is appreciably contaminated with calcium (41). Incorporation of sodium and potassium salts in magnesium cell mixtures in concentrations as high as

90% KCl-10% $MgCl_2$ and 70% NaCl-30% $MgCl_2$ deposit satisfactorily pure magnesium at low potentials. However, with normal operating potentials and greater current densities the sodium and potassium contents must be considerably lowered to prevent alkali metal impurity deposition (41).

In contrast to some of these results, Ruff and Busch (135) found that in fluoride melts the order of increasing deposition potential was K, Na, Mg, Ba, Li and Ca, and they particularly condemned the inclusion of Na and Ba fluorides in magnesium baths. They found that incorporation of LiF and CaF_2 permitted production of commercially pure magnesium directly. From the above, despite some apparent contradiction, it is clear that magnesium has a lower deposition potential than calcium in general and in particular from fluoride melts. A considerable body of information substantiates this conclusion, for example the work of Grube and Jaisle (56) and Grube and Henne (55) may be mentioned.

With respect to strontium and barium fluorides it should be noted that the melting points of 1400° and 1353° respectively make them inherently somewhat undesirable as additives since the prospects of obtaining a low melting eutectic mixture with calcium fluoride are poor. Their deposition potentials have been reported by Arndt and Willner (3) to be so close to that of calcium in chloride melts that the difference is negligible in practice. Barium fluoride has been used interchangeably with calcium fluoride in some experimental electrolyses (56) (55) (66) (47) (61) as an additive without significant differences being noted.

Troutz (170) has shown that, in chloride melts, strontium (97%) deposits from a 32% KCl-68% $SrCl_2$ mixture. Neumann and Bergve (117), working with a 26% KCl-74% $SrCl_2$ melt,confirmed this behaviour, but under comparable conditions obtained no yield of barium metal. Probably the best conclusion that may be drawn from these results is that K, Ca, Sr and Ba are closely grouped with respect to decomposition potential, and that in all likelihood Sr and Ba do not represent suitable additives, particularly if a considerable lowering in melt temperature is necessary.

Information on the relative deposition potential of sodium is relatively clear cut as the great majority of reports show that it deposits ahead of calcium, from most melts, and from fluoride melts in particular. Pertinent information in this respect is given by numerous investigators (135) (56) (55). The work reported by Danneel, Stockem and von Kuegelgen (21) is slightly contradictory in that it reports an interchange of the normal positions of sodium and calcium when temperatures exceed 800° in chloride melts. The evidence is,however,quite conclusive that sodium fluoride should not constitute a suitable additive for the purpose of this work.

The information with regard to the relative position of potassium is confused, some reports indicating that it falls below calcium (135) (41), others indicating approximately the same range for both (114) (43) (21), and still others indicating that potassium has the higher deposition potential (114) (117). The apparent conflicts are probably caused in part by temperature and composition factors, but the evidence indicates that calcium and potassium are close together with respect to deposition potential, with potassium probably slightly the higher of the two.

The position of lithium is likewise uncertain with respect to calcium. Less information is available, and the conclusion is that calcium and lithium are likewise very close together, with somewhat less disagreement among the reports that place lithium slightly above (21) (118) and slightly below calcium (135). The work of Guntz (60) indicates that lithium and potassium are close together with lithium being predominantly deposited from chloride melts. The commercial preparation of alloys of lithium and calcium in widely varying proportions by single step electrolysis of fused lithium-calcium halide mixtures, as noted by Osberg (122) and Val'dman (171) is further indication of the similar electrolytic behaviour of these elements.

The remaining element, beryllium, has special characteristics that distinguish it from those previously mentioned. Probably beryllium, in an uncomplexed form, would deposit at a lower potential than calcium, as one investigator has placed it below sodium in the potential series (25), and its preparation from melts containing barium fluoride has been commercialized.

The complexing tendencies of beryllium are quite strong, however, and it shows considerable ability to form stable complex halo-beryllates such as $M_2^{I} BeX_4$ and $M^{II} BeX_4$. It was observed that at lower temperatures, such as near the melting point of Na_2BeF_4 at about 700-800°, only cathodic deposition of sodium was obtained (44), whereas in the case of higher melting $MgBeF_4$ or $BaBeF_4$ at about 1000° considerable dissociation apparently occurred, and Be, rather than Mg or Ba, was obtained in the cathodic deposit.

In view of the absence of highly suitable additives, it was decided that beryllium fluoride should be tried as a constituent of the melt on the theory that at lower temperatures it might be complexed so completely that it would be present in substantially only the anionic form. An additional advantage anticipated was that the addition of a substance forming another species of anion would be more effective in producing the desired lowering than would the addition of a substance contributing only fluoride anions.

From the above information it was concluded that potassium and lithium were the best available simple cationic additives, although their deposition potentials so closely approach that of calcium that in practice selective deposition of calcium might not be possible. As discussed in the next section, a method was sought by which the effective deposition potentials might be shifted to favor calcium deposition.

Effect of Liquid Metal Cathodes on Potential

The information in the preceding section referred to deposition potential relationships of the metals in substantially pure form. Deposition of a metal upon the surface of another liquid metal with formation of an alloy might be expected to decrease the effective deposition potential by an amount dependent upon the heat of formation of the alloy. Thus it might be possible to selectively deposit calcium in the form of an alloy with some liquid metallic cathode without substantial deposition of additive cations such as lithium or potassium.

The conscious use of this method for the purpose of shifting deposition potentials in commercial fused salt electrolysis has not been found in the literature, but a few experimental studies have been made which appeared encouraging. Jellinek and Czerwinski (77), working with mixtures of varying proportions of sodium chloride with alkaline earth chlorides, showed that up to approximately ten times as much of the Group II metal was selectively deposited in a molten lead cathode for approximately equimolar mixtures of the salts. For mixtures containing approximately 90 mole percent of sodium chloride, the weight percents of sodium and Group II metal deposited were approximately equal.

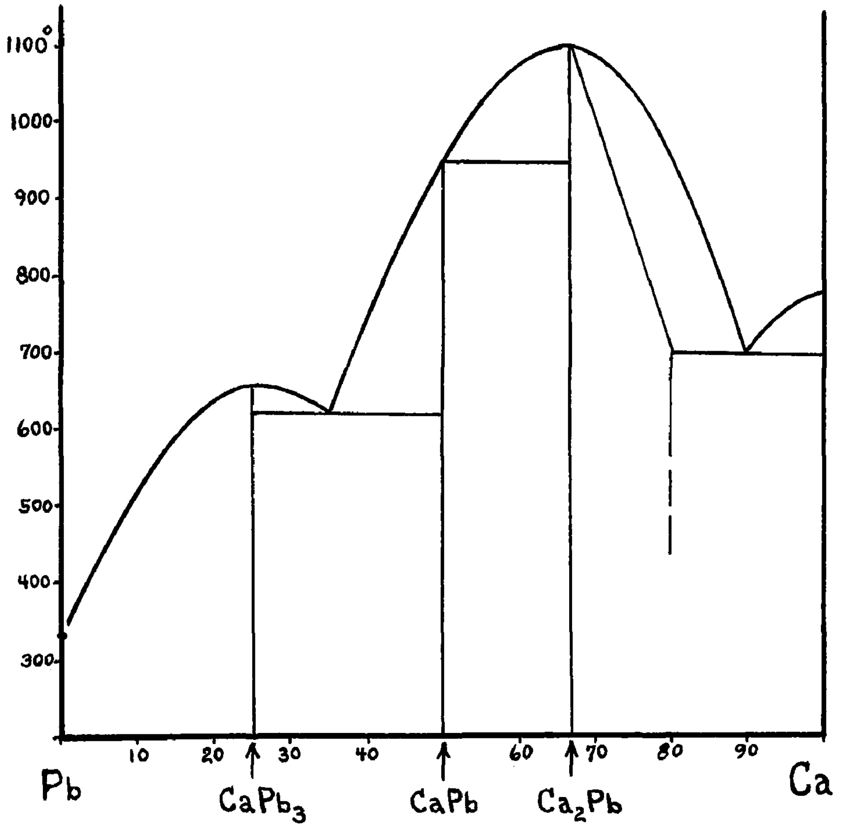
Considerable commercial preparation of calcium-lead alloys has been carried out in melts using additives of sodium chloride or potassium chloride, usually to calcium chloride melts which used molten lead cathodes. Numerous references are given for this process by Englehardt (45). While such processes are operable it has been noted that it is very essential to provide large cathode areas, preferably with agitation and continual presentation of fresh lead surfaces. The extremely slow diffusion rates of the deposited calcium and the compound Pb_3Ca apparently are controlling and if the process is not assisted in some way the surface becomes saturated with calcium and the deposition potential is shifted to a more normal value (114).

Information on various common low melting metals was collected with respect to the alloy systems which they form with potential constituents of a calcium fluoride melt. Based on later information as to the probable operating temperature certain eliminations were possible. Considerations such as relative availability and alloying tendencies with calcium, lithium, potassium, and beryllium indicated that probably lead was generally most suitable, particularly as the information was less complete for other possible alloying metals such as cadmium, zinc, tin and bismuth. References to pertinent alloy systems are given in Appendix 4.

Calcium-lead alloys have been prepared from baths containing sodium chloride or potassium chloride as additives (112) (139), and the partially selective depoistion of calcium on a molten lead cathode ahead of sodium from chloride melts had been demonstrated by Jellinek and Czerwinski (77). It was decided to try the combination of calcium, lithium and beryllium fluorides in conjunction with a lead cathode to see whether calcium would be deposited even more selectively in the presence of lithium. In the event that this proved not to be the case, it was felt that potassium fluoride might be substituted for the lithium fluoride, to see whether the normal order of increasing deposition potential of potassium, lithium and calcium, as given by Ruff (135) for fluoride melts, could be shifted to favor calcium deposition.

Insufficient heat of formation data were available to permit estimation of the relative effect of alloy formation on the deposition potentials of lithium and calcium. For lithium-lead compounds no information was found. For calcium, the heats of formation of the compounds Ca_2Pb and CaPb have been reported to be 47 and 25 Kcal./mole respectively (88), but no data are available for the compound $CaPb_3$ which is of most interest. An estimate of 10-15 Kcal./mole for a minimum value of the heat of formation of the latter compound would probably be reasonable. The lithium-lead compounds are considerably lower melting than the calcium compounds which might be indicative of somewhat lower heats of formation for the lithium alloys.

The phase diagram of the calcium-lead system (88) is given below to illustrate the point that operation is not possible at very low temperatures with very appreciable calcium contents.



Available Information on Phase Relations and Anticipated Behaviour

At the start of this work, no information was available on the binary systems and the ternary system formed by calcium fluoride, lithium fluoride and beryllium fluoride. A survey of information on analogous systems was made to learn whether there might be any correlation which would permit prediction of the general behaviour of the systems of interest in this investigation. References to information obtained in this preliminary survey, and to subsequently published reports, have been summarized in Appendix 1.

Information on the thermal and other physical properties of the three constituents, calcium, lithium and beryllium fluorides, has been collected in Appendix 2.

Since information on compounds formed in the ternary and binary systems might have been reported independently of any phase diagram studies, a literature search was made for the methods of preparation and properties of compounds which might be expected to form. Pertinent information and references have been assembled in Appendix 3.

Based on the above information the following behaviour was anticipated for the binary and ternary systems.

The calcium fluoride-lithium fluoride system was expected to show a simple eutectic behaviour with no compound formation. It was believed that the eutectic would occur at approximately 30 mole percent of calcium fluoride at about 750°.

In the calcium fluoride-beryllium fluoride system formation of the compound $CaBeF_4$ was expected and two eutectics were anticipated. No reliable estimates could be made as to the positions or melting temperatures of the eutectics or of the compound.

In the lithium fluoride-beryllium fluoride system, compound formation was anticipated, at least for Li_2BeF_4 and possibly for other compounds. The eutectic in the region of 30 mole percent BeF_2 was expected to be rather shallow with respect to the peak for the compound Li_2BeF_4. The latter was expected to have a melting point in the range of 450 to 500°. Another lower eutectic was anticipated in the region of about 50 mole percent BeF_2 at a temperature of about 400-450°.

In general, the anticipated binary systems have a fairly close resemblance to those actually found. However, for the anticipated ternary system, the prognostications proved less accurate. No information was available to indicate the formation of a compound <u>within</u> the ternary system. From the number of components and the anticipated binary invariant points, a minimum of three invariant points was expected within the ternary system. These points were estimated as probably lying out in the region of 10 to 20 mole percent CaF_2, a considerable over-estimate in the light of subsequent data. Temperatures of the invariant points naturally were expected to lie somewhat below the binary invariant points, but not as low as proved to be the case.

In the beryllium fluoride rich section of the system some difficulty was expected because of the formation of glasses rather than crystals, but the severity of the effect and its rather wide area of influence was not anticipated.

These estimates of the possible behaviour have been given since they outline the point of view used in interpreting initial results. A perfectly unbiased approach to the study of a ternary system is probably as poor as the opposite extreme of retaining preconceived ideas, as the treatment is best handled by variations to test the correctness of interpretations.

The Phase Rule

The complication of phase relations caused by the introduction of a third component, with the consequent possibility of interactions between ternary compounds, binary compounds and the three components, increases the possible permutations into the order of hundreds for only moderately complicated systems. Consequently no text dealing with phase relations may reasonably hope to explain and illustrate more than a very small fraction of the possible cases.

Unfortunately in most texts in English, the subject of three component systems has until quite recently received only a very sketchy treatment, with the exception of the important systems formed with water. While there is no formal difference between aqueous and non-aqueous systems, there is the practical difference that most of the work on aqueous systems is presented in isothermal studies, so that complete descriptions of behaviour over a wide range of temperature are a rarity. Hence such descriptions are usually not helpful for the non-isothermal studies of fused salt systems.

The unrecognized contributions to Phase Rule theory by Gibbs (51), were revived in an exhaustive treatment in the German language by Roozeboom (133). Based on the latter work, Masing (109) wrote a much less complete text in German, which has been translated into English by Rogers (130). Also in English there is a treatment by Marsh (105), based in part on Masing's text. Until the appearance during the past year of several new and revised texts, those of Rogers and Marsh were the only available helpful summaries in English on the subject of ternary systems.

In discussing the subject of the Phase Rule and phase diagrams certain conventional assumptions will be made. The systems will be treated as "condensed systems" unaffected by normal pressure changes, magnetic and gravitational fields, etc. In addition, except where stated to the contrary, the absence of solid solutions will be assumed for two reasons. Firstly, the presence of solid solutions greatly complicates the phase diagrams and secondly, no evidence was found in the present work for the occurrence of any substantial mutual solubility of the solid phases. Naturally such a complete lack of miscibility of the solids is impossible. However, if it is small in extent, it practically reduces to the case of complete immiscibility, with certain exceptions as will be noted.

It is also implicitly assumed that equilibrium conditions prevail and that all phase transformations occur in a completely theoretical manner, although it will be shown that such is not always the case in the system under discussion.

The Phase Rule of Gibbs deals with the equilibria existing among the homogeneous portions of a heterogeneous system. The homogeneous portions, usually called phases, are regions having uniform physical properties and compositions, separated from each other by distinct physical boundaries. Pressure and temperature are assumed to be uniform throughout the heterogeneous system. The fundamental hypothesis forming the basis of the Phase Rule is that the properties of a phase are uniquely determined by specifying values for a minimum number of independent variables, an empirically verified fact.

It has been determined that for a phase made up of "n" components, the equation of state required to completely determine the properties of the phase must contain $n + 2$ variables in the case of non-condensed systems. In such cases, two of these variables must be taken from the trio of interdependent variables, p, T and v (specific volume); while $n - 1$ concentration variables must be chosen from the n possible concentration values describing the composition of the phase. Then specification of any pair of the p, v, T variables automatically specifies the third, and the concentration of the "n th" component is automatically determined by specification of $n - 1$ concentration variables. Hence it is apparent that the arbitrary choice of $2 + (n-1) = n+1$ variables will in theory permit calculation of the "n th" variable from the equation of state, i.e. the phase properties are completely fixed.

Thus for a homogeneous phase made up of n components, with an equation of state of the form --

$$f\,[\,C_1, C_2, \ldots\ldots C_{n-1}, p, T(\text{or } v)\,] = 0 \;,$$

the specification of T and p (or v) and n-1 concentrations automatically determines the specific volume (or T or p) and other properties of this phase.

Some explanation of the meaning of "components" is necessary. The number of components of a heterogeneous system is the minimum number of substances whose concentrations in the different phases may be varied independently of each other, under the conditions of the experiment. The significance of the latter phrase may be clarified by several examples.

A closed container having liquid water and water vapor present at ordinary temperatures and pressures would be considered a one component system. At much higher temperatures and pressures the same system would be a two component system since differential solubility effects would cause the composition of the partially dissociated gas phase to be different from that of the initial starting material, water. Likewise the composition of the liquid phase would be different from the starting material, water, for the same reasons. Thus even though all derived from a single substance, the system must be treated as a two component system, since addition of water would not change the relative concentrations of H_2, O_2 or H_2O in the two phases. Hence an additional component is necessary to permit independent variation of the concentrations in the two phases and the system is one of two components under these conditions.

If H_2, O_2 and water (liquid and vapor) are present in a container at low enough temperature so that reaction does not occur, the system must be treated as one of three components. Here addition of water would in no way alter the composition of the gas phase, nor would addition of O_2 or H_2 permit independent alteration of the concentrations in the liquid phase (H_2O + dissolved O_2 and H_2), constant total pressure being assumed. It is apparent that in order to vary the concentrations independently in both phases, all three substances must be classed as components for these circumstances.

If the above system were heated to higher temperatures where reaction and dissociation occur in accordance with the Mass Action Law,

$$K = \frac{C_{H_2}^2 \, C_{O_2}}{C_{H_2O}^2} \quad ,$$

the system becomes a two component one (if entirely gaseous). This follows, since specification of any two of the concentrations determines the third, and consequently there must be two components whose concentrations are independently variable to permit specification of a system of any arbitrary composition. Thus the conditions and any mass action relationships must be considered in determining the number of components of a particular system.

For a non-condensed system the Phase Rule is usually written as $P + F = n + 2$ where P signifies the number of phases present, n the number of components and f the number of degrees of freedom. The 2 arises from the assumed possibility of temperature and pressure variation. In the event that either or both temperature and pressure are arbitrarily held constant the expression has the forms

$$P + F = n + 1 \text{ , for constant T or p.}$$

$$P + F = n \text{ , for constant T and p.}$$

In the present work, the conventional condensed system is assumed with constant pressure, i.e. the effect of vaporization is assumed to be negligible and only liquid and solid phases are presumed to affect the behaviour of the ternary system.

For a condensed system of n components and P phases the Phase Rule may be derived in the following manner. If the n components can be present in each phase, then since $n - 1$ concentration variables are sufficient to define the composition of each phase, a total of $P(n - 1)$ concentration variables are needed to specify the compositions of P phases. In addition 1 must be added for the temperature variable, pressure being considered fixed. Then the total number of variables that need to be specified in order to define the state of the system are equal to $P(n - 1) + 1$.

The chemical potential, or escaping tendency, of each component of a phase is equal at equilibrium to its chemical potential in all other phases of the system. If the variables of temperature and composition are defined completely, then the chemical potential of each component is theoretically expressible as a function of these variables. Then, with respect to a phase containing all the components in equilibrium with $P - 1$ other phases, there are available $P - 1$ relations for each component showing the equality of the chemical potential for each component. For all n components there are $n(P - 1)$ equations available which interrelate the compositions of all phases.

For a system requiring the specification of $P(n - 1) + 1$ variables to define the system, for which only $n(P - 1)$ equations are available, the difference of

$$[P(n - 1) + 1] - [n(P - 1)] = n - P + 1 = F$$

is the number of possible independent changes of state, also called "degrees of freedom". These represent the changes in concentrations or temperature which are possible within the system without violation of the $n(P - 1)$ equations relating the compositions in all P phases. In order to completely define the system, F variables must be arbitrarily fixed so that the remaining variables will be determined by the equilibria existing among components in the different phases.

Thus for a condensed system, in general, $F = n - P + 1$ and for a three component or ternary system

$$F = 3 - P + 1 = 4 - P$$

Then for a ternary system, the presence of two phases permits two degrees of freedom, i.e. fixing of one composition variable and the temperature is necessary in order to define the system. For three phases present, it is only necessary to fix one variable, e.g. the temperature, in order to define the system. Finally for four phases present, there are no possible degrees of freedom, i.e. this circumstance occurs as a singular point at only one temperature and set of composition values, and the system is called invariant since one of the phases must vanish before any change is possible among the temperature and composition variables.

Confining the discussion to ternary condensed systems in which one of the phases is a liquid and the others solids, two types of invariant points are possible. Symbolizing the phases as melt, A, B and C, two possible types of equilibria may be written--

$$\text{melt} \rightleftharpoons A + B + C$$

and $$\text{melt} + A \rightleftharpoons B + C$$

The first relation is that of the ternary eutectic point at which a melt, simultaneously saturated with respect to A, B and C solid phases, exists at equilibrium with them at a particular over-all composition value and a fixed temperature. By withdrawal of heat, the equilibrium is driven to the right, until finally with the disappearance of the last of the melt, the system becomes univariant and temperature or composition variation of the remaining phases becomes possible.

The second relation is characteristic of the ternary peritectic point at which a melt saturated with A reaches a particular composition and temperature at which it is also saturated with respect to B and C. Upon withdrawal of heat, it is commonly explained that the melt "reacts" with A to form B and C. A better way of stating the situation is that upon deposition of B and C the melt becomes unsaturated with respect to A and some of it dissolves. On continuation of this process it can be seen that one of two conclusions may be reached, depending upon the relative amounts of A and melt which are present. Either A may be in excess in which case complete solidification occurs at the ternary peritectic point, or the melt may be in excess in which case A vanishes and the system made up of melt, B and C is again a univariant system free to undergo change of temperature or composition variables.

Analogous singular points occur in binary condensed systems except that the number of solid phases participating is reduced by one.

It should be noted that in practice peritectic "reactions" may not proceed as completely as theory requires, because of insufficient time to attain equilibrium, effective isolation of previously deposited solid by a coating of a new phase, and similar difficulties. Likewise the formation of a solid phase may occur in a non-theoretical manner in that supercooling may occur to small or large extents so that thermal analyses may yield deceptive results.

Certain generalizations and specific cases describing the behaviour of ternary systems have been given in Appendix 5. The interpretation of the experimental results depends upon the proper application of these ideas which are derived from general Phase Rule theory and the geometrical system of representation which is used.

EXPERIMENTAL

EXPERIMENTAL

Preparation of Materials

Preparation of the melts required for the study of the binary and ternary systems furnished a serious problem in one respect. While calcium fluoride and lithium fluoride were readily available, beryllium fluoride was more difficult to obtain and consequently much of this material was prepared or reclaimed by the methods to be described.

Through the courtesy of Mr. Carl Anderson of the Ozark-Mahoning Company, there were provided several lots of high grade, hand selected, natural fluorspar ore. One lot of this material, of a quality which would be called "optical grade", was used almost exclusively during this work. The transparent material was again hand selected to remove pieces with any visible inclusions of foreign matter. The material was then crushed and mixed to form a homogeneous sample. The standard method of analysis for lower grade fluorspar was applied (103), but the inherent inaccuracies of the method are such that they showed essentially no impurities present, except for possibly 0.1% of acid soluble carbonate, with negligible traces of impurities such as silica and heavy metals. The calcium fluoride was therefore considered to be nearly 99.9% pure and in all computations was considered to be 100% pure. Details of analyses and results have been collected in Appendix 15, Part A.

Lithium fluoride used was J. T. Baker Analyzed grade and no attempt at purification was made. The total of listed impurities indicated by their analysis was approximately 0.1%.

Lithium carbonate, J. T. Baker Analyzed grade, was used in synthetic wet preparation of Li_2BeF_4. Indicated impurities of approximately 0.5% of other alkali metals probably did not introduce any significant impurity into the product.

Ammonium fluoride and bifluoride used in the preparation of $(NH_4)_2BeF_4$ were of various degrees of purity. Impurities and preparative methods were such that it was unlikely that they contributed impurities which were not eliminated during one of the preparative steps or in the various reclamation steps carried out on the mother liquor residues from the $(NH_4)_2BeF_4$ preparation.

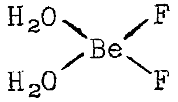
The supply of the necessary beryllium fluoride presented much more difficulty. One commercial lot of material (1 pound) was obtained from the Brush Beryllium Corporation. This beryllium fluoride, stated to have approximately 99% purity, tended to form slightly cloudy melts with the other fluorides. Analysis confirmed the purity as 99% calculated from the analysis for beryllium metal as the oxide. (See Appendix 15, Part B.) Subsequent attempts to obtain additional quantities were unsuccessful, but after the conclusion of the thesis work, the American Beryllium Corporation indicated that it could then make available a probably better grade of material.

Beryllium fluoride used in about the first quarter of the work on beryllium fluoride systems were prepared from an old lot of about 400 g. of Kahlbaum "beryllium carbonate" which was available. Analysis of this material is covered in Appendix 15, Part B.

In the very last stages of the work, some so-called beryllium basic carbonate was obtained from the A. D. MacKay Company. The material was not analyzed, but was put through the regular basic acetate purification process described below. Considerable quantities of iron were removed and only a 50% yield of theoretical was obtained indicating that the original material did not correspond to the conventional basic carbonate formulated as $(BeO)_5:CO_2:5H_2O$.

Other than by the reaction of the elements, beryllium fluoride in pure anhydrous form has apparently only been prepared by the classical method of LeBeau (96) in which anhydrous $(NH_4)_2BeF_4$ is heated in a protective atmosphere to drive off $2NH_4F$ leaving the anhydrous BeF_2. While the method appears quite elegant and no difficulties are described in the literature, the procedure on a laboratory scale quickly gets into difficulties, although it is apparently used by both large commercial producers in this country. Briefly, as NH_4F is evolved the mass of material melts to a thin liquid which becomes thicker and thicker as it approaches the composition of BeF_2. The combination of viscous liquid and evolving NH_4F causes formation of prodigious quantities of foam resembling "Foamglas". The preparation in quantities, even as small as 5 to 10 grams, requires manipulations that are highly incompatible with the requirements for carrying out the reaction in an atmosphere of dry carbon dioxide.

Although the beryllium fluoride for the initial investigation of the CaF_2-BeF_2 system was prepared in the above manner by heating $(NH_4)_2BeF_4$, on subsequent work it was found that the NH_4F could be reliably evolved in a considerably smoother manner if either calcium or lithium fluorides were present to lower the viscosity of the liquid mass. Reasonably good results were obtained by heating such mixtures in a platinum dish under an inverted funnel through which dry carbon dioxide was passed at a high rate. Quantitative checks indicated that all the NH_4F was evolved after the melt ceased rapid evolution and the only visible gas bubbles were a few adhering to the bottom of the dish. This was true at temperatures as low as 400°, whereas with $(NH_4)_2BeF_4$ alone, considerably higher temperatures or evacuation is necessary to remove the last of the NH_4F.

Beryllium fluoride is quite hygroscopic and unusual with respect to its high coordinating ability. Its aqueous solutions will yield basic salt mixtures unless the coordination requirements are satisfied by some other means. The process of solution in water is very slow in reaching equilibrium since beryllium fluoride is essentially a polymer. On reaching saturation, however, it is found that almost 18 moles of BeF_2 per liter of original water are present, which has lead to the proposal that a structure like  is present (98).

Since preparation from aqueous solution leads to indefinite oxyfluoride mixtures, an attempt was made to determine whether the use of anhydrous liquid hydrogen fluoride might be more successful. Since no oxygen-free beryllium salt was available, beryllium carbonate was added slowly to a considerable excess of anhydrous hydrogen fluoride. Upon removal of excess hydrogen fluoride, however, a mixed gummy oxyfluoride was obtained, indicating that the beryllium fluoride formed (not soluble in the medium) was able to retain the water evolved in the reaction despite the extreme dehydrating effect of the anhydrous hydrogen fluoride.

Subsequent preparations were confined to the ordinary wet methods involving the formation of $(NH_4)_2BeF_4$. The use of NH_4HF_2 is much more economical than the method using NH_4F as may be seen from the stoichiometric relations below, but the purity of the available NH_4HF_2 is considerably poorer. Both methods were used depending on available material.

Essentially the method consisted of precipitating, filtering and washing the hydrated beryllium hydroxide, dissolving it in a solution of either NH_4F or NH_4HF_2, filtering to remove impurities, evaporating, cooling, and crystallizing out $(NH_4)_2BeF_4$. The latter was filtered and washed with dilute (50%) and then more concentrated (80%) ethanol-water solution to remove mother liquor, and then dried at 110° to give the anhydrous product. The reactions involved are:

$$Be^{++}: x\ H_2O + 2NH_4OH \longrightarrow Be(OH)_2: x\ H_2O + 2NH_4^+$$

$$Be(OH)_2: x\ H_2O + 2NH_4HF_2 \longrightarrow (NH_4)_2BeF_4 + (2 + x)\ H_2O$$

$$\text{or}\quad Be(OH)_2: x\ H_2O + 4NH_4F \longrightarrow (NH_4)_2BeF_4 + 2NH_3 + (2+x)\ H_2O$$

The preparation has been described by Ray (128).

Certain practical difficulties should be mentioned. If the starting quantity of beryllium is not accurately known, excess of NH_4F will tend to lower the purity of the product. If an attempt is made to govern the amount of NH_4F by the addition of just enough to dissolve the $Be(OH)_2$, the attainment of completion of the reaction is slow, or too much NH_4F may be added if small amounts of insoluble cloudy material are present (as was the case in the reclaimed beryllium solutions of the present work). On the other hand the hydrated beryllium oxide can also be peptized by the strongly ammoniacal solution. If excess NH_4F is present it does not usually substantially affect the purity of the first crop, but very definitely does tend to be present in subsequent crops of crystals.

The extreme solubility of $(NH_4)_2BeF_4$ (probably considerably greater than 100 g./100 g. of H_2O) makes the recovery process a slow one. Likewise the initial washing of the crystalline crop must not be carried out with too concentrated an ethanol solution lest the adherent mother liquor be subjected to a salting out effect. On the other hand the losses by effective washing are usually very severe, and consequently the entire process is a long drawn-out one since the mother liquor may only be reconcentrated on the steam bath because of the "bumping" difficulties produced by faster evaporation.

Proper adjustment of the ethanol content of the wash solution permits a considerable reduction in the solubility of the $(NH_4)_2BeF_4$. Some workers have used ethanol addition as a substitute for evaporation, but a trial of this method indicated that the yield had somewhat lower purity. In general, preparations of $(NH_4)_2BeF_4$, made during many recovery stages in this work, ranged from about 99 to 85% pure. The balance, consisting of NH_4F, had only one harmful effect, i.e. it made more difficult the determination of the amount of BeF_2 being introduced into a melt. See Appendix 15, Part C.

As the beryllium content of the melts was salvaged and reused many times during the work, a description of the reclamation process is in order. The pulverized melts were treated with 80% perchloric acid-water mixtures and boiled to drive off all fluorine as HF. (Use of **sulfuric** acid was not satisfactory because of formation of insoluble calcium sulfate.) The perchlorate solution was then diluted and the beryllium precipitated as the hydroxide with excess ammonium hydroxide. Nickel present as an impurity (from the nickel stirring rods used in the melts) was separated as the soluble ammonia complex. Calcium and lithium trapped in the precipitate were removed by additional reprecipitations. Occasionally the recovered beryllium hydroxide was given an 8-hydroxyquinoline purification treatment to remove iron and aluminum impurities which might otherwise have tended to accumulate (70).

In the latter part of the work, when the inadequacy of the analytical method for beryllium made it very desirable to obtain 100% pure $(NH_4)_2BeF_4$, an attempt was made to arrive at this by preparing a pure beryllium compound, the basic acetate, or $Be_4O(CH_3COO)_6$. It was hoped that with this as a starting material it might be possible to avoid any excess of ammonium fluoride in the $(NH_4)_2BeF_4$.

The preparation of $Be_4O(CH_3COO)_6$ involved addition of the purified precipitated hydroxide to glacial acetic acid and evaporation to dryness on the steam bath. Filtration prior to evaporation removed some silica and possibly additional insoluble residues resulting from attack on the glassware used in the perchloric acid treatment where HF was evolved. The $Be_4O(CH_3COO)_6$ was redissolved in boiling glacial acetic acid and filtered hot with the removal of a considerable amount of troublesome insoluble material, the identity of which was unknown, but which was tentatively ascribed to silica or to the possibility of cross-linked basic acetates. The product was separated by filtration from the cool solution and was twice recrystallized from glacial acetic acid and finally dried at about 150°.

This $Be_4O(CH_3COO)_6$ product was of high purity such that the inaccuracies of the beryllium analysis did not permit distinguishing it from 100% purity. See Appendix 15, Part D. The hoped-for improvement in the $(NH_4)_2BeF_4$ purity was only partly attained, however, for various reasons such as the uncertainty in composition of the NH_4HF_2 used, etc., but the method was retained throughout the balance of the work as a means of preventing recycling and buildup of impurities.

The recrystallization of beryllium basic acetate has been described by Booth (8). The earlier work on its preparation and properties for atomic weight purification purposes was described by Parsons (126) and more recently by Hönigschmid (73).

For preparation of $(NH_4)_2BeF_4$, the basic acetate was converted to nitrate by boiling with nitric acid and, contrary to literature reports, the treatment must be made quite drastic, as judged from the prolonged period of acetic acid evolution, if freedom from acetate is to be attained. Precipitation of the hydroxide from the nitrate solution was followed by conversion to the chloride which gives a more washable type of hydroxide precipitate. The latter was then used in the $(NH_4)_2BeF_4$ preparation process previously described. The electrolytic preparation of a "crystalline" form of beryllium hydroxide has been described by Booth (8) as the best way to obtain a product free of occluded foreign electrolytes.

In another attempt to obtain a melt of definitely known composition, the general method described by Ray (128) was tried in which $Li_2BeF_4{:}1H_2O$ was prepared by the addition of Li_2CO_3 to a solution of $(NH_4)_2BeF_4$. When this was tried in a modified way using hot solutions and rapid evaporation, a poor looking product with indications of the presence of oxy-fluorides was obtained. Another attempt was made using a cold solution of Li_2BeF_4 prepared by dissolving the product of a dry fusion of the stoichiometric quantities of LiF and $(NH_4)_2BeF_4$. The resulting solution was then evaporated at room temperature (or lower) in a large vacuum desiccator. Upon reaching the volume at which saturation with $Li_2BeF_4{:}1H_2O$ should have occurred (according to Ray), no solids were present. After several more weeks of evaporation translucent crystals, with an index of refraction almost identical with that of water, commenced to form. After about another week of evaporation, to reduce the volume to that amount which should have been easily capable of holding any soluble impurities, the solids were equilibrated for several weeks with the solution. The product was separated by filtration and was washed sparingly with cold water and then with a very little ethanol followed by ether.

Analysis of the resulting product showed nearly the theoretical composition. See Appendix 15, Part E. Actually the errors of analysis were such that the purity probably was 100% with the possible exception that the extent of hydration might not have been exactly according to theory. This product, when heated to constant weight to drive off the water, gave a perfectly clear melt with which the melting point of Li_2BeF_4 could be determined with more certainty.

The attractiveness of the Ray Li_2CO_3 method is somewhat decreased by the knowledge of the relative solubilities involved. In order to prepare one mole of Li_2BeF_4 (98.9 g.), it would be necessary to start with about 5 liters of water in order to dissolve the Li_2CO_3. The solubility of about 13.2 g. per liter claimed by Ray (128) for Li_2BeF_4 would make necessary the vacuum evaporation of approximately 4.9 liters of water in order to obtain about 90% yield. Actually the Li_2BeF_4 is considerably more soluble, a rough figure of 23 g. per liter being obtained in this work from analysis of the undiluted mother liquor. (See Appendix 15, Part E).

Equipment

The principal equipment used in the work consisted of a specially constructed furnace and a potentiometer-recorder for automatic plotting of the time-temperature curves.

Since some of the work involved temperatures of 1400° and higher, the usual types of wire wound furnaces were not suitable. For this study a furnace was constructed using Carborundum "Globar" resistance heating units which are limited to a recommended maximum temperature of 1450°. Eight of these heating units were distributed symmetrically in a circle, surrounding and parallel to a vertical 3" I.D. "Alundum" tube. Surrounding the circle of heating elements was a shell of cast refractory closed at top and bottom ends by heavy cast refractory pieces through which the cooler end sections of the heating elements passed. Electrical contacts were made to the elements on the outer faces of the refractory end plates. The active heating region of the elements, about 6" in length, was thus permitted to directly radiate to the central tube where the sample container was located. Heat losses from the elements were held to reasonable values by about 4" thicknesses of refractory on the ends and laterally by about 5" of refractory, plus about 2" of exfoliated vermiculite placed between the refractory and the outer shell. The ends of the "Alundum" tube were closed by about 4" of refractory except for a small hole to permit observation, stirring operations, etc.

The refractory used was deliberately chosen to obtain minimum possible heat storage capacity compatible with good insulation qualities. Johns-Manville "Light Weight Firecrete" was used even though the deterioration of the refractory was severe during the short period of use at temperatures higher than its recommended peak service temperature of 1300°.

Power supply was controlled by a 45 ampere capacity "Powerstat" autotransformer with voltmeter and ammeter indication of the secondary power demands. Connection to the elements was made thru a bus-board arrangement permitting alteration of the series-parallel circuits as the elements increased in resistance with ageing.

A Leeds and Northrup "Micromax" Potentiometer-Recorder was used in conjunction with a platinum-platinum, 10% rhodium thermocouple. A chart speed of 6" per hour was used. The fixed scale of the recorder was adjusted during calibration, and all subsequent critical temperature measurements were made from the fixed scale rather than the chart record, as the latter is subject to expansion-contraction and tracking errors. By using the glass face of the instrument as a mirror and lining up the pointer with the pupil of the eye it was possible to estimate temperatures to less than 1° over the 1600° range.

The same thermocouple was used throughout the work, although gradually shortened by numerous breakages and rewelding operations. Leeds and Northrup compensating leads were used between the thermocouple and the recorder which was equipped with a cold-junction compensator for ambient temperature correction. Internal accuracy of the instrument was excellent and other uncertainties are believed to have been larger than any instrumental error. Auto-standardization occurred at regular 45 minute intervals against the internal standard cell and for critical measurements the instrument was hand-standardized to remove slight errors due to drift of the operating dry cell voltage.

The thermocouple was calibrated on numerous occasions at a variety of fixed points over the range of 100° to about 1100°, and once the fixed scale had been adjusted no further change was found necessary. The calibration points used were the following (91):

Boiling water 100°*
Freezing tin 231.85°
Freezing lead 327.4°
Melting potassium dichromate 397.5°
Freezing zinc 419.45°
Freezing antimony 630.5°
Melting potassium chloride 770.3°*
Melting sodium chloride 800.4°*
Melting potassium sulfate 1069.1°

The uncertainties in the determination of the fixed points were variable, usually from 1 to 2°, but in the cases indicated with an asterisk agreement was better, probably to within less than 1°. In general therefore a ±1° error in absolute accuracy was possible, but the relative errors were probably in the order of ±3/4° or less. With respect to the highest ranges above 900° no definite statement can be made as to the accuracy although it is believed that ±2° would be a reasonable estimate of the probable error. An attempt was made to obtain a calibration with nickel at 1452°, but the attempt was unsuccessful and was not repeated because of the extreme overload placed upon the furnace and power supply at this temperature. The check obtained on the calcium fluoride melting point with the value given by Naylor (116) indicates an error of no greater than 5° at the 1400° level. This is quite understandable in view of the large radiation errors which may occur at this temperature.

Calibrations in which metals were used necessitated the use of a thermocouple well (glass or graphite), but in all other cases, and during all of the phase diagram work, the couple was immersed directly in the melt. Breakage was more severe at high temperatures, but below 800° a single weld would frequently last the equivalent of 300 to 500 hours of continuous operation. The use of bare thermocouples was not only a convenience, but was a necessity due to the relative shallowness of the melts used. Use of protective wells in the phase diagram work would have created large opportunities for conduction errors. No effect of direct immersion upon the welds was observed, breakage normally occurring at a point where corrosion tended to be most severe, i.e. just at the surface of the melt.

In use the couple was immersed to a point slightly above the bottom of the container, in a manner comparable to that used in calibration. Almost all melts were hand-stirred with a nickel rod, either continuously or at sufficiently short intervals so that temperature differentials within the melts were minimized at all points of critical interest. As unstirred melts in some of the systems gave erratic results, several mechanical agitation systems were tried, including propellors and spring-loaded plungers. None were very successful and breakage of the bare thermocouple was frequent in the freezing melt.

As the benefits of observation and "feel" during stirring were considerable, hand stirring was used in most of the work. Nickel welding rods, which are relatively poor conductors of heat and fairly stable to attack by the melts, were used.

As sample containers, carbon crucibles (about 3" O.D. and 2" I.D. by 2 1/2" deep) were machined from carbon electrodes. These were used for most of the work on the CaF_2-LiF system, but on subsequent work shallow platinum dishes (about 40 ml. capacity) were used, primarily because they permitted a more satisfactory check of the changes in the weight of the melt.

For electrolytic work a direct current supply was constructed. A selenium rectifier, arranged for full wave rectification was fed by the secondary of a Powerstat auto-transformer. The D.C. output was filtered by a double LC type of filter, using high capacity electrolytic condensers and specially constructed low resistance (iron core) choke coils. With this arrangement low ripple currents of 30 amperes at low voltage (10 V) could be provided, as well as small currents (1 to 2 A) with negligible ripple at higher voltages such as 50 V.

Electrolytic apparatus is described in the section covering that phase of the experimental work.

General Procedure

Certain pertinent comments and the general procedure followed in the work on the phase diagrams are given below in some detail for the different systems studied.

Mixtures for the preparation of the melts were usually made with oven-dried materials weighed to within the nearest 0.0005 g. The total weights used varied considerably, the principal determining factor being the requirements for beryllium fluoride. Since the latter was difficult to prepare, particularly in large quantities, melts containing larger proportions of this material were usually made up to total weights of about 30 g. Other melts requiring less beryllium fluoride were made on a somewhat larger scale, but the size of the available platinum dishes restricted the maximum amounts used.

The beryllium fluoride used was obtained in three general ways. For the CaF_2-BeF_2 system, the initial set of runs was made using beryllium fluoride prepared by decomposition of $(NH_4)_2BeF_4$ in large carbon crucibles in the absence of other fluorides A few runs made on this system at a much later date utilized beryllium fluoride prepared in the presence of calcium fluoride. For work on about two-thirds of the LiF-BeF_2 system and the ternary system, beryllium fluoride obtained from the Brush Beryllium Corporation was used. This material had been placed in a large number of small jars using dry box technique, and the jars were kept in a desiccator over magnesium perchlorate. During weighing, the material was exposed to the atmosphere as little as possible and the mixture was immediately placed in the furnace to avoid moisture pickup. For the balance of the work, the beryllium fluoride was prepared by the decomposition of weighed quantities of $(NH_4)_2BeF_4$ in the presence of either or both of the other fluorides. This operation was carried out under an inverted funnel supplied with a rapid flow of dry carbon dioxide. After the evolution process was complete the platinum dish and load were weighed to permit calculation of the actual weight of beryllium fluoride present. Calcination of the calcium and lithium fluorides showed slight losses over the oven-dried weights and small corrections were made to the weighed quantities to compensate for such losses where uncalcined materials were used.

All melts were then positioned in the same relative vertical position in the furnace, using as a support a number of inverted porcelain Gooch crucibles in an attempt to minimize the heat storage of material in immediate contact with the container and melt. The top opening of the central "Alundum" tube of the furnace was closed with a split refractory plug leaving only a small access hole for the suspended thermocouple and stirring rod. A slow stream of thoroughly dried carbon dioxide was passed in through a copper inlet tube projecting down into this opening.

Melts were generally heated 100 to 150° above the anticipated region of interest and thoroughly mixed. The cooling rate was controlled by the appropriate setting of the power input which was varied in accordance with the particular range of operation so that cooling rates were roughly comparable. The approximate time involved per cycle averaged about 1.5 hours, figured from peak temperature to peak temperature on successive melts. Usually about 20-25 minutes of cooling occurred prior to an invariant point. The holding time at such points was about 15-20 minutes depending on eutectic content of the melt. Subsequent cooling and reheating usually required about 40 minutes.

During cooling the melt was stirred occasionally and the temperature reading from the fixed scale of the recorder was noted on the chart. In the region of points of interest stirring was usually made as continuous as possible and, particularly during the invariant process, stirring was carried on as long as the melt was liquid enough to permit mixing of the plastic mass. Actually, however, judging from the thermal holding times, about 25-30% of the process remained to be accomplished when the melt was too solid for further stirring, due to a large amount of non-apparent liquid present in the solid mass.

The thermal effects observed, particularly with respect to primary crystallization of a single component were variable. In regions of shallow slope of the temperature vs. composition curve, the effects of primary and secondary crystallizations showed up unmistakably. In other regions of much steeper slope, where very little primary solids might be deposited during a drop of 100° or more, the effects varied from reasonably detectable to no observable thermal effect, in the sense of a relatively good inflection point on the cooling curve. The fact that the furnace was built and insulated for work at high temperatures in part aggravated this condition at the lower temperatures.

Because of the uncertainty in a few of the results of the CaF_2-BeF_2 system, observations were made on the cooling melt and it was found that a visible effect occurred on the surface just prior to obvious points of crystallization. This was attributed at the time to the removal of small surface dust particles during the formation of the first surface crystals. On subsequent work in the binary LiF-BeF_2 and ternary systems, when thermal effects became uncertain, observation using a powerful spotlight was used and it was found possible in most cases to detect the initial crystallization from surface effects just prior to observable thermal effects. In the case of calcium or lithium fluorides appearing as the first crystals, the effect was quite sharp, as if suddenly a coating of tiny shining oil droplets developed on the surface. While quite similar in their initial appearance, the behaviour of the "droplets" differed sufficiently during the next minute or two of crystallization so that the two could be differentiated. In the case of Li_2BeF_4 crystallization, the surface of the melt suddenly developed rapidly growing needle crystals which would cover the surface in a very few seconds. Both the above effects preceded the thermal effects (where observed) by about 1 to 2° depending on the cooling rate, the surface of the melt tending to be slightly cooler due to radiation, despite constant stirring.

The primary crystallization of $CaBeF_4$ was not as a rule observable by a surface effect. Although the material is needle shaped and might be expected to initially appear on the surface if the other crystalline forms could, it characteristically seemed to form below the surface and sometimes would be attached somewhat to the platinum dish. This would result in a gritty feeling as the hand manipulated stirrer passed across the bottom of the platinum dish. In certain cases where the initial crystallization of the $CaBeF_4$ was accompanied by no apparent thermal effect still another technique was tried. It was found somewhat accidentally that if a cold 1/8" nickel rod was plunged to the bottom of the melt and immediately withdrawn, small needles were observable sticking out from the thin shell of frozen material on the end of the rod. This method of detection of $CaBeF_4$ deposition had to be used in a small region of the melt where no other methods worked. The reproducibility of this method was checked and in some cases was found to be good to within about 5°, but in other cases it was poorer, possibly because of other interferences. These results accordingly were treated as doubtful. No difficulty was occasioned by the fact that both calcium and lithium fluoberyllates have needle-like shapes, since that of lithium is not stable above approximately 460° and characteristically it always appears first as surface crystals.

For the binary systems, CaF_2-LiF and CaF_2-BeF_2, mixtures were prepared with compositions spaced closely enough to adequately define the liquidus curves of the system. The ingredients of the melts were weighed permitting calculation of the composition, and generally the resulting melt was afterwards sampled and analyzed for purposes of checking the calculated composition.

The binary LiF-BeF_2 and ternary systems were largely investigated jointly. The difficulty in the preparation of beryllium fluoride and its poor handling properties made it desirable to economize on effort and avoid exposure of the material to the atmosphere by many weighing operations. Consequently the general procedure used was to prepare a melt on the LiF-BeF_2 side of the ternary diagram and determine its thermal behaviour. Then a weighed amount of calcium fluoride was introduced into this melt, shifting the composition along a straight line toward the opposite calcium fluoride vertex of the ternary diagram. Repetition of this process permitted "sectioning" of the ternary system along this line. Deviations may occur after several such steps for a number of reasons to be discussed. Consequently the ternary melt was sampled at intervals and the melt reused unless the temperature level or indications of hydrolysis made further use undesirable. Such a method had one large advantage in addition to economy. This advantage was that relative temperature values were obtained with more certainty than if two separate melts were prepared, since there was very little uncertainty in the relative compositions of two melts differing only by a small addition of the calcium fluoride. In general the method worked quite satisfactorily, but in one region the resultant uncertainties undoubtedly caused as much work as the method saved in other ways.

Deviations of the melt composition from that calculated from the ingredients occurred for a number of reasons. The principal ones were as follows:

1) Small volatility losses from the initial ingredients on first heating. These were compensated for by corrections based on experience of previous losses.
2) General volatility losses can be quite severe from such melts particularly at temperatures above 850 degrees. Losses due to this item might be as large as 1/4 to 1/2% by weight in the

course of several thermal cycles. The possible fractionation effect produced is unknown.

3) Creepage losses represent a difficult problem in the CaF_2-LiF system and introduce some uncertainties in the other systems. Generally creepage would occur up to the rim and occasionally over the edge and partially down the side of the dish. From experience gained, the melt was removed and the material broken off the sides and exterior before it had a chance to completely escape.

To compensate for losses on items 2) and 3) the melt was withdrawn and weighed with the container at frequent intervals, sometimes after each run in the later stages of the work. Allowance was then made in the calculation of the composition for all such losses on the assumption that the composition of the loss was representative of the melt. Allowance was made also for the weight and character of any samples removed. By means of such compensated calculations agreement was usually obtained with the results of analysis to within 1 mole percent. Since the over-all analytical accuracy was probably no better than this, the calculated values of composition were usually considered more trustworthy, unless special reasons existed for believing otherwise.

While the above uncertainties were smaller, or not of great significance, in other portions of the ternary system, they presented serious problems in the vicinity of the Li_2BeF_4 portion of the system where much less uncertainty was desirable. Here several variations were used in an attempt to decrease the relative composition uncertainties.

In addition to sections directed toward the calcium fluoride corner of the triangle, several other types of sections were employed. Master batches of melts were prepared at about the 20 mole percent .CaF_2 point of the CaF_2-LiF binary system and at about the 50 mole percent CaF_2 point of the CaF_2-BeF_2 binary system. Addition of portions of one or the other of these batches to melts in the LiF-BeF_2 system caused composition shifts directed along sections terminating at the compositions of these batches. In addition master batches of melt were prepared, with the approximate composition of Li_2BeF_4, which were then shifted in either direction along the binary LiF-BeF_2 side of the melt by the addition of one or the other of the pure components. A great many crisscrossing sections were thus obtained along which were distributed a great many points, sometimes as close together as 0.1 mole percent. While this method furnished detailed information about the contours along a given section, discordant relative points on different sections were possible because of the relatively serious effect in this region of small errors in composition and temperature.

For melts with original compositions far from that of an invariant point, the thermal analysis was only carried as far as the primary or secondary crystallization break, since invariant reactions in the presence of too much previously deposited solids tend to yield low temperature values. The detection of secondary crystallization points furnishes additional information provided the initially crystallized species is known, since the point of secondary crystallization lies on a straight line directed away from that species. The intersections of such lines, for melts of different original compositions but the same secondary crystallization temperatures, serve to locate points along lines of two-fold saturation for the simpler ternary cases.

For melts with compositions close to that of an invariant point the thermal analysis was followed through the primary and secondary crystallizations and through the invariant point. In general the process was then followed below this point to an extent sufficient to indicate the relative completeness of the solidification at the invariant point. Because such a variety of weights and cooling conditions were used, the resulting data were not susceptible to the simplified procedure of tabulating "reaction times" and "holding times" on a "per gram" basis.

In place of this method, a direct comparison was made only between closely related melts cooled under similar circumstances. For example successive melts of a given section differed in weight only by the small amount of the additive component and were cooled under similar conditions and hence their thermal behaviours were almost directly comparable on the basis of the chart records. Other melts of different compositions (but the same weight) cooled from much different temperature levels were not directly comparable.

Samples of the solidified melts were examined from two standpoints, that is with respect to gross composition and the determination of the phases present. The samples were analyzed generally in groups of 10 to 20 for cation content, no attempt being made to determine fluorine content. Briefly the complete analyses covered removal of fluorine as hydrogen fluoride by perchloric acid treatment, followed by precipitation of $Be(OH)_2$ which was ignited and weighed as the oxide, BeO. The filtrate was treated to precipitate calcium as CaC_2O_4 which was separated and determined volumetrically with standard $KMnO_4$. The filtrate of the calcium determination was treated to substitute chloride for other anions and remove ammonium salts. A volumetric determination of lithium was then performed on this residue based on the precipitation of a complex lithium periodate. Iodine liberated by the reaction of the periodate with potassium iodide was determined with standard sodium thiosulfate. More complete details are given in Appendices 14 and 15 concerning the methods and results of these analyses.

Optical and X-ray methods were used for the determination of phases present in the samples. A polarizing microscope and suitable immersion media permitted general identification of the constituents where the habits (i.e. cubic, needle-shaped, or glassy) alone were insufficient for this characterization. For most cases special immersion liquids were prepared using glycerine-water mixtures as most of the phases of interest have unusually low indices of refraction.

For X-ray analysis, powdered samples were mounted in Lindemann glass capillaries and exposed to Copper K_α radiation, using a North American Phillips X-ray Diffraction apparatus with 11.459 cm. diameter cameras. Measurement of the pattern or direct comparison was sufficient to determine the presence or absence of phases present in the different regions of this ternary system. The sensitivity of this method appeared to be higher than normal as it is believed as little as 2% of a particular phase was detectable, with the exception of beryllium fluoride. The latter, appearing only as a central halo on the pattern (typical of the behaviour of a semi-amorphous substance), probably was not detectable in amounts less than 4%. The generally high sensitivity is believed to be due to the low absorption power of the constituents, since generally the atomic numbers of these elements were lower than those present in usual mixtures. Also, as a consequence of this fact, it was not necessary to dilute the samples in the customary way.

THE SYSTEM CALCIUM FLUORIDE-LITHIUM FLUORIDE

THE SYSTEM CALCIUM FLUORIDE-LITHIUM FLUORIDE

The CaF_2-LiF system was the first to be studied. The relative simplicity of the system and the greater availability of the components permitted nearly complete characterization of the system on the first attempt. There remained, however, a slight uncertainty as to the exact eutectic composition and the exact location of the steeply sloping liquidus line immediately adjacent to the eutectic on the calcium fluoride rich side. Considerably later, repeat determinations were made on these points using visual observation as well as thermal analysis, and the uncertainties were greatly reduced.

In connection with this study the melting point of calcium fluoride was redetermined. A value of approximately 1413° was obtained, but because of the lack of calibration in this range and the probability of larger errors, the 1418° value obtained by Naylor (116), has been used in the figure describing the system. Likewise the figure of 845° for the freezing point of lithium fluoride given by other workers (143)(166) has been used instead of the value of 850° obtained in this work.

The principal differences in procedure from that generally described in the preceding section involved the amounts of melt prepared and the containers used. For this work the weights were larger, generally about 100 g., and large carbon crucibles were used. The creeping tendencies of these melts are fairly great and the lithium fluoride has appreciable volatility at the higher temperatures, both of which effects tend to cause some discordance between the calculated and analyzed compositions. Hydrolysis became more severe at these high temperatures than was the case with the other systems, and a faint odor of hydrogen fluoride and traces of oxide-like material on the walls above the melt were noticeable.

For this binary system analyses were at first made only for calcium, and because of difficulty in removing the melt from the carbon crucible without contamination, no great reliance was placed on the analyses for the first series of runs. On the subsequent check determinations platinum containers were used and analyses were made for both calcium and lithium.

On the later set of runs a master batch of mixture was prepared which was split and carried (by addition of one or the other component) in both directions from the eutectic region in order to more accurately obtain the relative temperature-composition data.

The results of the thermal analyses for the two series of runs have been tabulated, together with the calculated compositions, in Appendix 7. The analytical results and comparisons of the calculated and analyzed melt compositions have been tabulated in Appendix 15, Part G.

In Figures 1 and 2, which follow, the results for the binary CaF_2-LiF system are shown graphically. Five values obtained on the first trials, concerning which there was great uncertainty, have been omitted where the subsequent determinations indicated that they were in gross error. The remaining values which deviate from the smooth curves would probably be improved by a redetermination, but this was not believed necessary in view of their relative unimportance for the main purpose of the problem. Following the figures a tabulation is given of the plotted values.

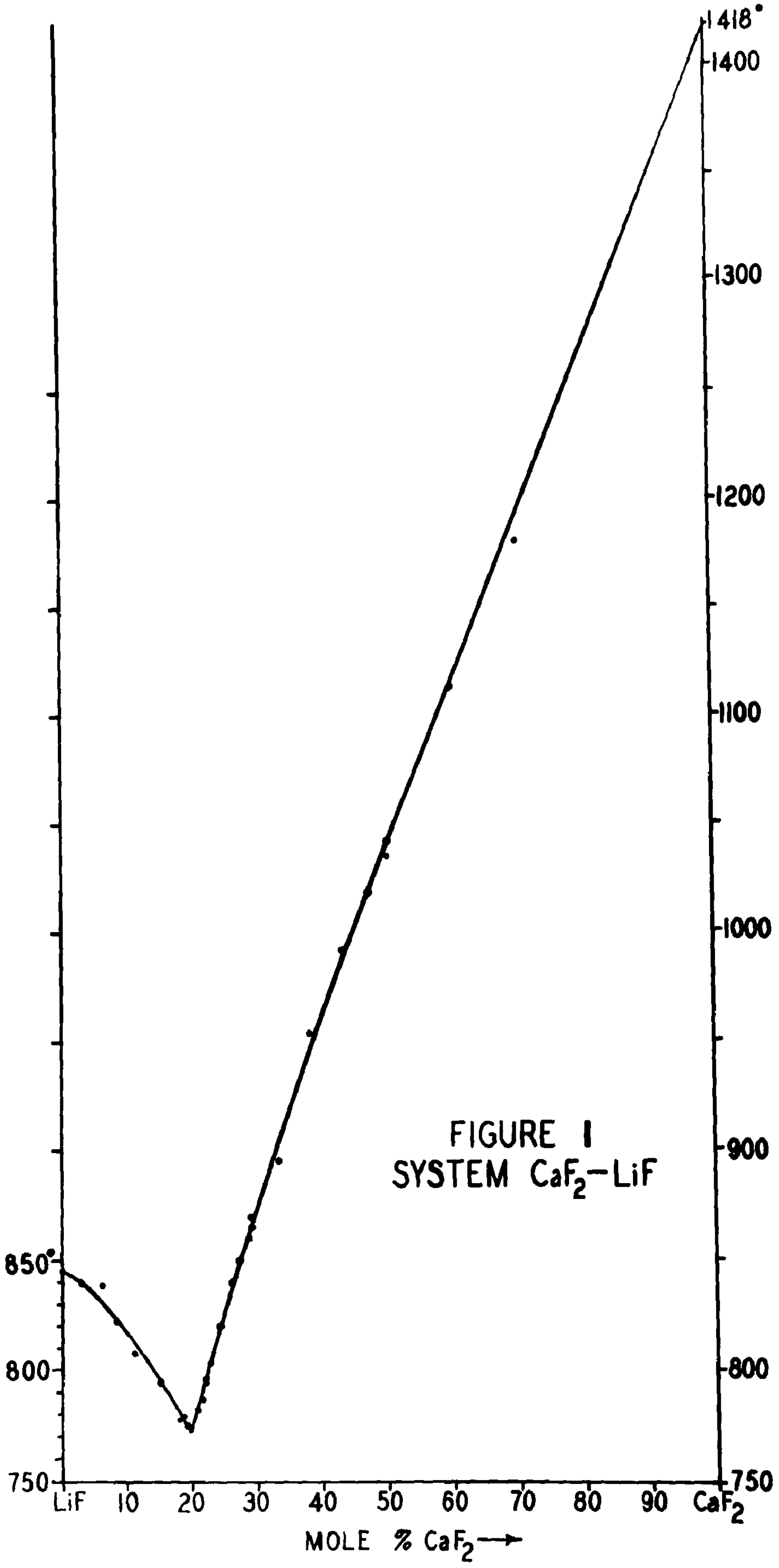


FIGURE I
SYSTEM CaF_2–LiF

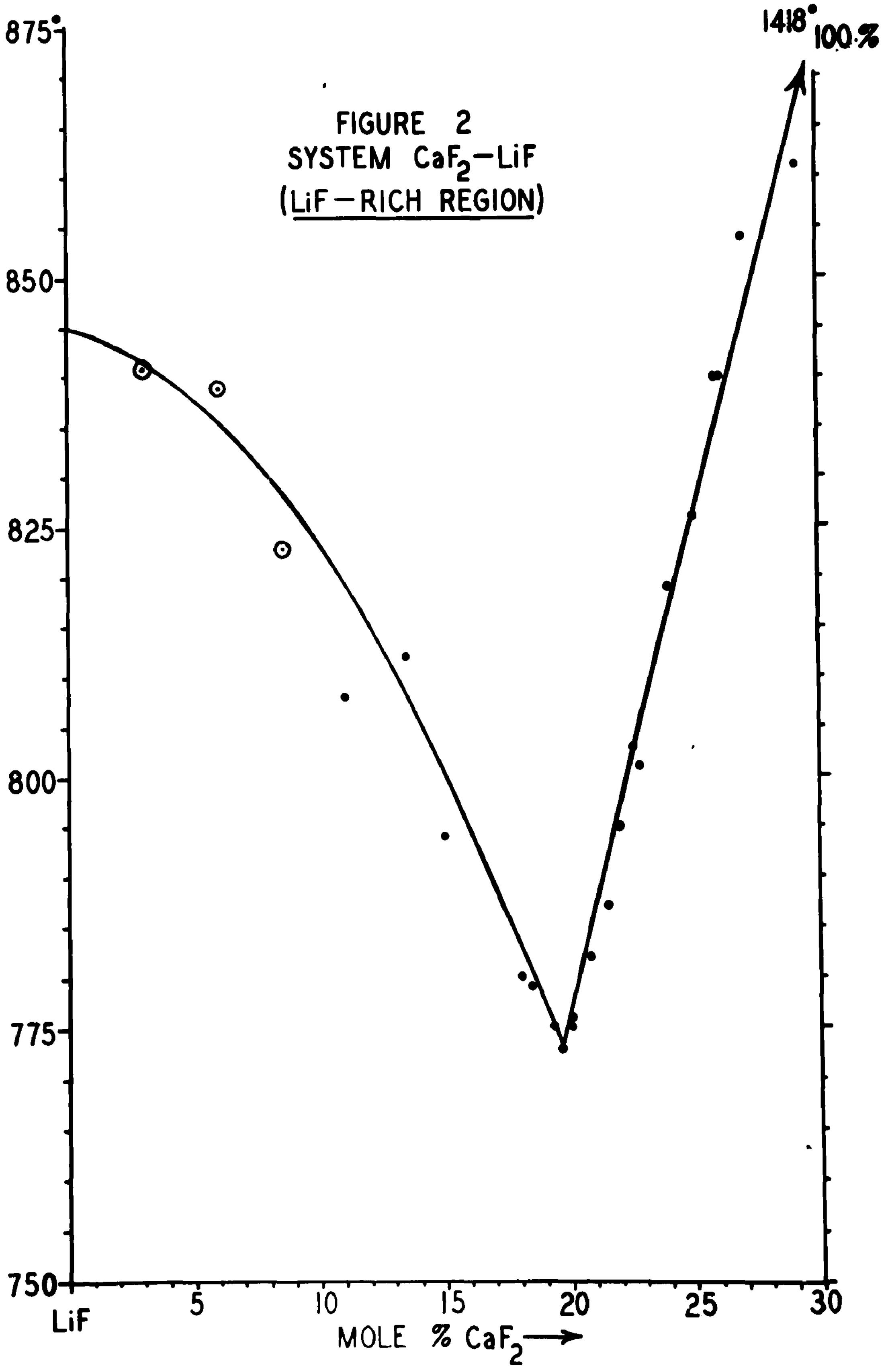


FIGURE 2
SYSTEM CaF_2—LiF
(LiF—RICH REGION)
875°
850
825
800
775
750
LiF
5
10
15
20
25
30
MOLE % CaF_2 →
1418°
100 %

TABULATION OF VALUES PLOTTED IN FIGURES 1 AND 2

Mole Percent CaF_2	Temp., ° C.	Mole Percent CaF_2	Temp., ° C.
0	845	22.5	803
3.0 (?)	841	22.8 (?)	801 (?)
5.9 (?)	839	24.0	819
8.6 (?)	823	25.0	826
11.1	808	25.9	840 (?)
13.5	812	26.0	840 (?)
15.0	794	27.0	854
18.0	780	29.2	861
18.3	779	32.1	898
19.3	775	38.0	955 (?)
19.6	773	43.0	993
20.0	777	47.0	1018
20.0	775	50.7	1035
20.8	782	60.0	1115 (?)
21.5	787	70.5	1180 (?)
22.0	795	100.0	1418

Note: (?) signifies more than normal amount of uncertainty as to composition or temperature. Other values probably are correct to within about ±.3% and ±2°. In the region from 18 to 22% the accuracy is probably good to within ±.1% and ±1°.

The system as shown is a simple eutectic whose only unusual feature is a rather sharply descending slope immediately to the right of the eutectic, which is somewhat out of line with the balance of the slope from the calcium fluoride melting point. The eutectic is believed to be located at 19.5 ± 0.2 mole percent of calcium fluoride with a solidification temperature of 773 ± 1° C.

The behaviour of the system is substantially the same as would be expected from the limited amount of data on analogous systems given in Appendix 1. For purposes of comparison rough plots follow in Figure 3 showing the relations of the known LiF-Group II metal fluorides and CaF_2-Group I metal fluorides systems.

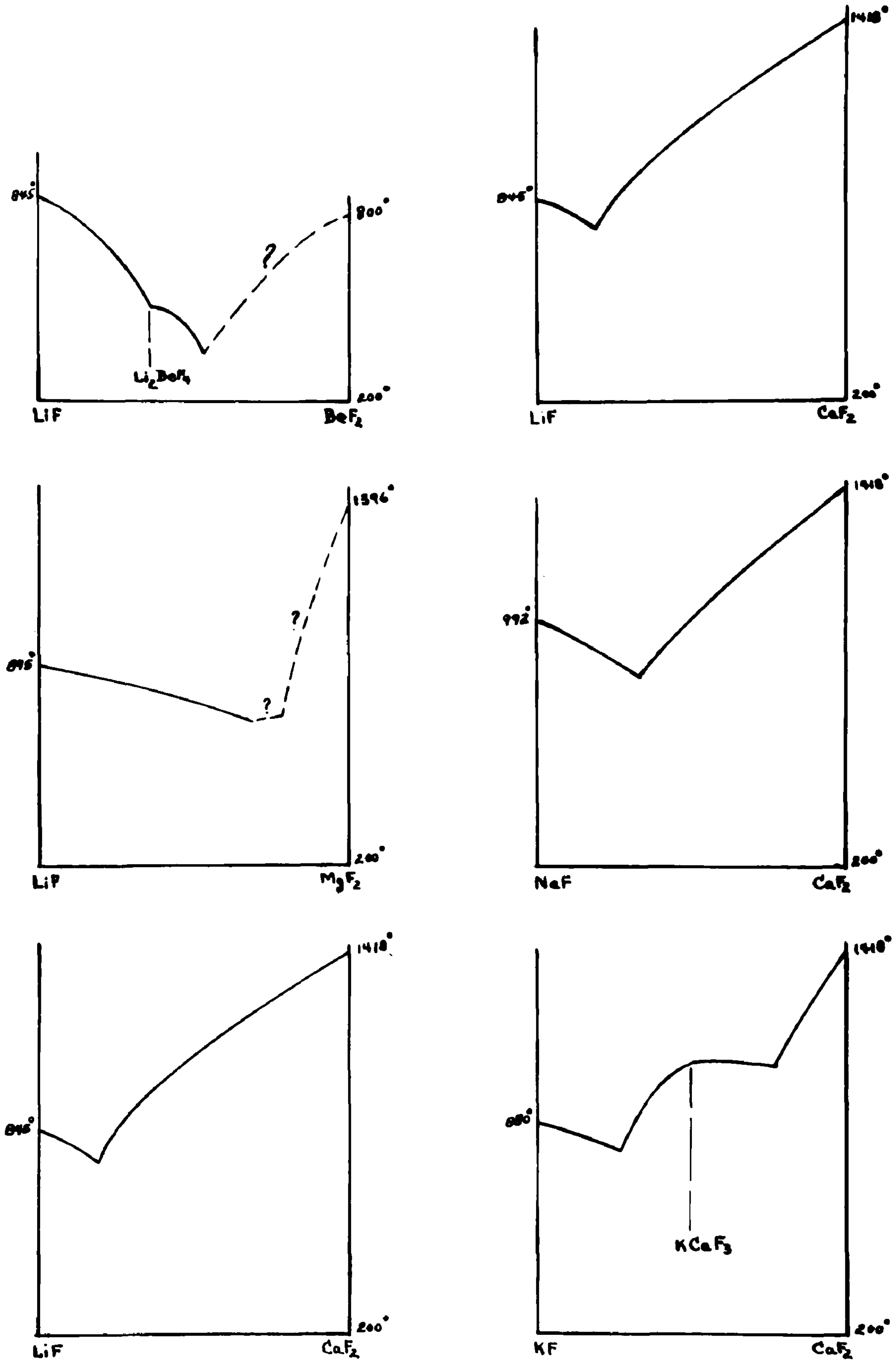

845°
800°
?
Li2BeF4
200°
LiF
BeF2
1418°
845°
200°
LiF
CaF2
1396°
?
845°
?
200°
LiF
MgF2
1418°
992°
200°
NaF
CaF2
1418°
845°
200°
LiF
CaF2
1418°
880°
KCaF3
200°
KF
CaF2

FIGURE 3

THE SYSTEM CALCIUM FLUORIDE-BERYLLIUM FLUORIDE

THE SYSTEM CALCIUM FLUORIDE-BERYLLIUM FLUORIDE

The work to obtain the phase diagram of the CaF_2-BeF_2 system was performed in two parts. In the first phase of the work the nature of the system was not well elucidated, and many of the results appeared to be inconclusive. The peculiarities of the system are such that they lead to results which deceptively resemble "delayed" crystallization effects. Also in the BeF_2-rich portion of the diagram no definite results were obtainable because of genuine delayed crystallization effects. At this stage therefore the system was not clearly defined.

Subsequent to the above work, the system was included among the topics presented in a paper by Osborn (124), but no information has been received and no publication on the work has appeared.

In later work on the ternary system, sufficient information was obtained to permit a better understanding of the binary CaF_2-BeF_2 system. Thereafter a new attack was made on the system which more closely defined it in the regions where crystalline products are obtainable.

For the preparation of these melts the beryllium fluoride was obtained exclusively from the decomposition of $(NH_4)_2BeF_4$. For the first phase of the work this decomposition was carried out in large carbon crucibles and the phase diagram runs were made in the same containers. Due to the oxidation of the crucibles this method did not permit maintaining an accurate check on the volatilization losses. Creepage and oxidation of material on the upper walls of the crucibles caused difficulties. In the later investigation of the system, platinum dishes were used as containers. The $(NH_4)_2BeF_4$ could be decomposed successfully in these smaller containers in the presence of calcium fluoride, and the compositions and volatilization losses could be followed more satisfactorily. Volatilization, either real or the result of hydrolysis reactions, becomes very appreciable from these melts at temperatures above 900° so that composition uncertainties become larger.

Because of the difficulties in the preparation of the beryllium fluoride, these melts were reused several times by the addition of portions of calcium fluoride to shift the compositions toward that side of the binary phase diagram. On too many such repetitions, particularly at the higher temperatures, these melts became seriously contaminated with beryllium oxides. The presence of the latter material probably accounts for some discordant temperature results obtained for an invariant point located near the center of the system.

The results of the thermal analyses have been tabulated in Appendix 8, omitting those runs which gave no conclusive results and which were later repeated. The complications of the cooling curves prevent an entirely adequate description of the results in tabular form, but an attempt will be made to describe these in general terms in the discussion which follows.

The results of the analyses of samples of melts have been assembled in Appendix 15, Part H. The calculated compositions based on input and volatilization losses are also indicated. Finally a tabulation is given of the calculated composition of the melts based on the results of the analyses, interpolation being necessary in the case of intermediate samples to take into account various losses.

Analytical results for the various preparations of $(NH_4)_2BeF_4$ are given in Appendix 15, Part C.

Within this system the binary compound calcium fluoberyllate occurs and a considerable amount of work was done on the wet preparation and X-ray characterization of this material. Synthetic work is covered in Appendix 9, and the X-ray investigation is discussed in Appendix 13. With respect to the latter material it may be remarked that it was not possible to index the lines of the powder diffraction pattern or to determine the unit cell dimensions of the compound. Apparently it is a member of one of the more complex crystalline classes such as monoclinic or triclinic which could not be characterized with the available equipment.

Optical examinations of the phases present in the melts are discussed in connection with the X-ray work. The calcium fluoride occurs as an isotropic phase, while the beryllium fluoride, tends to form a strained isotropic glass. The compound $CaBeF_4$ occurs almost exclusively as prismatic material so oriented on the microscopic slide that it is anisotropic when examined with polarized light. When beryllium oxide was present it was readily observable as small hexagonal prisms of much higher refractive index than the other components of the melts. Qualitative determination of the phases present was therefore quite readily accomplished with optical methods.

The phases were examined with respect to the constancy of refractive index using microscopic immersion methods. In general no good indications of changes of this property with melt composition were obtained, but the strained character of the beryllium fluoride prevented good observations.

In X-ray examinations for the determination of constituent phases, a slight apparent change of about 0.01 A^o shrinkage of the lattice plane separations of $CaBeF_4$ was noted as the composition was shifted away from the BeF_2-rich side of the system. Whether this is due to solid solution of BeF_2 in $CaBeF_4$ is not known and probably is not determinable due to the glass forming properties of melts in this region where the BeF_2 itself does not crystallize. The difference of 0.01A^o is however larger than the normal measuring error and hence is believed to be at least partly real.

Inspection of the tabulated results of the thermal analyses in Appendix 8, will show considerable discordance among the values, in particular those of the invariant point occurring near the center of the system. The results will be discussed with respect to certain regions of the diagram and an attempt will be made to explain the peculiarities of the system. The phase diagram of the system is given in Figure 4 for assistance in following the discussion. A tabulation of the experimental values used in plotting the diagram follows the figure.

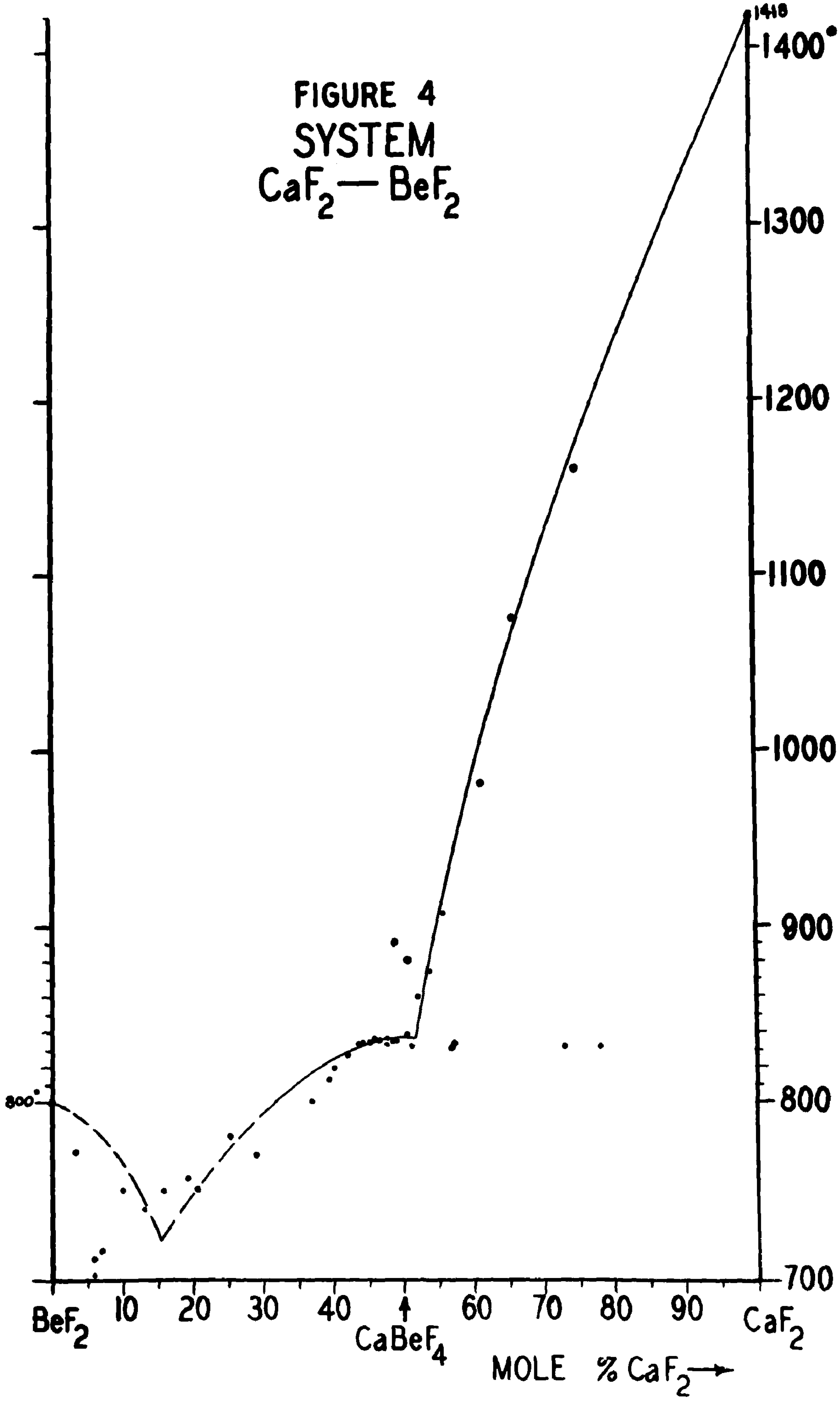


FIGURE 4
SYSTEM
CaF_2—BeF_2

TABULATION OF COMPOSITION-TEMPERATURE VALUES FOR FIGURE 4

Composition, Mole Percent CaF_2	Temperature, °C.	Composition, Mole Percent CaF_2	Temperature, °C.
ca. 3.3	772	45.8	836
6.0	712	46.4	835
6.2	702	47.6	832
7.1	716	47.7	836
10.1	750 (?)	48.6	834
13.1	740	48.8	ca. 890
ca. 15.8	750	49.0	834
ca. 19.2	757	50.4	838
20.5 (?)	751	50.5 (?)	880 (?)
25.2	780	51.0	831
ca. 29.0	770	52.0	859
ca. 37.0	800	53.7	874
39.5	813	55.6	907
ca. 40.0	818	56.8	831
40.0	819	57.0	833
42.0	828	61.0	ca. 980
43.4	833	64.5 (?)	900
ca. 44.1	833	66.0	ca. 1075
44.1	833	73.0	831
45.2	834	75.0	ca. 1160
		78.0 (?)	831

Note: 1) Symbol "ca" signifies approximately ±1/2 mole percent composition uncertainty.

2) Symbol (?) signifies greater than normal uncertainty, possibly ± 1 mole percent or more.

3) It will be noted that on a number of the melts above 50 mole percent the initial crystallization was undetected and the eutectic temperature is given as the first observed thermal effect.

4) Values for seven melts, probably contaminated with BeO impurity, have been omitted from the plotted values.

As previously mentioned the beryllium fluoride normally exists in a polymeric glassy form without a true melting point. At 800°, the so-called "melting point", there is no large observable change in a gradual softening process which probably is noticeable as low as 700°. At 800° the material is extremely viscous and not until about 900° does the material exhibit a reasonable resemblance to a liquid. Volatility of the beryllium fluoride is sufficient at this temperature to be visibly evident.

The left hand portion of the binary system from 0 to about 20 mole percent CaF_2 is not determinable on the basis of the results of this work. In this region the effect of the addition of calcium fluoride is merely to relatively lower the gradual transition zone of the pure beryllium fluoride. The melts are progressively less viscous for the same temperature but no definite liquidus line is determined.

It is believed that a eutectic theoretically occurs in the vicinity of 10 mole percent CaF_2 but no good indications of its position were obtained. Consequently this region of the phase diagram is shown by the dotted lines which give estimated general behaviour if the melts would crystallize. This "theoretical" eutectic might possibly be as high as 750° based on solidification temperatures of melts with higher calcium fluoride contents.

In the general region of 20 to 50 mole percent CaF_2 the initial work on the system showed the following characteristics. As the calcium fluoride content was increased the point of initial crystallization rose to a maximum of approximately 836°. The thermal effects observed shifted from small flat plateaus to much longer plateaus showing a very flat initial portion followed by a gradual slope and then a rapid temperature drop which approximately coincided with the disappearance of the last apparent liquid. The general behaviour therefore greatly resembled an invariant crystallization process in which about one-half to two-thirds of the melt solidified at nearly constant temperature and then the balance solidified over a much larger temperature range. For compositions of about 45 mole percent CaF_2, the melts appeared to largely solidify within about a 10° range, with apparently about 80% of the process occurring within a 1° range. To add to the confusion this solidification process did not occur at a particular temperature for melts of nearly the same composition, but instead in about one-half the cases occurred at about 833°, while the balance of the solidification processes were scattered over lower temperatures down to about 820°. (The latter results are now believed to have been due to the effect of contamination of the melt by beryllium oxide.) From the results obtained at this stage of the work, it was strongly suspected that most of the thermal effects obtained in the 20 to 50 mole percent CaF_2 region might all represent the same invariant equilibrium process, distorted however by hindered crystallization effects which were dependent on composition.

In the region of 50-100 mole percent CaF_2 the initial results were generally more conclusive but also in part confusing. Melts in the region of 50 to 55 mole percent showed the same thermal effects as before, with no apparent initial crystallization at higher temperatures than about 833°. Suddenly for melts of about 60 mole percent and higher, apparent initial crystallization appeared at temperatures of about 975° and higher. Subsequently, by the time the lower invariant point of about 833 was reached, either very little or no apparent liquid remained. This peculiar behaviour, indicative of a eutectic located to the right of the compound $CaBeF_4$, was apparently not confirmed by melts in the general region of 50-55 mole percent CaF_2. Instead the latter exhibited much the same thermal effects as melts to the left of 50 mole percent. (Here again the presence of beryllium oxide which is increasingly produced at higher temperatures added to the confusion by contributing a number of results in the 820° range.)

At this stage these results, if they could be believed, indicated a eutectic at about 50 mole percent CaF_2, while the preceding work indicated, if anything, a peritectic reaction in this vicinity. Work was then discontinued on this system to see if later results on the ternary system would contribute anything to the understanding of this system. It is now believed that the general deceptiveness of the system with a tendency for quite flat plateaus (followed by gradual slopes) in the 20 to 50 mole percent region arises from two causes. The first cause is believed to be that the system actually has a rather shallow slope of the liquidus line, which in the vicinity of 45 to 50 mole percent becomes practically horizontal. The second cause is that crystallization is initially slightly delayed and consequently, even when started, it cannot proceed rapidly enough to raise the supercooled melt temperature to the proper value. This results in a flattening-out of the upper portion of a sloping thermal analysis curve which really represents a univariant process.

After work on the ternary system showed approximately the same behaviour in the vicinity of the binary CaF_2-BeF_2 system, except with better indications of a eutectic process, a reinvestigation was made of the center of the binary system. Improved techniques permitted a better determination of the phase relations, while the use of platinum containers seemed to greatly decrease tendencies for beryllium oxide formation which previously had contributed discordance to the results.

In this later work a master batch of melt was prepared with 40 mole percent CaF_2 composition, and the batch was split in two parts which were carried up to and beyond 50 mole percent by the addition of portions of calcium fluoride. Cleaner melts permitted visual observation and more certainty as to composition. The following results were obtained.

The initial crystallization point, as indicated by the appearance of surface needles of $CaBeF_4$ and the start of a thermal plateau, was gradually shifted toward higher temperatures with increasing CaF_2 content. The plateaus, at first sloping slightly, again became relatively flat above 45 mole percent CaF_2; while the point of final disappearance of apparent liquid rose from about 770° to about 810°. At 47.6 and 47.7 mole percent no initial crystallization of CaF_2 was observed prior to the plateau. On a subsequent melt calculated to be 48.8 mole percent, possible CaF_2 deposition was observed at about 890° but this may have been impurity. Another melt at 48.6 mole percent did <u>not</u>, however, show this behaviour, showing only an 834° plateau.

On the next two melts at 53.7 and 55.6 mole percent, initial deposition of CaF_2 was observed at 874° and 907° respectively. These liquidus points were considerably different in location from the prior doubtful observation at 48.8 mole percent and more weight was placed upon them as they were in better agreement with other data. Above this region the liquidus curve was a steep slope leading upward toward the CaF_2 melting point.

The behaviour is interpreted as that of a somewhat defective binary eutectic reaction in the vicinity of about 52 mole percent CaF_2. The fact that some liquid was apparent below the invariant point for melts with greater than 50 mole percent CaF_2 content is not explainable on either a peritectic or eutectic basis for a compound of that composition, except as a slightly incomplete phase reaction. Only slight evidence for a dip of about 2 to 4^o exists for the valley lying between 50 and 52 mole percent. A similar dip extends out into the ternary system for some distance and, as discussed there, the evidence as a whole points toward a barely congruently melting $CaBeF_4$ with a closely adjoining eutectic at about 52 mole percent CaF_2.

The peak value obtained for $CaBeF_4$ deposition was 836^o and the indicated value of the eutectic was about 832^o, the latter value generally falling in the range 830 to 833^o (all temperatures based on cooling cycles). Based on heating cycles, which tend to be somewhat higher for various reasons, the indicated values would be less than 840^o for the $CaBeF_4$ peak and greater than 836^o for the binary eutectic point.

The failure to observe the eutectic which should exist in the range of 0 to 50 mole percent CaF_2, probably around the 10-15 mole percent region, is probably a result of the inability of the melts to overcome the high viscous resistance to crystallization at these lower temperatures. There were slight indications that the eutectic lies as high as about 770°, since in one case a very short plateau was obtained at 775° on a 37 mole percent mixture, and in many cases apparent solidification occurred by about 770 to 780°.

In all probability, because of the complexity of beryllium fluoride and its solutions in the region of 0 to 30 mole percent CaF_2, the system is one of many components rather than binary, with the concentration and types of species being a function of the calcium fluoride content. Under such circumstances ordinary phase rule relationships would not be expected to be completely valid for processes taking place in relatively finite time intervals during which equilibrium is approached at the slower rates characteristic of glasses.

THE SYSTEM LITHIUM FLORIDE-BERYLLIUM FLUORIDE

THE SYSTEM LITHIUM FLUORIDE-BERYLLIUM FLUORIDE

The investigation of the LiF-BeF_2 system was carried out in conjunction with the study of the ternary system. In general, after use of a melt to determine a point on the liquidus line of the binary system, calcium fluoride (or a suitable mixture of calcium fluoride and lithium or beryllium fluoride) was added to shift the composition of the melt into the ternary system along a "section" directed toward the composition of the additive. This procedure reduced the necessary handling and preparation of beryllium fluoride to a minimum.

In the region of the compound lithium fluoberyllate, Li_2BeF_4, the above procedure could not reliably furnish relative compositions with the accuracy necessitated by the peculiarities of the binary system. Here it was necessary to proceed by a method involving successive additions (usually of lithium fluoride) to an initial melt in the binary system, to cause shifts in composition across the region of compound occurrence. While this procedure furnished quite satisfactory relative data, analytical errors made the data insufficiently accurate on an absolute basis. In attempts to overcome the latter problem attempts were made to synthesize the pure compound, Li_2BeF_4, to remove the absolute uncertainties. (See Appendix 11).

Before commencing the work on this binary system the reports of recent work by Thilo and Lehmann (166) and Roy, Roy and Osborn (134) became available. These investigators reported quite divergent results which coincided with their different concepts of the silicate systems for which LiF-BeF_2 should constitute a Goldschmidt (52) "model" system. The comparative results will be discussed at the end of this section, but at this point it may be mentioned that in the present work good agreement was obtained with about one-half of the work of each group. These divergent results largely were responsible for the somewhat excessive investigation of this system in the present work, although accompanying difficulties in the ternary system also caused additional work.

The system may be broken down into four portions for purposes of discussion of procedure and results.

In the region of 0 to 25 mole percent BeF_2 it may be seen in Figure 5 that the slope of the liquidus line is relatively gradual and consequently in this region satisfactory thermal effects were obtained upon the initial crystallization of lithium fluoride and no special difficulties were encountered.

In the region of 25 to 36 mole percent BeF_2, the system is peculiar in several respects and the interpretation of results is subject to a number of difficulties. In the region of 25 to 30 mole percent the liquidus becomes steeper and only slight thermal effects of initial crystallization were obtained, which had to be confirmed by visual detection of the initial crystallization. In the region from 30 to about 33.5 mole percent the slope of approximately 50° per mole percent becomes so steep that no reliable thermal effect was obtained on cooling when the liquidus line was reached. Here visual detection had to be used exclusively to determine the temperature of initial deposition of lithium fluoride. Although visual detection was reasonably satisfactory because of the characteristic "oily" appearance of the first lithium fluoride surface crystals, slight inaccuracies of composition resulted in discordant temperature values. By contrast, in the region from about 33.5 to 36 mole percent the system is quite flat, and the initial deposition of lithium fluoberyllate, Li_2BeF_4, in characteristic needle form, was accompanied by a strong thermal effect during which all melts in this region seemed to solidify at practically the same temperature.

Here again, as in the CaF_2-BeF_2 system, the practical coincidence of an invariant process and a compound with a very blunt peak on the liquidus curve causes considerable difficulty in interpretation. As there are three possible invariant processes; i.e. peritectic with incongruent compound, eutectic with congruent compound, and the singular case of an "exactly" congruently melting compound, considerable effort and consideration was given to this region as discussed later in this section.

In the region of 36 to about 53 mole percent BeF_2 it may be seen in Figure 5 that the liquidus has a very gradual slope to a binary eutectic point at about 358°. In this region initial crystallization produced strong thermal effects and no difficulties were encountered except in the general vicinity of 380 to 360° where the viscosity of the melts caused the initial crystallization to become somewhat sluggish. It should be noted, however, that all cooling curves of melts in the 36 to 53 mole percent region showed initially a flat plateau, the length of which decreased gradually until it became little more than an inflection point in the region of 45 to 53 mole percent. This behaviour is worthy of note in connection with the evidence of Thilo and Lehmann for compound occurrence with the composition $Li_3Be_2F_7$ at 40 mole percent BeF_2.

In the region of 52 to 100 mole percent BeF_2 the glass-like characteristics of beryllium fluoride completely prevented satisfactory determination of the liquidus curve, if indeed one actually exists. A binary eutectic at about 358° and 52 mole percent was apparent, but the balance of the BeF_2-rich melts showed only gradual thickening. The broken curve in this region of Figure 5 indicates this general behaviour by points of greatest change in the viscosity of the melts.

The other investigators of the binary system apparently had little better success with this portion of the system. Thilo and Lehmann gave only a fragmentary portion of the curve and made no extravagant claims as to its significance. Osborn et al. showed a complete liquidus line obtained by the "quenching" technique, but the results are in complete conflict with the properties of beryllium fluoride and it is believed that the curve has no real significance other than as a measure of solid phase reaction rate as a function of temperature and composition.

The results of the LiF-BeF_2 binary system work are shown graphically on the following figures. The general picture of the entire system is given in Figure 5. It should be emphasized that the shape of the liquidus curve in the 30 to 35 mole percent region was drawn from a consideration of the more accurate data given in succeeding figures, rather than on several relatively inaccurate points, shown in this region on Figure 5.

The results of thermal analyses used in plotting the diagrams of Figures 5, 6 and 7 are tabulated in Appendix 10. The values in Figure 5 are given in the tabulation immediately following Figure 5. The values for Figures 6 and 7 are available in segregated form in Appendix 10. The analytical results, which in some cases are the bases for the tabulated compositions are given in Appendix 15, Part I.

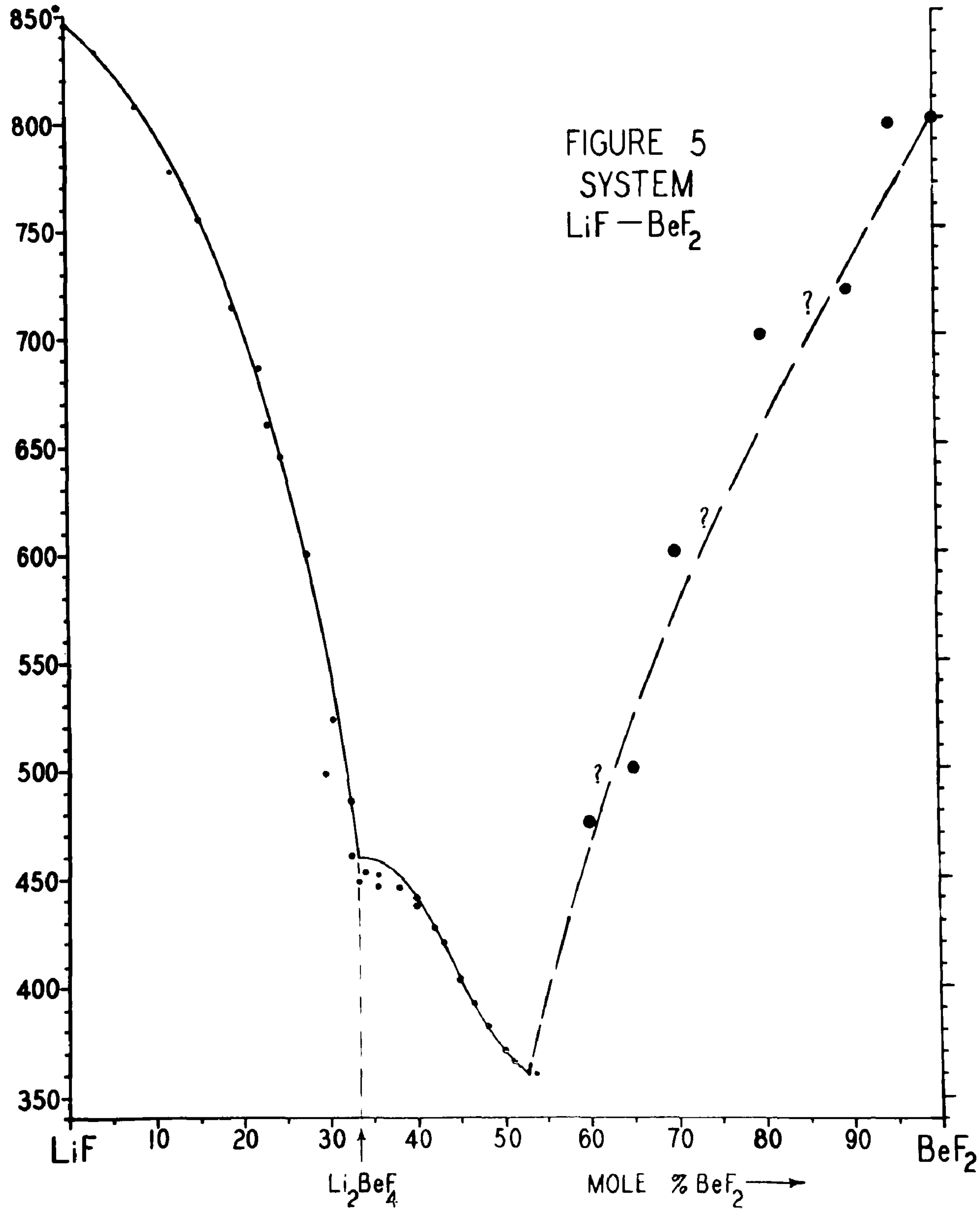


FIGURE 5
SYSTEM
LiF — BeF$_2$
850
800
750
700
650
600
550
500
450
400
350
LiF
10
20
30
40
50
60
70
80
90
BeF$_2$
Li$_2$BeF$_4$
MOLE % BeF$_2$ →
?
?
?

TABULATION OF VALUES USED IN FIGURE 5

Composition, Mole % BeF_2	Temperature, °C.	Composition, Mole % BeF_2	Temperature, °C.
4.1	833	40.0	437
8.1	808	40.0	441
12.0	777	42.0	427
15.2	756	43.0	420
19.0	715	45.0	403
22.1	687	46.4	392
23.0	ca. 660	48.1	382
ca. 24.3	ca. 645	ca. 50.0	372
ca. 27.5	600	51.0	366
ca. 29.5	498	53.6	ca. 360
30.4	ca. 521	56.7	---
32.4	486	60.0	ca. 475 (thickening)
ca. 32.5	460?	65.0	ca. 500 "
33.3	448	70.0	ca. 600 "
34.0	452	80.0	ca. 700 "
35.9	451	90.0	ca. 720 "
36.0	445	95.0	ca. 800 "
38.0	445		

Note -- "ca." signifies more than normal uncertainty.
Normal uncertainty approximately ±0.5 mole % and
± 2°.

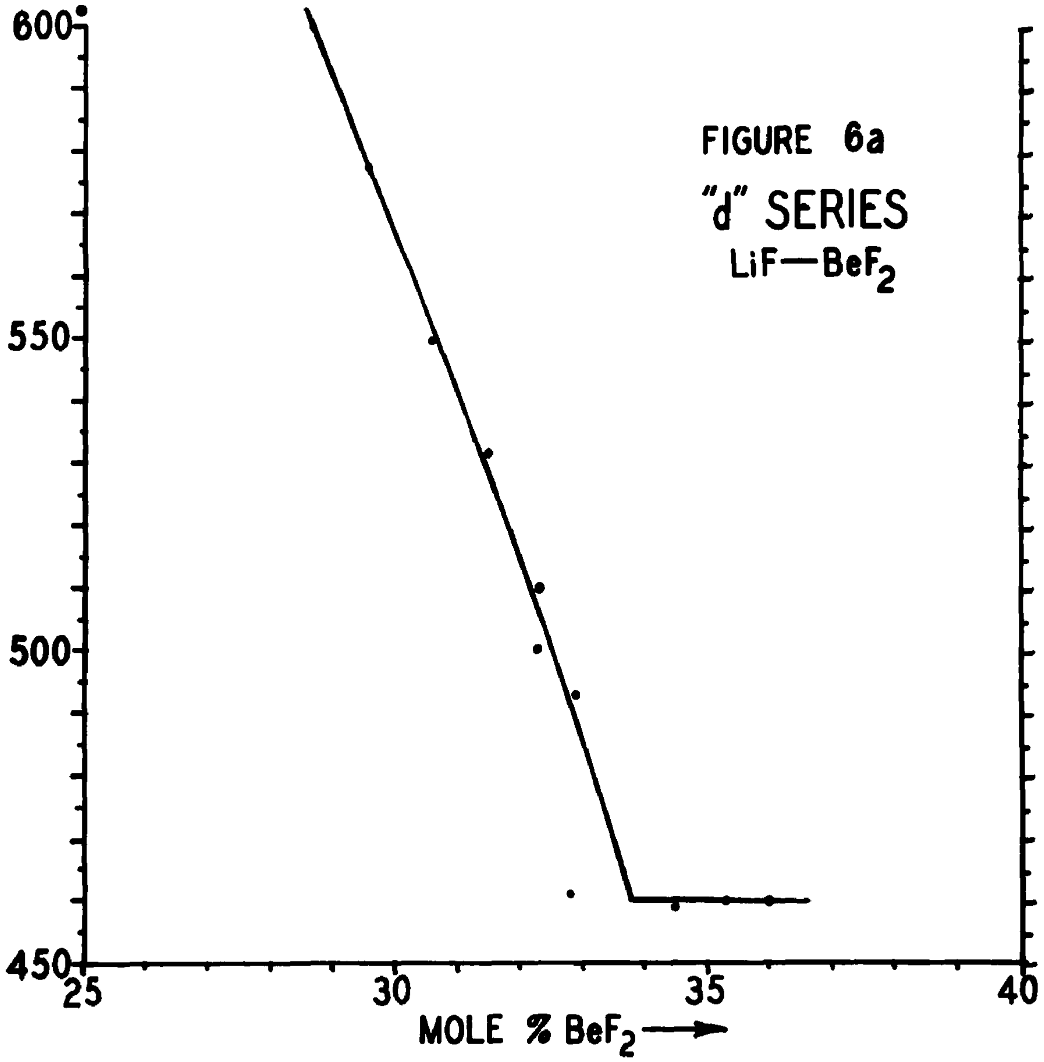


FIGURE 6a
"d" SERIES
$LiF—BeF_2$

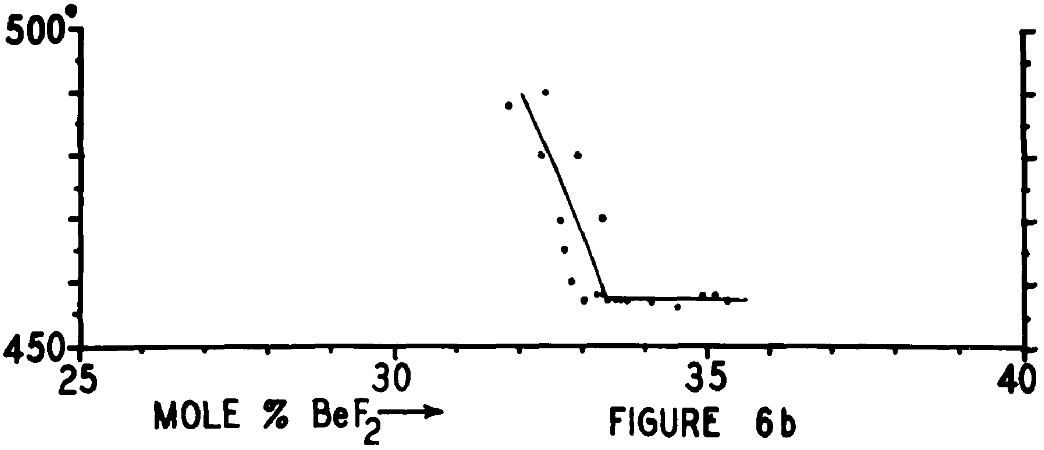


FIGURE 6b
"R" SERIES & MELT 1S
$LiF—BeF_2$

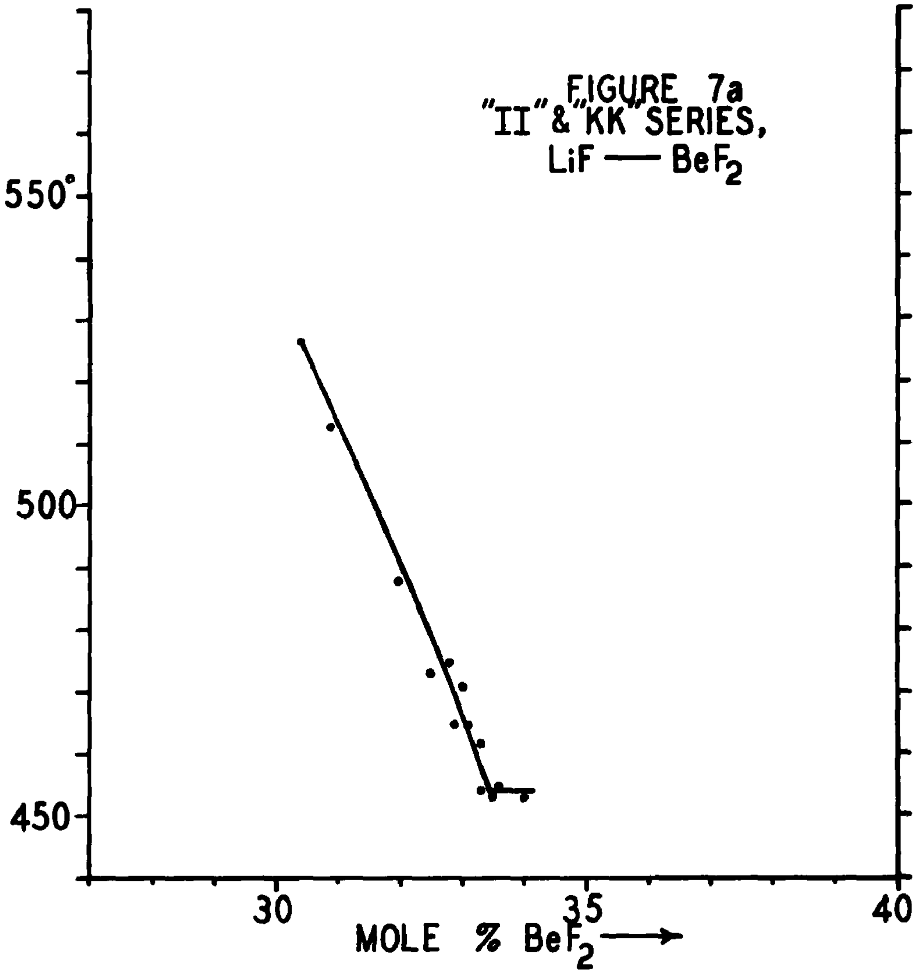


FIGURE 7a
"II" & "KK" SERIES,
LiF — BeF$_2$

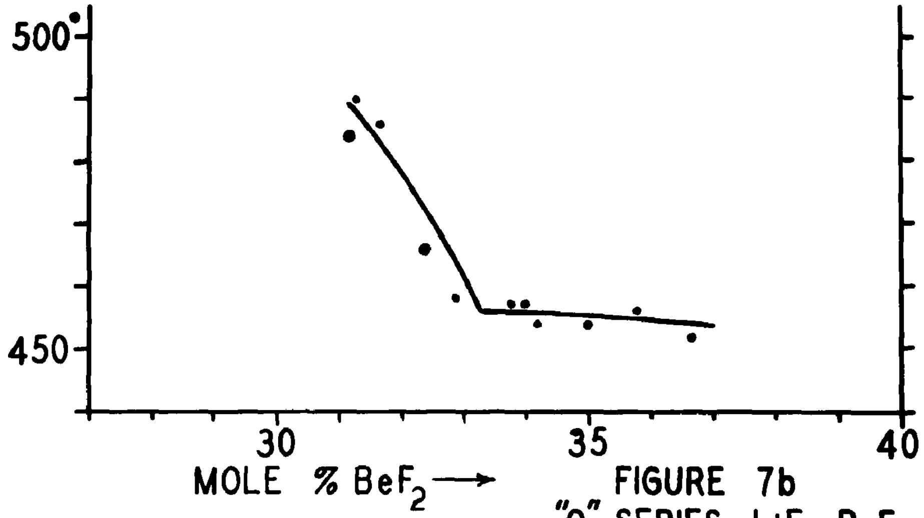


FIGURE 7b
"Q" SERIES, LiF-BeF$_2$

The special studies of the 30 to 35 mole percent region are shown in Figures 6a, 6b, 7a and 7b to avoid confusion of the points. These curves are substantially superimposable within limits of about ± 1/2 mole percent or less. The slightly lower temperature values in the region of 33 to 35 mole percent are not significant but are probably the result of slight impurities. The higher values are considered to be the more reliable ones.

Two of these curves, Figures 6a, and 6b were obtained using synthetic Li_2BeF_4 as a starting material. In only one case, that of Figure 6a, was the product considered to be very satisfactory, but analytically the material did not show the exactly theoretical composition. The product used for Figure 6b, on the contrary, was poor in appearance, but did have the proper analytical composition.

The results shown in Figures 7a and 7b were obtained from melts prepared from Brush BeF_2 and LiF. The results of Figure 7a were obtained by shifting the composition of two melts, while those of Figure 7b represent a series of independently prepared melts which consequently show slightly greater relative deviations.

The most accurate data on the 30 to 35 mole percent region is that of Figure 6a. The data is believed accurate to within at least ± 1/4 mole percent and the temperature to $\pm 1^{\circ}$. Some of the other figures are based on equally good relative data but the absolute values of composition are less certain and the temperatures generally were several degrees lower.

The only portion of the binary system requiring detailed consideration is the region immediately adjacent to the compound Li_2BeF_4. Here a knowledge of the exact type of binary invariant reaction would facilitate the interpretation of the ternary system. Solidified melts containing as little as 4 mole percent BeF_2 showed faintly the characteristic X-ray powder pattern of Li_2BeF_4 in addition to stronger lines of LiF. As the BeF_2 content was increased the relative intensities were reversed and the duration of the invariant process in the region of 450 to 460° was increased to a maximum at approximately the composition of Li_2BeF_4. Melts containing very little liquid upon reaching the invariant point naturally tended to exhibit abnormally low invariant temperatures. Solidification was apparently complete at this point for melts containing less than 33.3 mole percent BeF_2. During this solidification process, the Li_2BeF_4 crystallized in quite massive forms resembling columnar prisms and there was no apparent tendency to form any finely crystallized "classical" eutectic mixture.

In the region of 33.3 to 34.5 mole percent, there were no reliable indications of the existence of liquid below the invariant temperature either during cooling or heating, but this did not preclude the possible existence of very small amounts of liquid within the solid mass.

At about 34.5 mole percent and therafter, the existence of liquid below the invariant temperature was definite and at 35 mole percent or more the lower invariant eutectic was also observable at approximately 358°. Such melts tended to show fairly flat thermal plateaus accompanying the initial deposition of Li_2BeF_4, probably as the result of slight initial undercooling of the melt, combined with the effect of a relatively gradual temperature-composition slope. No discontinuities were observed other than the initial plateau which gradually sloped off to a curve falling smoothly to the lower invariant point at 358°, and accordingly no additional compound formation was indicated in the 33.5 to 53 mole percent region.

Inspection of the various liquidus curves of Figures 6a, 6b, 7a and 7b shows a quite consistent tendency for the projected steep slope to strike the flat slope at about 33.5 to 34.0 mole percent BeF_2. There is no apparent slight depression in the plateau to indicate a small binary eutectic valley to the left of the compound location. The type of crystallization at the invariant point is more characteristic of a peritectic than a eutectic reaction. Hence on the basis of the information obtained in this work, the invariant point must be interpreted as a peritectic reaction located at a composition of approximately 33.5 mole percent BeF_2. Because of analytical uncertainties it is not impossible that the compound is one which is exactly congruently melting, but there is no indication of a eutectic reaction in this region.

Reference is now made to the work of Thilo and Lehmann (166) and of Roy, Roy and Osborn (134) for comparison of the results reported for this system. The phase diagrams which they reported are reproduced in Figures 8 and 9. Both sets of investigators were studying the system for theoretical reasons connected with the resemblance of the system to certain silicate systems.

According to the Goldschmidt theory of "model" systems (52) a "weakened" model system is obtainable by the substitution of elements having similar sizes but lower valencies. Such a weakened system would be expected to exhibit the same general phase relationships and have the same general structures, but would be much less stable and hence susceptible of investigation at much lower temperatures than a corresponding silicate system. This general theory due to Goldschmidt was apparently first tested by O'Daniel and Tscheischwili (121) and is currently being investigated by Thilo and Osborn as judged by more recent articles (167) (125). While the results have been of interest in their partial verification of the Goldschmidt theory, it will be seen that the investigators may have been too quickly convinced when their first efforts gave the desired results needed for full agreement with the theory.

To illustrate the Goldschmidt approach the following tables of crystal radii are reproduced to show some of the possible substitutions permitted by this "weakened" model theory. In the left hand portion are shown compounds primarily of interest in high melting silicate systems and opposite each is shown a compound of elements of nearly equivalent size, but decreased valence, which constitutes the weakened model system.

MODEL STRUCTURES

Reinforced					Weakened				
Substance	Ionic Radii, A°.				Substance	Ionic Radii, A°.			
SiO_2	0.39	1.32	---		BeF_2	0.34	1.33	---	
MgO	0.78	1.32	---		LiF	0.78	1.33	---	
TiO_2	0.64	1.32	---		MgF_2	0.78	1.33	---	
SnO_2	0.74	1.32	---						
ThO_2	1.10	1.32	---		CaF_2	1.06	1.33	---	
Zn_2SiO_4	0.83	0.39	1.32		Li_2BeF_4	0.78	0.34	1.33	
$SrTiO_3$	1.27	0.64	1.32		$KMgF_3$	1.33	0.78	1.33	
$BaSO_4$	1.43	0.3	1.32		$RbBF_4$	1.49	0.2	1.33	
$CaMgSi_2O_6$	1.06	0.78	0.39	1.32	$NaLiBe_2F_6$	0.98	0.78	0.34	1.33

The above material is reproduced from the Osborn article using Goldschmidt's ionic or crystal radii.

Thilo and Lehmann used the Pauling ionic radii values shown below and consequently arrived at slightly different conclusions.

Coord. No. for Oxygen	Structural Unit in Silicates	Ionic A°	Radii, A°	Structural Unit in Fluoberyllates	Coord. No. for Fluorine
---	O^{-2}	1.40	1.36	F^{-1}	---
4	Si^{+4}	0.41	0.31	Be^{+2}	4
6	Mg^{+2}	0.65	0.60	Li^{+1}	6
6	Zn^{+2}	0.74	---	---	---
6-8	Ca^{+2}	0.99	0.95	Na^{+1}	6-8
8	Sr^{+2}	1.13	---	---	---
8	Ba^{+2}	1.35	1.33	K^{+1}	8

Goldschmidt originally believed that willemite, Zn_2SiO_4, or phenacite, Be_2SiO_4, should be related to Li_2BeF_4, whereas Thilo and Lehmann believed the MgO-SiO_2 system should be analogous to the LiF-BeF_2 system on the basis of better similarity of ionic sizes. Hence forsterite, Mg_2SiO_4, and clinoenstatite, $MgSiO_3$, would be expected to resemble Li_2BeF_4 and $LiBeF_3$.

Osborn et al. believed that willemite, Zn_2SiO_4, should resemble Li_2BeF_4 and that the ZnO-SiO_2 system should be the reinforced model system of which LiF-BeF_2 was the weakened model.

Chronologically, Thilo and Lehmann published first and it is doubtful, because of the timing, that Osborn et al. were aware of their prior publication.

Osborn et al. claimed on the basis of their results that there was a considerable similarity between the systems ZnO-SiO_2 and LiF-BeF_2 in that the general features of eutectics and compound formation occurred at practically the same compositions. The following comments may be made with respect to their work, which is shown graphically in Figure 8.

For the melting point of lithium fluoride a value of 870° was taken from the 1922 edition of Mellor (111). A single liquidus point was obtained in the region from 0 to 33.3 mole percent BeF_2 and based upon this result a eutectic was reported at about 20 mole percent. Both the procedure and the conclusion were erroneous and this region of the diagram may be considered to be worthless.

In the region from 33.3 to 52 mole percent BeF_2 the Osborn results and those of the present work are in quite good agreement for the four liquidus points which they show.

Over the 52 to 100 mole percent region their values, which represent the liquidus for the "low-quartz" form of beryllium fluoride, lead to an extrapolated value of 540° for the melting point of this form of beryllium fluoride. Since they obtained somewhat discordant results from a "crystobalite" form obtained by the decomposition of $(NH_4)_2BeF_4$, it is

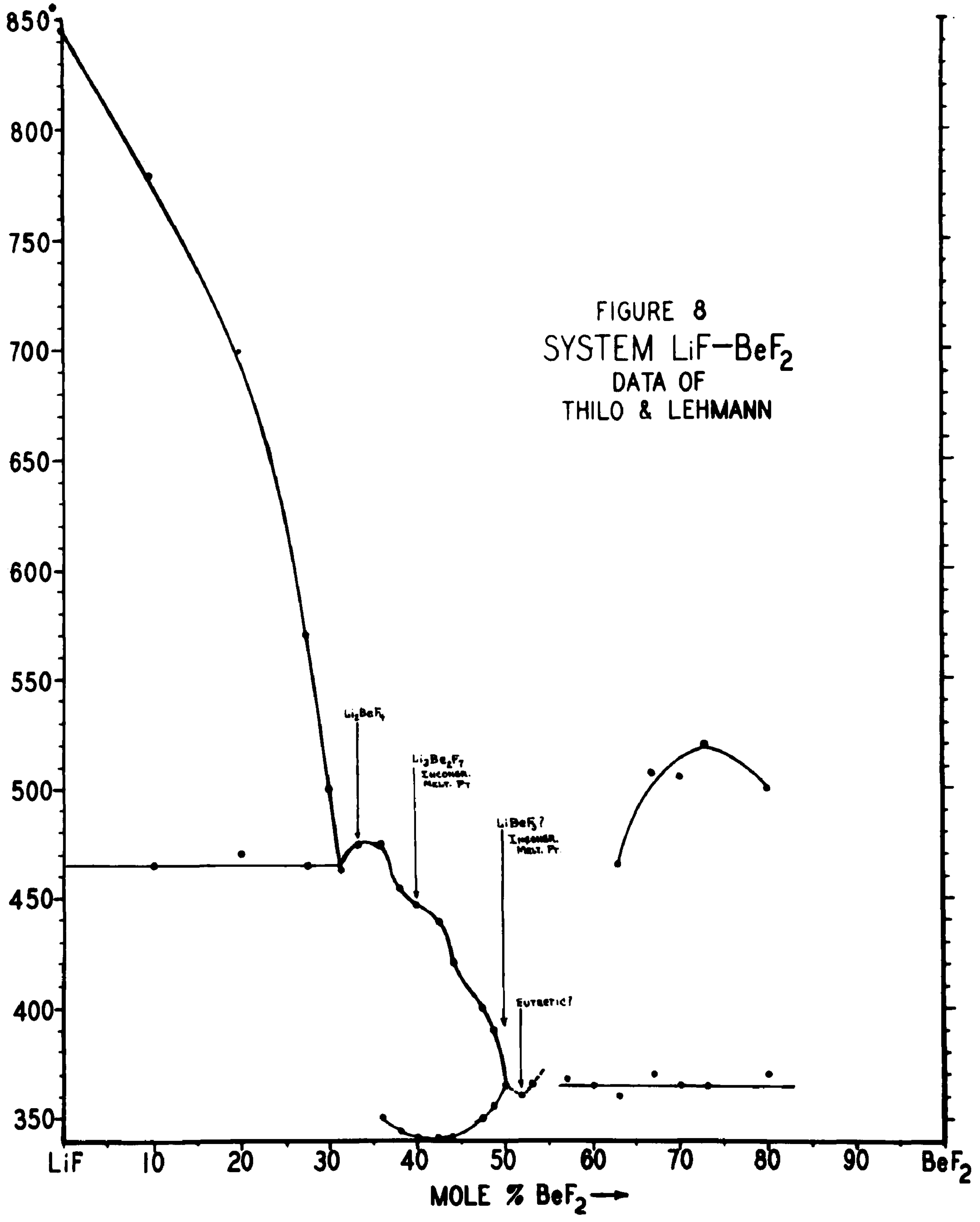


FIGURE 8
SYSTEM LiF–BeF$_2$
DATA OF
THILO & LEHMANN

suggested that the entire matter is unsettled, particularly as they give no information on the X-ray examinations of what were probably at best only strained amorphous samples poorly suited to structural determinations.

The work of Thilo and Lehmann (See Figure 9) was a much more thorough investigation in which adequate thermal analyses were apparently used at reasonably spaced intervals, and in which very extensive crystallographic and temperature relationships were shown between the $MgO-SiO_2$ and $LiF-BeF_2$ systems. Very complete agreements were obtained and, based upon the supposed complex forming ability of fluoberyllate ions, an extensive analogy was made with silicate systems with regard to the formation of linear, branched and multidirectional anionic complexes. Despite the thoroughness and imagination exhibited by this report several criticisms may be made which would lead to a different interpretation.

These investigators worked with undisturbed melts (i.e. unstirred) and experience in the present work has indicated that lack of a positive means of obtaining temperature uniformity in the melt normally tends to give somewhat spurious results, either high or low, depending on the exact position of the thermocouple within the solidifying mass. Differentials in the unstirred liquid usually amount to several degrees even in small volumes.

With respect to the region of 0 to about 30 mole percent BeF_2 quite good agreement exists between their values and those of the present work for the liquidus points. Throughout this region there was a gradual increase in their "eutectic" holding time per gram and the only peculiarity was a variation in the temperature of the "eutectic" reaction in the order of 465°, 470°, 465° and 472°. While a variation is normal, the usual tendency

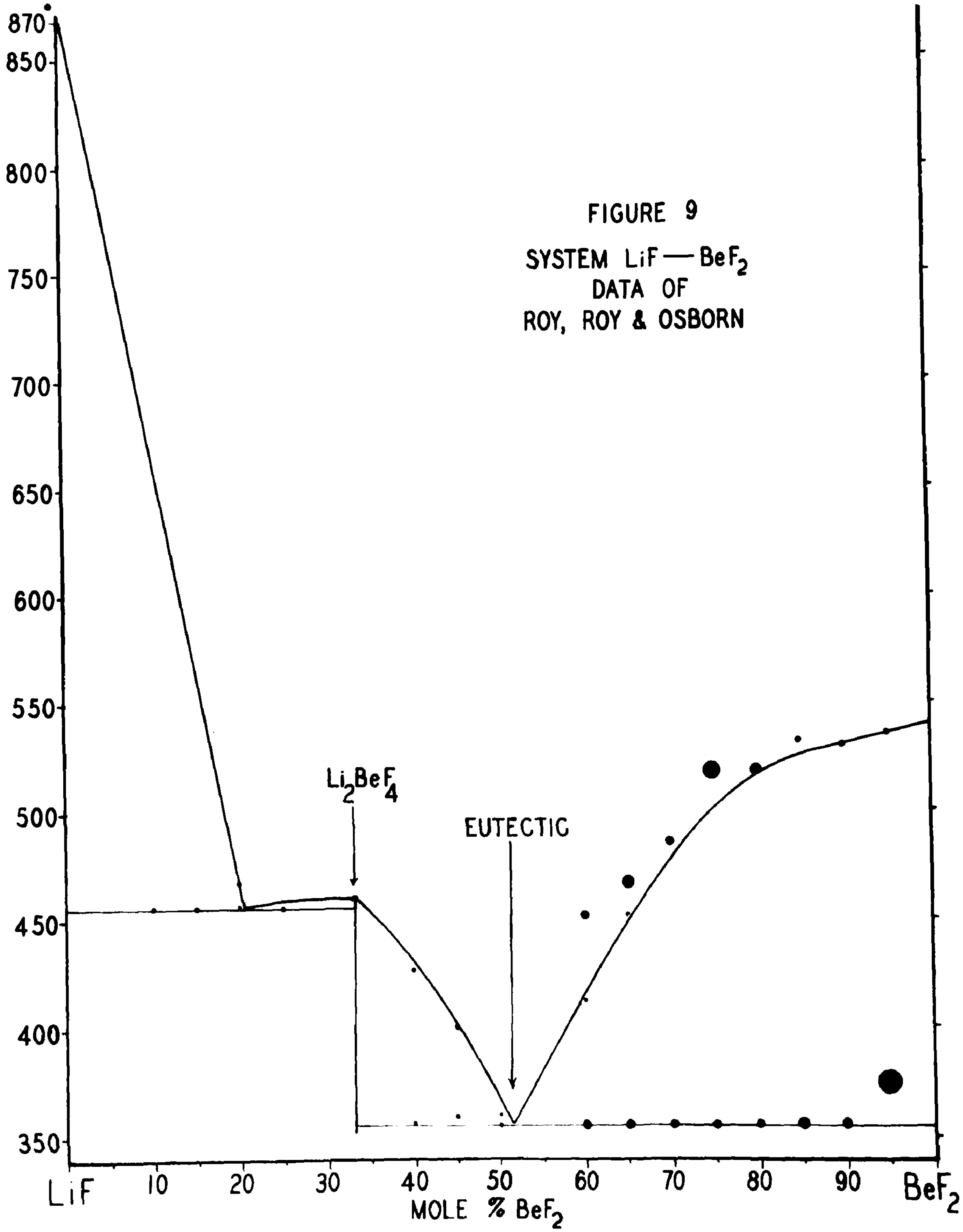


FIGURE 9

SYSTEM LiF — BeF$_2$
DATA OF
ROY, ROY & OSBORN

would be to have a gradual increase as the eutectic composition was approached.

On the next melt at 31.5 mole percent they found no initial crystallization inflection for LiF deposition, but only a "eutectic" at 462°. Strangely their holding time per gram at the eutectic was about two-thirds that of the preceding melt instead of being greater. The discordance between the 462° value and some of the previous higher values apparently did not bother them and they established the "eutectic" at 462° and 31. mole percent BeF_2, in good agreement with a eutectic in the $MgO-SiO_2$ system at "about 30 mole percent" according to the work of Andersen and Bowen (2).

On the next two melts at 33.3 and 36. mole percent BeF_2 they obtained liquidus values of 475° and 475°, and they gave "holding times of first crystallization" which were respectively about 5 and 10 percent less than that of the preceding "eutectic" holding time. (At this point comparison is made with the very similar flat plateaus of gradually decreasing length obtained in this work in the same region, which have however a 460° maximum value.) On their next melt at 38 mole percent the liquidus value dropped to 453° with the same "holding time of first crystallization" as the preceding melt at 36 mole percent.

Up to this point their thermal results closely paralleled those obtained in this work, except for the temperature values exceeding 460°. It is suggested however that their 470° figures show internal inconsistencies, as do the eutectic holding times. Since they relied completely on thermal effects, the possible initial deposition of LiF along the very steep liquidus curve at 31.5 mole percent might have occurred without detection, and the fortuitous combination of a low point of 462° might be accepted without reasonable doubt as a probable eutectic point. If any temperature uncertainty of large extent were apparent, however, some reinvestigation would seem necessary, but these workers apparently were satisfied despite the discordance of temperature and holding time values. The two succeeding values of 475° confirmed their eutectic diagnosis, although the decreased "holding times of first crystallization" are not explainable on the same basis.

Summarizing this region of the Thilo and Lehmann work, there was substantially complete agreement of their thermal results with the present work as to general behaviour. With respect to temperature, their results indicate a maximum melting temperature of 475° for Li_2BeF_4, whereas in this work a maximum temperature of 460° was obtained on carefully prepared wet synthesized material. The remaining differences may be due to composition errors.

Here their experimental data is not sufficient to permit a decision. Their compositions were based entirely on the input of pure LiF and of $(NH_4)_2BeF_4$ containing some NH_4F. The beryllium content of the $(NH_4)_2BeF_4$ was determined by conversion to $BeSO_4$ and subsequent reduction to BeO. The control analyses based on a pure beryllium basic acetate were stated to fluctuate, but no indication of the precision of the over-all analysis is obtainable from their report.

With respect to the 33 to 50 mole percent BeF_2 region the results of the present work are in good agreement with the report of Osborn et al., and in fair agreement with Thilo and Lehmann except for their claim of the occurrence of a compound $Li_3Be_2F_7$ at the 40 mole percent point. Several reasons exist for believing that this assumption is incorrect. Osborn et al. reported no such indications in their work. In the present work a complete series of gradually shortening plateaus were obtained as the liquidus curve was studied throughout this region. Thilo and Lehmann arbitrarily assumed that because there was a large difference in the "holding time of initial crystallization" between their 38 and 40 mole percent results, that such a compound existed. Their liquidus curve also shows an inflection at that point which would be absent if their high values of 475° were changed to 460° for the 33.3 and 36. mole percent results. They frankly admitted that only Li_2BeF_4 separates along the curve throughout the region 33.3 to 50 mole percent and that $Li_3Be_2F_7$ was not detected in any other manner. They state that the cooling curves in the region are anomalous and offer an explanation based on gradual exothermic decomposition of higher complex ions to permit further deposition of Li_2BeF_4. The "anomalous" curves, although inadequately described, would appear to have been purely due to partial solidification followed by undercooling and then renewed solidification, a combination which was sometimes observed in the present work when the melt was not sufficiently agitated.

The claim of Thilo and Lehmann for the existence of the compound $LiBeF_3$ is not based on any definite thermal data, but rather on the isolation of a different type of crystalline product best obtained by chilling melts with the ratio $LiF/BeF_2 = 4.9/5.1$ in a moderately rapid manner; other cooling rates yielding Li_2BeF_4 rather than $LiBeF_3$. These crystals of "$LiBeF_3$" showed a strong resemblance to monoclinic pyroxene, presumably in the form of clinoenstatite, or enstatite, $MgSiO_3$. The isolated material could not be analyzed satisfactorily using their sulfate method, and hence was characterized only by X-ray powder pattern. Thilo and Lehmann gave a comparison of X-ray lines for three samples: a) Li_2BeF_4, b) Sample of slowly solidified melt with over-all composition of $LiBeF_3$, and c) "$LiBeF_3$" isolated by the controlled chilling process. This tabulation is reproduced in Appendix 13, together with values obtained for Li_2BeF_4 in this work.

In considering the Thilo and Lehmann data the following points should be considered. According to them the product of b) would show only the lines of Li_2BeF_4 rather than $LiBeF_3$. They state that b) values are intermediate between those of a) and c), which conclusion is hardly confirmed by inspection of the results. From the manner of arrangement of the 52 listed lines, 16 are apparently supposed to be unique for $LiBeF_3$, 19 for Li_2BeF_4, and 17 lines common to both compounds. By comparison of their b) and c) data, however, it is apparent that even more similarity exists, 27 values of lines being the same for both b) and c), leaving only 6 lines as unique for c) if the author's implied precision is accepted.

If, however, there is a shift in the position of the Li_2BeF_4 lines, as indicated by comparison of the a) and b) values, either real or due to experimental error, the claimed difference between the b) and c) values may be purely imaginary. On this basis probably 31 or 32 of the total of 33 lines are common to both b) and c), the remaining differences being largely in estimated intensity. Such a complete similarity of the X-ray powder patterns of two related compounds is not probable, except for the latter one-third of the list where the lines caused by the small separations of planes of high index values naturally tend to show closely spaced values.

The general conclusion with respect to this data is that the reality of any difference between Li_2BeF_4 and "$LiBeF_3$" remains undemonstrated, or that at best some distortion of the Li_2BeF_4 structure occurs as a function of composition. The demonstration of the Goldschmidt "model" behaviour is reduced to a much smaller degree of similarity between the LiF-BeF_2 and the MgO-SiO_2 systems. Until the latter has been adequately investigated, the analogy must remain incomplete.

On the basis of the present work it is concluded that the LiF-BeF_2 system exhibits two invariant points and one incongruently melting compound, Li_2BeF_4. The lower invariant point, representing the eutectic mixture of Li_2BeF_4 and BeF_2 occurs at approximately 52 mole percent BeF_2 and at about 358°. The upper invariant point occurs as a peritectic reaction at approximately 33.5 mole percent BeF_2 and at about 458-460°. The region from 52 to 100 mole percent BeF_2 yielded no definite liquidus line information.

No similarity exists between the ZnO-SiO_2 and LiF-BeF_2 systems as proposed by Osborn et al. The extent of similarity between the MgO-SiO_2 and LiF-BeF_2 systems as proposed by Thilo and Lehmann is actually much less than they believed, and such similarity as there is may be considered fortuitous on the basis of present knowledge.

THE TERNARY SYSTEM CALCIUM FLUORIDE--LITHIUM FLUORIDE--BERYLLIUM FLUORIDE

THE TERNARY SYSTEM CALCIUM FLUORIDE--LITHIUM FLUORIDE--BERYLLIUM FLUORIDE

Part A -- General

The ternary system was investigated concurrently with the work on the binary LiF-BeF_2 system. During much of the work on the ternary system the exact natures of the invariant reactions were uncertain in two of the contiguous binary systems near the compounds Li_2BeF_4 and $CaBeF_4$. The slight composition differences separating the invariant points and the compound locations created difficulties in determining whether a peritectic or eutectic phase reaction was involved. As a consequence of this uncertainty, the already large number of possible variations within the ternary system was greatly increased.

For a three component system, whose contiguous binary systems show two additional compounds and no solid solutions, three invariant points will occur within the ternary diagram. For systems, such as those of the present work, in which none of the binary systems show a continuous series of solid solutions, one of the ternary invariant points must be a ternary eutectic. It is not possible to predict the nature of the other two ternary points, even with full knowledge of the binary systems. These two points may be either peritectic and peritectic, or peritectic and eutectic in character.

The three constituent binary systems have been described in the preceding sections. The CaF_2-LiF system is purely eutectic. The system CaF_2-BeF_2 shows two eutectics with a compound which barely melts congruently.

The LiF-BeF$_2$ system shows both peritectic and eutectic reactions with a barely incongruently melting compound.

From the relative temperature levels of the significant points of the binary systems it is possible to make some estimates as to the probable behaviour. Thus, the lines of two-fold saturation extending inward from the invariant points of the binary systems must descend toward lower temperatures within the ternary system. In addition, in the absence of solid solution regions extending far into the ternary system, phase rule theory permits drawing conclusions as to which lines of two-fold saturation cannot intersect. The theory, however, permits no choice between other alternative arrangements of the paths and intersections of the lines of two-fold saturation which are not in violation of the theory. According to the assumed arrangements and positions of such intersections, however, the theory will describe the resultant phase reactions along such lines and at the points of intersection.

Before referring to the experimental results it seems best to give some consideration to the theoretical possibilities in order that the results may be interpreted from the standpoint of their agreement with these possibilities. The general theory is covered more completely in Appendix 5, hence the discussion here will be more specific. The effect of solid solutions is omitted from the considerations, not because these solutions are not present, but for three main reasons. Firstly, the invariant points are so distant from all except one of the compounds that extreme miscibility ranges would be necessary to affect the interpretation of results. Secondly, no such solid solution formation was apparent from optical and X-ray examination. Finally, in the case of the compound Li_2BeF_4, which is very close in composition to one of the invariant points, solid solution formation cannot be excluded entirely. Here, the thermal results and phase reactions show no indications that solid solutions need be taken into account in the interpretation.

If the binary systems are placed in the usual triangular arrangement, with the binary phase diagrams indicated by projection along the sides of the triangle of Figure 10, certain forbidden and permitted possibilities may be described. For purposes of discussion, the BeF_2 rich portions of the binary systems are shown as approximate estimates, although the exact nature of these regions was not determined. The temperatures corresponding to the binary invariant points are also shown. *Considerable distortion of the diagrams with respect to composition has been made for clarity*, in order to separate closely spaced points, of interest for this discussion. *Assumed* lines of two-fold saturation within the ternary system are shown projected upon the ternary triangle.

As fully discussed in Appendix 5, it is not possible for the pair of two-fold saturation lines from F and G (or from H and I) to intersect prior to their intersection with other two-fold saturation lines, in the absence of extensive solid solution regions. It follows as a consequence that the line from H must intersect the line from G at point K. K must also be a ternary eutectic point since G has the lowest binary invariant temperature.

In addition, because point F and the observed ternary invariant points have temperatures considerably below those of points within the triangle AEC, this region may be excluded from the present discussion. The possibilities then remain that the three lines of two-fold saturation leading from F, I and J may intersect in a variety of ways. These variations may include both the order of the intersections and the location of the intersections among the three triangles AED, BDE and CDE.

One such combination is illustrated in the figure with the lines from J and F intersecting at the peritectic point M, followed by intersection of the line from M with that from I at another peritectic point L. From L the line of two-fold saturation falls to the final ternary eutectic point K. Had another equally possible combination been chosen in which points M and L were located within the composition triangles ACD and CDE respectively, the two invariant reactions at these points would have been eutectic rather than peritectic.

Normally, such a large number of possibilities does not greatly hamper analysis of the phase diagram when thermal-composition data have been obtained. In the present case, however, the invariant points M and L were very close to each other in temperature and composition. Also, because of their close proximity to point D they were necessarily close to the dividing lines DC and DE. This combination of circumstances, together with the accompanying uncertainties of the nature of the reactions in the binary systems at points F and I, made the interpretation of the behaviour in this region rather difficult. In addition, experimental errors with respect to the determination of temperature and composition approached too closely the magnitudes of the differences between the points M and L.

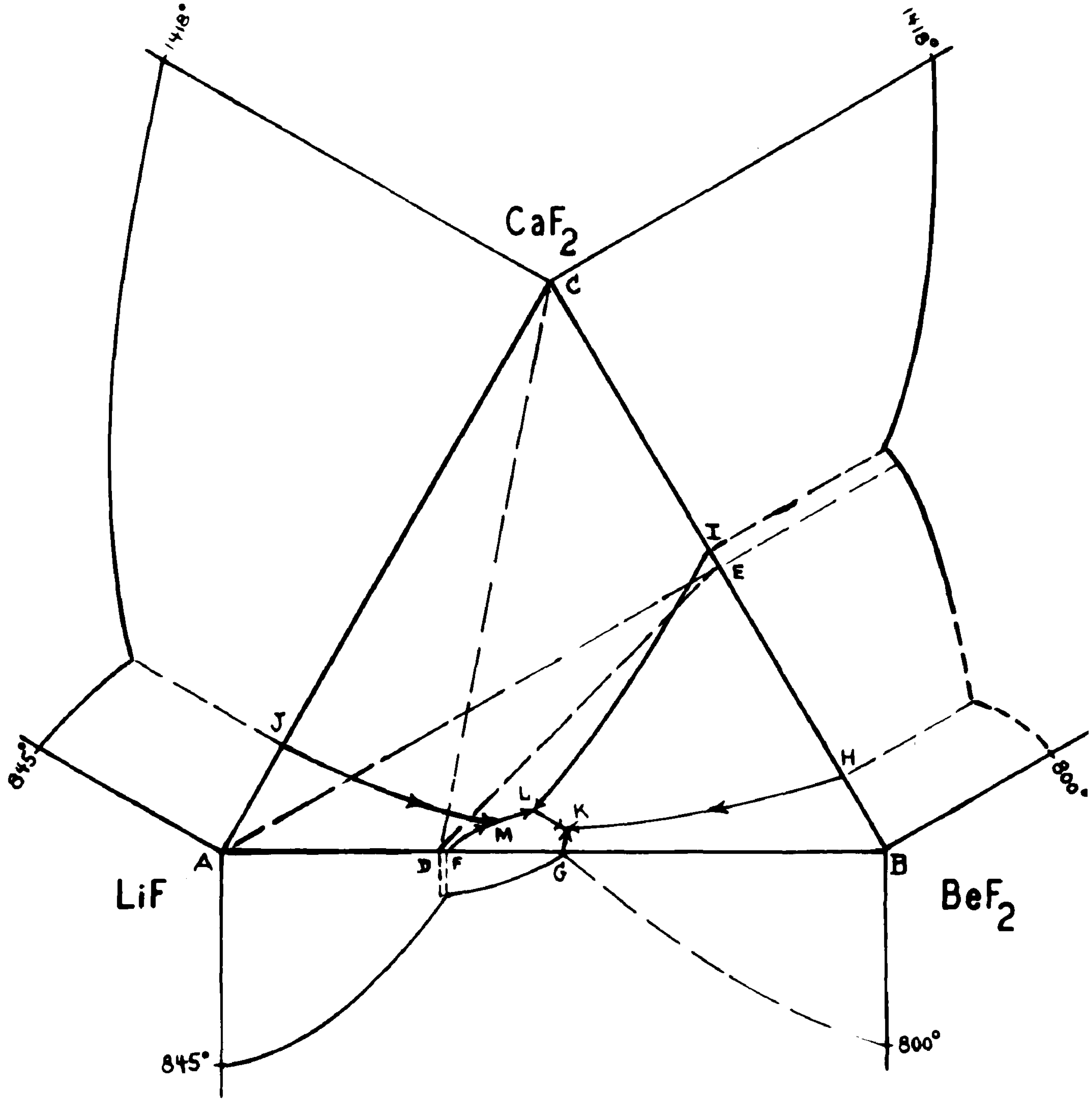


FIGURE 10
DISTORTED VIEW
TERNARY SYSTEM
CaF_2 — LiF — BeF_2

For clarity the discussion of the ternary system results is divided into four parts corresponding approximately to the following regions: (See Figure 10)

Part B) Region within ADMJ and to a limited extent above line MJ; i.e. the LiF-rich portion.

Part C) Region within BHILKG and to a limited extent above line IL; i.e. the BeF_2-rich portion.

Part D) Region within FGKLM and the immediately adjacent areas; i.e. the Li_2BeF_4-rich portion.

Part E) The ternary system as a whole.

The area lying in general above a line from I to J was not investigated for several reasons of which the following are most pertinent. Since there was no reason to expect complexity within the upper portion of the diagram, and no evidence was found for ternary compound formation there, the liquidus surface may reasonably be extrapolated from the binary curves. The high temperature involved (from about 800° to 1400°) made the region of no interest for the original purpose of the investigation. The cost, as well as the uncertainty of results due to volatilization and hydrolysis reactions, made it seem unwise to investigate this region.

The thermal-composition data and analytical results have been assembled in Appendices 12 and 15. The thousands of items of data involved make it impossible to describe the results of the excessively large number of thermal studies except as generalizations. The results are best followed by consideration of the trends obtained as the ternary system was "sectioned" along lines, usually extending from the LiF-BeF_2 side toward some point such as the CaF_2 corner of the diagram. Usually the procedure of making successive additions of a component was followed as a means of obtaining better relative composition values.

Part B -- The LiF-Rich Portion of the Ternary System

The general region covered by this section is shown in Figure 11, a partial phase diagram of this corner of the ternary system. The liquidus temperatures are shown adjacent to the composition points. The temperature contour lines have been drawn on the basis of both liquidus temperatures and information obtained by consideration of the temperatures of secondary inflection points, or observed changes in the character of the crystallization processes. The points may be identified with particular melts listed in Appendix 12 from the letter (indicated on the LiF-BeF$_2$ edge) from which a series of melts proceeds out along a straight line into the ternary system in the sequence A-1, A-2, etc. The temperature values along the LiF-CaF$_2$ and LiF-BeF$_2$ edges have been taken from the smooth curves drawn for the liquidus lines of the two binary systems.

Referring to Figure 11, the temperature contour lines show in general the behaviour to be expected for the region. They indicate a drop from the LiF peak toward the lower temperature regions of the valley leading down from the LiF-CaF$_2$ binary eutectic point, in the direction of the compound Li$_2$BeF$_4$. On the other side of the valley the slope climbs steeply toward the CaF$_2$ peak. In the left half of this region no difficulties were presented and the thermal results were in good agreement with the expected behaviour. The only peculiarity is the rather shallow slope of the bottom of the valley.

In the right hand portion of the figure, at about melt F-1 and subsequent melts of series G, H, etc., there is less and less temperature

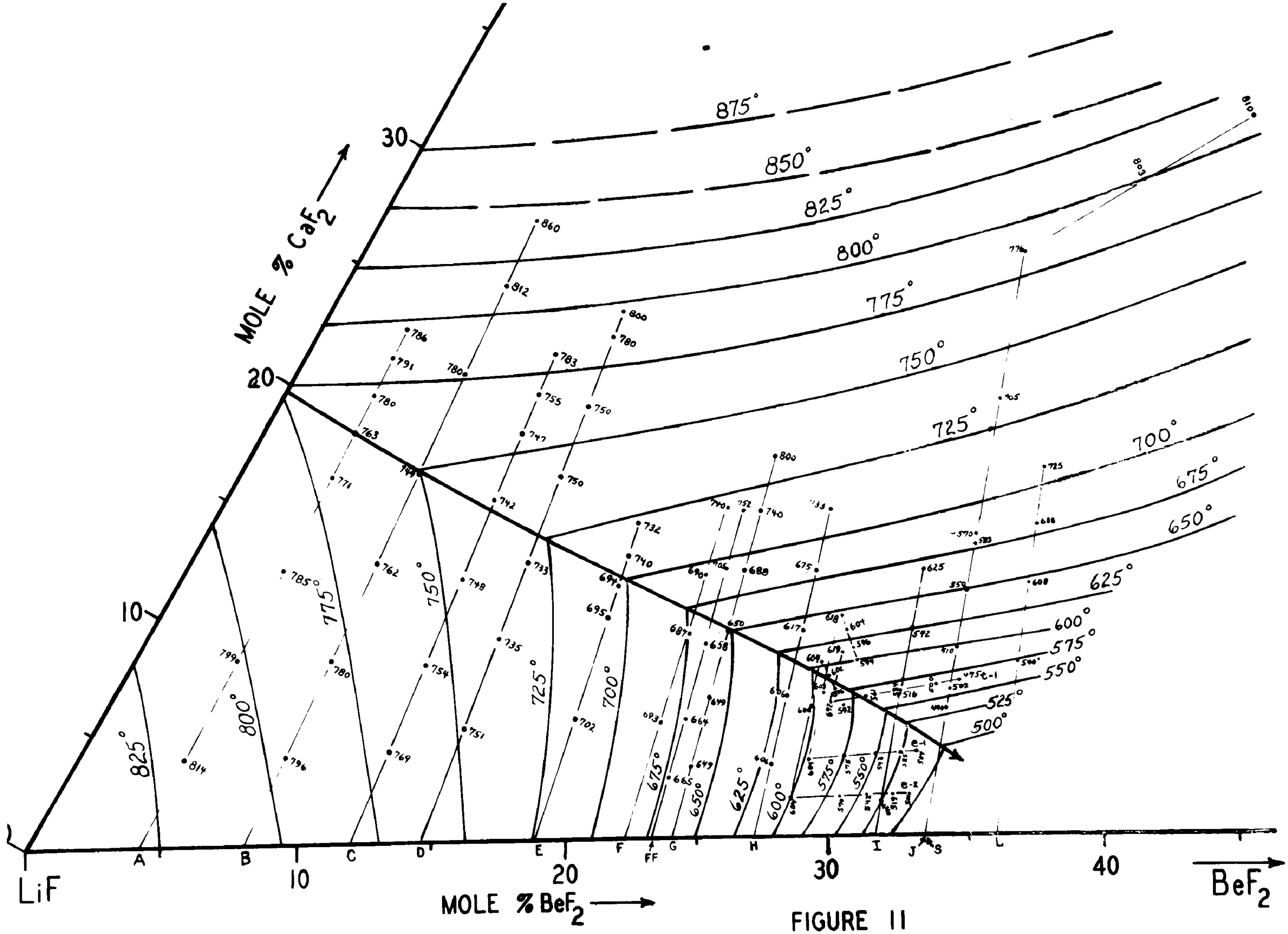


FIGURE 11

LiF-RICH REGION

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drop along each section and, as will be seen, there is subsequently an experimental rise in temperature as the ternary system is entered. This flat region, extending in from the LiF-BeF_2 side, explains the shallow slope of the valley leading down into it, since apparently the addition of CaF_2 is not exerting a normal lowering effect on the LiF-BeF_2 binary system. The exact location of this valley becomes difficult because of shallow slopes prior to the valley and the very steep slope on the CaF_2 side. For this slope thermal liquidus effects were poor and observation of initial CaF_2 crystallization became necessary to reliably determine the liquidus temperature.

Subsequent to the H series of melt an additional complicating feature appeared. In that region of the diagram, a precipitous slope occurs directed toward the Li_2BeF_4 region, corresponding to the steep slope in the adjacent part of the LiF-BeF_2 binary system. Initial deposition of LiF could then only be detected by observation as the thermal effects became poorer and poorer. This steep drop near the LiF-BeF_2 side is accompanied by a corresponding increased slope of the valley from the LiF-CaF_2 binary eutectic with its steeply sloping CaF_2 side. Along the section lines the system changes from relatively flat to a condition in which sections show a small initial rise of about 5 to 10°, while passing over a slight promontory extending in the general direction of the compound Li_2BeF_4. After passing over this hump the thermal sections show a slight and gradually decreasing fall into the valley from the LiF-CaF_2 eutectic, so that the bottom of the valley becomes more poorly defined. The far side of the valley, where CaF_2 deposits initially, becomes somewhat less steep as the Li_2BeF_4 region is approached.

At this point the valley from the LiF-CaF_2 binary eutectic (originally about 20 mole percent CaF_2) has extended to a point in close proximity to the LiF-BeF_2 side, that is only about 5 mole percent CaF_2 at about 30 mole percent BeF_2. The balance of this region is more appropriately discussed in Part D on a larger composition scale. The melts lying along lines identified by "e" and "t" were handled in a somewhat different manner, being shifted toward the points LiF, CaF_2 or Li_2BeF_4 as indicated by the path of their guide lines.

Summarizing the results in this section of the diagram, it may be said that the behaviour is that which might be generally expected from a consideration of the binary systems. The relatively small lowering effect of CaF_2 on the LiF extends out into the system and becomes progressively poorer. The moderate lowering effect of the Li_2BeF_4 on the LiF extends within the ternary system until a critical BeF_2 content is reached at about 25 mole percent, following which the lowering effect of the Li_2BeF_4 becomes much more drastic.

With respect to observed solid phases, LiF, CaF_2 and Li_2BeF_4 were found in significant amounts. Small traces of BeF_2 increased in the right hand portion as a result of an incomplete phase reaction in the vicinity of Li_2BeF_4. All melts in this region seemed to be completely solidified prior to or on reaching an invariant reaction at about 454° as more fully discussed in Part D. Thermal results occasionally indicating to the contrary were probably due mainly to arrival at the invariant point with insufficient liquid to produce a good plateau, or to slightly incomplete conversion of LiF to Li_2BeF_4.

In general the temperature contours may be drawn without too much omission of discordant points. Beyond the ternary eutectic valley (descending from the CaF_2-LiF eutectic) the situation becomes poorer as composition uncertainty and melt degradation increase with the rapidly rising temperature levels of that region.

Part C -- The BeF_2-Rich Portion of the Ternary System

As previously mentioned, the portion of the system with very high BeF_2 content solidifies in glassy form with no definite liquidus temperature at reasonably low cooling rates. Consequently the region of Figure 12 containing the broken contour lines is only a rough estimate which may be entirely without reality, the contours being inserted primarily for clarity in visualizing the phase diagram.

The same general "sectioning" procedure was followed on most of the melts in this region and the points are identifiable in a similar manner as were those in the preceding section. The temperatures along the BeF_2-CaF_2 side are taken from the liquidus curve of that binary system.

Assuming the presence of a valley leading down from an assumed binary eutectic in the BeF_2-CaF_2 system (at about 10 mole percent CaF_2), neither of which phenomena were definitely observed, it may be said that no good liquidus points were determined between this valley and the LiF-BeF_2 side of the diagram. On the other side of the valley, and definitely within about 5 mole percent from it, $CaBeF_4$ was initially deposited with apparent thermal effects. Thereafter, with increase in CaF_2 content, very strong thermal effects were obtained upon $CaBeF_4$ deposition over most of the region, primarily because of the relatively shallow slope of the space surface representing saturation with this component. A corresponding shallow slope is present in the binary system for the liquidus curve of this compound. When the space surface of CaF_2 deposition was encountered (at a valley leading down from the CaF_2-$CaBeF_4$

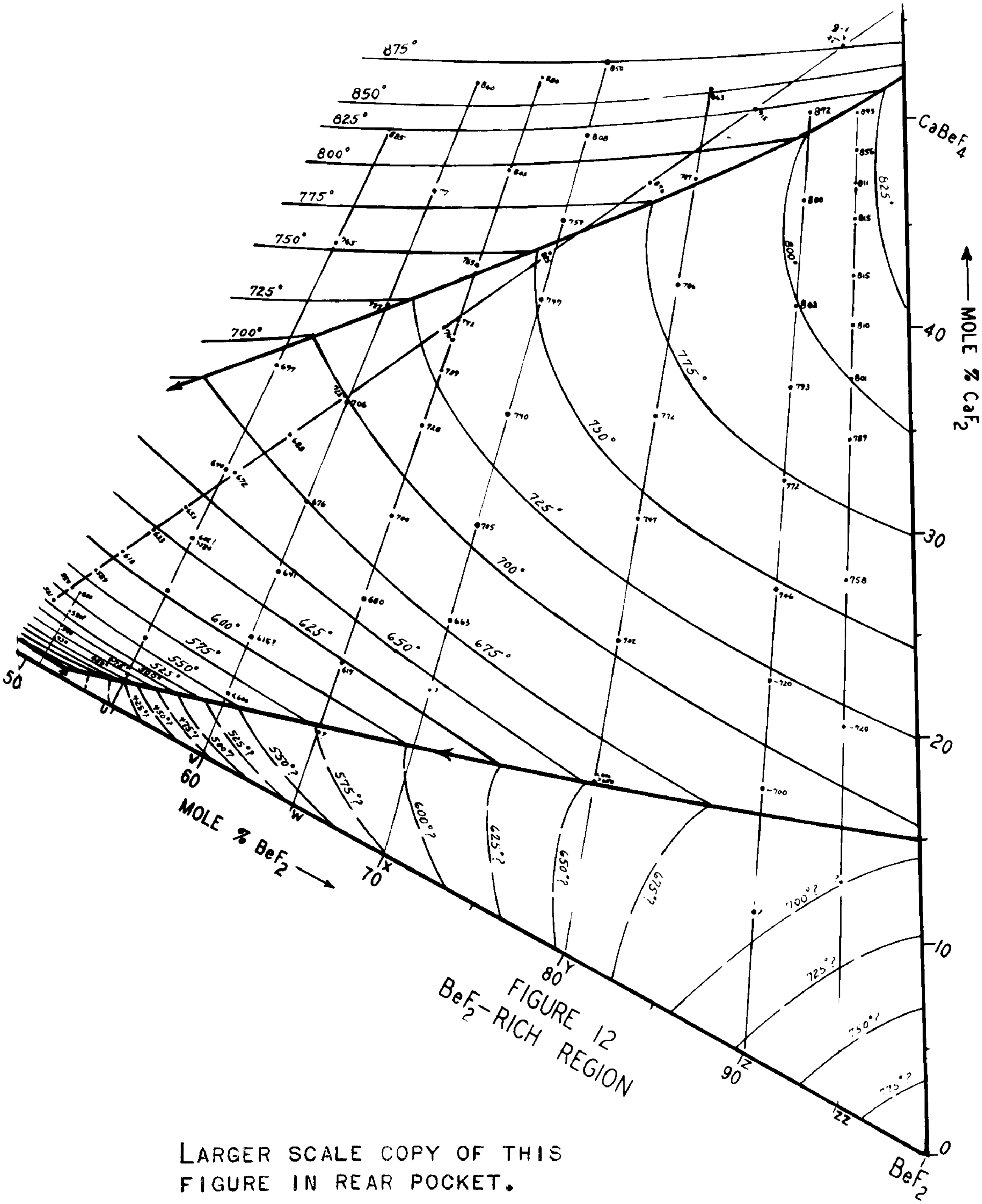


FIGURE 12
BeF_2-RICH REGION

LARGER SCALE COPY OF THIS
FIGURE IN REAR POCKET.

eutectic), this favorable thermal effect vanished. Beyond this valley, initial deposition of CaF_2 had to be detected visually.

Referring to Figure 12, covering this section of the ternary diagram, the results may be generalized briefly as follows, detailed results being given in Appendix 12.

Sections passing into the ternary system near the BeF_2-CaF_2 side showed a gradually rising slope, with slight evidence of passing over a small hump extending out from the vicinity of the compound $CaBeF_4$. Thereafter, they fell very slightly to a valley leading down from the CaF_2-$CaBeF_4$ eutectic at approximately 51 mole percent CaF_2. Beyond this valley, the slope of initial CaF_2 deposition rose very steeply and much more discordant values were obtained as a result of the high temperature degradation of the melts.

Sections more removed from the BeF_2-CaF_2side, such as the Y, X and W series, showed the same initial slow rise of temperature for $CaBeF_4$ deposition with strong thermal effects. They did not however show indications of passing over a small rise prior to reaching the valley leading down from the CaF_2-$CaBeF_4$ eutectic. A very slight valley is indicated by the contour arrangement (since it is theoretically necessary), but the intersections of contour lines at the valley appear to become increasingly oblique. Thereafter, the valley only made itself apparent as a strong thermal effect following initial CaF_2 deposition.

For these melts (located reasonably distant from the BeF_2-CaF_2 side of the system) it became experimentally possible to follow the solidification process to completion in order to determine the ultimate destination of solidifying mixtures. Of the melts which were thus cooled, it was found that one or the other of two destinations were reached. One of these was the lowest temperature point of the system. This was the ternary eutectic point (approximately 350°) in the near vicinity of the binary Li_2BeF_4-BeF_2 eutectic (about 52 mole percent BeF_2). The other alternative destination was found to be at a higher temperature near 450° at a location closer to the Li_1BeF_4 region as further discussed in Part D.

Significantly, the first destination at the lower temperature was shown by melts initially depositing $CaBeF_4$ and also by those very close to the LiF-BeF_2 side which had no definite liquidus point. The second (higher temperature) destination was shown by those melts initially depositing CaF_2, i.e. those *beyond* the eutectic valley representing the two-fold saturation line for $CaBeF_4$ and CaF_2. This behaviour and the liquidus thermal effects were used in estimating the location of the valley.

Between these two extremes of behaviour, there was a third class represented by melts which had compositions somewhat below the CaF_2 content of the eutectic $CaBeF_4$-CaF_2 valley. Such melts exhibited a *second inflection* at temperatures intermediate between 350° and 450°. Eventually they reached the 350° destination with apparent thermal effect, unless too small an amount of liquid remained. These two inflections, due to initial $CaBeF_4$ deposition and subsequent intersection with a valley representing a two-fold saturation line for $CaBeF_4$ and Li_2BeF_4, will be further discussed in Part D.

For melts still farther from the BeF_2-CaF_2 side of the system, such as the V series, the slope representing $CaBeF_4$ deposition was initially steeper and indicated a rapid decline toward the ternary eutectic located near the 52 mole percent BeF_2 region. This initially steep slope for $CaBeF_4$ deposition increased in abruptness for the regions to the left of this series so that thermal effects were not obtained and special technique was necessary in detecting $CaBeF_4$ deposition as further discussed in Part D. Thermal effects were obtained only after the initial slope had undergone an inflection to form a short sloping plateau below the eutectic $CaBeF_4$-CaF_2 "valley", which extends toward the Li_2BeF_4 region. In the region under discussion the "valley" has extended to about the composition point of 20 mole percent CaF_2 and 40 mole percent BeF_2.

One series of melts extends across this region along a straight line from point g-1 (near 55 mole percent CaF_2 on the BeF_2-CaF_2 side) directed toward the 48 mole percent BeF_2 point of the LiF-BeF_2 side. These points were obtained differently from the previously mentioned melt series in that they represent a "section" surveyed by addition of material of the latter composition to original material of the composition g-1. The general results were in agreement with those of the other sections prepared by addition of CaF_2 to melts of the LiF-BeF_2 side of the system.

Summarizing the behaviour of this region of the ternary system, a line of two-fold saturation (representing a eutectic reaction forming CaF_2 and $CaBeF_4$) extends down from the corresponding binary eutectic point at about 51 mole percent CaF_2. Beyond this gradually sloping valley, a steeply ascending slope is found extending across the region (the surface of saturation with respect to CaF_2), in agreement with the similar slope found beyond the LiF-CaF_2 eutectic line in Part B.

On the lower side of the valley, a broad (gradually sloping) promontory extends inward from the $CaBeF_4$ composition point. This agrees with the considerably dissociated character indicated for this compound by the "rounded-off" peak which it shows in the binary BeF_2-CaF_2 system. The over-all effect is one produced by a very inconsequential lowering by CaF_2 of the $CaBeF_4$ liquidus and, by contrast, a fairly strong lowering effect of the $CaBeF_4$ upon the CaF_2 liquidus surface.

In the region nearer the compound Li_2BeF_4 there is an indication that substantial lowering effect of the Li_2BeF_4 upon the $CaBeF_4$ is obtained only after a fairly critical composition of the former is reached, following which the effective lowering is very abrupt.

With respect to the BeF_2-rich portion adjacent to the LiF-BeF_2 side of the system no results of significance were obtained. The lowering produced at the ternary eutectic point, as compared with the adjacent Li_2BeF_4-BeF_2 binary eutectic point, was very small and is discussed in Part D.

In general, throughout the region covered by this section the thermal results were in reasonable agreement with the indicated temperature contour lines. Some exceptions occur particularly in the high temperature region above the $CaBeF_4$-CaF_2 eutectic valley, principally because of composition uncertainty and contamination by hydrolysis products. Some imagination was necessarily employed in estimating the contour shapes and location, as their fine structure could not be obtained except by an excessively large number of experimental points.

Part D -- The Li_2BeF_4-Rich Portion of the Ternary System

The central portion of the ternary diagram along the LiF-BeF_2 side (from 30 to 50 mole percent BeF_2), extending into the system to a concentration of about 15 mole percent CaF_2, will be discussed in this section. The previously described portions of the ternary system were those lying roughly within the ranges of 0 to 30 mole percent BeF_2 and 50 to 100 mole percent BeF_2. In the region from about 30 to 50 mole percent BeF_2, the major experimental and interpretive difficulties were encountered.

Because of the large number of melts of closely spaced compositions which were prepared in this region, it has been necessary to present the results on an enlarged scale. While the scale does not give a false impression of the accuracy of gravimetric preparation of the melts, the possible absolute composition errors are much larger than the scale of Figure 13 might indicate. Because of the formulation of the melts from generally the same materials in similar manners, the relative positions are <u>theoretically</u> known to an accuracy somewhat closer to the scale of the diagram. The disturbing factors such as creepage losses, slight volatilization and hydrolysis introduce, however, much larger uncertainties of probably at least ± 1/4 mole percent under the best of circumstances. Such uncertainty must be kept in mind for closely spaced melts and the results must be interpreted in terms of trends despite the presence of occasional discordant values.

With respect to temperature values, a somewhat analogous situation exists, primarily because of the very small differences (such as 5 to 10°) in temperature levels between significant points. Here a 1° error will appear as a discordant value. It will be appreciated that even with good temperature detection, occasional undercooling or failure to detect first crystallization may readily create errors of this magnitude or greater. For largely solidified melts, temperatures representing the ends of certain thermal effects are considerably more in error because of the much poorer temperature equilibrium within the sample container.

Finally, and of even more importance, there is the discordance which may be introduced by any incompleteness of the phase reactions. Peritectic reactions, of which two are present in this region, are notoriously bad offenders in this respect. Consequently, should any effective isolation of a solid component occur during solidification, such that it is not in equilibrium with the melt, the melt will necessarily behave like one of different over-all composition. All melts were mixed as effectively as possible until the solidification prevented further stirring. As previously mentioned, considerable quantities of non-apparent liquid (up to 25%) might still remain as judged by the continuance of the thermal effect.

All these effects must be considered together with visual observation of the character of the crystallization. The data have been tabulated in Appendix 12 in a way that best permits consideration from the standpoint of the changes which occur throughout a particular section. A great many melts must be considered, of which about one hundred were concentrated in the immediate vicinity of the Li_2BeF_4 point in an attempt to obtain a detailed picture of the thermal contour complications in this region.

Because of the peculiarities of the system in this region, even this super-abundance of data does not permit a purely objective conclusion. Considerable judgment still was necessary to choose among the numerous possible explanations of the data, in the light of the previously mentioned uncertainties as to exact compositions and temperatures.

In Figure 13 all results obtained in this region have been indicated by a composition point and an associated temperature value representing the observed liquidus temperature. Several types of "sections" were made in this region. Some were shifted from the LiF-BeF_2 side in the direction of the CaF_2 corner of the system. Others were directed from the vicinity of the Li_2BeF_4 composition point toward either the $CaBeF_4$ composition point or another point at approximately the location of the binary LiF-BeF_2 eutectic. Light guide lines are indicated, extending out from the identified initial melts on the LiF-BeF_2 side, to indicate the path of each section. The few exceptions to this general procedure, series "e", "t", "g" and S, were prepared and carried along other sections in a manner which is apparent from an examination of the direction followed by their respective guide lines. The identification of a particular composition point may be made by reference to the origin of its guide line, the numbering for example following the sequence S, S-1, S-2, etc., or 12Q, 12Q-1, 12Q-2, etc.

In the discussion of Part B it was noted that starting at about the 30 mole percent BeF_2 point, a perceptible and gradually increasing

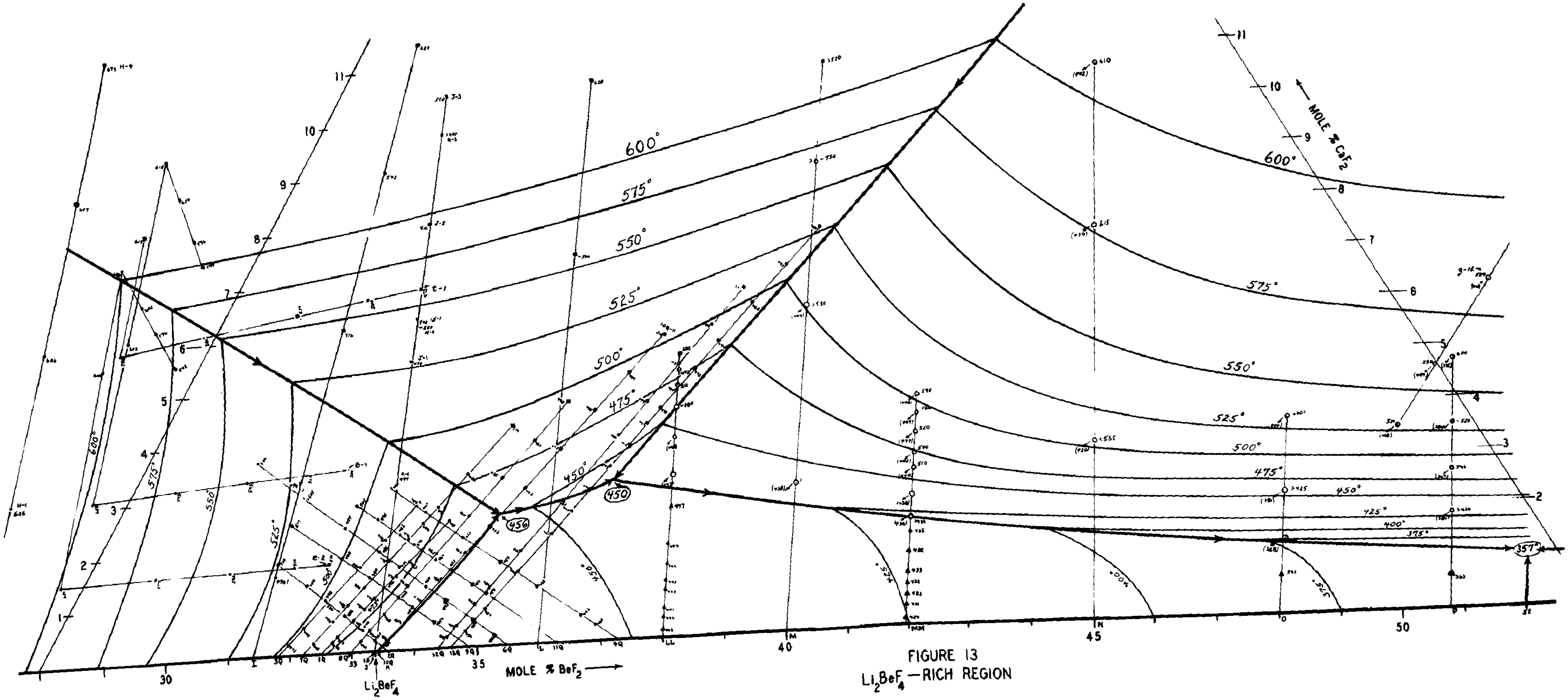


FIGURE 13
Li$_2$BeF$_4$—RICH REGION

Larger scale copy of this
figure in rear pocket.

initial rise was found as a binary LiF-BeF_2 melt was carried out into the ternary system by addition of CaF_2. On such sections the small initial rise was shortly followed by a small temperature drop as the CaF_2 content was increased. All sections originating in the region of 30 to about 32.5 mole percent BeF_2 showed this same behaviour, indicating that the sections were cutting through a small promontory extending down toward the Li_2BeF_4 point. The relative temperature levels of the sections dropped sharply as the BeF_2 content increased. Accordingly, throughout this region initial LiF deposition had to be detected visually for lack of thermal effects. The reliability of such a detection was probably very good in this region, and better than would be indicated by some apparent discordant values.

Subsequent to the small rise and fall mentioned for melts carried into the ternary system (from the region of 30 to 32 mole percent BeF_2), a rise in the liquidus temperature was encountered at concentrations of approximately 3 to 4 mole percent CaF_2. Here there was a small region where it was difficult to decide the identity of the initially deposited solid by visual methods, i.e. whether LiF or CaF_2. Up to this region LiF definitely deposited first. Beyond this region CaF_2 was observed as the initially deposited solid, the liquidus temperature rising rather steeply for these melts. The region of uncertainty corresponds roughly (± 0.5 mole percent) with the path of the two-fold saturation line for LiF-CaF_2 deposition. In order to bring out this observation the points of the figure have been shown as solid circles or squares corresponding to the deposition of LiF or CaF_2 respectively as the initial solid.

The melts starting from the region of 32.5 to 33.5 mole percent BeF_2 on the LiF-BeF_2 side likewise showed LiF as the initial solid. Also they tended to show less and less initial rise, until by 33.5 mole percent the liquidus slope extending into the ternary system was very slight. On extension to concentrations greater than 2.5 to 3 mole percent CaF_2, there was a moderately sloping rise in the liquidus temperature accompanied by initial deposition of CaF_2.

The above discussion refers to binary melts to the left of the Li_2BeF_4 peritectic point which were shifted into the ternary system in the direction of the $CaBeF_4$ composition point. To the right of the Li_2BeF_4 peritectic point, two melts were carried along sections directed toward the $CaBeF_4$ point. The following comments refer to these melts of the 12Q- and 13Q- series. The initially deposited solid was Li_2BeF_4 (triangular symbols) and the liquidus temperature fell very slightly until the CaF_2 concentration reached about 3 mole percent. The liquidus temperature then rose quite gradually accompanied by a shift to CaF_2 as the initially deposited solid. The transition region corresponds to the two-fold saturation line ML which connects the two ternary invariant points of Figure 10.

Most of the melts to the right of the Li_2BeF_4 peritectic point (i.e. those with 33.5 to 37 mole percent BeF_2) were shifted along sections directed toward the vicinity of the CaF_2-LiF binary eutectic point. The location of these sections was such that primarily they were only useful in establishing the approximate location of the two-fold saturation line extending in from the Li_2BeF_4 peritectic point. Thus, as may be seen from Figure 13, all these melts showed initial deposition of Li_2BeF_4 (indicated by a triangular symbol), with only a slight upward trend of the liquidus temperature as the composition was shifted upward toward the left. Upon passing the two-fold saturation line, there was a shift to initial deposition of LiF accompanied by a rather rapid increase in the liquidus temperature, in reasonable agreement with the previous points obtained in that area.

From the region of 37 to 50 mole percent BeF_2 a number of series of melts were shifted into the ternary system along sections directed toward the CaF_2 vertex of the diagram. Most of these melts showed normal thermal effects, corresponding to the initial deposition of $CaBeF_4$ (open circle symbols), only after a minimum concentration of about 3 to 4 mole percent CaF_2 had been reached. Thereafter the thermal results showed the presence of a gradually sloping plateau. The latter represented the continuation of the plateau falling from the vicinity of the $CaBeF_4$ point as described in Part C of this section.

Nearer the LiF-BeF_2 side, however, there is apparently a very steep slope, representing the drop from the above plateau to the two-fold saturation line leading toward the ternary eutectic point. This drop, amounting to as much as 150° in some places, occurs in a very narrow region located between 0 and 3 mole percent CaF_2 up from the LiF-BeF_2 side of the diagram. In this region, the initial deposition of $CaBeF_4$ exerted no detectable thermal effect, as only a very small amount of solid formed in dropping through a large temperature range. This corresponded to the behaviour in three other parts of the ternary diagram where very steep slopes were encountered.

The situation in this region was worse, however, since $CaBeF_4$ deposited without any surface indication that crystallization was occurring. Solidification occurred as a gradual accumulation of needle shaped crystals, characteristically very tiny compared to the usual needle and prismatic habits of Li_2BeF_4. Occasionally the solidification was detectable by a sudden gritty feeling produced as the hand operated stirrer passed over the bottom of the platinum sample container.

For lack of a better method the following variation of quenching technique was used, with only partial success, in an attempt to detect initial $CaBeF_4$ deposition in this region. By plunging a cold nickel stirring rod (1/8" diam.) to the bottom of the melt and instantly withdrawing it, it was possible to withdraw a rapidly chilled sample from which the $CaBeF_4$ projected in the form of a fuzz of tiny needles. The needles, usually about the size of human hair and from 1/8" to 1/4" long, were identified by X-ray methods. While in some cases the method was shown to be reproducible to within 5° as a method of detection, in other cases it gave only very discordant results. This might not have been the fault of the method, but rather a shift in the point of crystallization to the upper, outer edge of the melt with subsequent adherence to the platinum container. Such a preferential tendency for $CaBeF_4$ to form adherent crystals on the platinum metal dish was noted in some cases.

Two very detailed melt series were run in this region (series LL- and MM-), at very small composition intervals (0.1 to 0.2 mole percent CaF_2)

in an attempt to characterize this steep slope, making use of the "quenching" technique. The results were only partially successful in that they indicated the probable location of the two-fold saturation line along the base of the slope, but in no way furnished details of the liquidus line until the latter decreased in slope at higher temperature levels.

Up to this point in Part D, the discussion has been exclusively confined to the results obtained for liquidus points throughout the general region of 30 to 50 mole percent BeF_2 near the LiF-BeF_2 side of the diagram. If all of these temperature and composition values were perfectly accurate and if the system were perfectly behaved, there would probably be no need for either additional information or discussion. Consideration of the data obtained and estimation of the accuracy (with relation to the peculiar requirements of the system) indicate that considerable supporting evidence is required to justify the proposed phase diagram.

Two additional sources of information are the X-ray examinations of the solidified melt samples and the supplementary thermal information obtained in conjunction with the liquidus values.

The X-ray examination of melt samples from this region is summarized and discussed fully in Appendix 13. The agreement is excellent with the proposed phase diagram behaviour, considering the fact that peritectic reactions are involved. Detailed consideration of the phases theoretically predictable for each of the melts (based on the location of their composition within certain composition triangles) is in good agreement with those actually found by X-ray analysis. In five cases, the "forbidden" situation of four coexisting solid phases was found, and these particular samples are noted to be ones lying right on the borderlines between two possible modes of behaviour. In addition to these cases there is evidence, throughout all the results, of a slight degree of incompleteness of the peritectic reactions, since at least traces of beryllium fluoride were always present in the samples. The X-ray data therefore are in accord with the proposed phase diagram, but they show that the system does not always behave perfectly, a conclusion which is particularly evident from the secondary thermal data.

While liquidus data are expressable by one or two pieces of information per point, the secondary thermal data are extremely voluminous and also, in this case, very deceptive. In tabulating the material in Appendix 12, only the more important features of the thermal behaviour could be shown. Such data as the points of first, second and third inflections, the types of solids formed, and a general description of thermal plateaus have been included. The latter values, however, are so dependent upon the particular conditions that exist for each melt that they should only be used for comparison with very adjacent melts of the same series. The amount of solids present prior to a plateau, the amount of liquid present at the end, etc., all affect the shape and temperature descriptions. Worst of all, in the vicinity of the Li_2BeF_4 point, there is a closely spaced combination of a ternary peritectic line, three ternary eutectic lines and two ternary peritectic points, in a narrow range of temperature and composition.

Mention is also made of the phenomenon (explained in detail at the end of Appendix 5) in which circumstances permit a melt to depart from a ternary peritectic line when a bivariant condition is created. Under these circumstances the ternary peritectic is not reached and the melt proceeds across a bivariant space surface until another two-fold saturation line is encountered.

This combination of possibilities may result in frequent transition from one type of phase reaction to another without thermal inflection. This blending together of univariant and invariant processes constituted the greatest obstacle to the interpretation of the behaviour, aside from the phenomena due to "forbidden" types of phase behaviour occurring in this same region.

For convenience in the following discussion Figure 14 is used as its exaggerated proportions make it possible to describe the secondary thermal behaviour in general terms more readily than do the detailed phase diagrams. The figure is the same as Figure 10 except that the binary systems have been omitted.

In Part C, the general solidification behaviour of melts in the right hand half of the ternary system was partially described. For cases where sufficient liquid remained at the start of the secondary solidification processes, it was possible to classify the subsequent behaviour into several catagories.

1. Melts with original compositions within the triangle CDE and above line ML, showed a <u>second</u> inflection at the point corresponding to L. The melts solidified at this point,

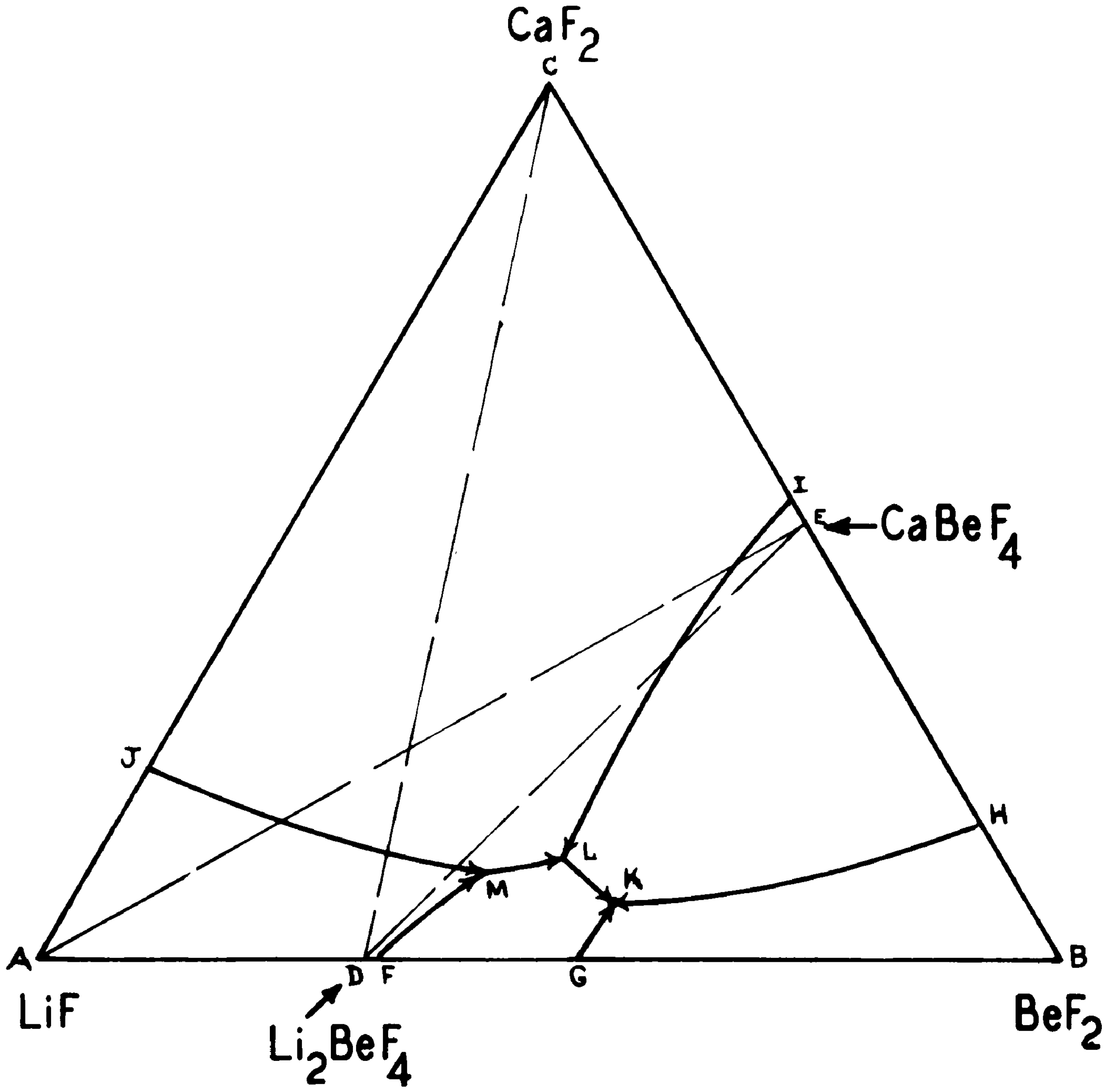


FIGURE 14

<u>DISTORTED VIEW</u>

TERNARY SYSTEM

CaF_2—LiF—BeF_2

except for melts in close proximity to point L, which are discussed later.

2. Melts within the area corresponding to the irregular figure EHKE ultimately solidified at the ternary eutectic point K. These melts did not show the required second inflection point upon reaching the ternary eutectic line HK, but only thickened gradually.

3. Melts lying between the areas of (1) and (2), i.e. in the irregular region EILKE, showed a <u>second</u> inflection upon reaching the ternary eutectic line KL. This line slopes from L, at first very gradually and then more steeply. Consequently the effect nearer L resembled a gradually sloping invariant reaction. For melts reading LK somewhat nearer point K, the second inflection came at a <u>lower</u> temperature and was neither as flat nor as (apparently) prolonged as those striking LK nearer to L. These melts all showed the third inflection corresponding to the ternary eutectic point K. The effect here was quite dependent on the amount of liquid remaining since in some cases apparent "undercooling" of 15° to 20° occurred. Melts containing reasonable amounts of liquid solidified at K at fairly consistent temperatures, which were practically the same as that of the binary eutectic at G.

The melts discussed in Part C show good agreement for their secondary thermal behaviour with that required by the proposed phase diagram. They were, however, too remote in original composition to be of much help in establishing the locations of significant points in the Li_2BeF_4 region.

In Part B, the behaviour of melts in the general region of area AFMJ was discussed. As a rule such melts to the left of 30 mole percent BeF_2 were not cooled to the point at which they might furnish usable information about the behaviour around line FM and point M. These melts showed a moderately good second inflection on reaching line JM if near the J end of the line. If they reached line JM somewhat nearer to M, the secondary inflections became nil. There was a blending together of the primary and secondary thermal effects as the space surfaces and space curve of two-fold saturation have quite similar slopes. Such melts (if allowed to cool sufficiently) solidified at J, but the temperature values were not conclusive as excessive solids were present on reaching the invariant point.

For the secondary thermal behaviour of melts in the general region of 30 to 50 mole percent BeF_2 a large amount of data is available, particularly that furnished by the different "Q" series of melts. Melts in the left hand portion of this region (i.e. slightly to the left of line FM) contained considerable liquid on reaching the ternary peritectic line FM. Melts in this vicinity, which were being shifted in the direction of the $CaBeF_4$ point, such as the series 1Q-, 3Q-, 7Q-, 8Q-, and 10Q- showed the following behaviour with respect to the second inflection temperature. For these melts (close to the LiF-BeF_2 side) the second inflection appeared at about 456° in the form of a nearly flat plateau during which the largest part of the melt solidification occurred. The end of the plateau at about 452° and 448° was accompanied by an abrupt drop in temperature coincident with the disappearance of apparent liquid.

As these same melt series were extended into the ternary system, the secondary inflection temperature gradually dropped to about 449° for melts lying below the line extending from point A to point M of Figure 14. The shape of the plateau at first sloped slightly more than the preceding melts, but as the initial plateau temperature decreased the slope became flatter. For secondary inflection temperatures of 449° the plateau became again very flat, terminating in an abrupt temperature drop-off. The abrupt drop-off was coincident in most cases with the disappearance of apparent liquid, but on subsequent reheating liquid was usually observed in small amounts at temperatures about 10° lower than that corresponding to the disappearance of liquid.

Another significant observation at this point was the behaviour during crystallization on the plateau. Previous melts had shown no tendency to form any crust on the surface when stirred in a normal manner. At this region a change occurred and the melt characteristically formed a crust over the surface and solidified as an adherent mass on the stirring rod. This shift in behaviour coincided quite well with the attainment of melt compositions at or beyond a line from point A to point M, and with the change to a flatter plateau at about 449°. Such a "crusting" phenomenon was unique for this region, and is believed to be due to a particular mode of crystallization of the CaF_2 as it solidifies at the ternary peritectic points near 450°.

Due to the proximity of point M to the line DE there was reason to feel that this different type of crystallization might be the result of a ternary eutectic rather than a peritectic reaction. While a few results seemed confirmatory of this hypothesis, the great majority indicated that the reaction was one in which large crystals were formed, unlike a classical eutectic type of mixture. The incomplete solidification (indicated on reheating) was also indicative of a non-eutectic reaction.

As these same melts of the series 3Q-, 7Q-, 8Q- and 10Q- were extended farther into the system the shift to initial deposition of CaF_2 occurred, and the secondary inflection appeared as a very flat plateau with initial temperatures gradually shifted downward from 449° to 447°. This behaviour is interpreted as the result of initial CaF_2 deposition which caused the melt composition to shift until the two-fold saturation line ML was reached. Here the secondary deposition of Li_2BeF_4 commenced and the melt followed the "eutectic" line ML to point L. The solidification theoretically required at point L (ternary peritectic point) was outwardly satisfied by the disappearance of liquid at 447°, but on reheating liquid was usually detectable in slight amounts as much as 5° to 10° lower than the apparent solidification temperature.

Here, two additional series of melts (12Q- and 13Q-) may be included in the discussion. These melts located just to the right of line FM were also shifted across the ternary system toward the $CaBeF_4$ point. Their behaviour was different from that of the preceding melts since Li_2BeF_4 was initially deposited. Here a very gradually sloping plateau was obtained as a first inflection, the initial deposition temperature gradually shifting downward from about 458° as the melts were shifted inward. At a composition value on the line ML, this value for the 12Q-series had declined to 449° and, for the 13Q series, to 444°. Thereafter these melts showed initial CaF_2 deposition and the reaction along the line ML appeared as a quite flat plateau accompanied by the previously mentioned "crust" formation.

Another set of the melts should be mentioned before leaving this region; that is the 4Q-, 6Q-, 9Q- and 11Q- series, started in the binary system to the right of point F, and shifted in the direction of the CaF_2-LiF binary eutectic (point J). These melts exhibited a transition in behaviour when the line FM was reached and thereafter followed the same general trends shown by other melts in the region to the left of line FM, as previously discussed.

Before these melts (4Q- etc) pass the line FM, and come under the control of the ternary peritectic reaction which takes place along it, they are free to proceed in a variety of directions. Their path during Li_2BeF_4 deposition is governed by the relation of the melt composition to the Li_2BeF_4 composition (point D). The reaction path of the melt may be such as to strike line LK well down toward point K. There will be a gradual upward shift of the secondary inflection point as the melt path intersects LK at points progressively approaching point L. In other cases the intersection of the melt path will be with the line ML, where a secondary inflection should occur if not masked by the very shallow slope of the Li_2BeF_4 primary crystallization surface.

The great variety of results required by these possibilities, may be seen in the tabulations of the data for the series 4Q-, 6Q-, 9Q-, and 11Q-. The initial decline to the ternary eutectic, the gradually rising value for the temperature of apparent sclidification along the line LK, the upper invariant reactions and other required secondary thermal phenomena, are present in substantially good agreement with the proposed phase diagram.

Up to this point the regions near point L (along line LI and just above line LK) have not been considered in detail. The principal sources of information for the former region are the melt series 12Q- and 13Q-. For the latter region, bordered by line LK, information is furnished by the two series LL- and MM-. The two sets of data will be considered jointly as they are mutually dependent.

The character of initial crystallization from the 12Q- and 13Q- series (when extended beyond line ML), the thermal liquidus values (obtained entirely visually), and the contours (above and to the left of point L) all required that there be a fairly definite valley leading up along line LI. The slope of this valley appeared at first to be gradual, then slightly steeper as the climb was made to the sloping plateau extending downward from the $CaBeF_4$ point along the line LI.

The data for the last members of the 13Q- series are not considered as reliable (See discordant results) as the data of the 12Q- series. Likewise, in this region there is the possibility that $CaBeF_4$ may initially deposit in characteristically unobservable fashion, so that the observed surface formation of CaF_2 corresponded to a secondary rather than a primary process.

Below the line LI in the vicinity of point L the situation with respect to reliable liquidus data is even poorer. In this region $CaBeF_4$ apparently initially deposits without detectable thermal effect, the slope of the liquidus surface being estimated to be about 30° per mole percent change in CaF_2 content. Until a temperature level of about 480 to 500° was reached, it was found that even the "quenching" method of dipping to detect $CaBeF_4$ formation was a failure.

On melts LL-11 and LL-12 results were obtained in reasonable agreement with the 12Q- and 13Q series results. For melts up to and including LL-8 it is felt that Li_2BeF_4 was initially deposited. Thereafter it is believed that the ternary eutectic line LK was passed and that subsequent $CaBeF_4$ deposition caused the upward displacement of the temperatures of second (?) inflection values (for LL-9 and LL-10) to slightly higher values representing intersections with LK at points closer to L.

For the adjacent series extending in from melt MM of the binary LiF-BeF_2 series entirely analogous results were obtained, the line LK apparently being passed at melt MM-8 and the first $CaBeF_4$ being detected at 500° to 515° on MM-10. The secondary inflections showed a considerably larger rise (after passing LK) corresponding to the increasing slope of the line LK in this region.

This upward trend in the secondary inflection points for the LL- and MM- series has been indicated in the phase diagram (by a small arrow showing direction of travel and by enclosing secondary inflection temperatures in parentheses) for those cases where primary inflection data are lacking.

Over the balance of the range from about 42 to 52 mole percent BeF_2 (i.e. to the left of, and close to, line GK of Figure 14) very little additional information was obtained as to the exact location of line LK. Here again melts shifted into the ternary system only gave information on the temperature level of Li_2BeF_4 deposition. $CaBeF_4$, however, was not detectable until temperature levels of 500 to 550° were reached. From the other contour information and these points, it is estimated that the slope of the $CaBeF_4$ liquidus surface is approximately 75° per mole percent change in CaF_2 content. The consequent lack of thermal effects is understandable. The line LK, leading down to the ternary eutectic point K, is believed to approach within about 1 mole percent of the LiF-BeF_2 binary side of the diagram by the time point K is reached.

Melts within the above region gave, under favorable circumstances, values of about 350 to 353° degrees <u>on cooling</u> for the temperature of the ternary eutectic point K. Because of the extreme sluggishness of melts at these low temperatures, there was considerable under-cooling of the melt. Consequently a range of 356° to 358° obtained <u>by careful heating</u> is a more reliable ternary eutectic temperature figure and an average value of 357° has been used. This is no more (and probably less) than 1° below the 358° value found for the binary Li_2BeF_4-BeF_2 eutectic point at G.

In all the previous discussions of Parts B, C, and D of this Appendix the values given have been in terms of the results obtained on cooling cycles. In the case of invariant reactions, it is possible (by slow heating and maintenance of temperature equilibrium by agitation) to obtain values usually about 2° higher than are obtained on cooling cycles. Since it was impossible to make very large numbers of check reheats at such points, all the reported values are consistently based on cooling cycles unless the contrary is stated. The values are therefore quite comparable and are so plotted. In reporting the important invariant points of the diagram it is desirable togive corrected values as shown in the summarizing Part E of this section.

In Parts B, C and D an attempt has been made to digest a large amount of data. It was hoped the discussion would be of assistance to any person interested in assessing the constructive evidence for the proposed interpretation of the ternary system phase relations. To have endeavored to have done otherwise would have completely defeated the purpose. Sufficient emphasis has been placed upon the uncertainties and the cause of discordant results so that it should be realized that they are present. It is felt that these factors are insufficiently important to vitiate the conclusions based on a preponderance of the evidence.

Part E -- The System CaF_2-LiF-BeF_2 as a Whole

In Parts B, C and D of this section, the results were discussed in general by reference to the distorted constructions of Figure 10 and 14. This was convenient because of the awkwardly large size of any over-all diagram which might be constructed to show the details on the necessary scale. A more realistic description may now be used.

In the small scale over-all view of the phase diagram of Figure 15, which is shown on the following page, certain values have been given for the invariant points which differ slightly from the results which were generally obtained on cooling cycles. As noted at the close of Part D, values which were approximately 2° higher were obtained on carefully controlled heating cycles. This procedure was only applicable to invariant points and not to the general liquidus surface values. In the complete system, shown in Figure 15, these slightly higher values have been used as they are not subject to the errors caused by undercooling, and because the large scale makes the change negligible. In connection with the contour lines it should be noted that 25° intervals destroy the fine structure, but any change in contour intervals to obtain fine detail would have to be made uniformly throughout the diagram to avoid a deceptive appearance. Reference must therefore be made to Figures 11, 12 and 13 for details.

The three invariant points of the ternary system, corresponding to points M, L and K of Figure 14, are respectively:

1. The ternary peritectic point located at approximately 34.3 mole percent BeF_2 and 2.5 mole percent CaF_2 at a temperature

Larger scale copy of this
figure in rear pocket.

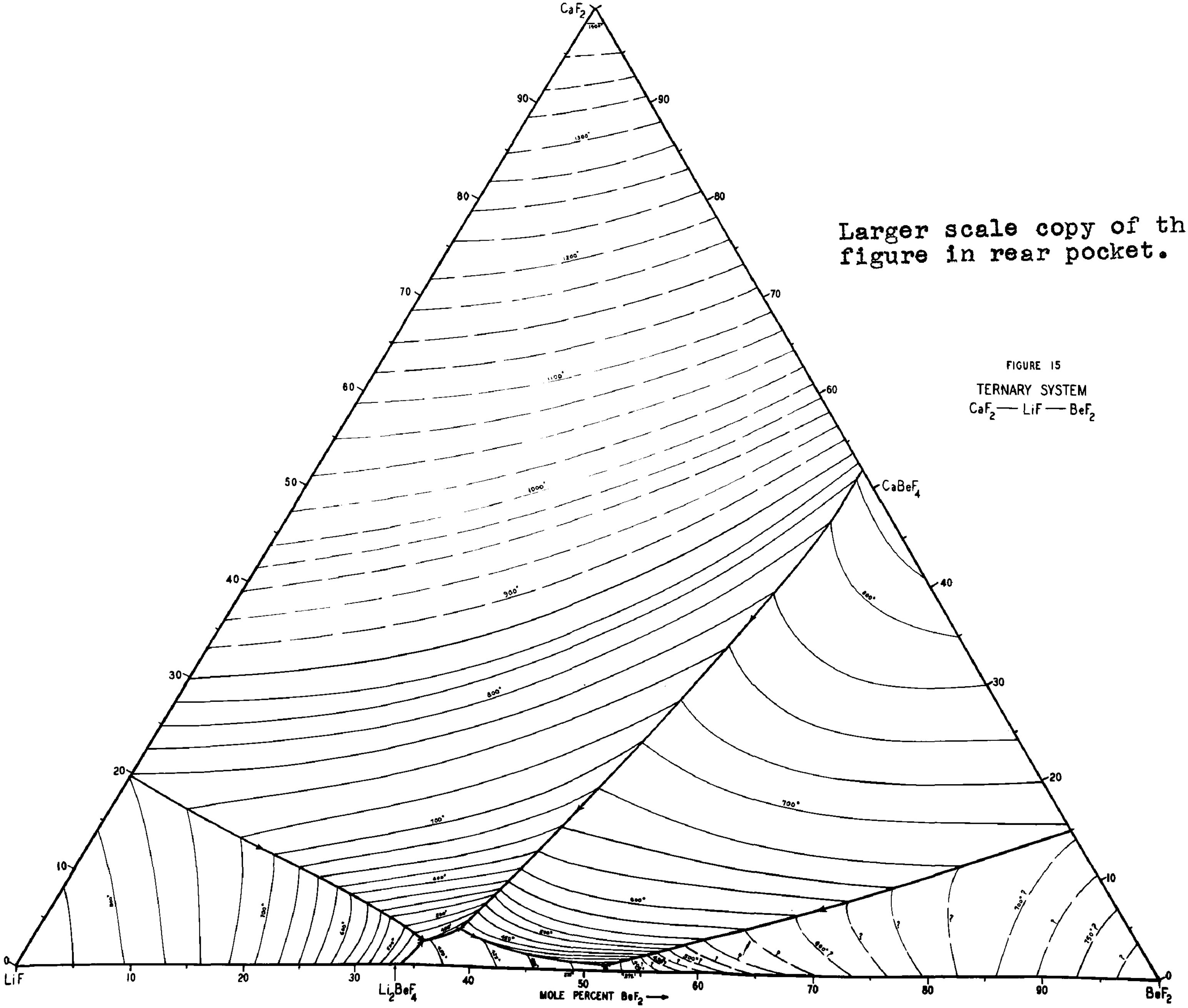


FIGURE 15

TERNARY SYSTEM

CaF$_2$ — LiF — BeF$_2$

of 456°. At this point the following equilibrium process occurs. $CaF_2 + LiF + melt \rightleftarrows Li_2BeF_4 + CaF_2$.

2. The ternary peritectic point located at approximately 36 mole percent BeF_2 and 3 mole percent CaF_2 at about 450°, at which point the following equilibrium process occurs. $CaF_2 + Li_2BeF_4 + melt \rightleftarrows CaBeF_4 + Li_2BeF_4$.

3. The ternary eutectic point at 357°, located with less certainty at approximately 52 mole percent BeF_2 and 1 mole percent CaF_2. The value with respect to CaF_2 composition is the more uncertain, the probable value being less than 2 mole percent and greater than 0.5 mole percent CaF_2. The equilibrium at this point is presumably; $CaBeF_4+Li_2BeF_4+BeF_2+Melt \rightleftarrows CaBeF_4+Li_2BeF_4+BeF_2$

Further summarizing the results, it was found possible to obtain very low melting mixtures of CaF_2 with BeF_2 and LiF, considerably below original expectations. However, the CaF_2 contents of such melts were also low and of the order of 1 to 3 mole percent, at the alternative temperature levels of about 357° and 450°.

Because of the close proximity of the two higher invariant points to the critical line connecting the composition point of Li_2BeF_4 with the $CaBeF_4$ point, there might be some question as to whether these points were ternary peritectic or eutectic. The possible analytical errors do not permit an absolute decision. In one case the invariant point was located almost on the dividing line between the two possible behaviours, the other being a little less than 1 mole percent away from the dividing line. The assignments of locations are dependent on a great many separate melt compositions so that a consistent error, rather than a few chance errors, would be necessary to seriously bias the interpretations.

A confirmatory factor was the solidification behaviour of melts upon reaching the invariant points. Certain melts were observed to pass through these points without solidification, in a manner permitted by the Phase Rule for particular original melt compositions. Others apparently solidified at the invariant points as required by the Phase Rule for those particular circumstances. Intermediate in behaviour were some cases which apparently failed to quite meet the complete solification test demanded by theory. This could arise from a type of behaviour described at the end of Appendix 5 in which it was shown that a process of solidification could depart from a line of ternary peritectic behaviour upon exhaustion of the substance being used up by the peritectic process. In these cases, however, it is believed that the isolation of LiF from equilibrium with the melt caused effective exhaustion to occur. This resulted in "forbidden" behaviour for melts which, in theory, should have followed the peritectic line to a final solidification at the invariant point.

This "forbidden" behaviour is characteristic of poorly behaved peritectic processes. It is, on the contrary, definitely not characteristic of the eutectic type of process in a ternary system where solid solutions are not involved. Here, the process is independent of previously deposited solids. The eutectic process along a two-fold saturation line is then "self regulating" and the path is followed in a completely theoretical manner. To do otherwise, the melt would have to heat itself to a higher temperature while at the same time it was depositing an excess of one solid. Simultaneously the solubility of this solid in the melt would be increasing as required by the higher temperature. Obviously there could be no continuation of such a thermodynamically improbable process, and accordingly eutectic lines of two-fold saturation show good agreement with Phase Rule requirements. The same holds true for a ternary eutectic point reaction.

It is the apparently defective nature of the processes (occurring along the **peritectic** line and at the invariant points in the Li_2BeF_4 region) that constitutes the best indication that they are peritectic processes rather than eutectic. As a consequence of the thermal data, and because of the above considerations, it is believed that the phase diagram interpretation is correct as shown in Figure 15, despite the uncertainties which indicate that other explanations of the behaviour might be possible.

ELECTROLYTIC INVESTIGATIONS IN THE TERNARY SYSTEM

ELECTROLYTIC INVESTIGATIONS IN THE TERNARY SYSTEM

The phase diagram of the ternary system contains one relatively low temperature region lying very close to the binary LiF-BeF_2 side in the range of 34 to 52 mole percent BeF_2, with a corresponding CaF_2 content ranging from 3 to 1 mole percent. Surrounding this region of low temperature (and low CaF_2 content) are steeply ascending slopes. The slope arrangements are such that temperatures of 550° to 600° would be necessary in order to liquify mixtures containing about twice the CaF_2 content of those which exist as liquids in the lower temperature region of about 350° to 450°.

Despite the unfavorably low CaF_2 contents of the lower melting mixtures it was decided to try them for electrolytic purposes. This decision was in part governed by the fact that it is practically necessary to operate at temperatures slightly above the melting points in order to avoid operating difficulties. Operation at temperatures in excess of 550° could only be expected to result in greatly increased reactivity of evolved fluorine, which promised more difficulty than the other alternative of operation using a melt containing very little CaF_2.

The determination of electrode products in such a process presents particular difficulties which were more fully described in the "General and Theoretical" section. The collection and detection of evolved fluorine (if not used up by attack on the electrode) would not be expected to be too difficult in a qualitative way. The deposited metal from the electrolytic process represents a more difficult problem in the case of calcium. The operating temperature in question is far below that required for formation of a coherent metal deposit. As a method of isolation of the cathode product, it was decided to use a molten lead cathode. If successful, this would have the advantage of preventing dissipation of the calcium metal throughout the melt. In addition a favorable effect on the deposition potential of calcium might be obtained as more fully discussed in earlier sections.

While electrolysis of fused salts on a small scale basis is particularly undesirable, practical considerations made it necessary to work with small containers and amounts of melt which could be handled at moderate current levels.

As a source of D.C. power for this work a full-wave, filtered output, rectifier was constructed. The output of a selenium rectifier, arranged for full-wave bridge type rectification, was passed through a filtering network to reduce the ripple voltage. This filter, a double L type, consisted of large electrolytic capacitors and very high inductance choke coils. The latter were specially constructed to have very low resistances. The output ripple from the filter varied from about 2 to 10% depending upon current loading. With this arrangement, supplied by a variable autotransformer, a maximum current of 30 amperes at any voltage from 0 to 100 V was available at the output terminals.

For purposes of making rough comparative conductance measurements and for electrolyses a small cell was constructed. A schematic drawing showing the construction is given in Figure 16. The nickel crucible

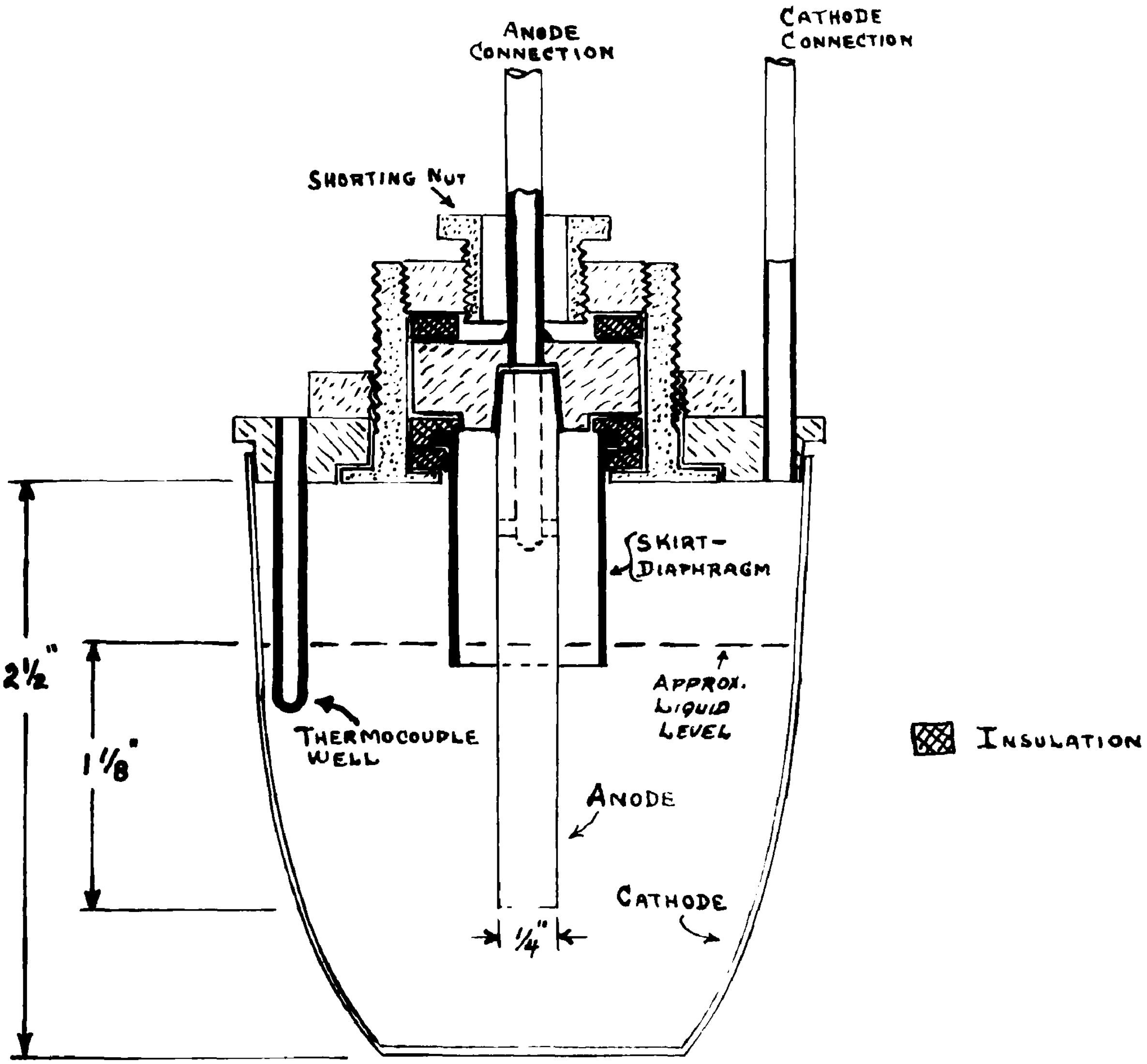


FIGURE 16
CELL
CONSTRUCTION

constituting the cell pot was interchangeable with carbon crucibles of slightly larger size which were used in some of the later work. The cell pot served as the cathode of the cell. Diaphragms of different lengths were prepared to permit isolation of the anode products in melts having different surface levels, the diaphragm being chosen so as to project only slightly below the melt surface. A central anode arrangement was used, carbon, nickel and copper rods being the alternative forms available. Anode gas take-off was by way of a hollow passage at the top of the anode, leading to a copper tube manifold.

The anode and diaphragm were insulated from each other and from the cover of the cell. The anode electrical connection was made through the copper exhaust manifold. The cathode electrical connection was made either through another copper line connected to the cover of the cell, or in other cases by means of a copper band attached to the carbon crucible walls.

For conductance measurements it was possible to determine the lead resistances by shorting the circuit (at a point just above the anode) with the aid of a movable shorting nut. These lead resistances were deducted to determine the cell resistance.

For resistance measurements, at the very low values which were found to exist, no very satisfactory equipment was available. A General Radio Impedance Bridge, Type 650-A, was used. The source of the A.C. measuring voltage was the self-contained 1000 cycle microphone hummer of the bridge. A 5" DuMont Cathode Ray Oscilloscope was used for detecting the null at the balanced position of the bridge. The measuring error for the higher resistance values was about 1%, but for those of most interest, at about 1 ohm, the error was probably at least 10%. The possible effect of insulating films on the electrode surfaces is not known.

For conductance measurements three melts located in the binary LiF-BeF_2 system were prepared. Thereafter, these melts (called 1EL, 2EL and 3EL) were shifted into the ternary system (to form melts 1EL-1, 2EL-1 and 3EL-1) to determine whether addition of CaF_2 caused much change in the conductance. Since BeF_2 is itself non-conductive as a liquid it was felt that such rough measurements of conductance were desirable. These would be of some help in deciding whether any peculiarly high resistance phenomena which might be encountered could properly be assigned to the melt or to a polarization effect.

As the results obtained on these conductance measurements were neither very significant nor conclusive, the data has been relegated to Appendix 16. The observations are briefly summarized by the following statements.

1. The two melts prepared with compositions (in the LiF-BeF_2 binary system) near 33 mole percent BeF_2 were approximately three to four times as conductive as the single melt with a composition of approximately 54 mole percent BeF_2.

2. The addition of CaF_2 caused a fairly large increase in the conductance of the latter melt when shifted to a composition of about 1 mole percent CaF_2 and 54 mole percent BeF_2.

3. The addition of CaF_2 to the other two melts (by which they were shifted to about 0.9 mole percent CaF_2 and 32.1 and 33.6 mole percent BeF_2) gave discordant results, one increasing and the other decreasing in conductance, neither effect being large.

4. It was concluded that a resistance of 0.5 to 1.0 ohm might be expected from either the high or the low BeF_2 content melts for the cell used, over the range of about 550 to 450°. The negative temperature coefficient of resistance was large, possibly about 1% per degree.

5. Very appreciable conductance in the solid state was noted.

The conductance value noted was somewhat lower than that of most fused salt melts. The usual range of values from excellent to average conductors is about 20 to 2 $ohms^{-1}$ $cm.^{-1}$ for the specific conductance. The irregular shape of the cell prevents more than a rough estimate that in this case the specific conductance could hardly have been higher than 0.1 to 0.2 $ohm^{-1}cm.^{-1}$. (See Drossbach (27) for a listing of specific conductivity for various fused salts.)

For the initial electrolytic work the cell described in Figure 16 was used, trying different electrodes, diaphragms, nickel and carbon crucibles, and molten lead cathodes as variations in attempts to overcome operating difficulties. Since this cell was closed at the top it was not possible to observe the causes of the trouble. The initial melts that were used were those mentioned above. Subsequently two other melts were prepared. The compositions were as follows:

Melt	Mole Percent CaF_2	 BeF_2	 LiF	Wt. of Melt, g.
1 EL-1	0.85	32.1	66.1	100.9
2 EL-1	0.88	33.6	65.5	97.9
3 EL-1	1.04	54.0	45.0	89.7
4 EL-1	0.84	33.3	65.9	101.6
5 EL-1	0.89	29.6	69.5	94.0

The attempts at electrolysis of these melts are described below.

On melt 3EL-1, a nickel crucible and carbon anode were tested using the diaphragm shown in Figure 16. There was only a momentary current flow when 5V was applied. Upon raising the applied voltage to 30V current again flowed, but in an irregular manner. No apparent anode gas product could be detected although the electrolysis was continued for about 20 minutes. During this time the cell temperature rose from about 390 to 480°. Upon shutdown and removal from the furnace it was found that a hole had been burnt in the crucible wall. This apparently was the result of an arcing short passing through a considerable amount of black frothy crust on the surface of the melt. The carbon anode had been considerably attacked and the nickel crucible had also lost some weight.

Melt 1EL-1 was next tried using a nickel anode and a molten lead cathode at a temperature of 500°. Although the current flow could be maintained at lower voltage, symptoms of erratic behaviour caused the test to be halted after only a few minutes. Upon inspection the same apparent shorting effect through the black frothy material was suspected. The nickel anode was found to have been slightly attacked. No gaseous product was observed. The lead cathode was reserved for analysis (marked "After 1 EL-1").

Melt 2 EL-1 was then used with a carbon crucible, molten lead cathode and carbon anode. The temperature rose from 510° to 580° as it was attempted to force a current to flow by the use of 50-75 volts. The current flow was very erratic and nearly negligible part of the time. Inspection indicated about the same conditions as were observed for the preceding trials.

Another trial was briefly made on the same melt using a carbon crucible, molten lead cathode and a nickel anode. The temperature rose from 470° to 520° and the behaviour observed on melt 1 EL-1 was repeated.

The diaphragm was then discarded for all subsequent work and the trial on melt 2 EL-1 was repeated using a carbon crucible, molten lead cathode and nickel anode. Operation was much more stable and a run of approximately 30 minutes was made at about 7V and 15A and 525° to 550°. On shutdown the lead cathode (weight 150 g.) was reserved for analysis (marked "After 2 EL-1"). The nickel anode was found to have been heavily attacked, but at no time was there any evidence of the evolution of fluorine by way of the anode gas manifold.

At this stage it was decided to transfer operations to an open carbon crucible (heated by gas) so that the behaviour could be observed directly. Only the central anode-holding portion of the cell top was used, minus the diaphragm. A carbon crucible, with molten lead cathode (100 g.) was used, first in conjunction with a nickel anode. Immediately upon the application of power a red-orange solid spread across the surface from the anode rod. This changed color and a black froth commenced to form as a result of rising bubbles. The latter did not, however, escape as the froth remained unbroken. The experiment was continued with the following schedule.

About 5 minutes at 10V, 1/2A.
About 6 minutes at 15V, 1A.
About 3 minutes at 17V, 4A.
About 13 minutes at 12V, 10A.

As noted the resistance dropped somewhat, the temperature rising from 460° to 540° largely as a result of internal heating. During the test there was no evidence of the escape of any fluorine. Upon removal of the anode it was found to have been very strongly attacked.

A carbon anode was substituted and it was found that the melt did not wet the electrode. When voltage exceeding about 1V was applied, sparks were observed over the surface of the anode. Upon removal of the anode it was found to be eroded, possibly because of the sparking action. Substitution of the nickel anode again permitted current flow at normal voltage. When a copper anode was tried, it likewise was considerably attacked in a brief period. The test was discontinued and the lead cathode weighing 150 g. was reserved for analysis (marked "After 3 EL-1").

To determine that the non-wetting phenomena for the carbon anode was not a property of the contaminated melt, a fresh melt 5 EL-1 was tried. An open carbon crucible was used with a carbon anode, the molten lead cathode being omitted at this stage. A very short trial was made with the same results, that is sparking from the anode to the melt with very erratic current flow, the temperature of the melt being 550°.

A nickel anode was then substituted to check on whether the red-orange anode product observed for a very short interval might not be due to lead contamination. This was shown to be incorrect as the phenomenon was immediately observed in the absence of the lead cathode. The colored product had only a transient existence and immediately disappeared in black froth which was next produced.

The molten lead cathode was then added and a 15 minute run at 550° was made at a current of 5A, the voltage being regulated between 5 and 10V in order to keep the current steady. The lead cathode removed on shutdown (weight 150 g.) was marked "After 5 EL-1" and reserved for analysis. The nickel anode had suffered a loss of about 15% by weight during this run, based on the immersed portion of the rod

During all these trials the only evidence of anode gas evolution was that a few bubbles could be observed rising to form a froth with the black material originating at the anode. The other indication of the anode process was the initial colored product and the black product which followed it. From these observations it might reasonably be concluded that evolved fluorine attacked the anode.

For a determination of the type and amount of metal deposited by the cathode process, an analysis of these heavily contaminated melts promised to be very unsatisfactory, when considered in conjunction with the analytical errors found in the earlier work. It was therefore decided to analyze the lead cathodes on a "before and after" basis to determine the change in composition. In order to do so, it was necessary to scrape the surface of the lead free of traces of the fused salt mixture. This may have had some bearing on the results obtained.

The analytical results have been tabulated in Appendix 15, part K. The results were quite anomalous in that they indicated no change in the analysis of the lead. The latter was originally chemically pure grade and the samples of the molten cathodes were only negligibly different with respect to Ca, Li and Be contents than the blank determinations shown by the starting material. Over-all recovery was checked at the same time by a lead determination and the analytical losses were found to be small.

The analysis is fairly difficult because it involves the separation of a small amount of "impurity" from the lead which interferes with the determination of the other metals of interest. The method used was a special one, but it is believed that it was adequate for the purpose. The only explanation then remaining is that the foreign metal content of the lead samples, <u>as analyzed</u>, must have been negligibly small.

While this conclusion appears improbable it might arise from one of two possible behaviours. Possibly any cathode product was never deposited on the lead cathode, but instead deposited on the wall of the crucible electrically connected to the lead. Alternatively, any material deposited on the lead was not present at the time of analysis. No indication of the former possibility was observed, but such an observation would be unlikely. With regard to the second possibility it is conceivable, for example, that $CaPb_3$ formed on the lead surface might not have been retained in the analytical sample.

Referring to the phase diagram for the Ca-Pb system and the discussion of the behaviour of molten lead cathodes given at the end of the section on the "Effect of Liquid Cathodes, etc.," it appears that such a possibility is conceivable. Either in the handling and separation of the melt from the lead cathode, or in cleaning the cathode metal to obtain analytical samples, any surface layer of $CaPb_3$ might have been removed. As these experiments were necessarily performed below the melting temperature of that compound, the alloying action with the liquid lead depends on absorption and such reactions have been observed to be very slow (114).

The electrolytic trials were therefore failures from two standpoints. The recovery of fluorine was not obtained, and its probable evolution could only be inferred from the formation of a reaction product accompanied by a strenuous attack on the anodes used. As no more suitable materials than nickel, copper or carbon were known, there did not appear to be any way of overcoming the anode construction problem except by reducing the temperature. On the other hand it was not found possible to recover the metal deposited in order to determine whether CaF_2 was decomposed. The solution to this difficulty apparently does not lie in the same direction, but rather in the direction of raising the temperature level.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The problems of developing a direct electrolytic method for the production of elemental fluorine from calcium fluoride have been discussed and a possible method proposed which involved the electrolysis of fused metal fluoride mixtures.

The use of the method required a knowledge of the solubility relations of the molten fluorides of calcium, lithium and beryllium. The binary and ternary systems formed by this combination of fluorides have been investigated and their phase diagrams described.

Comparison has been made of the results obtained for the lithium fluoride-beryllium fluoride system with those reported by two previous groups of investigators. It was concluded that neither of these reports was completely accurate.

The syntheses and X-ray examinations of compounds existing in the ternary system have been described.

The most favorable region of the ternary system of calcium, lithium and beryllium fluorides was used to test the proposed method for the decomposition of calcium fluoride. The results of electrolytic investigations have been described in which it could not be demonstrated that the original purpose was achieved.

Inability to recover fluorine as a product of the electrolysis has been attributed to chemical reaction with the anode material. The possible reasons for failure to recover and identify the cathodically deposited metal have been considered.

APPENDIX I

APPENDIX 1

SUMMARIZED REFERENCES ON PHASE RELATIONS OF CALCIUM FLUORIDE--LITHIUM FLUORIDE--BERYLLIUM FLUORIDE AND ANALOGOUS COMPOUNDS

A) Calcium Fluoride Systems and Analogs.

CaF_2-LiF-MgF_2, report of lowest melting ternary mixture as 665°, no phase diagram studies, used for magnesium production. (135)

Ternary reciprocal system of F^- and Cl^- of lithium and calcium, contains no report of LiF-CaF_2 system. (13)

Quaternary CaF_2-LiF-BaF_2-MgF_2 system. -- lowest melting mixture 603°. (83)

CaF_2-NaF-KF, phase diagrams of binaries and ternary.

The CaF_2-NaF system, simple eutectic melting at 810°.

The CaF_2-KF system, two eutectics at 782° and 1060° with congruently melting compound KF:CaF_2 at 1068°.

Ternary system shows peritectic point at 772° and ternary eutectic at 682°. Recent report (1951) by Silber et al. (149)

CaF_2-NaF-BaF_2, partial data given, lowest point approximately 750°, used for magnesium production. (56)

CaF_2-NaF-MgF_2, phase diagrams of binaries and ternary.

CaF_2-NaF system, simple eutectic, 810°, at about 50 mole percent.

CaF_2-MgF_2 system, simple eutectic, 945°, at about 50 mole percent.

MgF_2-NaF system, two eutectics at 815° and 985° with congruently melting compound $NaMgF_3$ at 1030°. (55)

CaF_2-ThF_4 (177)

CaF_2-YF_3 (177)

CaF_2-SnF_2, study of solid solutions formed. (138)

CaF_2-MgF_2, eutectic at 970° and 52 mole percent MgF_2. (160)

CaF_2-BaF_2, eutectic at 1277° and 50 mole percent BaF_2. (160)

CaF_2-MgF_2-BaF_2, lowest point of system, 817°. Used for magnesium production. (50)

MgF_2-KF and MgF_2-RbF, phase diagrams.

Two systems similar in that compounds M^IMgF_3 and $M^I_2MgF_4$ are formed with congruent melting points; two eutectics are present. (36)

MgF_2-KF-RbF, ternary system described. (36)

MgF_2-NaF-BaF_2, binary and ternary systems given.

MgF_2-NaF, two eutectics and intermediate compound.

BaF_2-MgF_2, two eutectics and intermediate compound (uncertain).

BaF_2-NaF, simple eutectic. (81) (57)

$MgCl_2$-NaCl, $MgCl_2$-KCl, $MgCl_2$-RbCl. These systems all show formation of M^IMgCl_3 and $M^I_2MgCl_4$ with congruent melting points for potassium and rubidium, but incongruent for sodium. (82)

BaF_2-SrF_2, minimum in system at 1270°. (7)

BaF_2-NaF-MgF_2, binary and ternary systems.

BaF_2-NaF system has simple eutectic at 825°. (57)

B) Lithium Fluoride Systems and Analogs.

See above under item A). Also the following

LiF-MgF_2, several conflicting reports. Probably simple eutectic (74) (164) (67)

LiF-MgF_2, NaF-MgF_2, KF-MgF_2, RbF-MgF_2

Systems become increasingly complex. For LiF probably simple eutectic; for NaF, two eutectics and compound $NaMgF_3$; for KF and RbF, two compounds M^IMgF_3 and $M^I_2MgF_4$. (81)

LiF-BeF_2, phase diagram. Two reports that were somewhat discordant. Described in connection with discussion of results on this system. Reported in 1949 and 1950. (166) (134)

NaF-BeF_2, phase diagram, substantially same as the LiF-BeF_2 system above. Three reports (1944, 1950, and 1951). Compounds $NaBeF_3$ and Na_2BeF_4 and others claimed. (120) (166) (134)

BeF_2

NaF-RbF, partial study. (134)

LiF-BaF_2-MgF_2, report of lowest point as 645°. (83)

$LiCl$-$CaCl_2$, simple eutectic reported at 496°. (58)

C) Beryllium Fluoride Systems and Analogs.

BeF_2-LiF, BeF_2-NaF, BeF_2-RbF. See under item B).

BeF_2-Mixtures with alkali and alkaline earth fluorides.

Refers to BeF_2-rich portion of systems where glasses formed which were the object of the study. (68)

BeF_2-MgF_2, describes patented process for Mg metal reduction of this melt to form Be metal. (80)

BeF_2-MgF_2, phase diagram study, uncertain results. (172)

$BeCl_2$ - Various metallic chlorides (Na, Li, Ag, Cd, Ba, Ca, Mg, Pb, Tl)

For NaCl -- shows eutectic and incongruently melting compound Na_2BeCl_4.

For $LiCl_2$ -- shows eutectic and compound Li_2BeCl_4. Uncertain whether congruent or incongruent.

For $CaCl_2$ -- eutectic only.

For $BaCl_2$ -- shows eutectic and congruently melting compound $BaBeCl_4$.

For $MgCl_2$ -- uncertain results, probably solid solutions. Very extensive article. (142)

NOTE: Russian investigators have been particularly active in the study of fused salt systems. Their accumulated data have permitted certain generalizations on the behaviour particularly with reference to the possible types of compound formation and their relative stabilities. Reference may be made to the work of Dergunov and Bergmann (13) (37) in which further references may be found to an extensive series of papers. Other pertinent references are to Gromakov (54) and Kryagova (87).

APPENDIX 2

APPENDIX 2

PHYSICAL AND THERMAL PROPERTIES OF CALCIUM FLUORIDE, LITHIUM FLUORIDE AND BERYLLIUM FLUORIDE

Calcium Fluoride.

Melting point -- While given as approximately 1325-1375° by most handbooks, more recent values would indicate that the older values were obtained using impure materials. Probably the best value is 1418° obtained by Naylor (116) using a drop-calorimetric method.

Modifications -- A transition from α to β form occurs at 1151° accompanied by absorption of energy. (116)

Specific Heat --Kelley (79) gives slightly different values than those given by Naylor (116) which are shown below.

CaF_2 (α) $Cp = 14.30 + .00728T + \frac{46,900}{T^2}$; Range 298-1424°K.

CaF_2 (β) $Cp = 25.81 + .00250T$; Range 1424-1691° K.

CaF_2 (liq.) $Cp = 23.88$; Range 1691-1800° K.

Heat contents and Entropy Values - Given by Naylor (116), for the above ranges, and by Todd (169) for lower range 52-298°K.

Heats of Transition and Fusion - As given by Kelley (79)

$\Delta H_{1424^\circ K} = 1,140$ cal./mole (transition).

$\Delta H_{1691^\circ K} = 7,100$ cal./mole (fusion).

Crystal System -- Cubic (fluorite structure), a = 5.451 A°.

Refractive Index -- $1.4339 = n_D$

Vapor Pressure and Volatility (137) (97) (4)

Hydrolysis Data (26)

Density of Liquid Calcium Fluoride. In unavailable reference (108).

Approximate value 3.0.

X-ray Data -- The lattice spacings given by Hanawalt (63) for powder diffraction patterns are as follows:

3.16 A° *
1.93 *
1.65 *
1.370
1.256
1.117
1.050
0.968
0.925
0.866
0.835
0.789
0.767
0.731
0.713
0.644

* Signifies strongest lines.

Preparation of Pure Calcium Fluoride. Stockbarger has described purification methods necessary for the preparation of optical quality material (155) (156).

Lithium Fluoride.

Melting Point -- Handbook values are approximately 840 to 845°, but more recent determinations with probably more carefully purified material give 845° (143) (166).

Thermodynamic properties -- Kelley (79) gives no data for lithium fluoride.

Crystal System -- Cubic (NaCl structure), a = 4.0173 A°.

Refractive Index -- 1.3915 = n_D

Boiling Point -- Approximately 1675°. (78)

Density of Liquid Lithium Fluoride, approximately 1.8 (78)

Structural Studies -- Numerous structural studies have been made. See collected references under (159).

X-Ray Data -- Powder diffraction lattice spacings given by Hanawalt (64) are as follows:

2.32 A° *
2.00 *
1.419 *
1.211
1.160

* Signifies stronger lines

Values obtained in this work for LiF are given in Appendix 11.

Preparation of Pure Lithium Fluoride -- The preparation of pure lithium fluoride by treatment of a saturated solution of lithium carbonate with carbon dioxide to yield the more soluble bicarbonate has been described. (157) The bicarbonate solution on treatment with hydrofluoric acid precipitates the less soluble lithium fluoride, thus affording a good separation from the more soluble alkali metal fluorides. An analogous procedure depending on formation of the bicarbonate was described by Schmitz-Dumont (143).

Beryllium Fluoride

Melting Point -- Since this substance is undoubtedly polymeric it has no true melting point. The customary handbook value is approximately 800°, but softening actually begins by about 750°, at 800° the mass is very viscous, and considerable fluidity is not obtained until about 900° according to the experience on this work. Polymorphic changes are reported at temperatures below 800°, such as 425° and 528° (120).

Modifications -- A report of a "crystalline" modification resembling α quartz has been given (120). Various other studies claim general resemblances to different quartz modifications.

Thermodynamic data -- No values are given by Kelley (79) for beryllium fluoride.

Crystal Structure -- Hexagonal α quartz structure with $a = 4.72$ Å, $c = 5.18$ Å has been reported (120).

Refractive Index -- Less than that of water = 1.333

X-ray and Structural Information -- Structural studies have been made by Warren and Hill (173); Novoselova, Zhasmin, et al. (120). Summarized information on older work is given in Strukturbericht references (158).

The powder diffraction pattern given by Novoselova, Zhasmin, et al. for their "crystalline" modification is given below. The data lacks confirmation and there may be interference from NaF or Na_2BeF_4 also present. Relative intensities are indicated on a scale of 10.

d,A°	Intensity	d,A°	Intensity	d,A°	Intensity
3.84	10	1.778	7	1.330	2
2.97	4	1.655	1	1.317	2
2.685	6	1.623	6	1.293	3
2.365	5	1.539	7	1.257	3
2.225	8	1.521	1	1.237	4
2.12	7	1.483	1	1.220	2
1.98	5	1.463	2		
1.92	5	1.423	3		
1.83	6	1.373	1		

Preparation of Pure Beryllium Fluoride -- Discussed in Experimental section on the preparation of materials.

APPENDIX 3

APPENDIX 3

SUMMARIZED INFORMATION ON FLUOBERYLLATES AND ANALOGOUS COMPOUNDS

With respect to the system formed by calcium fluoride and lithium fluoride, no compound formation was anticipated.

In the calcium fluoride-beryllium fluoride system, several references indicated that compound formation would probably occur. The compound calcium fluoberyllate, $CaBeF_4$, had been mentioned in several foreign patents (17), but the physical properties were not described and the methods of preparation indicated that the compound was not isolated in pure condition. Several methods have been given by Ray (129) for the preparation of the anhydrous compound, one of which was claimed to yield a pure product, despite several good reasons why an impure product might be expected.

The preparations of the compounds $BaBeF_4$ and Ba_2BeF_6 have been described in an unavailable publication (75). Sarker and Ray claimed the preparation of $BaBeF_4$ in an article (140) which was the first of a very extensive series of reports made by Ray in the German literature on the subject of the general isomorphic relation between the $BeF_4^=$ ion and the $SO_4^=$ ion. In summary, the compound $CaBeF_4$ was definitely expected to occur in the calcium fluoride-beryllium fluoride melts in view of the thermal stability indicated by Ray (129). A compound of the type Ca_2BeF_6 was not expected to occur.

Prior to the appearance of recent reports on the lithium fluoride-beryllium fluoride system, one or two compounds were expected to occur based on the reported existence of compounds of the types M^IBeX_3 and $M^I_2BeX_4$.

Numerous chloroberyllates of both types have been reported as solids and still others claimed in ionic form (36). Of the fluoberyllates, the compound Li_2BeF_4 had been prepared by Ray (128) and two patent references (38) (76) indicated the preparation of $NaBeF_3$ and K_2BeF_4 in somewhat adulterated forms. No thermal data was available from these sources, but the general character of the lithium fluoride-beryllium fluoride system could be predicted from the available phase diagram due to Novoselova, Zhasmin et al. (120) on the sodium fluoride-beryllium fluoride system. The later conflicting reports (166) (134) which were made shortly before the start of actual work on the system LiF-BeF_2 confirmed the generally anticipated behaviour, except that the extent of the temperature lowering was greater than expected.

APPENDIX 4

APPENDIX 4

INFORMATION ON ALLOY SYSTEMS

The following references cover the available information on alloy systems pertinent to the choice of a metallic cathode for this work. The content of the reference is indicated by a brief description.

Calcium Alloy Systems

Ca-Pb, phase diagram, heats of formation (88) (46).
Theoretical (141). Preparation and behaviour (154) (143) (112) (139)

Ca-Bi, phase diagram, heats of formation (90) (88).

Ca-Zn, phase diagram (161).

Ca-Na, phase diagram (162).

Ca-Mg, phase diagram (163).

Ca-Li-Pb, descriptive (65).

Ca Alloy Survey (72).

Lithium Alloy Systems

Li-Ca-Pb, descriptive (65).

Li-Pb (148).

Li-Pb-Na (148).

Li-Pb, phase diagram, also numerous Li-metal systems (123).

Li-Zn-Mg, phase diagrams (15).

Potassium Alloy Systems

K-Pb, K-Bi, K-Zn, K-Cd, K-Sn, partial study (153).

K-Pb, K-Sn, phase diagrams (84).

K-Bi, phase diagram (85).

K-Cd, K-Zn, phase diagrams (86) (176).

Barium Alloy Systems

Ba-Pb, Ba-Bi, Ba-Sn, heats of formation (89).

General Survey (16).

APPENDIX 5

APPENDIX 5

GENERAL PHASE RELATIONS IN TERNARY SYSTEMS

Several generalizations used in the discussion and interpretation of experimental results will be described. The ternary system is represented using the conventional Roozeboom method which employs an equilateral triangular right prism to express the relationship of temperature and the three composition parameters. For convenience the lines of two-fold saturation (at the intersection of two space-surfaces of single-fold saturation) are shown by projection onto the base of the prism. When required, the binary systems (i.e. the side walls of the prism) are shown in "folded down" projections along the edges of the triangular base of the prism.

From the manner of use and the properties of an equilateral triangle it follows that the ratio of the components B and C is a constant along any line connecting component A with the opposite side (BC) of the triangle, as shown in Figure 17.

As a consequence of this it is also true that if but one solid component B is separating in a pure form from a melt with the composition M_1, the composition of the melt will follow the straight line m_1 m_2, etc. until a different solid phase appears, as at point p in Figure 18. Here the occurrence of a new solid phase C causes the system to become univariant and the composition of the melt follows the line of two-fold saturation et with simultaneous deposition of B and C until the ternary eutectic point t is reached. Here solid A commences to form and the

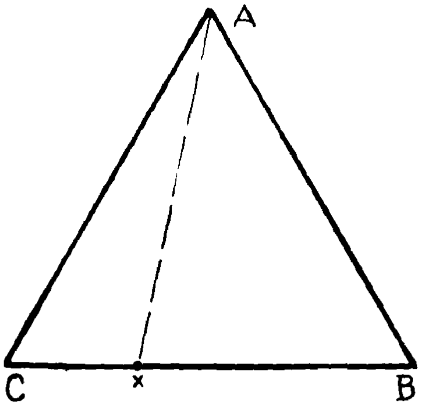


FIGURE 17

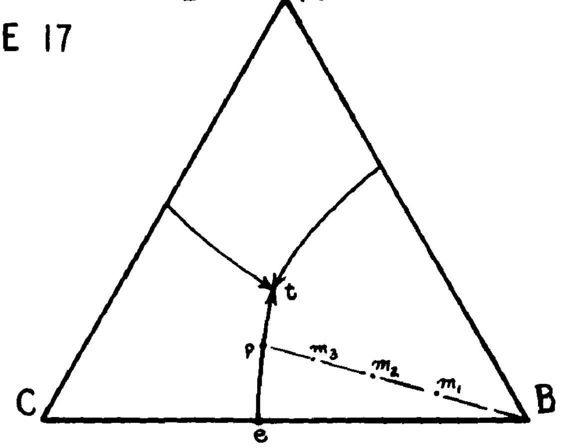


FIGURE 18

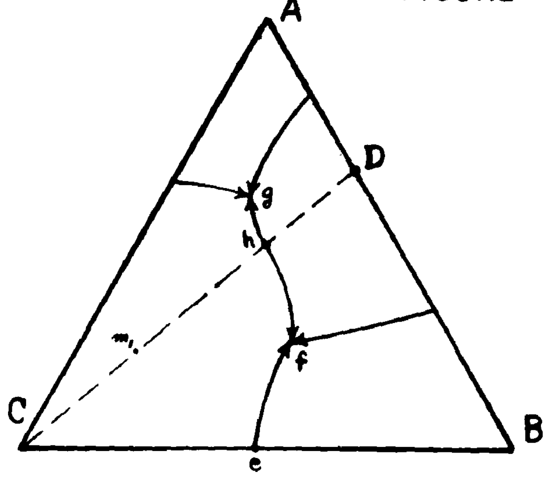


FIGURE 19

system is invariant until the liquid phase vanishes. The arrow heads denote the direction of lower temperatures, and the three binary systems are in this case assumed to be simple eutectic ones.

Any system consisting of two phases has a total composition represented by a point on the straight line connecting the compositions of the two phases (either solid or liquid).

In the event of the occurrence of a binary congruently melting compound D in the binary system AB of Figure 19, several cases are possible. The other two binary systems are considered to be simple eutectic ones.

1.) Section CD is quasi-binary. If a vertical section CD through the ternary system exhibits all the characteristics of a binary system of C and D the section is called quasi-binary and the entire system may be treated as two independent ternary systems ADC and BDC. It can be shown that the ternary eutectic points f and g must lie on opposite sides of the line CD and that point h, representing the lowest point on line CD (eutectic of the binary system of C and D), is a point from which the temperature decreases in passing from h to either g or f. Also any melt with an original composition lying on line CD, such as m_1, will solidify to form C and D only, in a normal binary system operation, without departure of the melt composition from the line CD.

2.) Section CD is not quasi-binary. (See Figure 20.)

If the section CD does not have the normal characteristics

Note: Pages 183 and 184 are non-existent due to numbering error.

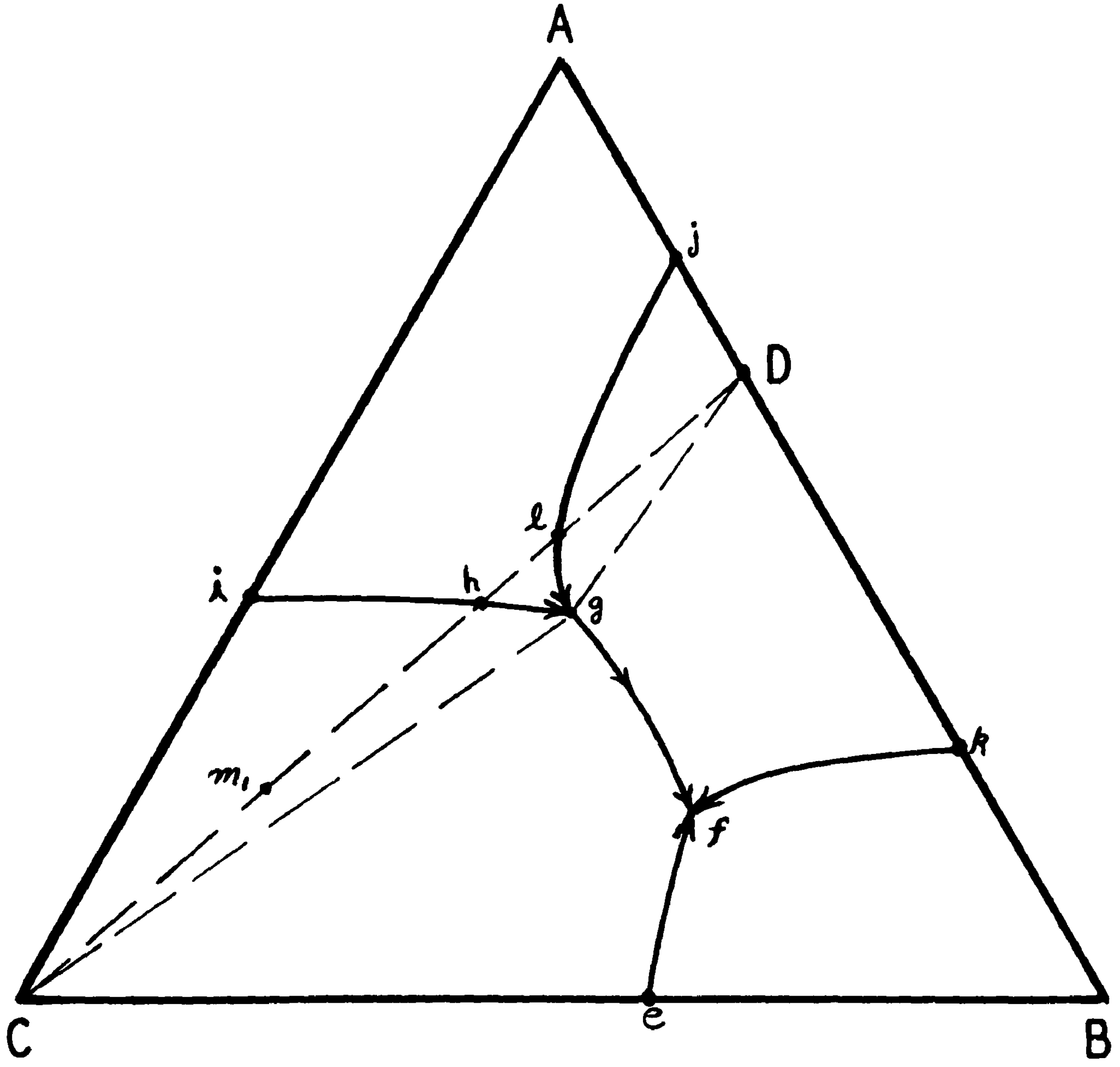


FIGURE 20

of a binary system, then it may be shown that the points g and f lie on the same side of line CD and that one of them is a peritectic and the other a ternary eutectic point. Again the systems A and C, and B and C, are considered as simple eutectic ones.

In this case the two parts of the system are not independent and the behaviour of different melt compositions may be described as follows.

A melt of composition m_1 will follow along line CD with deposition of solid C until point h is reached. Solid A will then also start to deposit and the melt composition will follow hg with the last of the melt solidifying just as point g is reached.

A melt within the area CihC will first deposit C, then follow along ihg depositing solids C and A, and will solidify before reaching point g, somewhere between h and g.

A melt within the area AjlhiA will follow a similar process, first with deposition of A, and then with deposition of A and, C (or A and D) along line ihg (or jlg) depending upon the exact relation of the eutectic lines. Again solidification will occur between h and g (or l and g), prior to reaching point g.

A melt within area DljD behaves analogously to one in the area CihC.

A melt within the area hlgh will first deposit solid A, and subsequently will follow along hg (or lg) depositing C and A (or D and A) until point g is reached. Then new solid phase D (or A) appears and the melt "reacts" to use up A at constant temperature with deposition of D until A vanishes. The melt then deposits C and D along line gf until the melt composition reaches f, the ternary eutectic point. There, complete isothermal solidification occurs with deposition of C and D and the new solid phase B. The amount of B formed is a function of the location of the original melt within the area hlgh, melts near the line hl forming almost no B at point f.

Melts within other areas require no detailed explanation except to say that melts in the area ChgC (or DlgD) will undergo a peritectic reaction at g subsequent to the primary deposition of C (or D) and secondary deposition of C and A (or D and A), with isothermal disappearance of A at point g. Thereafter the melt proceeds to point f where B, C and D phases deposit isothermally with complete solidification.

Two generalizations are illustrated by the above behaviour. (Figure 20).

1.) A melt having an original composition located within the triangular area ACDA solidifies with formation of A, C and D only, there being no possibility of deposition of B, since then the composition of the solid residue would be expressible only by a location within the triangle BCDB. This, however, is impossible since the original melt and final solid residue must have the same composition location.

Similarly melts of original composition within the triangle BCDB show finally only solids B, C and D in the final solid residue.

2.) From the relative behaviours of Figures 19 and 20 the generalization may be drawn that no line of two fold saturation may pass across a quasi-binary section. Thus in Figure 19, the lines gh and fh are two different space curves with a common terminus at h, but in Figure 20, lines ihg and jlg are continuous space curves which do cross the quasi-binary section CD.

It may be asked whether it would not be possible for the binary eutectics on either side of compound D to join at a peritectic point or eutectic point before intersecting the lines of two-fold saturation from the other two binary systems AC and BC, as shown in Figures 21 and 22. Such a construction is impossible in cases where no solid solutions are formed for the following reasons.

It will be observed for both figures that melts having the original composition m_1 will in general first deposit solid D, then will reach line kg and pass down along that line with deposition of solids D and B until point g is reached at which the new solid phase A appears. In the case of Figure 22 where a ternary eutectic is indicated at g, the remaining melt of composition g would solidify to form solids A, D and B having a final composition equal to the original composition of the melt m_1. It will be noted that the solid mass of composition m_1 does not lie within a triangle whose vertices are the solid phases making up the solidified

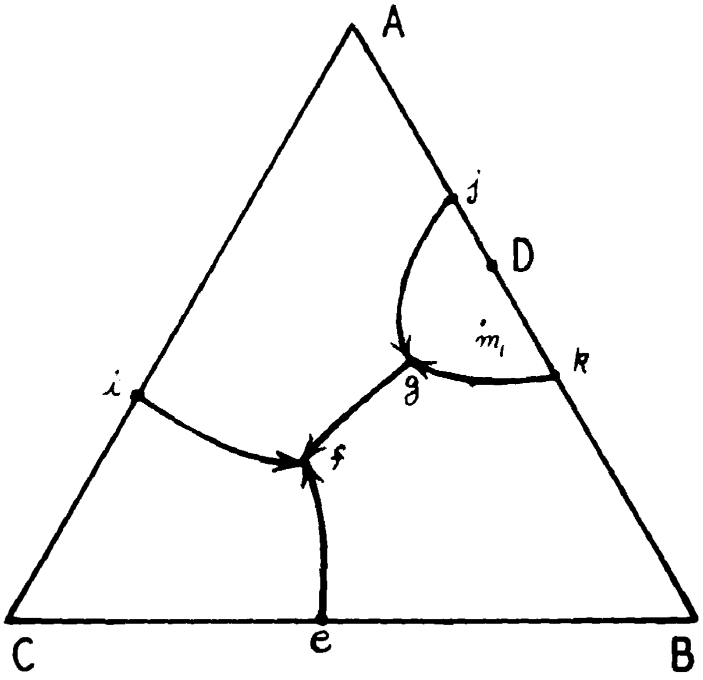


FIGURE 21

IMPOSSIBLE CONSTRUCTIONS

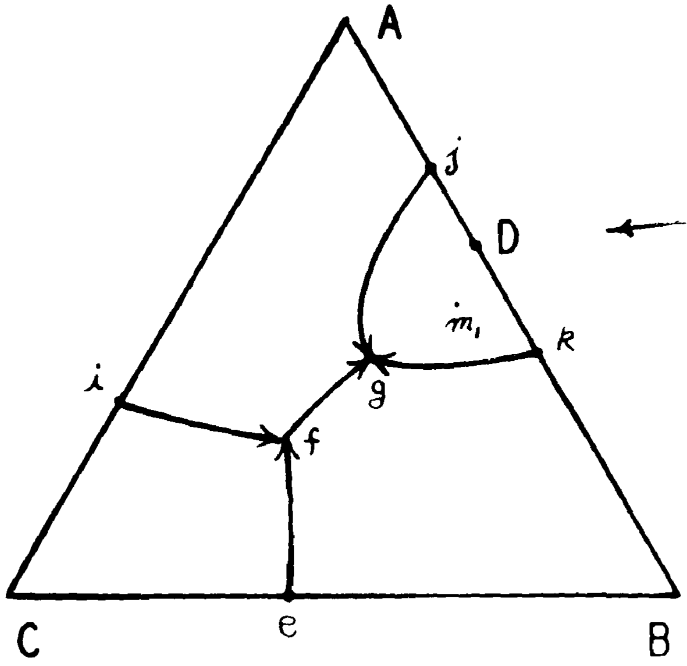


FIGURE 22

mass, i.e. within a triangle ABD. Hence it is impossible to express the composition m_1 in terms of A, B and D and the situation of Figure 22 is impossible.

In Figure 21, where a peritectic point is indicated at g, it will be noted that the shape of the area gADBg (formed by connecting the invariant point g with the solid phases present at the point g) is not a quadrangle with no re-entrant angles. It may be shown however that such a form is necessary for a peritectic reaction, and hence the construction of Figure 21 is impossible.

In the event that solid solutions are formed, either a peritectic or eutectic reaction may occur depending on the extent of the regions of stability of the solid solutions α, β and δ as shown in Figures 23 and 24. Points α, β and δ represent the compositions of solid solutions of A, B and D which are in equilibrium with the melt of composition g. (These are not the same for melts of different compositions.) It is seen that in the peritectic case of Figure 23, the reaction at g is one in which solid solution δ is used up in the equilibrium, δ + melt g $\rightleftarrows \alpha + \beta$.

Masing (131) terms the reaction at point g in Figure 24 a "eutectic" one of the type $\delta \rightleftarrows$ melt g + α + β, and further states that solid solution δ cannot be in equilibrium with the melt g at temperatures below that point: The system $\alpha\delta\beta g\alpha$ is one of a quadrangle containing a re-entrant angle, so that the reaction cannot be one of the usual peritectic type.

The above justification of Figure 24 leads to no impossible cases provided the following interpretation is applied. Melts having original

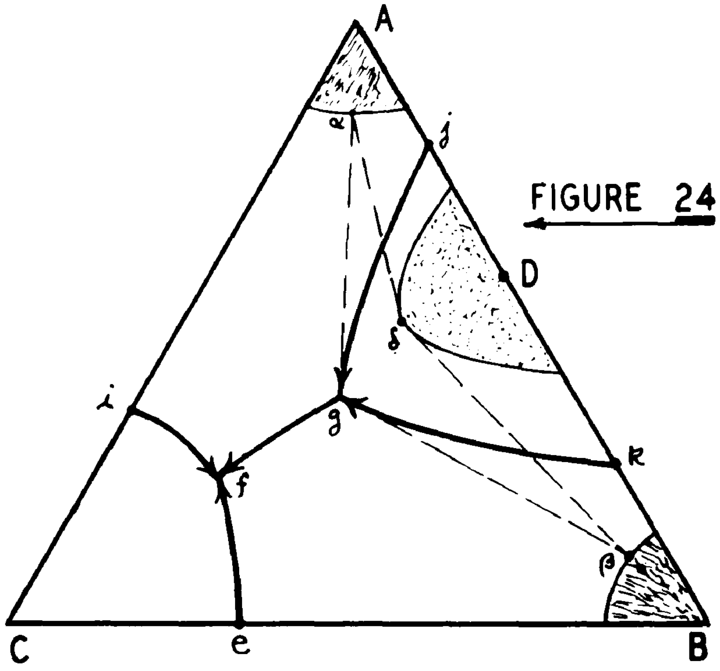


FIGURE 24

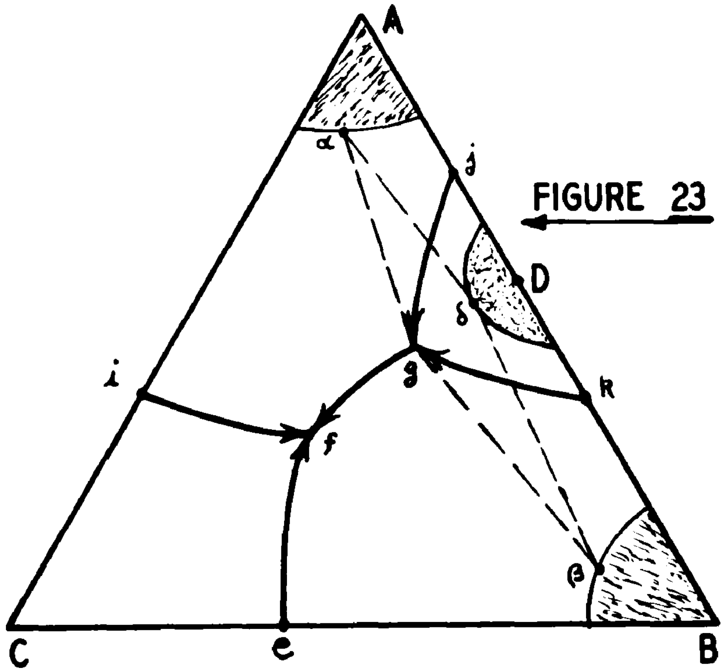


FIGURE 23

compositions to the right of line $\alpha\delta\beta$ solidify before reaching point g, or at that point any residual solid D reacts to form $\alpha + \beta + \delta$. If, however, the original melt lies within the area $\alpha\delta\beta g\alpha$ there may remain at g (after conclusion of the reaction) one of the following combinations; (1) $\alpha + \delta$ + melt g, (2) $\alpha + \beta$ + melt g, (3) $\beta + \delta$ + melt g. It must be assumed that if any δ remains, it takes no further part in any reaction according to the Masing interpretation. The melt g must then pass along the line gf with formation of α and β, until it reaches the ternary eutectic point f, where component C is also deposited as such or as a solid solution (not shown). It is apparent from the above discussion that if there is a limiting boundary for solid solutions of D, there is no possibility that points g and f may be ternary eutectic and peritectic respectively. Instead point f necessarily must be the ternary eutectic.

The above arguments for a system exhibiting an "open maximum" (congruently melting compound D) are equally applicable to the case of the occurrence of an incongruently melting compound in the system AB. Again it is impossible that the two lines of two-fold saturation may meet before first encountering some other line of two-fold saturation, except for the case of extensive solid solution formation such as that described above.

Mention should be made of a method of study which permits a quicker determination of the type of system present, provided circumstances are favorable. This is the "Klarkreuz" method due to Guertler (59) (131) (106). Figure 25 shows a system in which two binary compounds D and E

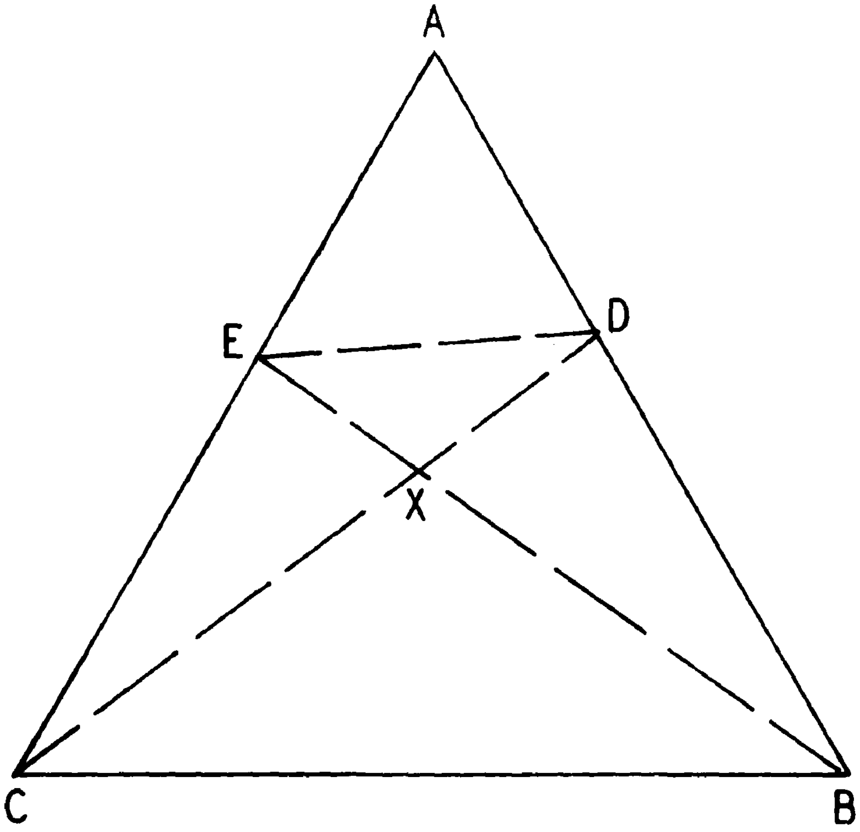


FIGURE 25

CD OR BE MAY BE QUASI-BINARY, BUT NOT BOTH.

occur, one in system AB and the other in system AC. If the system consists only of cooling solid phases having the over-all composition of the original melt, the phase rule for a condensed system states that only 3 solid phases may be present for a 3 component system, if the temperature is still a variable. That is

$$F = n - P + 1 = 3 - P + 1 = 1$$

and $P = 3$ for $F = 1$ = temperature degree of freedom.

Consequently within the solid mixture only three solid phases may coexist. Possible combinations are obtained by cutting the system into partial systems by the lines ED and EB, or lines ED and CD. From these divisions of the system, the following combinations are possible for the three coexisting solid phases.

(1)	A + D + E B + C + E B + D + E	and	(2)	A + D + E B + C + D E + C + D

If only lines CD, or BD, were drawn, possible combinations would be the following:

(3)	A + C + D B + C + D	(4)	A + B + E C + B + E

It will be noted that according to the particular combination chosen, certain solid phases are or are not capable of coexistence. These are as follows:

Combination (1) E + B can coexist, A + C cannot.

Combination (2) C + D can coexist, E + B cannot.

Combination (3) C + D can coexist, E + B + A cannot.

Combination (4) E + B can coexist, A + C + D cannot.

The Guertler method consists of preparing a melt with the composition X (Figure 25) which is common to the various possible ways of dividing the system. The melt is allowed to solidify and the coexisting solid phases are determined. According to the possible combinations it is possible to eliminate unallowable methods of dividing the system into smaller systems which may then be treated as discrete systems. This does <u>not</u> necessarily mean that the quasi-binary sections are determined, but rather that the method discloses where they are <u>not</u> possible. In this respect the method is entirely general.

For systems in which ADB and AEC binary systems show <u>only simple eutectics</u>, the method conclusively decides whether CD or BE is a quasi-binary section, since in the two cases only two solid phases will be formed, either C + D, or B + E. If one is a quasi-binary system then the other cannot be quasi-binary, since two such systems can never cross each other. Here the coexistence of C and D (or B and E) solid phases means that CD (or BE) is a quasi-binary section.

When the binary systems show any peritectic reactions, the method is not as conclusive for two reasons. The first is that, practically, peritectic reactions may not go to completion and definite results may not be obtained. The second reason is that neither CD, nor BE, necessarily has to be a quasi-binary section, so that the method can only at best say that one or the other is <u>not</u> a quasi-binary system.

Other generalities which are applicable to ternary systems are the following.

For those systems, in which <u>all</u> the binary systems show one invariant point, there exists but one ternary invariant point.

For each additional invariant point in any of the binary systems there exists another ternary invariant point. (Such an additional invariant point in the binary system arises from the occurrence of a congruent or incongruent compound, so that in the case of the former, it should not be counted as an invariant point for this purpose).

An example would be that of Figure 25 where as a consequence of the eutectic behaviour of the binary systems (in which five invariant minimum points appear), three invariant points must occur in the ternary system, of which at least one must be a ternary eutectic. The other two may both be peritectic, but if one of them is ternary eutectic, then the other is necessarily ternary eutectic. Thus the only possibilities in this case are: (1) One ternary eutectic, two ternary peritectic points,

or (2) Three ternary eutectic points.

If three ternary eutectics are shown, then two quasi-binary sections are present. If a ternary peritectic point occurs, no quasi-binary section is possible for this (Figure 25) ternary system, since another peritectic point must also be present. As a consequence the lines of two-fold saturation (leading to each peritectic point) cut across the two sections preventing them from being quasi-binary.

A special case may be mentioned in which the normal order of solidification processes will not follow the order of: (1) primary crystallizations, (2) peritectic reaction, (3) secondary crystallization and finally (4) ternary eutectic solidification. With reference to Figure 26, assume that the binary system AB forms compound D with an incongruent melting point. If the two fold saturation lines hk, ek, kt, tg and ft meet in

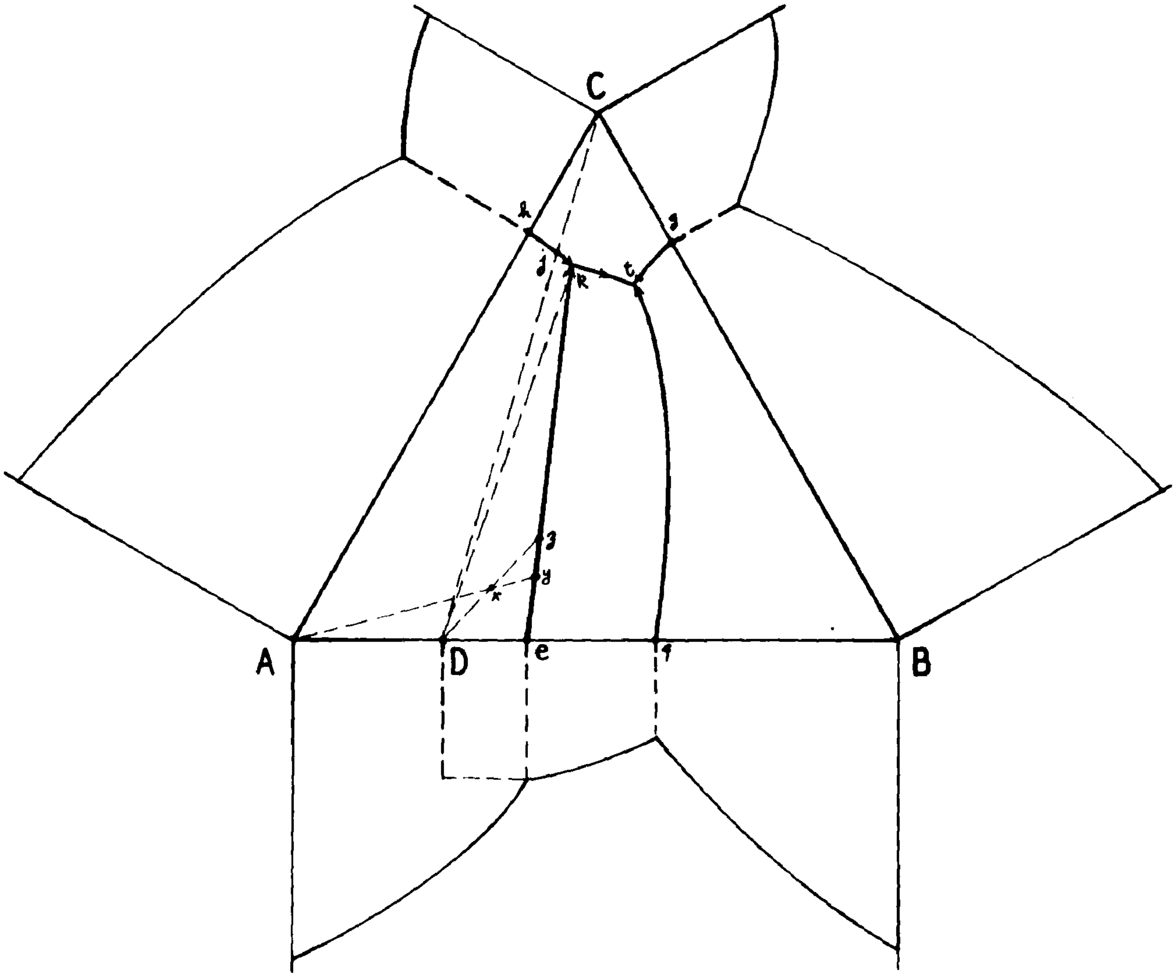


FIGURE 26

the manner shown, the point k represents a ternary peritectic and point t a ternary eutectic. All melts in the triangular area ACD will therefore solidify on reaching point k. Melts in the region jkd show the normal primary crystallization, then a peritectic reaction at k, and then secondary crystallization along line kt to final solidification at the ternary eutectic t.

Melts in the triangular area kde show a somewhat unusual order with respect to types of crystallization. A melt originally at composition X first deposits solid A and the melt composition follows line XY to an intersection with the line of "binary" peritectic reaction ek. A peritectic reaction occurs in which previously deposited A reacts with melt to yield compound D while the melt composition follows the peritectic two-fold saturation line ek. This reaction is not isothermal as only two solids and the melt are present. Since, $F = n - P + 1 = 3 - 3 + 1 = 1$, the system is univariant. Upon reaching point z, however, the system becomes bivariant because the solid A has been exhausted by the peritectic reaction and the system now consists of solid D and melt z, the original composition X lying on the straight line joining z and D. As the system has become bivariant, the composition of the melt is no longer restricted to following line ek, and the melt deposits solid D while proceeding to intersect either line kt or ft, where secondary deposition of two solids occurs, and finally the ternary eutectic point t is reached.

The point illustrated is that melts lying in exceptional areas, such as the one shown above, may exhibit somewhat unusual behaviour. Here the size of area kDe was purposely exaggerated, but if it were decreased so that the circumstances resembled those shown in Figure 14 it can be seen that melts closely related in composition would differ in thermal behaviour in an apparently anomalous manner.

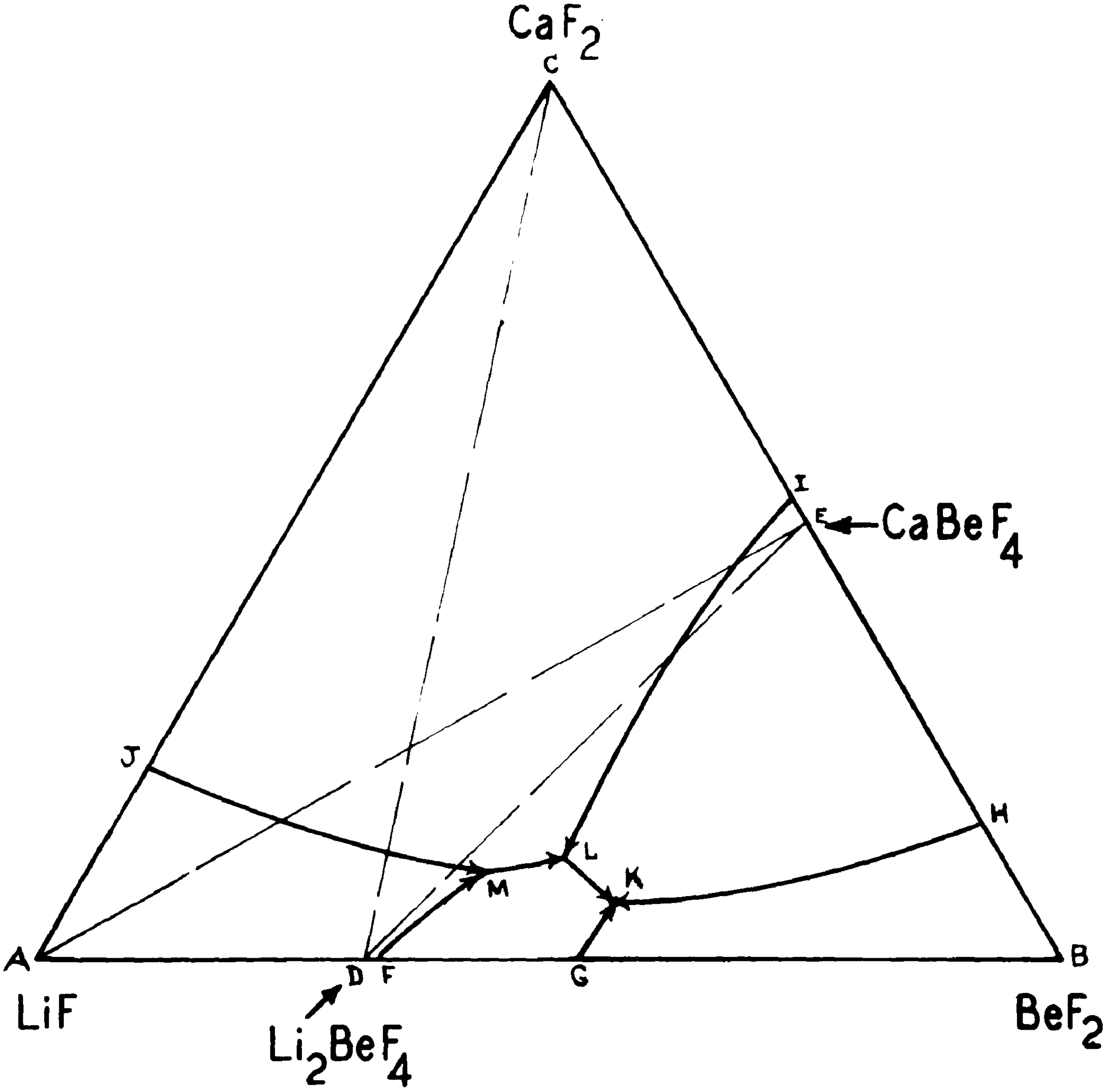


FIGURE 14

DISTORTED VIEW

TERNARY SYSTEM

CaF_2—LiF—BeF_2

APPENDIX 6

APPENDIX 6

SAMPLE NUMBERING SYSTEMS

The melts investigated in the binary CaF_2-LiF and CaF_2-BeF_2 systems were identified in a generally simple fashion. In the former case the melts were identified by either the approximate mole percent CaF_2, or by letters A, B, C, etc. starting from near the LiF side of the system. One special series of related melts near the eutectic of this system was identified by 1CL, 2CL, etc. Similarly in the CaF_2-BeF_2 system the melts were identified as A, B, C, etc. starting near the BeF_2 side of the system. One special series of related melts near the center of this system was identified by 1a, 2a, etc. Thus in these two systems the general relative melt location is indicated by the alphabetical sequence, or by the approximate percentage figure.

The same general method was used on the LiF-BeF_2 system, starting at the LiF side. Due, however, to the great number of melts studied in this system, other designations such as MM, LL, etc. became necessary to indicate melts in the vicinity of melts M and L etc. In addition a large number of series of related melts were studied in the Li_2BeF_4 region of this system. These melts were designated as 1II, 2II, etc.; 1KK, 2KK, etc.; 1R, 2R, 3R, etc.; 1d, 2d, etc.; 1e, 2e, etc. In this same region a large number of melts designated by 1Q, 2Q, 3Q, etc. were studied which were independent (unrelated) melts. Because of these complications it is necessary to consult the phase diagrams or tabulated compositions in the appendices to be certain of the relative composition locations of these melts.

Within the ternary CaF_2-LiF-BeF_2 system, all melts are designated by identifying symbols which terminate in a numerical suffix. The first portion of the symbols identifies the binary parent melt from which the ternary melt was derived. The numerical suffix indicates the relative order of the ternary melt in the series derived from the binary melt. Thus, for example, A-1 is the first ternary melt derived from melt A (of the LiF-BeF_2 system) by the addition of CaF_2. A-2 would be the second ternary melt obtained by further addition of CaF_2. As a more complicated example; 12Q-5 would signify the fifth ternary melt obtained from binary melt 12Q of the LiF-BeF_2 system.

All ternary melts were derived from binary LiF-BeF_2 melts, except for two special series designated t-1, t-2 etc. and g-1, g-2, etc. All ternary melts with the exception of the t, g, and Q series were started into the ternary system by the addition of CaF_2 to LiF-BeF_2 mixtures. All ternary system melts designated by upper case letters such as A-1, MM-5, etc. were carried across the system by the addition of CaF_2 only, with the exceptions of the Q and S series. The latter and a number of those designated by lower case symbols such as p, t, etc. were shifted along sections by the addition of mixtures or of other components, as more particularly described in the discussion of procedure and results.

APPENDIX 7

APPENDIX 7

RESULTS OF THERMAL ANALYSES OF CaF_2-LiF SYSTEM

(Note - See footnotes for significance of abbreviations.)

Date	Sample No.	Calc'd.Comp., Mole % CaF_2	Method of Detection	Primary Cryst. Temp.,°C.	Eutectic Temp.,°C.	Comments
11/7/49	--	0.0	S	852-50	---	Pure LiF
11/13/49	--	0.0	S	852-50	---	
11/8/49	A	ca. 3.0	S	841	769	
11/8/49	B	ca. 5.9	S	839	777	
11/9/49	C	ca. 8.6	S	823	772	
11/13/49	"11.1"	11.1	VS	808	773-2	
11/9/49	D	13.5	S	812	771	
11/16/49	"15"	15.0	VS	795-93	---	
11/17/49	"18"	18.0	V	780	772	
6/6/51	10CL	18.3	VS	779	---	
6/6/51	9CL	19.3	V	775	772	
6/6/51	8CL	19.6	V	773	773-2	See Note 3
11/9/49	E	20.0	S	803? 800-790?	777	Cooled too slowly
11/13/49	"20"	20.0	V	777	773-2	
11/17/49	"20'"	20.0	V	775	772	
6/6/51	7CL	20.8	V	782	773	
6/6/51	6CL	21.5	V	787	---	
6/6/51	1CL	22.0	V	796	773	Both runs on same master batch.
6/6/51	5CL	22.0	V	795	---	
11/17/49	"22"	22.0	V	778?	772	Removed special sample
6/6/51	2CL	22.5	V	803	---	
11/17/49	"23.3"	ca. 23.3	V	ca. 801	772	Removed special sample
6/6/51	3CL	24.0	V	820	---	
11/17/49	"24"	24.0	V	819	ca. 772	
11/17/49	"24"	24.0	V	815	ca. 772	Repeat
11/10/49	F	25.0	S	ca. 800?	778	
11/11/49	H	25.0	S	?	772-1	
11/17/49	"25"	25.0	VS	826	ca. 772	

Continued next page

RESULTS OF THERMAL ANALYSES OF CaF_2-LiF SYSTEM - Continued

Date	Sample No.	Calc'd.Comp., Mole % CaF_2	Method of Detection	Primary Cryst. Temp., °C.	Eutectic Temp., °C.	Comments
6/6/51	4CL	25.9	V	ca. 840	---	
11/16/49	"26"	26.0	V	ca. 840	776	
11/16/49	"27"	27.0	VS	855-53	777	
11/14/49	"29"	29.0	V	861-2	773	
11/10/49	G	33.3	S	860?	777	
11/12/49	G	33.3	V	898	771	Special samples removed.
11/11/49	I	33.3	S	?	775	
11/12/49	J	33.3	S	898	778-9,772	First melt stirred much.
11/12/49	"38"	38.0	S	ca. 942		
11/14/49	"38"	38.0	S	955	---	Repeat
11/14/49	"43"	43.0	VS	993	---	
11/14/49	"47"	47.0	VS	1018	---	
11/14/49	"50"	ca. 50.0	VS	ca.1043	ca. 772	
11/15/49	"50'"	50.0	V	1035	---	
11/15/49	"60"	60.0	V	ca.1115	---	
11/15/49	"70"	ca. 70.0	VS	1181-79	---	
11/4/49	--	100.0	S	ca.1413	---	Pure CaF_2

Notes:
(1) V signifies visual observation of point of primary crystallization.
(2) S signifies inflection point in thermal analysis curve at point of primary crystallization.
(3) Shift in type of primary crystallization occurred at sample 8CL. Melts above 8CL deposited LiF initially while those below it deposited CaF_2 initially.
(4) "Ca." signifies more than normal uncertainty of composition.

APPENDIX 8

APPENDIX 8

RESULTS OF THERMAL ANALYSES OF CaF_2-BeF_2 SYSTEM

In listing the results of these thermal analyses the compositions given in column 2 represent calculated values based on input to the melts. The melts analyzed subsequent to the tests are indicated by a sample letter in column 3 and an accompanying analytical result is given in column 4. The other composition values given in column 4 in square brackets represent interpolated values based on starting compositions, analytical results and observed weight losses during the tests. If an asterisk is shown in column 4, the composition value is that of the main part of the melt, additional analyses having been made on other samples of material on the walls of the crucible, etc. (See Analytical Appendix 15, Part H).

The description of the thermal behaviour shows the temperature of initial deposition of $CaBeF_4$ or CaF_2 in columns 5 and 6, actual observation of deposition being indicated by an X in column 7.

In column 8 the initial temperature of plateaus is shown,with a description of the type in column 9, i.e. short flat, short sloping, long flat, long gradually sloping.

In column 10 the temperature of disappearance or appearance of apparent liquid is given accompanied by C or H to indicate cooling or heating. In cases where the initial crystallization was not observed, thermal inflections were observed.

The initial studies were made in 1950. The second trials which were considerably better in general accuracy are represented by the underlined series of "a" samples of the period February 13 to 15, 1951.

A number of the earlier runs on melts contaminated by BeO are tabulated even though their low values are obviously discordant. These samples are indicated by triple question marks (???) in column 4. A single question mark indicates a larger than normal uncertainty of composition, possibly ± 1 mole percent.

Above 50 mole percent CaF_2 it will be noted that on many of the samples the initial CaF_2 deposition was not detected by thermal effects and at that time visual detection was not being used. The observed temperatures therefore represent the beginning of the eutectic reaction in these cases.

(1) Date	(2) Calc'd.Comp., Mole % CaF_2	(3) Sample	(4) Anal.Comp., Mole % CaF_2	(5) Temp. of Initial $CaBeF_4$	(6) Temp. of Cryst. CaF_2	(7) Obsvd.	(8) Start of Plateau	(9) Type Plateau	(10) Apparent Liquid
2/19/50	3.5	D	3.3(?)	--	--	--	772	Series of short	--
2/16/50	7.2	A	6.0	--	--	--	712	Short	--
2/17/50	---	-	[6.2]	--	--	--	702	Very short	--
2/20/50	7.1	-	---	--	--	--	716	Short Sloping	--
2/20/50	---	E	10.1	--	--	--	750	Very short	--
2/17/50	11.8	B	11.9	--	--	--	734	Short	--
2/21/50	---	-	[13.1]	--	--	--	740	Sloping	--
2/21/50	---	-	[15.8(?)]	--	--	--	750	Short	--
2/21/50	---	-	[19.2(?)]	--	--	--	757	Short	--
2/21/50	20.(?)	G	*20.8	--	--	--	751	Short	--
2/18/50	25.0	C	25.2	--	--	--	780	Very short	--
3/23/50	29(?)	-	--	--	--	--	770	Short	<770 C
3/23/50	37.(?)	-	--	800	--	X	800	Sloping to short 775°	775 C
4/22/50	39.5	-	--	--	--	--	813	Short flat, then slop'g	770 C
3/23/50	40.0	R	*40.3	--	--	--	818	" " " "	<800 C
2/13/51	40.0	a	Ca.40.0	819	--	X	819	" " " "	785 H 760 C
2/13/51	42.5	1a	[42.]	828	--	X	828	Flat, then sloping	780 C
2/22/50	44.1(?)	J	*48.1	--	--	--	823	Long, sloping	--
3/24/50	44.5	-	(???)	--	--	--	823	Short flat, then slop'g	--
2/15/51	44.3	7a	[43.4]	833	--	X	833	Flat, then sloping	790 CH
2/14/51	45.0	2a	[44.1]	833	--	X	833	" " "	780 CH
5/4/50	47.0	-	(???)	--	--	--	822	Sloping	<810 C
2/15/51	47.0	8a	[45.8]	836	--	X	836	Flat, then sloping	805 C
2/14/51	46.2	3a	[45.2]	834	--	X	834	" " "	--
2/14/51	47.5	4a	[46.4]	835	--	X	835	" " "	780 C
2/14/51	48.7	5a	[47.6]	832	--	X	832	" " "	780 CH
2/15/51	48.75	9a	[47.7]	836	--	X	836	" " "	815 H
3/7/50	49.0	-	--	--	--	--	834	Gradually sloping	--
2/15/51	50.0	10a	48.6	--	--	--	834	Flat	--
2/14/51	50.0	6a	48.8	--	890(?)	X(?)	830	Very flat	815 H
4/22/50	50.0	X	*49.7(???)	--	--	--	821	Long, then sloping	815 C
3/10/50	50.4	-	--	--	--	--	838	Long flat	--

Continued next page

Continued

(1) Date	(2) Calc'd.Comp., Mole % CaF_2	(3) Sample	(4) Anal.Comp., Mole % CaF_2	(5) Temp. of Initial Cryst. $CaBeF_4$	(6) Temp. of Initial Cryst. CaF_2	(7) Obsvd.	(8) Start of Plateau	(9) Type Plateau	(10) Apparent Liquid
3/24/50	50.5	T	50.5(???)	--	880	--	823	Short, then sloping	--
3/7/50	51.0	-	--	--	--	--	831	Sloping	--
3/7/50	52.0	-	--	--	859	--	839	Long, then sloping	--
2/15/51	52.7	11a	[53.7]	--	874	X	832	Flat, then sloping	--
2/15/51	54.8	12a	55.6	--	907	X	832	" " "	--
5/4/50	53.5	CC	*53.5(???)	--	--	--	821	Flat, then sloping	800 C
2/22/50	56.8	-	--	--	--	--	831	Flat, then sloping	--
3/10/50	57.0	N	56.7	--	--	--	833	Long, then sloping	--
4/23/50	57.(?)	-	--(???)	--	--	--	829	Sloping	820 C
4/23/50	59.(?)	-	--(???)	--	--	--	825	Flat	--
5/5/50	59.3	DD	59.3(???)	--	--	--	821	Short, sloping	815 C
3/11/50	61.0	-	--	--	980	X	834	Short	ca.830 C
4/23/50	64.5	AA	*64.6(???)	--	900	X	820	Short	--
3/11/50	66.0	-	--	--	1075	X	834	Short	--
3/7/50	73.0	-	--	--	--	--	831	Sloping	ca.831 C
3/11/50	75.0	P	*75.4	--	1160	X	829	Sloping	--
3/7/50	78.(?)	M	*77.6	--	--	--	831	Sloping	--

APPENDIX 9

APPENDIX 9

RESULTS OF THERMAL ANALYSES OF LiF-BeF_2 SYSTEM

Explanatory Notes

Table A and B give the data for the over-all phase diagram of Figure 5.

Tables C, D, E and F give the data for the more detailed study of the region near 33 mole percent BeF_2, plotted in Figures 6a, 6b, 7a and 7b.

Abbreviations

Under Composition, one or more of three headings appear, signifying the following:

ORIG. signifies composition calculated from input of LiF and apparent weight of BeF_2 after driving off NH_4F from $(NH_4)_2BeF_4$, or based on input of BeF_2 and LiF.

RECALC. signifies composition calculated from input based on subsequent analysis of $(NH_4)_2BeF_4$ used.

ANAL. signifies an analyzed melt. If result is given in parentheses it indicates a value obtained by back extrapolation from a ternary system sample analysis.

Under First Inflection, the abbreviations signify: S, sharp; G, good or definite; F, fair or less definite; P, poor or indefinite; VP, very poor or barely sufficient for recognition.

Under Plateau, the types shown have the following significance.

Long, flat -- flat or very slightly sloping within temperature range shown, followed by abrupt drop in temperature. Length about

10-20 minutes approximately.

Flat, sloping -- denoting behaviour in which quite flat pleateau occurs, followed by a smoothly sloping transition to a resumption of original general slope. Length of flat portion variable from about 10 to 15 minutes.

Sloping - denoting behaviour in which plateau is never very flat, but instead shows gradual drop of about 1°/min. followed later by a more rapidly cooling section, without any abrupt transition.

Gradually sloping - same as above, but with even more slope.

Short, sloping -- denoting behaviour where a short plateau of about 5 minutes or less duration occurs, followed by a non-abrupt transition.

Short -- denoting a short plateau of less than 5 minutes duration followed by an abrupt type of transition to more rapid cooling.

In the columns headed "Binary Eutectic" or "Apparent Liquid" the letters H and C indicate observations made during heating and cooling respectively. "Apparent Liquid" results are entirely based on observation of the disappearance (or reappearance) of the last (or first) liquid during cooling or heating of the melts.

TABLE A

Date	Melt	Composition, Mole % BeF_2			First Cryst. Observed,		First Inflect.,		Plateau,		Temp. Apparent Liquid
		Orig.	Recalc.	Anal.	Temp.	Type	Temp.	Type	Temp.	Type	
6/13/50	A	3.3	4.2	(4.)	--	--	833	S	--	--	--
6/14/50	B	7.9	8.1	(8.1)	--	--	808	G	--	--	--
6/19/50	C	11.8	12.0	(12.)	770	--	775-9	F	--	--	--
6/22/50	D	13.8	15.4	(15.)	756	--	756	G	--	--	--
6/23/50	E	18.8	19.0	(19.)	713	--	715	F	--	--	< 600 C
6/25/50	F	22.0	22.3	(22.)	--	--	687	F	453	Flat, sloping	< 460 C
7/7/50	FF	23.0	23.0	(23.)	665	--	ca. 655	VP	451-447	Flat	451 C
6/27/50	G	24.3	23.8	(25.)	640	--	640-9	P	455-50	Flat	455 C
6/27/50	H	27.5	26.9	(28.)	600	--	ca. 600	P	450-447	Long, flat	--
6/29/50	I	29.5	28.7	(30.5)	500	LiF	496	F	449	Long, flat	449 C
9/12/50	II	30.4	--	--	ca. 521	LiF	ca. 521	F	454-2	Very flat	450 C
5/8/51	e	32.2	32.5	--	486	LiF	none		462-55	Long, flat	455 C
7/1/50	J	32.5	31.7	(33.2)	460?	LiF?	none		450-445	Flat, sloping	--

TABLE B

Date	Melt	Composition, Mole % BeF_2 Orig.	Composition, Mole % BeF_2 Anal.	First Cryst. Observed, Temp.	First Cryst. Observed, Type	First Inflect., Temp.	First Inflect., Type	Plateau, Temp.	Plateau, Type	Binary Eutectic, Temp.	Apparent Liquid, Temp.
8/16/50	K	33.3	--	448	Li_2BeF_4	448	S	448-5	Very flat	--	--
9/11/50	1KK	34.0	--	453	"	452	S	452-1	Very flat	356 H	450 C 400 H
9/7/50	1L	35.9	--	451	"	451	S	451-50	Long flat	342 C	350 C
8/17/50	L	36.0	--	445	"	445	S	445	Long, sloping	--	--
9/8/50	LL	38.0	--	447	"	445	S	445	Long, sloping	347 C 356 H	390 C 370 H
8/20/50	M	40.0	--	442	"	437	S	437	Long, sloping	333 C 350 H	380 C 360 H
6/5/51	3p	40.0	--	441	"	441	S	441	Long, sloping	350-47 C	--
9/7/50	MM	42.0	--	429	"	ca. 427	G	427	Sloping	347 C 358 H	--
6/5/51	2p	43.0	--	420	"	420	G	420	Flat, sloping	--	--
8/20/50	N	45.0	--	407	"	403	G	403	Grad., sloping	--	350 C 350 H
2/8/51	U*	?55.?		403	"	403	G	403	Short, sloping	355 C	--
6/5/51	1p	46.4	--	392	"	392	G	394	Short	--	--
8/29/50	O	48.1	--	ca. 382	"	382	F	382	Sloping	330 C	--
6/5/51	p	50.0	50.9	372	"	372	G	372	Short	358-55 C	--
9/2/50	P	50.9	--	365	"	364	G	364	Long, sloping	357 C 358 H	--
6/5/51	3n	50.9	51.1	364	"	364	G	364-66	Short	356 C	--
6/5/51	2n	53.6	--	Shows only long plateau ca. 360.							
6/4/51	1n	56.7	--	Shows only long flat plateau 356.							
6/4/51	n	60.0	60.3	Shows only long plateau 360-50.							
2/6/51	V	60.0	--	Gradually thickened below 475.							
2/11/51	W	65.0	--	Gradually thickened below 500. Shows lower eutectic.							
2/3/51	X	70.0	--	Gradually thickened below ca. 600.							
1/31/51	Y	80.0	--	Gradually thickened below ca. 700.							
1/29/51	Z	90.0	--	Gradually thickened below ca. 720.							
2/10/51	ZZ	95.0	--	Gradually thickened below ca. 800.							

Note: * The composition of Melt U is uncertain. All indications are that by mistake it was compounded as 45 mole percent BeF_2-55 mole percent LiF instead of the desired value of 55 mole percent BeF_2-45 mole percent LiF.

TABLE C

Date	Melt	Composition, Mole % BeF_2			First Cryst. Observed,		First Inflect.,		Plateau,		Apparent Liquid,
		Orig.	Recalc.	Anal.	Temp.	Type	Temp.	Type	Temp.	Type	Temp.
5/6/51	10d	29.0	28.7	28.7	600	LiF	--	--	--	--	--
5/6/51	9d	30.0	29.6	--	578	"	--	--	--	--	--
5/6/51	8d	30.8	30.6	--	550	"	--	--	--	--	--
5/6/51	7d	31.8	31.5	31.5	532	"	--	--	--	--	--
5/6/51	6d	32.5	32.3	--	510	"	--	--	--	--	--
5/4/51	1d	32.8	32.3	--	500	"	--	--	460	Very flat	460 C
5/6/51	5d	33.2	32.9	--	493	"	460	S	460	Very flat	--
5/2/51	d	33.3	32.8	32.5	461	Li_2BeF_4	461	S	461-57	Long flat	457 C
5/4/51	2d	34.9	34.5	34.7	459	"	459	--	460	Long flat	460 C
5/5/51	3d*	35.7	35.3	--	460	"	458	--	458-56	Long flat	442 H
5/5/51	4d*	36.4	36.0	36.0	460	"	460	--	460-56	Long, then sloping	{400 C 420 H

* Notes -- 4d showed lower eutectic at about 350°.
3d showed no apparent lower eutectic.

TABLE D

Date	Melt	Composition, Mole % BeF_2		First Cryst. Observed,		First Inflection,		Plateau,		Temp. Apparent Liquid
		Recalc.	Anal.	Temp.	Type	Temp.	Type	Temp.	Type	
12/24/50	8R	32.4	32.0	ca.490	LiF	--	--	457-55	Very flat	455 C
"	7R	32.9	--	480	"	--	--	457	Very flat	--
"	6R	33.3	--	470	"	--	--	457-55	Very flat	455 C
12/23/50	5R	33.7	--	457	Li_2BeF_4	457	S	457-55	Long flat	455 C
"	4R	34.1	--	457	"	457	S	457-55	" "	455 C
"	3R	34.5	--	456	"	457	S	457-54	" "	454 C
"	2R*	34.9	--	458	"	459	S	459-56	" "	456 C
12/26/50	19R	31.8	32.3	488	LiF	--	--	457-56	Long flat	456 C
"	18R	32.3	--	480	"	--	--	--	--	--
"	17R	32.6	--	470	"	--	--	458	--	--
"	16R	32.7	--	465	"	--	--	458	--	--
"	15R	32.8	--	460	"	--	--	459-55	Long flat	455 C
"	14R	33.0	--	457	Li_2BeF_4	458	S	458-57	--	--
"	13R	33.2	--	458	"	458	S	458-56	Long flat	456 C
"	12R	33.3	--	458	"	458	S	458-57	--	--
12/25/50	11R	33.5	--	457	"	457	S	457-54	Flat	{454 C 454 H
"	10R	33.6	--	457	"	459	S	459-55	"	455 C
"	9R	35.1	--	458	"	458	S	458-53	Flat, sloping	400 C
12/22/50	1R*	35.3	--	456	"	456	S	456	Flat, sloping	{350 C 360 H
1/25/51	**S****	--	33.4	457	"	458	S	458-56	Long flat	456 C

Notes -- *Compositions of 1R and 2R calculated on the basis of effective 35.3 mole percent BeF_2 in the starting material, Li_2BeF_4 product of 12/19/50.

Starting material for **S was Li_2BeF_4 product of 1/19/50.

TABLE E

Date	Melt	Composition, Mole % BeF_2		First Cryst. Observed,		First Inflect.,		Plateau,		Apparent Liquid, Temp.
		Orig.	Anal.	Temp.	Type	Temp.	Type	Temp.	Type	
9/12/50	II	30.4	--	ca. 521	LiF	ca.521	F	454-52	Very flat	452 C
"	1II	30.9	--	513	"	--	--	455-52	Flat	--
"	2II	32.0	--	488	"	--	--	454-53	Very flat	--
9/14/50	3II	32.8	--	475	"	--	--	455-53	Very flat	ca.445 H
"	4II	33.0	--	ca. 471	"	--	--	455-53	Long flat	420 C
"	5II	33.1	--	465	"	--	--	455-53	Long flat	{425 C 448 H
"	6II	33.3	--	462	"	--	--	455-53	Long flat	425 C
"	7II	ca.33.6	34.1	455	Li_2BeF_4	455	S	455-54	Long flat	--
9/16/50	5KK	ca.32.5	32.3	473	LiF	--	--	454-53	Very flat	{430 C 447 H
"	4KK	32.9	--	465	"	--	--	455-53	Very flat	435 C
9/14/50	3KK	33.3	--	454	Li_2BeF_4	454	S	454-52	Very flat	ca. 450 H
9/12/50	2KK	33.5	--	453	"	453	S	453-51	Very flat	{> 440 C > 440 H
9/11/50	1KK*	34.0	--	453	"	452	S	452-51	Very flat	{400 H ca. 450 C

* Showed slight break at 356° eutectic on reheating.

TABLE F

Date	Melt	Composition, Mole % BeF_2 Orig.	First Cryst. Observed, Temp.	First Cryst. Observed, Type	First Inflect., Temp.	First Inflect., Type	Plateau, Temp.	Plateau, Type	Apparent Liquid, Temp.
10/6/50	3Q	31.2	484?	LiF	456	S	456-55	Long flat	455 C
10/18/50	5Q	31.3	ca. 490	"	454	S	454	" "	454 C
"	7Q	31.7	486	"	454	S	454	" "	"
11/2/50	8Q	32.4?	466	"	456	S	456-54	" "	454 CH
11/7/50	10Q	32.9	458	"	456	S	456-55	" "	455 C
12/4/50	12Q	33.8	457	Li_2BeF_4	457	S	457-55	" "	"
12/5/50	13Q	34.0	457	"	457	S	457-55	" "	"
11/3/50	9Q	34.2	454	"	456	S	456-54	Long, sloping	410 C
10/19/50	6Q	35.0	454	"	454	S	454	Long, sloping	< 450 C
11/8/50	11Q	35.8	456	"	455	S	455-50	Flat, sloping	< 450 C
10/8/50	4Q	36.7	452	"	452	S	452	Sloping	< 400 C

Notes -- All melts prepared from Brush BeF_2 and LiF.
Composition of 8Q uncertain due to probable weighing error.
On 3Q and 5Q the initial observations of surface crystallization were uncertain.

APPENDIX 10

APPENDIX 10

CALCIUM FLUOBERYLLATE; RESULTS OF WET AND DRY SYNTHESES, OPTICAL AND X-RAY DATA

References for the existence of the compound $CaBeF_4$ were given in Appendix 3. The method of wet synthesis of $BaBeF_4$ briefly described by Sarker and Ray (140) was tried in several modified forms in an attempt to prepare pure $CaBeF_4$. X-ray and analytical data both indicate that all the products were contaminated with calcium fluoride.

Essentially the Ray method comprises mixing a cold saturated solution of a soluble alkaline earth metal salt with a cold saturated solution of $(NH_4)_2BeF_4$. The somewhat microcrystalline product is washed by decantation with several solvents to remove soluble salts and finally water. The principal modification made was to use centrifugal decantation, but other methods of combining the solutions and different digestion methods were also tried.

The first product, "A", was prepared by rapidly mixing cold saturated solutions of $(NH_4)_2BeF_4$ and $Ca(NO_3)_2$ followed by successive centrifugal decantation and washing with four portions of water, three portions of absolute ethanol, two portions of hot glacial acetic acid, and three portions of absolute ethanol.

The alcohol suspension was then evaporated to dryness on the steam bath, yielding a white impalpable powder with an average size of about 1 to 2 microns. As the $(NH_4)_2BeF_4$ was known to contain NH_4F as impurity, a 50% excess was used. Calcium fluoride would be expected to be present in the product under such conditions. Upon analysis, the molal ratio of CaF_2/BeF_2 was found to be approximately 1.9, but the analytical results did not total 100% by weight. X-ray examination indicated the presence of five of the stronger lines of calcium fluoride, in addition to about thirteen other lines identical to those observed for $CaBeF_4$ occurring in the samples from the CaF_2-BeF_2 system melts.

In an attempt to prepare purer $(NH_4)_2BeF_4$ the same starting material was fractionally recrystallized to yield a product which turned out to be about 95% NH_4F on subsequent analysis. Needless to say the $CaBeF_4$ preparations "B" and "C" obtained with this "purified" product were poor.

In another attempt using about 50% purity $(NH_4)_2BeF_4$, a dilute solution of one reagent was slowly added to a dilute solution of the other with agitation. While considerable calcium fluoride impurity would be expected, analysis of the product, "D", showed a ratio of CaF_2/BeF_2 of about 1.2.

Fractional precipitation was also tried in the hope of removing most of the contaminating fluoride ion in the first half of the precipitated product. The product of the second part of the precipitation, "F", showed a molal ratio of 1.12.

X-ray examination of these products, "D" and "F", showed slight amounts of calcium fluoride contamination. None of the analytical results showed 100% recovery, the totals generally being in the range of 89 to 93%. This recovery could be accounted for if the oven-dried material had an empirical composition $CaBeF_4:1/2H_2O$, or if it were otherwise solvated.

Although all of the above results were obtained using $(NH_4)_2BeF_4$ contaminated by NH_4F, it is still probable that difficulty would be encountered in obtaining complete freedom from calcium fluoride even though pure $(NH_4)_2BeF_4$ were used. Since the latter material probably dissociates in solution to form some fluoride ions, slight precipitation of calcium fluoride would be expected at the least, and if the mixing operation was carried out very gradually, substantial calcium fluoride formation might be possible. In addition hydrolysis of the product, $CaBeF_4$, may occur with possible oxyfluoride and calcium fluoride formation. The hot glacial acetic acid used in the wash treatment is supposed to remove hydrolysis products, but it does not have a large solvent effect on calcium fluoride.

Because of the apparent practical and theoretical difficulties of preparing $CaBeF_4$ in pure form by the above method, some attention was given to another possible procedure. The complexing agent nitrilotriacetic acid, $N(CH_2COOH)_3$, shows considerable specificity as to the types of calcium compounds with which it forms soluble complexes. Considerable work was done on the preparation of this reagent and trials were made of its possible value in dissolving $CaBeF_4$ to leave the insoluble CaF_2 as a residue but no satisfactory results were obtained.

The formula of the compound formed by CaF_2 and BeF_2 is probably $CaBeF_4$ for several reasons. The original dry-synthetic product reported by Ray (129) showed the proper analysis. In addition it may be seen that as the products of this work were obtained in purer form the analytical molal ratio of CaF_2/BeF_2 approached the value of 1 from the high side.

Conversely the sample J' consisting of single crystals of $CaBeF_4$ (removed from melt J of the CaF_2-BeF_2 system) gave a molal ratio of about 0.9, yet both products by X-ray methods were identical. (See Appendix 15, Part H). It is therefore concluded that the formula of Ray correctly expresses the composition.

Since no X-ray structure or powder pattern data had ever been published for this compound, an attempt was made to determine the crystalline system and unit cell dimensions of $CaBeF_4$.

Optical examination shows practically exclusively one crystalline habit, that of a thin prismatic crystal lying on its broad face and presenting the appearance of very elongated parallelograms with $45^\circ \pm 1^\circ$ angles at the acute corners. The crystals when viewed in this position are anisotropic and show parallel extinction.

The indices of refraction were determined using calibrated water-glycerine mixtures (for both tungsten and sodium lamp illumination) by the Becke line method, using dispersion effects for final matching. In the crushed samples on the microscopic slide some nearly isotropic sections were rarely observable (not always perfectly oriented) which had an index of refraction of $n_{NaD} = 1.386$. If the crystals were uniaxial this would determine the index of the ordinary ray as being $\omega_{NaD} = 1.386$.

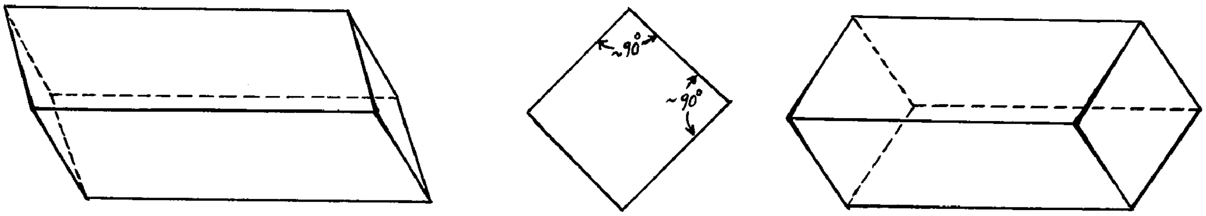
For the anisotropic prismatic crystals (lying on their broad faces) two indices of refraction were obtained for the ordinary and extraordinary rays, $\omega_{NaD} = 1.386$ and $\varepsilon_{NaD} = 1.401$, assuming again that the crystals are uniaxial and that in this orientation the optic axis lies perpendicular to the axis of the microscope. The refractive index values are probably accurate to within ± 0.005.

Interference figure observations made on the isotropic sections always showed at best incomplete uniaxial crosses, in which the center was slightly outside the field, but the arms of the cross were observable on rotation. Tests with quartz, mica and selenite retardation test plates showed positive optical sign. Tests with the selenite test plate on anisotropic sections (with the long axis of the crystal parallel to the slow ray vibrational direction of the test plate) showed a blue coloration, indicative of positive elongation.

Interference figures observed on the anisotropic sections gave what appeared to be "flash figures" (consisting of two hyperbolae which enter from opposite quadrants and leave by the other two quadrants), which might be indicative of <u>either</u> a uniaxial structure, or of biaxial "optic normal" and "obtuse bisectrix" figures.

The results of the above observations strongly indicated a uniaxial structure for $CaBeF_4$, but were not absolutely definite in excluding a biaxial structure. The orientation of the few isotropic sections observable was not sufficiently perfect to permit certainty that the observed ω value was identical with the ω value shown by the anisotropic sections. The failure to obtain centered uniaxial cross interference figures on the isotropic sections also indicates a slight defect in the orientation. The fact that only two indices of refraction were observed for the anisotropic sections does not unequivocally mean that these are the exact values of ω and ε since a very predominant crystalline habit might cause the crystals to always lie in the same orientation, with the optic axis non-parallel to the stage in a consistent manner. The anisotropic interference figures could be interpreted as being due to either uniaxial or biaxial structure "flash figures". The only positive indication of uniaxial character was the occasional observation of a poor uniaxial cross. The agreement of the ω values for the isotropic and anisotropic sections may be taken as confirmatory.

Larger macro-crystals of $CaBeF_4$ have a somewhat rhombohedral appearance except that the elongated faces meet at approximately 90° angles. The ends of the crystals, because of characteristic habit, or prominent cleavage, have a rough resemblance to rhombs as indicated in the following sketch.



Irregularity of the faces prevented any satisfactory measurement of the angles.

By means of X-ray examination an attempt was made to determine the crystal system and unit cell dimensions. The powder diffraction pattern furnished accurate interplanar spacing information, but the indexing of the observed lines was not obvious from the pattern as would be the case for the cubic system. Attempts were made to index the lines, using alignment charts for the tetragonal, simple hexagonal and hexagonal rhombohedral crystal systems in the manner outlined by Bunn (14). For all three systems it was found that no axial ratio value gave a satisfactory fit between the observed and theoretical lattice plane separations, indicating that the $CaBeF_4$ crystals did not have uniaxial character.

Crude attempts were made, using the powder cameras, to obtain rotating single crystal patterns. Due to the lack of suitable orientation controls, and because of the restricted axial length of these cameras, only a few distorted layer lines were obtained. Use of the approximate unit translation values thus obtained (for three different orientations of the crystals) was found to furnish no help in determining the true axial ratio. Attempts were made using these values, and to a limited extent by trial and error, to index the crystal in the orthorhombic and monoclinic systems without success.

Using analogous structures, such as $CaSO_4$ (with which $CaBeF_4$ might be expected to be isomorphous) as a possible clue to axial ratios, additional trials were made but again no completely satisfactory indexing was possible. It was decided that proper indexing would only be possible by the use of suitable single crystal cameras which were not available.

The X-ray examination is thus at odds with the optical microscopic results in that it is indicated that the $CaBeF_4$ structure is not uniaxial. It is worthy of note that the structure of $CaSO_4$ is also in some doubt, as it does not entirely fit the rhombohedral system according to some investigators. It would be expected from the studies of Ray on the isomorphism of $BeF_4^{=}$ and $SO_4^{=}$ that these compounds should be quite similar. The interplanar spacings from powder diffraction patterns are not very identical, but here scattering ability plays a large part so that comparable sizes would not necessarily mean identical X-ray behaviour.

The analytical results for several of the wet preparations are tabulated briefly below. For other details see Appendix 15, Part H.

Date of Analysis	$CaBeF_4$ Prep.	Sample Wt., g.	Wt. BeO, g.	Wt. % BeO	Vol. $KMnO_4$, ml.	Wt. % CaF_2	Molal Ratio, CaF_2/BeF_2
5/29/50	"A"	0.4000	0.0455	21.4	133.3	67.3	1.89
"	"D"	0.3950	0.0647	30.8	123.0	62.9	1.23
"	"F"	0.4000	0.0692	32.5	119.25	60.2	1.12

Data on the X-ray powder diffraction patterns of $CaBeF_4$ and $CaSO_4$ are given below. The material used for the former was a crushed sample of material (containing a little CaF_2) removed from Melt J of the CaF_2-BeF_2 system. The latter was obtained from a residue of one of the salvage operations which was found to be $CaSO_4$. The Hanawalt (63) values given for CaF_2 and $CaSO_4$ are also tabulated. Relative intensities are given by: VS, very strong; S, strong; M, medium; W, weak; VW, very weak; and D, diffuse. The lines marked with an asterisk in the $CaBeF_4$ column may be due in whole or in part to the presence of CaF_2 which interferes at these points, but it is believed that they are due to $CaBeF_4$ primarily. Additional lines were present in the back reflection region, but these were not measured in this case. The faint lines, known to be due to CaF_2, in the $CaBeF_4$ pattern are not tabulated.

The possibility of interference by CuK_β radiation was checked for the $CaBeF_4$ pattern and no indications are present that any of the listed lines are due to anything except CuK_α radiation.

While some apparent similarities may be noted from the coincidences of $CaSO_4$ and $CaBeF_4$ lines, it is believed that this is purely coincidence.

COMPARISON OF $CaBeF_4$ AND $CaSO_4$ X-RAY PATTERNS

Hanawalt CaF_2 Values, A°	$CaBeF_4$ Sample J, Film #9, A°	$CaSO_4$ Sample, Film #17, A°	Hanawalt $CaSO_4$ Values, A°
	Ca. 4.55 MD	3.72 VW	3.89
	3.41 VSD	3.47 VS	3.49 S
3.16 S		3.15 VW	3.11
		2.84 S	2.85 S
		2.79 VW	
	2.56 M	2.46 W	2.46
		2.32 S	2.32 S
	2.27 S	2.27 VW	2.26
		2.20 S	2.20 S
	2.14 S	2.17 VW	
		2.08 W	2.08
		1.99 W	1.99
1.93 S	1.93* M	1.93 W	1.93
	1.82 S	1.86 M	1.86
	1.76 S	1.74 W	1.74
	1.72 M		
1.65 S	1.68 VW	1.64 M	1.64
		1.59 VW	1.59
		1.56 VW	
		1.52 VW	1.52
	1.50 VW	1.49 W	1.487
	1.43 M	1.43 W	1.420
1.37	1.39 VW	1.40 W	1.395
			1.360
	1.35 M	1.32 W	1.318
	1.30 M	1.30 VW	1.296
	1.26* VW	1.29 W	1.275
1.256	1.25*?VW	1.23 VW	1.215
		1.22 VW	
	1.16 M	1.18 VW	1.197
	1.15 VW	1.12 M	1.103
	1.14 VW		
1.117	1.12* VW		
	1.10 VW		
	1.09 VW		

The general accuracy of measurement is to within 0.01A$^{\circ}$, except for the first two lines for $CaBeF_4$ which are so diffuse that 0.02 to 0.03A$^{\circ}$ error might be quite possible.

Examinations of other melt samples and the wet-synthesis products gave essentially the same values for the $CaBeF_4$ lines as those shown above.

APPENDIX 11

APPENDIX 11

LITHIUM FLUOBERYLLATE; RESULTS OF SYNTHESES OF MONOHYDRATED AND ANHYDROUS COMPOUNDS; X-RAY DATA

In part E of Appendix 15, the details of analysis and calculation are given for preparations of $Li_2BeF_4{:}1H_2O$ and Li_2BeF_4 obtained by a combination of wet and dry syntheses. The first product, Li_2BeF_4, prepared from analyzed $(NH_4)_2BeF_4$ and LiF by volatilization of NH_4F had an analysis of 33.4 mole percent BeF_2. This checked excellently with the calculated input of the reagents and with the weight of product obtained following volatilization.

This product was converted to the monohydrate by solution in water and vacuum evaporation. In the recovery operations the resulting product probably lost a little of the theoretical water of crystallization. The hydrated product had the following analysis.

Wt. Percent			Total	Mole Percent		
H_2O	LiF	BeF_2	Wt. Percent	H_2O	LiF	BeF_2
13.9	46.1	39.7	99.7	23.0	52.2	24.8

Despite the good analytical recovery, the values show more deviation from the theoretical values than would be expected from the probable error of about ± 0.5 mole percent. Slight dehydration of the product would explain most of the deviation.

After thorough dehydration (requiring more than 110°), the same sample had the following analysis calculated on the dry basis.

Wt. Percent		Total Wt. Percent	Mole Percent	
LiF	BeF_2		LiF	BeF_2
53.5	46.1	99.6	67.8	32.2

This result disagrees with the theoretical value by about 1.1 mole percent.

A similar result was obtained on analysis of Melt "d" of the LiF-BeF_2 system, which had been prepared from the same monohydrated product. This material, after use in one thermal analysis, had the composition 67.5 mole percent LiF and 32.5 mole percent BeF_2.

The solubility determined for the compound (See Appendix 15, Part E) was approximately 23 grams of Li_2BeF_4 per liter of water as determined by analysis of the mother liquor. This checked fairly well with an estimated solubility of 26 g./liter based on first appearance of permanent crystals during evaporation. These results are about double the value of 13.2 g./liter given by Ray (128).

In connection with the tabulation of the X-ray powder diffraction pattern for Li_2BeF_4 obtained in this work additional patterns are shown for results due to Thilo and Lehmann (166). These authors have presented evidence for the existence of the compound $LiBeF_3$. In the section discussing the results for the LiF-BeF_2 system this X-ray evidence was questioned. Their data is reproduced in conjunction with measurements made on Li_2BeF_4 (as obtained from melts during this work) and a sample of pure LiF. The latter is included for comparison since, in this work, at least traces of LiF tended to be present in the solid products although forbidden by a theoretically complete phase rule "reaction" process. For both LiF and

BeF_2 certain lines were found by experience to be present in melts of widely differing compositions, and these lines are identified accordingly.

The Thilo and Lehmann data covers three different samples, designated "a", "b" and "c". Their "a" sample was believed to be Li_2BeF_4. The "b" sample represented material from a normally cooled melt having the over-all composition of $LiBeF_3$. According to them such a melt would form Li_2BeF_4 instead of $LiBeF_3$ because special cooling technique was not used. The "c" sample was believed to be $LiBeF_3$, obtained by special cooling of a melt containing a slight excess of BeF_2 over the stoichiometric requirements.

The tabulated values are in terms of θ (called $\theta/2$ by Thilo and Lehmann) where θ is the Bragg angle. For convenience the values given for Film #33 of this work have been shown also in A° units.

The intensities are shown by the following abbreviations.

VS	very strong	VW	very weak
S	strong	VVW	very, very weak
M	medium	D	diffuse
W	weak	β	Cu K_β line

The samples of melts of the LiF-BeF_2 system, whose patterns are shown, had the following compositions.

Film #33; Melt B, containing approximately 8 mole percent BeF_2.

Film #76; Melt 3Q, containing approximately 32 mole percent BeF_2.

Film #52; Sample consisted of crushed Li_2BeF_4 single crystals dipped from Melt O (while cooling), composition of the melt approximately 48. mole percent BeF_2.

Film #32; LiF, reagent grade, powder.

COMPARISON OF X-RAY POWDER PATTERNS

Thilo and Lehmann Data			Results of this Work					
Sample "a" Li_2BeF_4	Sample "b" Composition $LiBeF_3$	Sample "c" "Compound" $LiBeF_3$	Film 33 Melt B	Film 76 Melt 3Q	Film 52 Sample O-c	Film 32 LiF	Film 33 Lattice Spacing in A° Units	Notes on Probable Identity of Lines in Columns 4-6.
Column 1	2	3	4	5	6	7	8	9
Units θ	θ	θ	θ	θ	θ	θ	A°	
			6.7 WD	6.7 D	6.6 D		6.7*	BeF_2
	10.6 W	10.3 S	10.7 W	10.68 M	10.67 W		4.11	Li_2BeF_4
11.6 W	11.6 W	11.5 VW	11.4 WD	11.44 SD	11.41 MD		3.86	Li_2BeF_4
12.6 VVW	12.6 VW							
13.4 S	13.1 S	13.1	13.38 M	13.40 S	13.36 S		3.33	Li_2BeF_4
	14.1 D	14.0 VVW			13.90 VW	14.12 VW	3.12	Li_2BeF_4?
			14.30 VW	14.24 W	14.37 VD			Li_2BeF_4
14.6 VVD			14.80 VW	14.85 VW	14.79 VW		3.02	Li_2BeF_4
	15.2 VVW	15.3 W			15.20 VW			Li_2BeF_4?
16.5 S	16.5 S	16.2 S	16.48 M	16.50 VW	16.45 M		2.72	Li_2BeF_4
						17.38 β VW		
17.9 W	17.9 W		17.82 W	17.81 M	17.82 W		2.52	Li_2BeF_4
	18.1 VW	18.3 S			18.16 VW			Li_2BeF_4?
19.2 VS	19.2 VS	19.2 VVW	19.15 M	19.11 VS	19.10 VS		2.35*	Li_2BeF_4
			19.32 VSD			19.38 VSD	2.33*	LiF
	20.0 VS	19.8 VS		19.80 VW	19.78 W			Li_2BeF_4
						20.15 β VW		
20.4 VS	20.8 VS	20.6 VS	20.28 S	20.28 VS	20.30 VS		2.22	Li_2BeF_4
21.0 VW	21.0 W				21.70 W			Li_2BeF_4
	22.0 W	21.9 VS			22.08 VWD			Li_2BeF_4?
22.4 VVD			22.42 VSD	22.45 VW		22.50 VSD	2.02*	LiF
		23.0 VW				23.40 VW		
23.7 S	23.7 S		23.62 W	23.65 W	23.63 W		1.92	Li_2BeF_4
24.7 S	24.7 S	24.9 W	24.62 W	24.68 W	24.65 VW		1.85	Li_2BeF_4
25.6 D	26.2 VD	26.4 VVW	25.62 VW	25.70 VW	25.6 VVW		1.78	Li_2BeF_4
				26.20 VW	26.3 VVW			Li_2BeF_4
27.1 VW	27.0 VW	27.1 S		26.85 VW	26.97 VVW			Li_2BeF_4
27.9 VVW	27.9 VVW			27.81 VW	27.81 VVW			Li_2BeF_4
28.6 S	28.6 S	28.4 W	28.48 W	28.50 M	28.48 W		1.62	Li_2BeF_4
			29.10 VW			29.20 VW	1.58*	LiF
				29.31 WD				LiF?

Continued next page

Comparison of X-ray Powder Patterns - Continued

Column 1		2		3		4		5		6		7		8	9
29.5	W	29.6	W	29.6	S	29.60	VW	29.65	W	29.51	VW			1.56	Li_2BeF_4
30.4	W	30.5	VW			30.22	VW	30.27	W	30.26	VW			1.53	Li_2BeF_4
31.3	W	31.3	W	31.2	VD	31.15	VW	31.21	W	31.15	VW			1.49	Li_2BeF_4
32.	VW							31.95	VW						Li_2BeF_4
		32.2	VW	32.5	S										
32.9	VVW					32.67	VS	32.75	VW			32.68	VSD	1.43*	LiF
		33.5	VVW	33.6	VVW										
34.6	S	34.7	S	34.5	VVW	34.51	W	34.54	M	34.57	W			1.36	Li_2BeF_4
		35.5	W	35.5	S					35.46	VW				Li_2BeF_4
36.2	S	36.2	S	36.4	VW	36.12	W	36.14	W	36.16	VW			1.32	Li_2BeF_4
37.1	S	37.1	W	37.3	VW	36.90	VW	36.94	W	36.95	W			1.29	Li_2BeF_4
								37.80	VVW						Li_2BeF_4
						38.55	VW	38.57	W	38.54	VW			1.25	Li_2BeF_4
38.6	S	39.5	W	39.5	W	39.27	M	39.32	W	39.31	VW	39.28	M	1.23*	LiF
				40.3	W										
						41.34	M					41.40	M	1.18*	LiF
41.8	W	41.8	W					41.70	VW	41.65	VVW				Li_2BeF_4
43.0	VVW	42.6	VW	43.2	VD										
44.1	W	44.0	VW					Other Lines Not Measured							
				44.3	VW										
45.6	VVW	45.6	VVW	45.4	VVW										
46.5	W	46.5	VW							46.48	VVW				Li_2BeF_4
		47.6	VW	47.2	W										
				47.9	W					Other Lines Not Measured					
48.5															
				49.2	W										
49.5	W	49.7	VW			49.8	WD					49.75	W	1.01*	LiF
				50.6	VW										
51.0	W	50.0	VVD												
51.9	VW	51.9	VW												
52.5	W	52.7	VW												
53.3	W	53.5	W												
						56.3	W					56.25	W	*	LiF
						58.6	MD					58.55	M	*	LiF
						69.3	MD					69.25	M	*	LiF

In the tabulation, the horizontal relationship given by Thilo and Lehmann for the various lines has been preserved, although obviously unjustified in several cases. In still more cases a realistic appraisal of their measuring accuracy, as judged from the internal consistency of the data, would indicate no significant differences between some values shown at different levels in Columns 1, 2 and 3. It is assumed that by so differentiating the values these workers claimed that they belonged to different compounds.

The results of this work, shown in Columns 4, 5, 6 and 7 appear to be internally consistent to at least $\pm 0.03^\circ$, except for very weak or diffuse lines where measurement becomes more difficult. From other evidence obtained during camera calibration, a general accuracy of $\pm$ 1 part per 1000 was found under favorable conditions. The camera size (twice the diameter used by the other workers) made more accurate measurement possible, but correspondingly lowered line intensities. As a consequence some lines were obtained by Thilo and Lehmann which were not observed in this work on 3 hour exposures at 35KV and 15ma with nickel filtered Cu K_α radiation.

A thorough inspection of the comparative data will indicate at most only two or three lines present in the "$LiBeF_3$" pattern which may not be reasonably attributed to Li_2BeF_4. The fact that the balance of the lines show good or fairly good matches with Li_2BeF_4 lines is strong evidence for concluding that the patterns were formed by the same compound.

In Column (8), the values of lattice plane spacings for Film 33 have been given in A° units. Those values believed to be due to LiF, or BeF_2, rather than Li_2BeF_4 have been marked with an asterisk.

The values given for the results of this work are uncorrected values since calibration indicated no significant correction (for film shrinkage and camera diameter) was necessary. The center-to-center measurements, made independently on patterns of melt samples show no significant difference in the Li_2BeF_4 product produced under a wide range of conditions. This range extended over melts from 8 to 48 mole percent BeF_2. None of these melts should have produced "$LiBeF_3$", according to the claim of Thilo and Lehmann, yet the similarity to their results (Column 3) makes it unlikely that there is any real difference in the samples.

APPENDIX 12

APPENDIX 12

RESULTS OF THERMAL ANALYSES OF CaF_2-LiF-BeF_2 SYSTEM

The order of arrangement of the tabulation is an alphabetical sequence in which all samples having a capital letter in their prefix have been placed ahead of all those identified by a lower case letter prefix.

The tabulation lists composition values and thermal results. Almost all composition values are based on the calculated starting compositions of the parent member of each series. This value was either based on the weights of BeF_2, LiF, and CaF_2 used, or on the weight of the melt after the evolution of NH_4F was accomplished in cases where $(NH_4)_2BeF_4$ was used. The A to K melts were corrected in composition by a compromise between the analyses and calculated compositions as the latter were not accurately known.

In order to permit condensation, the mole percent of LiF (obtainable by difference from 100) has been omitted. Except for the Q series and the e, g and t series, CaF_2 was the additive substance used to shift the composition in all other cases.

In cases where more than two inflections occurred the third inflection has usually been placed in the following line under the second inflection, or has been otherwise noted.

Where the column shows a dash it is indicated that the melt was not cooled to the level at which the expected process would have occurred.

Abbreviations

In column 4, the abbreviations used to signify deposition of $CaBeF_4$ and Li_2BeF_4 are CB and LB respectively.

In columns 5 and 9, X signifies visual detection of first or second crystallization. T signifies thermal detection. With respect to the type of inflections the following were used: S, sharp; G, good or definite; F, fair or less definite, P, poor or indefinite; VP, very poor or barely sufficient for recognition. D signifies detection by dipping sample from melt. M signifies that melt only thickened with no definite liquidus point.

In column 8, the shapes of plateaus are indicated by:

Long flat -- flat or very slightly sloping, within the temperature range shown, for about 20-25 minutes, followed by abrupt drop in temperature.

Flat -- same as above, except about 10-20 minutes.

Long sloping -- same as above, but with a decrease of about 5 to 7 degrees during a period of about 20-25 minutes, about two thirds of drop occurring in last 10 minutes.

Flat sloping -- flat plateau of about 10-15 minute duration followed by smooth transition to a resumption of the original slope.

Sloping -- plateau with gradual slope of about 1°/min. followed by smooth transition to more rapidly cooling section.

Short sloping -- short plateau of about 5 minutes or less duration followed by smooth transition.

Short -- same as above except with more abrupt transition to more rapidly cooling section.

In column 9, "crust" signifies unusual type of solidification mentioned in text. "Abrupt" signifies unusually sharp drop in temperature at end of a plateau.

Where an asterisk is used the value may be either approximate or uncertain.

In column 10, the temperatures of disappearance of last apparent liquid or appearance of first liquid (during cooling or heating) are indicated by C or H. CH is used if the two temperatures were nearly the same. These temperatures are very approximate, although they should be comparable with one another.

Large inflections after heating through an invariant point are indicated by "Jump-".

Melt	Composition, Mole Percent		1st. Cryst. or Inflection,			Plateau (or 2nd. Inflection),			Comments	Apparent Liquid
	BeF_2	CaF_2	Type	Obsv.	Temp.	Type	Temp.	Shape		
1	2	3	4	5	6	7	8	9	10	11
A-1	3.2	3.9	LiF	TS	814	CaF_2	720	TF		
-2	3.1	7.8	"	"	799	"	742	TF		
-3	2.9	11.7	"	"	785	"	751	TS		
-4	2.8	15.7	"	"	771	"	*755	"		
-5	2.7	17.6	LiF?	TF	763	"	755	"		
-6	2.7	19.2	CaF_2?	TP	*780	LiF	756	"		
-7	2.6	20.7	CaF_2	"	791	"	756	"		
-8	2.6	22.0	"	"	786	"	758	"		
B-1	7.6	3.7	LiF	TS	796	CaF_2	672	TF		
-2	7.2	7.8	"	"	780	"	715	TS		
-3	6.9	12.0	"	"	762	"	735	TG		
-4	6.6	15.8	"	TG	749	"	745	"		
-5	6.4	20.0	CaF_2?	TP	780	LiF?	754	"		
-6	6.0	23.8	CaF_2	"	815	LiF	753	TS		
-6	6.0	23.8	"	XTP	812	"	751	"		
-7	5.8	26.6	"	"	860	"	751	"		
C-1	11.4	3.8	LiF	XTG	769	--	--			
-2	10.9	7.6	"	XTS	754	CaF_2	687	TG		
-3	10.5	11.2	"	TF	748	"	712	TS	Shows 440° plateau	
-4	10.1	14.5	"	XTG	742	"	721-5	TG		
-5	9.8	17.4	CaF_2?	XTF	747	LiF?	729	TS		
-6	9.6	19.0	CaF_2	TP	755	LiF	737	"		
-7	9.3	20.8	"	"	783	"	736	"		
D-1	13.1	4.8	LiF	XTF	751	--	--	--		
-2	12.6	8.7	"	XTG	735	CaF_2	692	TP	Shows 437° plateau	
-3	12.3	11.8	"	XTF	733	"	713	TF		
-4	11.8	15.4	CaF_2?	TP	*750	LiF	724	TS		
-5	11.4	18.5	CaF_2	"	*750	"	726	"	Shows 437° plateau	
-6	11.0	21.4	"	"	*780	"	729	"		
-7	10.9	22.4	"	XTP	*800	"	735	"	Shows 447° plateau	

Continued next page

1	2	3	4	5	6	7	8	9	10	11
E-1	17.9	5.1	LiF	XTG	702	CaF_2	*670	TF		
-2	17.0	9.5	"	"	695	"	670	"		
-3	16.8	10.9	LiF?	"	694		None		Only one inflection	
-4	16.5	12.2	CaF_2?	TP	*750	LiF	694	TS		
-4	16.5	12.2	"	"	*740	"	709	TG		
-5	16.2	13.6	"	"	*732	"	713	TS		
F-1	*20.9	*5.0	LiF	TS	695	--	--			
-1	*20.9	*5.0	"	XTG	693		620?	--		
-2	*20.1	*8.7	"	XTF	687		650?	--		
-3	*19.5	*11.3	CaF_2?	X	690	LiF?	678	TS		
-4	*18.9	*14.1	CaF_2?	XTP	740	"	680	TG		
FF-1	22.4	2.6	LiF	XTP	*665	LB	439-2	Short sloping		
-2	21.9	5.1	"	"	664	--	--			
-3	21.1	8.4	LiF?	XTF	658	--	--			
-4	20.4	11.5	CaF_2?	TP	*705	LiF	668	XTF		
-5	19.8	14.0	CaF_2	XTP	752	"	671	XTG		
G-1	23.5	3.1	LiF	XTP	*649	--	--			
-2	22.8	6.0	"	"	649	--	--			
-3	22.2	8.8	"	XTF	650	--	--			
-4	21.5	11.5	--	--	--	LiF	650	TG		
-4	21.5	11.5	CaF_2	XTG	688	"	650	"		
-5	20.9	14.0	"	XTP	*740	"	652	"		
-6	20.3	16.4	"	XTG	*800	"	*654	TP		
H-1	26.1	3.1	LiF	X	595	--	--		Inflect. 606 also	
-2	25.3	6.0	"	X	597			Inflect.441-450	" " "	
-3	24.6	8.8	LiF?	XTG	617	LB	439	Sloping	" " "	
-4	23.9	11.4	CaF_2?	X	*658	LiF?	606	"		
						LB	439	Sloping		
-4	23.9	11.4	CaF_2	TF	*695	LiF	*619		Took avg. 675°	
-5	23.2	14.0	"	"	*733	LiF	618	TG		

Continued next page

1	2	3	4	5	6	7	8	9	10	11
I-1	31.4	1.6	LiF	X	496	LB	456	Long sloping		<440 C
-2	31.0	3.2	"	X	496	"	443	" "	Jump 452H	
-3	30.2	6.1	CaF_2?	X	516	"	440	Long flat		
-4	29.5	9.0	CaF_2	X	542	"	440	" "	Jump 450H	
-5	28.9	11.4	"	X	625	"	440	" "		
J-1	32.5	2.8	LiF	X	469?	LB	444-30	Long sloping	Jump 450H	
-2	31.6	5.5	CaF_2?	X	490	LB	438-30	" "		437 H
						CB	*490	D	Needles dipped 490H	
-3	30.6	8.1	CaF_2	X	510	CB	500	D		
						LB	440	Long flat		
-4	29.7	10.5	**CaF_2**	X	550	LB	440	Flat sloping	Jump 450H	
-5	29.0	12.9	?	X	*570	"	442	" "		
-5	29.0	12.9	CaF_2	TG	*688	--	--			
K-1	32.2	3.2	LiF?	XTP	497	LB	446	Long sloping		
-2	31.2	6.2	?	X	*500	"	440	Long flat		
-3	30.1	9.8	CaF_2	X	>490	"	441	Flat	Jump 442H	
-4	29.0	11.9	"	XTP	560	"	441	"		
-5	28.1	15.7	"	XTP	683	--	--			
L-1	34.5	3.8	--	--	--	LB	441	Long, flat	Erratic results	
-2	33.2	7.4	CaF_2	X	*540	"	440	" "		
-3	32.0	10.7	"	XTG	608	"	444	Flat		
-4	31.1	13.3	"	XTP	688	--	--			
-5	30.2	15.7	"	XTG	725	--	--			
LL-1	37.9	0.13	LB	XTS	446	CB	446	Long sloping		
-2	37.8	0.18	"	X	450	"	446	" "		
-3	37.7	0.64	"	X	448	"	445	" "		
-4	37.6	0.9	"	X	447	"	445			<420
-5	37.6	1.1	"	X	448	"	445	Short sloping		
-6	37.5	1.4	"	X	447	"	446	Flat sloping		<425
-7	37.3	1.8	"	X	447	"	445	" "		
-8	37.0	2.5	"	X	447	"	445	Long flat		
-9	36.8	3.1	--	--	--	LB	447	" "		
-10	36.5	3.8	--	--	--	"	448	" "		
-11	36.3	4.4	CB	D	482	"	448	" "	Very flat	440 C
-11	36.3	4.4	CB	D	475?	--	--			
-12	36.1	4.8	CB	D	512	LB	449	Long flat		
-13	36.0	5.1	CB	D	>472	LB	448			
-14	35.8	5.4	CaF_2	X	*500	CB	>460			

Continued next page

1	2	3	4	5	6	7	8	9	10	11
M-1	38.9	2.8	--	--	--	LB	438	Flat sloping	Plateau 325C	400 C
-2	37.6	6.2	CB	D	> 530	"	444	" "		*440 CH
-3	36.6	8.9	CB	DTP	> 550	CaF_2?	505	X		
						LB	444	Long flat		441C 430H
-3	36.6	8.9	CB	D	550	--	--	--		
-4	35.6	10.8	CaF_2	X	> 520	CB	500	D	Erratic dip.	435 H
MM-1	41.9	0.18	LB	XTS	424	--	--		No 2nd infl.	
						BeF_2	343	Flat sloping		358 H
-2	41.8	0.36	LB	X	431	CB?	426	" "		
-3	41.7	0.54	"	X	433	CB?	427	" "		
-4	41.6	0.78	"	X	432	CB	428	Short sloping		
-5	41.5	1.0	"	X	433	"	430	" "		
-6	41.4	1.4	"	X	432	"	430	Sloping		
-7	41.2	1.8	"	X	435	"	432	"		
-8	41.1	2.1	CB?	X	> 439	LB	434	XTS Sloping		
-9	40.9	2.5	--	--	--	"	438	XTS Flat		
-10	40.7	3.0	CB	D	515	"	440	XTS Flat		
-10	40.7	3.0	"	D	500	--	--			
-11	40.6	3.3	CB?	D	< 500	LB	442	XTS Flat		
-12	40.5	3.7	CB	D	520	"	444	XTS Flat sloping		420C 410H
-13	40.2	4.1	"	D	*560	"	447	XTS Flat		
-14	40.1	4.4	"	D	*590	"	448	XTS Flat		
N-1	43.4	3.5	CB	D	< 550H	"	420	Short sloping		333 C
-2	41.6	7.5	"	D	615	"	439	" "		390C 370H
-2	41.6	7.5	"	D	605-10	--	--			
-3	40.1	10.6	"	D	*610	LB	442	Short sloping	Jump 448H	440C 430H
-3	40.1	10.6	"	D	625	--	--			
-4	38.5	14.5	CaF_2	X	660	CB	*640	D		
			CaF_2?	TF	670	LB	420	Long sloping	Jump 440H	430 H
O-1	47.8	0.7	LB	XTF	391	BeF_2	347	Long flat		345?H
-2	47.4	1.4	--	--	--	LB	388	XTG		
						BeF_2	346	Long flat	Jump 357H	*350 H
-3	46.9	2.3	CB	X	> 425	LB	391	XTS		
						BeF_2	347	Long flat		
-4	46.4	3.7	CB	D	600	LB	404	XTS		
						BeF_2	345	Flat		

Continued next page

1	2	3	4	5	6	7	8	9	10	11
P-1	50.6	0.6	LB	DTS	363	BeF_2	353	Long flat	No 2nd inflect.	
-2	50.0	1.8	CB?	X	>430	LB	364	DTS		
						BeF_2	349	Long flat	Jump 358H	
-3	49.6	2.6	CB	D	540	LB	369	DTS		
						BeF_2	350	Long flat		
			--	--	--	--	--	Repeat, erratic results on dip of CB		
-4	49.1	3.5	CB	D	<520	LB	381	DTS		
						BeF_2	353	Flat sloping		
-5	48.6	4.7	CB	D	*600	LB	392	DTS		
1Q-1	32.6	0.2	LiF	X	485	LB	455	Long flat, abrupt	Jump 457-460H	452 C
-2	32.7	0.3	"	X	484	"	455	" "		
-3	32.8	0.6	"	X	482	"	454	--		
-4	32.9	0.8	"	X	>468	"	452-47	Flat sloping		
-5	33.0	1.0	"	X	479	"	452-39	" "		440 CH
-6	33.0	1.4	"	X	476	"	451-36	" "		440 CH
-7	33.2	1.7	"	X	483	"	449-44	" "		446 H
-8	33.5	2.4	"	X	481	"	457	X		
						CaF_2?	448-40	Flat	Abrupt drop	444 CH
2Q-1	33.5	0.1	LB	XTS	456			Long flat		450 C
-2	33.2	0.2	LiF	X	463	LB	455	" "		
-3	33.1	0.4	"	X	470	LB	456-52	" "	Jump 457H	452C 448H
-4	32.6	0.7	"	X	482	LB	455-47	Flat sloping		442 H
-5	32.1	1.0	"	X	496	LB	454-45	" "	Jump 456H	450C 444H
-6	31.7	1.3	"	X	499	LB	452-41	" "	Jump *450H	445 CH
-7	31.0	1.7	"	X	510	LB	450-42	" "		436 H
3Q-1	30.8	0.2	LiF	X	493	LB	455	Long flat	Jump 458H	452C 447H
-2	30.9	0.5	"	X	499	"	455	" "		452C
-3	31.0	0.95	"	X	506	"	454	" "	Abrupt drop	438C 440H
-4	31.2	1.3	"	X	501	"	452	" "	Crust formed	446C 444H
-5	31.5	2.1	"	X	496	"	449	" ", flatter	" "	445H
-6	31.8	2.8	LiF?	X	489	"	446	Very flat, long	" "	445H
4Q-1	35.8	0.3	LB	XTS	452	--	--	Flat sloping		<400C
-2	35.4	0.5	"	XTS	453	--	--	" "		400C 410H
-3	34.5	1.1	"	XTS	453	--	--	" "		438 CH
-4	33.6	1.6	"	XTS	452	--	--	Long flat	Jump 451H	441C 437H
-5	32.8	2.1	LiF	X	453	LB	451	" "	Crust formed	444H
-6	32.0	2.6	LiF?	X	469	"	447	" ", flatter	" "	444H
-7	31.2	3.1	CaF_2?	X	488	"	447	Very flat, long	" "	443H

Note - No 5Q series, converted to 7Q.

Continued next page

1	2	3	4	5	6	7	8	9	10	11
6Q-1	34.2	0.2	LB	XTS	455			Long flat	No lower inflect.	440 H
-2	33.7	0.5	"	XTS	454			" "	Jump 455H	
-3	33.2	0.9	"	XTS	453			" "		443 H
-4	32.7	1.2	LiF	X	460	LB	454	" "	Crust formed	438 H
-5	32.1	1.6	"	X	474	"	454	" "	" "	438 H
-6	31.5	1.9	"	X	486	"	452	Long sloping	" "	
-7	30.8	2.4	"	X	497	"	451	Long flat	" "	445 H
-8	29.8	3.0	"	X	505	"	449	Flatter	" "	445 H
-9	28.8	3.7	"	X	536	"	450	Very flat,long	" "	445 H
7Q-1	31.2	0.2	"	X	490	"	455	Long flat		442 H
-2	31.4	0.6	"	X	490	"	454	" "	Crust formed	442 H
-3	31.5	0.9	"	X	488	"	453	" "	" "	449C 444H
-4	31.7	1.2	"	X	486	"	452	" "	Less crust	441H
-5	31.8	1.7	"	X	478	"	450	Long sloping	No crust	438H
-6	32.0	2.1	LiF	X	475	LB	449	Long sloping	Crust formed	445C 444H
-7	32.1	2.4	"	X	479	"	448	" "	" "	433H
-8	32.2	2.7	LiF?	X	478	"	447	" "	Crust,Jump 451H	438H
-9	32.4	3.3	CaF_2	X	482	"	449	Very flat	Crust,Jump 456H	444H
-10	32.7	4.2	"	X	502	"	448	" "	" " 456H	444H
									Shows no lower inflect.	
8Q-1	32.0	0.2	LiF	X	468	LB	456	Very flat		448H
-2	32.1	0.4	"	X	470	"	455	Long flat		
-3	32.2	0.7	"	X	468	"	455	" "	More slope	440H
-4	32.3	1.2	"	X	465	"	453	" "	More slope	437H
-5	32.5	1.8	"	X	463	"	453	" "	Abrupt drop	
-6	32.7	2.5	"	X	460	"	451	" "	Very abrupt	447H
-7	33.0	3.2	CaF_2	?	455	"	449	Very flat		
-8	33.2	3.9	"	X	482	"	448	" "	Crust formed	437H
-9	33.4	4.6	"	X	498	"	448	" "	" "	433H
9Q-1	33.1	0.5	LB	XTS	456	"	456	Long flat		438H
-2	32.7	0.8	"	XTS	455	"	455	Long sloping		436H
-3	32.3	1.0	LiF	X	463	"	454	" "		440H
-4	31.9	1.2	"	X	473	"	453	" "		437H
-5	31.6	1.4	"	X	480	"	452	" "		440H
-6	31.0	1.8	"	X	490	"	451	Long flat		440H
-7	29.9	2.5	"	X	517	"	449	" "		439H

Continued next page

1	2	3	4	5	6	7	8	9	10	11
10Q-1	32.5	0.2	LiF	X	458	LB	455	Long flat		447H
-2	32.6	0.5	"	X	457	"	455	" "		440H
-3	32.7	0.9	"	X	455	"	453	Long sloping		440H
-4	32.8	1.3	"	X	456	"	453	" "	Abrupt drop	
-5	33.0	1.8	"	X	455	"	451	" "	" "	440H
-6	33.2	2.3	"	X	453	"	449	Long flat	" "	438H
-7	33.4	3.0	--	--		"	451	Long sloping	Crust,abrupt	440H
-8	33.7	3.7	CaF_2	X	473	LB	455	X		
						CB	449	Long sloping	Crust formed	435H
-9	34.0	4.4	CaF_2	X	498	LB	453	X		
						CB	448	Very flat	Crust formed	440H
-10	34.2	5.1	CaF_2	X	497	LB	448	" "	Abrupt drop	432H
-11	34.5	5.8	"	X	510	"	447	" "	" "	
11Q-1	33.7	1.0	LB	XTS	453			Long sloping		<433H
-2	33.3	1.2	"	XTS	453			Long flat		440H
-3	32.9	1.5	"	XTS	453			Long sloping	Abrupt drop	440H
-4	32.5	1.7	LiF	X	463	LB	452	" "	" "	445H
-5	32.0	2.0	"	X	472	"	450	" "	Very abrupt	441H
-6	31.6	2.2	"	X	483	"	449	Very flat	" "	445H
-7	31.2	2.5	"	X	495	"	448	Long sloping	Abrupt drop	
-8	30.8	2.8	"	X	505	"	448	Long flat	Jump 452H	
12Q-1	33.4	0.2	LB	XTS	457			Long sloping		437H
-2	33.4	0.4	"	XTS	457			" "		437H
-3	33.6	0.8	"	XTS	456			" "		430H
-4	33.7	1.1	"	XTS	455			" "		436H
-5	33.9	1.8	"	XTS	452			" "		440H
-6	34.2	2.7	"	XTS	449			" "		
-7	34.5	3.9	CaF_2	X	466	LB?	449	Long flat	Crust formed	410H
-8	34.7	4.5	"	X	477	CB?	449	Long sloping	" "	<378H
-9	34.9	5.2	"	X	474	"	449	More slope	" "	<378H
-10	35.1	5.9	"	X	494	"	449	" "	Jump 453H	400?H
-11	35.3	6.6	"	X	511	"	450	" "		430H

Continued next page

1	2	3	4	5	6	7	8	9	10	11
13Q-1	33.6	0.3	LB	XTS	457			Long sloping		440H
-2	33.7	0.7	"	XTS	456			More slope		
-3	33.9	1.4	"	XTS	453			" "		440H
-4	34.2	2.1	"	XTS	453			" "		440H
-5	34.3	2.5	"	XTS	445			Flatter		< 430H
-6	34.4	2.9	"	XTS	444			"	Crust formed	< 400HC
-7	34.6	3.3	CaF_2	X	447	?	445	Long flat	" "	< 420H
-8	34.7	3.7	"	X	458	"	445	" "	" "	< 400CH
-9	34.8	4.1	"	X	455	"	445	" "	" "	
-10	34.9	4.4	"	X	458	"	445	" "	" "	< 400CH
-11	35.1	4.7	"	X	464	"	446	" "	" "	< 400CH
-12	35.2	5.1	"	X	470	"	447	" "	" "	
-13	35.3	5.6	"	X	472	"	447	" "	" "	
-14	35.6	6.3	"	X	466	CB?	449	D		< 400CH
						LB	447	Long flat	" "	
-15	35.8	7.0	"	X	473	CB	453	D		
						LB	447	Long sloping	" "	
-16	36.0	7.7	"	X	484	CB	454	D		
						LB	447	Long sloping	More slope	

Note -- R series was entirely in $LiF-BeF_2$ system.

1	2	3	4	5	6	7	8	9	10	11
1S-1	31.2	6.3	CaF_2	X	502	LB	451	Flat sloping	Crust formed	444C
-2	29.2	12.5	"	X	583	"	450	Short sloping		
-3	27.0	18.8	"	X	705	"	449	" "		
-4	25.0	25.0	"	X	776	--	--			
-5	27.9	27.9	"	X	803	LB?	446	Short sloping		($CaBeF_4$ added)
-6	30.7	30.7	"	X	810	CB	600	TSX		(" ")
-6	30.7	30.7	--	--	--	"	590	TS		
-6	30.7	30.7	--	--	--	"	604	D	No inflection	

Note -- There was no T series in ternary system.
The composition of U is uncertain (may be approx. 10% less BeF_2 than shown).
All the initial melts of the U to ZZ series show only a gradual thickening rather than an inflection. (Indicated by M).

Continued next page

1	2	3	4	5	6	7	8	9	10	11
U-1	54.0	1.9	BeF$_2$	M	412	LB	355	Long sloping	Ternary eutectic	Jump 417H
-2	52.7	4.2	?	X	460	?	411	Sloping		
-3	51.2	7.0	CB?	X	506	?	422	"		
-4	49.4	10.3	CB	XD	602	LB?	442	Grad. sloping		Inflect.448H
-5	47.0	14.6	CB	XTG	640	--	--			
-6	43.4	21.1	CaF$_2$	X	697	CB	648	XTP		
-7	39.2	28.7	"	X	765	--	--		Infl. 460H	
-8	35.4	35.7	"	X	885	CB	648	X		
V-1	57.8	3.7	BeF$_2$	M	600	LB	353	Long sloping	Ternary eutectic	
-2	55.7	7.1	CB?	TP	615	LB	345	" "	" "	
-3	53.4	11.0	CB	TG	641	--	--	No inflect. at 450.		
-4	50.9	15.2	"	XTS	676	--	--			
-5	47.3	21.2	"	XTS	706	LB	432	TF	Reheating inflect. at 360 and 432	
-6	43.7	27.1	CaF$_2$	X	727	CB	715	XTG		
-7	39.7	33.9	"	X	777	"	711	XTF		
-8	35.8	40.4	"	X	860	"	712	TF		
W-1	62.3	4.2	--	--	--	--	--	Inflect. 360 H		
-2	59.7	8.2	CB?	X?	600	--	--			
-2	57.2	12.0	CB	DTF	617	--	--			
-3	54.1	16.7	"	D	680	--	--			
-4	50.7	22.0	"	TF	700	--	--			
-5	48.6	25.3	"	TS	728	--	--			
-6	46.6	28.3	"	XTS	739	--	--			
-7	44.6	31.4	"	XTS	742	--	--	Inflect. about 450H.		
-8	44.6	31.4	CaF$_2$	X	763	CB	741	Sloping		
-9	41.0	37.0	"	X	805	"	735			
-10	37.4	42.5	"	X	880	"	734	Short		
						LB	446	Short flat		
X-1	63.5	9.3	--	--	--					
-2	60.7	13.3	CB	TG	663	--	--			
-3	56.9	18.7	"	TG	705	--	--	Supercooled	Inflect. 720H	
-4	52.5	25.0	"	TG	740			"	Inflect. 360H	
-5	48.0	31.5	"	TG	747				Inflect. 360H, none at 450.	
-6	44.8	36.0	"	TG	754	LB	445	Short sloping		
-7	41.4	40.8	CaF$_2$?	X?	800	CB	755	TG		
-7	41.4	40.8	CaF$_2$	X	808	"	754	TG	Inflect. 450H	
-8	38.5	45.0	"	X	850	"	754	TG		

Note -- There was no T series in ternary system.
The composition of U is uncertain (may be approx. 10% less BeF$_2$ than shown). All the initial melts of the U to ZZ series show only a gradual thickening rather than an inflection. (Indicated by M).

Continued next page

1	2	3	4	5	6	7	8	9	10	11
Y-1	72.7	9.1	CB?	TP	690	--	--		Definite solids by 650 C	
-2	66.6	16.8	CB	TG	702	--	--		Inflect 350H	
-3	61.4	23.3	"	TS	747	--	--			
-4	56.9	28.9	"	TS	772	--	--		Inflect. 344C	
-5	51.3	35.9	"	TS	786	--	--	Supercooled		
-6	46.7	41.6	"	TS	787	LB	444	Short sloping	Jump 456H	
-7	42.9	46.4	CaF_2	X	863	CB	787	TS		
Z-1	83.6	7.1	--	--	--					
-2	78.0	13.3	CB?	TP	700	--	--		Inflect. 700H also.	
-3	73.1	18.8	CB	TF	720	--	--			
-3	73.1	18.8	"	TG	760	--	--			
-4	68.8	23.5	"	TS	746	--	--		Inflect. 760H	
-5	63.8	29.1	"	TS	772	--	--		Inflect. 790H	<425C
-6	59.5	33.9	"	TS	793	--	--	Supercooled	Inflect. 798H	
-7	55.7	38.1	"	TS	802	--	--	"	Inflect. 806H	
-8	50.9	43.5	CaF_2	?	?	CB	800	Short sloping		
-9	46.8	48.0	CaF_2	X	872	"	799	" "	No inflect. at 450 or 360CH.	
ZZ-1	85.1	10.9	--	--	--					
-2	77.8	18.5	CB?	TP	*720	--	--			
-3	70.8	25.9	CB	TG	758	--	--	Supercooled		
-4	64.1	32.9	"	TS	789	--	--	"		
-5	61.2	35.9	"	TS	801	--	--	"	Inflect.*350H	
-6	58.6	38.6	"	XTS	810	--	--	No supercooling		
-7	56.2	41.1	"	XTS	815	--	--	" "		
-8	53.5	44.0	"	XTS	815	--	--	Slight supercooling		
-9	52.0	45.6	CaF_2?	X	811	CB	811	X Sloping	Observed both at once.	
-10	50.3	47.3	CaF_2	X	856	"	810	XTS		
-11	48.5	49.2	"	X	895	"	809	XTS	No inflect. at 450 or 350C	
								Possible slight inflect.at 460 and 360H.		

Continued next page

1	2	3	4	5	6	7	8	9	10	11
	Note the melts marked "e-" actually were two series prepared from the same master batch. Sequence indicated below.									
e-1	31.3	3.5	LiF	X	504	LB	453	Long sloping	Crust formed	440H
e-3	30.7	3.4	"	X	525	"	454	" "	" "	(LiF added)
e-4	29.8	3.3	"	X	543	"	450	" "		(" ")
e-5	28.7	3.2	"	X	575	"	449	Long flat		(" ")
e-6	27.4	3.1	"	X	604	--	--			(" ")
e-11	26.7	6.1	LiF?	X	603	--	--			(CaF_2 ")
e-12	25.7	9.5	CaF_2	X	618	--	--			(" ")
e-13	26.3	8.8	"	X	604	--	--			(Li_2BeF_4")
e-14	26.8	8.0	"	X	596	--	--			(" ")
e-19	27.2	7.5	"	X	594	--	--			(" ")
e-2	31.9	1.7	LiF	X	501	--	--			
e-7	31.3	1.7	"	X	519	--	--			(LiF added)
e-8	30.3	1.65	"	X	542	--	--			(" ")
e-9	29.1	1.60	"	X	570	--	--			(" ")
e-10	27.6	1.55	"	X	604	--	--			(" ")
e-15	26.5	5.6	"	X	600	--	--			(CaF_2 ")
e-16	25.9	7.5	CaF_2?	X	604	--	--			(" ")
e-17	26.5	6.8	"	X	602	--	--			(Li_2BeF_4")
e-18	27.2	6.3	LiF?	X	596	--	--			(" ")
e-20	27.6	5.6	LiF	X	592	--	--			(" ")
	Note -- The g- series was carried from near the $CaBeF_4$ point toward a composition point at about 49 mole percent BeF_2 (in the LiF-BeF_2 system).									
g-1	45.	52.	CaF_2	X	927	--	--			
-2	45.7	46.7	"	X	915	CB	795	TS		
-3	46.2	40.2	"	X	876	"	765	TS		
-4	46.5	34.0	"	X	825	"	743	TS		
-5	46.9	27.5	"	X	760	"	717	XTS		
-6	47.2	21.4	"	X	723	"	705	XTS		
						LB	452	Sloping plateau		
-7	47.3	18.1	CB	XTS	688	--	--			
-8	47.6	14.7	"	"	672	--	--			
-9	47.8	11.7	"	TG	653	LB	430	TF	Inflect. 430H	
						BeF_2	336	TF	Inflect. 360H	
-10	47.9	9.7	"	TF	633	LB	424	TF	Inflect. 428H	

Continued next page

1	2	3	4	5	6	7	8	9	10	11
g-11	48.0	7.8	CB	TF	610	--	--			
-12	48.1	6.1	"	TF	589	LB	411	Sloping plateau		
-13	48.2	4.6	"	TP	550	LB	404	" "	Inflect. 360H	
-14	48.2	3.5	"	TP	521	LB	407	" "	Inflect. 400H	
						BeF_2	338	Ternary eutectic	Inflect. 360H	

Note - The "t-" series of melts were handled specially as noted below.

t-1	30.9	6.9	CaF_2	X	475	LB	455	Long sloping	Crust formed	
-2	30.2	6.8	"	X	500	"	453	" "	" "	(LiF added)
-3	29.1	6.5	"	X	534	--	--			(" ")
-4	27.8	6.2	CaF_2?	X	561	--	--			(" ")
-5	26.6	5.9	"	X	592	--	--			(" ")
-6	26.0	8.1	CaF_2	X	619	LB	451	Long sloping	Crust formed	(CaF_2 ")

APPENDIX 13

APPENDIX 13

QUALITATIVE X-RAY DATA FOR TERNARY SYSTEM SAMPLES

X-ray diffraction patterns were obtained for numerous samples as a means of detecting the compounds present as separate phases in the solidified melts. The results obtained on binary system samples are not discussed here as the only noteworthy result, an indication of incompleteness of the Li_2BeF_4 peritectic reaction, is illustrated by the data in Appendix 11. This same tendency for some incompleteness of peritectic reactions extended into the ternary system and somewhat complicated the interpretation of results. Thus occasionally four solid phases were detected in the solidified melt where the Phase Rule forbids more than three coexistent solid phases under non-isothermal conditions.

An additional difficulty is that BeF_2 is detectable by only one effect, a diffuse halo at a low value of the Bragg angle, no lines being attributable to this amorphous form. Occasionally this halo was too indistinct for positive detection and its presence had to be inferred on the basis of stoichiometric necessity. Thus a melt containing only a very small percentage of CaF_2 might not show a pattern for either CaF_2 or $CaBeF_4$ and the presence of one or the other might have to be inferred until on succeeding melts the concentrations had been increased to detectable levels. Another example of such a situation might be one in which the added LiF and CaF_2 were insufficient to combine with the BeF_2 present, so that its presence would be necessary, even though not detectable.

Both CaF_2 and LiF exhibit only a few X-ray lines, due to their cubic structure, and these lines do not interfere seriously with each other. On the other hand, $CaBeF_4$ and Li_2BeF_4 have quite complex X-ray patterns and much overlapping of the lines occur. Fortunately, however, at least one fairly intense line exists for each of the four compounds at locations free of interference. It was therefore fairly simple to detect the presence, or apparent absence, of particular phases by merely matching the patterns visually with other X-ray patterns. Naturally the method cannot prove the absence of very small amounts of a particular phase in such a routine way, but the sensitivity in this case is probably better than 5% and possibly as good as 2%. This unusually high sensitivity is apparently due to the low atomic numbers of the elements involved. This sensitivity may be illustrated by the large number of lines given for Li_2BeF_4, Film 33 in Appendix 11, where the actual Li_2BeF_4 content was approximately 25% of the whole. Practically the same results were obtainable when this value was reduced to 10%, i.e. for melts containing about 97% LiF and 3% BeF_2.

The results have been tabulated only for a region of particular interest, i.e. in the Li_2BeF_4-rich portion of the ternary system. It is understood that outside of this region the X-ray examinations showed only those phases which would be expected from the nature of the system, except for faint traces of components present because of incomplete phase reactions.

The first tabulation shows the rough estimates of the amounts of components present, in all cases Li_2BeF_4 being the most prominent phase. All these samples showed at least traces of BeF_2, an effect which was noted after the addition of only a few percent of BeF_2 to any melt. Consequently the presence of BeF_2 is only mentioned where the increased intensity warranted the notation.

The second tabulation groups the results of the first into one of three major combinations. It will be noted that five results show the presence of a "forbidden" component. The choice of which component was the "forbidden" one was based on relative intensities of the X-ray patterns. These combinations of phases are as follows:

(1) $LiF + Li_2BeF_4 + CaF_2$.

(2) $Li_2BeF_4 + CaF_2 + CaBeF_4$.

(3) $Li_2BeF_4 + CaBeF_4 + BeF_2$.

TABLE 1

ESTIMATED RELATIVE AMOUNTS OF PHASES

Note -- All samples show the presence of some BeF_2

Sample	Phases Present
H-3	LiF, Li_2BeF_4, CaF_2, moderate.
K-2	LiF, slight. Li_2BeF_4, CaF_2, strong.
K-5	LiF, small. Li_2BeF_4, strong. CaF_2, moderate.
L-2	Li_2BeF_4, strong. CaF_2, small. ($CaBeF_4$ inferred). No LiF
L-5	LiF, small. Li_2BeF_4 strong. CaF_2 moderate.
LL-14a	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2, moderate.
LL-14e	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2, moderate.
M-1	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2, moderate.
M-2b	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2, moderate.
M-3b	Li_2BeF_4, $CaBeF_4$, strong. CaF_2, trace.
M-4	Li_2BeF_4, $CaBeF_4$, CaF_2, moderate.
MM-12a	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2 moderate.
MM-12c	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2 moderate.
MM-12d	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2 moderate.
MM-12f	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2 moderate.
N-3	Li_2BeF_4, strong. $CaBeF_4$, moderate. BeF_2, moderate.
N-4f	Li_2BeF_4, $CaBeF_4$ strong. CaF_2, present.
O-2b	Li_2BeF_4 moderate. $CaBeF_4$, trace. BeF_2, moderate.
1Q-4	LiF, slight. Li_2BeF_4, strong. CaF_2, small.
1Q-6	LiF, slight. Li_2BeF_4, strong. CaF_2, small.
1Q-8	LiF, trace. Li_2BeF_4, strong. $CaBeF_4$, slight. CaF_2, small.
2Q-3	LiF, slight. Li_2BeF_4, strong. CaF_2, small.
2Q-4	LiF, slight, Li_2BeF_4, strong, CaF_2, small, more than 2Q-3.
2Q-5	LiF, slight. Li_2BeF_4, strong. CaF_2, small, more than 2Q-4.
2Q-7	LiF, slight. Li_2BeF_4, strong. CaF_2 small, more than 2Q-5.
3Q-2	LiF, slight. Li_2BeF_4, strong. CaF_2, moderate.
3Q-4	LiF, slight. Li_2BeF_4, strong. CaF_2, moderate.
3Q-5	LiF, slight. Li_2BeF_4, strong. $CaBeF_4$, CaF_2, small.
3Q-6	LiF, slight. Li_2BeF_4, strong. $CaBeF_4$, CaF_2, small.
4Q-2	Li_2BeF_4, strong. ($CaBeF_4$, inferred). No CaF_2 or LiF. BeF_2, small.
4Q-3	Li_2BeF_4, strong. $CaBeF_4$, slight. BeF_2, small.
4Q-4	Li_2BeF_4, strong. $CaBeF_4$, CaF_2, small.
4Q-5	Li_2BeF_4, strong. $CaBeF_4$, slight. CaF_2, moderate.
4Q-6	LiF, slight. Li_2BeF_4, strong. $CaBeF_4$, slight. CaF_2, moderate.
4Q-7	LiF, slight. Li_2BeF_4, strong. $CaBeF_4$, slight. CaF_2, moderate.

TABLE 2

Combination (1) LiF + Li_2BeF_4 + CaF_2	Combination (2) Li_2BeF_4 + CaF_2 + $CaBeF_4$	Combination (3) Li_2BeF_4 + $CaBeF_4$ + BeF_2
H-3	--	LL-14a
K-2	--	LL-14e
K-5	--	MM-12a
L-5	L-2	MM-12c
1Q-4	--	MM-12d
1Q-6	1Q-8 + LiF trace	MM-12f
2Q-3	M-3b	M-1
2Q-4	M-4	M-2b
2Q-5	N-4f	N-3
2Q-7	--	O-2b
3Q-2	3Q-5 + LiF trace	--
3Q-4	3Q-6 + LiF trace	--
4Q-6 + $CaBeF_4$ trace	4Q-4	4Q-2
4Q-7 + $CaBeF_4$ trace	4Q-5	4Q-3

The results are shown graphically in Figure 27, a portion of the ternary diagram near the Li_2BeF_4 point. The different phase combinations are indicated by the different symbols plotted at the composition points. Since the compositions are subject to some uncertainties the boundaries of these regions are not sharp when plotted on a large scale. It is apparent, however, that the phase reactions divide the system into several regions. The projections of lines of two-fold saturation have been indicated to permit comparison of predicted and actual solidification behaviour. It will be noted that melts showing a forbidden phase (in addition to BeF_2) are those lying quite close to the invariant points.

In general the agreement is quite satisfactory considering the uncertainties and the apparent tendencies for formation of "forbidden" phases. This agreement furnishes additional confirmation for the

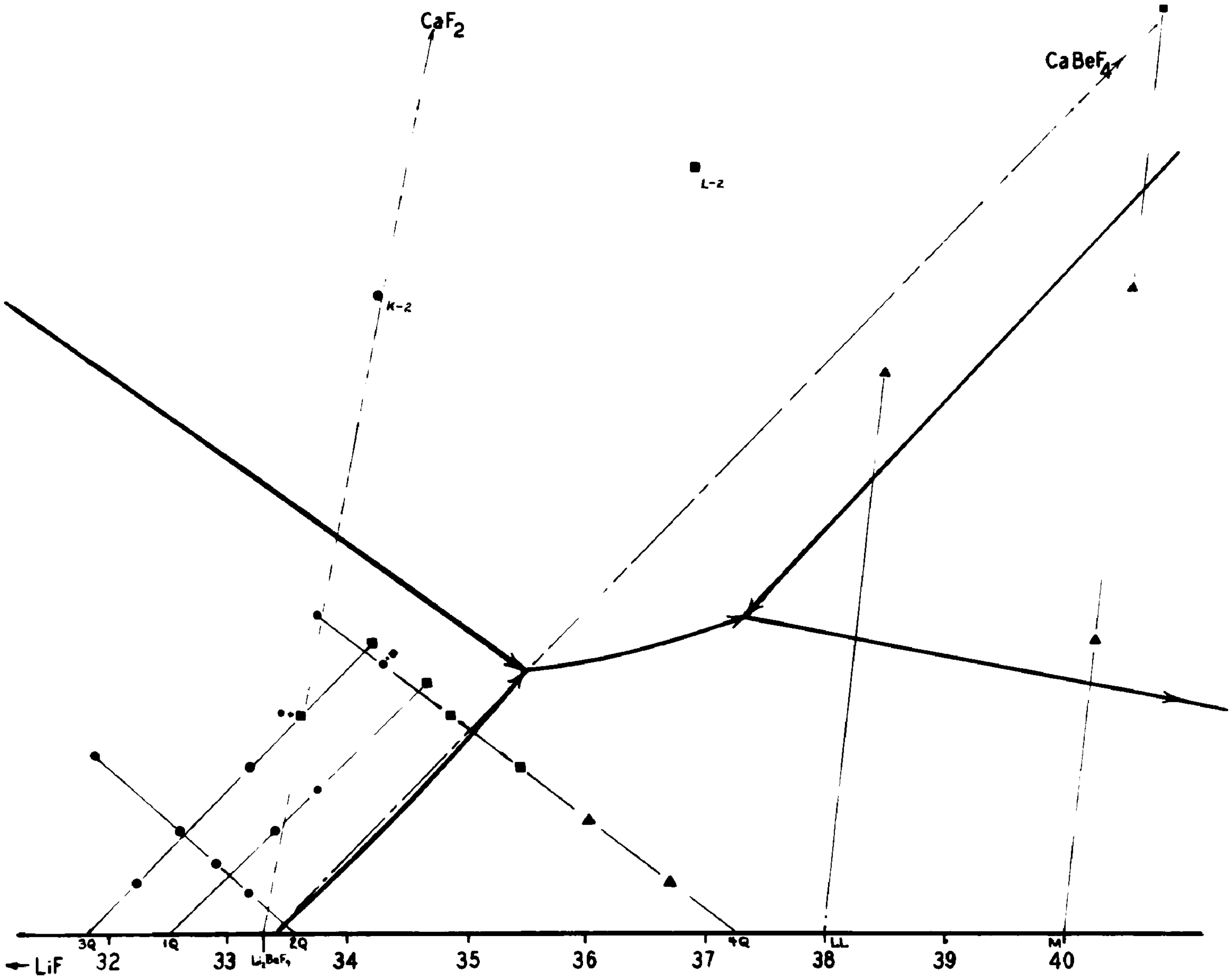


FIGURE 27
X-RAY SURVEY

interpretation of the thermal data. A detailed consideration of the data shows that the ultimate components of the solidified melts are determined by the location of the original melt in a particular composition triangle, corresponding to one of the three combinations noted above. The anomalous behaviour of several melts lying almost on a boundary line between two such regions is understandable. The thermal data is also in general agreement with the results of the X-ray examination. Thus solidification by the time a particular invariant point is reached precludes the formation of another solid component, which appears only if the melt is capable of reaching another nearby invarient point. A number of results of this type are apparent, the 4Q series being an example, where the melts showed a transition through three invariant points as the composition was shifted. The thermal and solid phase studies showed corresponding results in agreement with the predicted behaviour.

One additional X-ray analysis of particular interest was that made on a sample of melt S-4. The composition value of this melt was intended to be that suitable for a test of the "Klarkreuz" method discussed in Appendix 5. The melt was prepared carefully(p.273) from Li_2BeF_4 and CaF_2 of high purity. The calculated composition was 25 mole percent CaF_2, 25 mole percent BeF_2 and 50 mole percent LiF, corresponding to the point of intersection of a line drawn between Li_2BeF_4 and CaF_2, and of a line drawn between LiF and $CaBeF_4$. After use the analytical composition was found to be 25.1 mole percent BeF_2, 25.7 mole percent CaF_2 and 49.2 mole percent LiF. It was therefore possible that some departure had occurred from the desired value during three preceding thermal analyses.

X-ray analysis of melt S-4 gave the following information on the constituent phases.

Strong CaF_2 content.
Moderate Li_2BeF_4 content.
No LiF content.
No $CaBeF_4$ content.
Trace BeF_2

This evidence that Li_2BeF_4 and CaF_2 may coexist, while LiF and $CaBeF_4$ do not show any such tendency, shows conclusively that the LiF-$CaBeF_4$ line does not represent a "quasi-binary section". Such a result would be expected from the thermal results for the ternary system, which show two lines of two-fold saturation cutting across the line joining LiF and $CaBeF_4$. Such lines of two-fold saturation cannot pass in a continuous manner across a "quasi-binary" section.

The fact that CaF_2 and Li_2BeF_4 are the coexisting solid phases does not necessarily mean that the section joining these points is "quasi-binary". The result merely indicates that it <u>might</u> be, since the "Klarkreuz" method (in the presence of peritectic reactions) can only indicate the absence of possibility, and not the definite presence of a "quasi-binary" section. This information is therefore not in contradiction with the thermal results which show a line of two-fold saturation cutting across the section Li_2BeF_4-CaF_2. The slight trace of BeF_2 noted is believed to have been due only to slightly imperfect phase reactions at the temperature of solidification.

APPENDIX 14

APPENDIX 14

ANALYTICAL METHODS

The major portion of the analytical work required the determination of calcium, beryllium and lithium, singly and in combinations. Most of the analyses were concerned with mixtures of the fluorides of these metals. As analytical methods for fluorine are neither convenient nor accurate, the determination of this component was always indirect by calculation from the weight of metals found. This assumed that only fluorides were present and in cases where this was not entirely true, because of degradation of the melts, the error became apparent when the calculated weight percentages failed to total to 100%.

Due to interferences of the cations, the procedure necessarily was one in which Be, Ca and Li were separated consecutively from the same sample. The fluorine must be completely removed by volatilization using perchloric acid for decomposition of the fluorides. Otherwise, beryllium will be incompletely precipitated due to formation of a soluble fluoride complex, and calcium will be partially left in insoluble form during the beryllium separation. The separation of beryllium as the hydrated oxide, permits a subsequent separation of calcium as the oxalate. The filtrate at this point must be treated to remove a considerable accumulation of ammonium salts prior to the lithium separation. For the latter procedure, a separation in the form of a complex mixture of lithium periodates was made, finishing with an empirical volumetric determination of the lithium based on an iodimetric method.

The different procedures are discussed briefly below and variations are mentioned in connection with the analytical results in Appendix 15.

1) Decomposition of Fluorides

It was necessary to make at least two volatilizations using 80% perchloric acid (about 10-15 ml. for each step for 1 g. powdered samples) to be reasonably certain of complete decomposition. Platinum dishes were found to be more satisfactory than crucibles. As the decomposition must be carried out near maximum temperature to be effective, and as the evolution of hydrogen fluoride is vigorous yet erratic, some spattering losses undoubtedly occur. Two evaporations represent the practical limit as the process has usually caused some creepage to the rim at this stage. The evaporations were continued to the saturation point, the dish contents were partially cooled, and then were rinsed into beakers for the beryllium separation.

2) Beryllium Separation and Determination

The above solution, containing a moderate amount of free perchloric acid, was diluted to approximately 175 ml. and the beryllium precipitated as the very voluminous hydrated oxide, using only a sufficient excess of ammonium hydroxide to permit a detectable odor. While it would be desirable to use a much larger volume to reduce occlusion errors, the filtration, recovery and washing operations required approximately two hours, even with this small volume. Recovery of material adhering tenaciously to the beaker walls was achieved by three successive treatments with dilute hydrochloric acid and reprecipitations with dilute ammonium hydroxide. These clean-up liquids and a total of about 150 ml. of slightly ammoniacal wash water were used in washing the precipitate which was filtered using Whatman No. 41 paper. The precipitate equivalent to about 0.1 g. BeO completely filled this size of paper.

After drying at 110°, the paper and contents were transferred to preweighed platinum crucibles, using acidified filter paper policemen to remove any material adhering to the funnel. The crucibles were ignited at the maximum heat of Fisher burners to convert to BeO.

The weighing operations for this material must take into account its extremely hygroscopic character. The following system was used to overcome the difficulty, particular care being necessary to keep the timing reproducible. The hot crucible was removed from the flame and immediately cooled on an aluminum plate under an inverted funnel supplied with a flow of dried nitrogen. During the cooling period, about two minutes, the preceding crucible was weighed and the succeeding crucible was started on its cooling cycle. Weighing was carried out at maximum possible speed (two to three swings of the balance), using preset weights. Either one or two preliminary weighings of each crucible were necessary to obtain the approximate weight with sufficient accuracy so that the final weighing might be possible with no more than a very minor rider admustment. The tare weight of the crucibles was obtained in an exactly similar manner.

By this method a weight of the BeO residue was obtained which was believed to be in error by no more than 0.0005 g. This was not, however, entirely satisfactory since the maximum practical residue to handle (in precipitate form) amounted to only about 0.1 g. Hence the final percentage error might readily be 0.2 to 0.3 mole percent, with possible relative errors of 0.5 mole percent. The possible errors due to occlusion of other ions is not known, several attempts using controls resulting in both positive and negative results, with about the same deviations shown by analyses made in the absence of other metal ions.

3) Calcium Separation and Determination

A standard oxalate separation was carried out on the filtrate of the beryllium separation, using a volume of approximately 400 ml. The solution, already containing considerable ammonium chloride, was sufficiently acidified to permit holding all oxalate in solution when a large excess of ammonium oxalate was added. Dilute ammonium hydroxide was then added until the first permanent precipitate of calcium oxalate appeared, and after about 15 minutes additional dilute ammonium hydroxide was added with stirring until the methyl red endpoint was reached.

The oxalate precipitate was digested, cooled, filtered, and washed in the usual manner with 40 ml. of cold water using Gooch-asbestos filtering crucibles. The determination was completed volumetrically by dissolving the precipitate in dilute sulfuric acid and titrating in a volume of about 200 ml. at about 60° with standard potassium permanganate solution. Concentrations of the latter ranged from 0.05 to 0.2 N and either 10 ml.

or 50 ml. burettes were used, depending upon the requirements of the particular samples being analyzed.

J. T. Baker "Special" grade of calcium carbonate was used as the primary standard. Control samples were carried through the entire process and others were run in which all steps prior to oxalate precipitation were omitted. Although good checks were obtained in general, indicating good calcium recovery, an occasional "wild" result indicated the inadvisability of basing normalities on the control samples. Accordingly the standardizations were based on simple conversion of the carbonate to oxalate under the same conditions used in the analytical calcium separations. Such standardizations usually checked to within 1-2 parts per thousand.

The accuracy of the actual calcium determinations was inferior to this, as judged by the reproducibility of results on duplicate samples carried through the entire process. An error of about 2 to 3 parts per thousand seems reasonable. While this does not create any very significant error in calculating compositions near the Li_2BeF_4 point, it exceeds the desirable maximum error near the $CaBeF_4$ point where the resulting calculated composition may be in error by 0.3 to 0.4 mole percent.

4) Lithium Separation and Determination

The filtrate of the calcium determination was concentrated and treated to remove the large concentration of ammonium and oxalate salts which otherwise might interfere in the lithium determination. To obtain complete decomposition of these salts, including oxalates, at steam bath temperature it was found necessary to make repeated treatments with mixed nitric and hydrochloric acids. (Free bromine has also been recommended for this step.) The oxalates do not decompose at all readily under simple nitric acid treatment, which does however effectively attack the ammonium ion.

The residual material was converted to the perchlorate form and transferred to a 100 ml. volumetric flask from which aliquots were taken for the lithium precipitation. These aliquots were evaporated to dryness on a sand bath to remove excess perchloric acid.

The lithium precipitation followed the method of Rogers and Caley (132) which requires the absence of all metal ions other than the alkali metals and low ammonium ion concentrations. Lithium was precipitated by dropwise addition of a solution of potassium periodate (KIO_4) dissolved in 5 molar potassium hydroxide. The precipitate has no definite composition and consists of a mixture of lithium periodates (?), with the approximate composition corresponding to Li_5IO_6. The conditions of precipitation, digestion, filtering and washing must accordingly be rigidly maintained to obtain consistent results.

The precipitate was then dissolved in dilute sulfuric acid, iodine was liberated by the addition of excess potassium iodide, and the iodine was determined volumetrically in the usual manner, generally with standard sodium thiosulfate solution. The titer of the latter was determined by carrying out similar precipitations and titrations of aliquot samples of known lithium content which were prepared using "J. T. Baker Analyzed" lithium carbonate as the primary standard.

The original method calls for dissolving the precipitate in "5 ml. of N H_2SO_4". In this work, even with more than 10 ml. of 2N H_2SO_4, the precipitate would not completely dissolve in any reasonable length of time. It was found to be much more effective to add a concentrated potassium iodide solution to the mixture of acid, precipitate and asbestos slurry in the Gooch filtering crucible somewhat in advance of titration. This procedure is open to criticism because of possible iodine volatilization. It was found, however, that the actual recovery was always much better than on precipitates handled in the usual manner. The latter lacks the effective dissolving power of the combination of acid and concentrated potassium iodide solution.

The method was modified by using a polyethylene bottle-pipette combination for storage and dispensing of the precipitating reagent. It was thought that some of the inherent error in the method might be due to the formation of relatively insoluble lithium carbonate, which might then become coated with the periodate complex during the precipitation. The reagent was therefore protected against carbon dioxide from the atmosphere. An attempt was made to prepare carbonate-free reagent solution by electrolytic preparation of potassium-mercury amalgam, but the process was not satisfactory for the production of solutions with concentrations greater than 1 to 2 molar.

Optional iodine evolution and titration methods are given in the original report, suited to larger or smaller amounts of precipitate, which involve arsenite titration with buffer solution added before or after addition of potassium iodide. The thiosulfate method was found to be much more satisfactory, since the precipitate amount could usually be predicted and the size of the aliquot governed accordingly. Then the potassium iodide might be used with the acid to obtain the superior dissolving action noted above.

The method is limited to approximately 50 mg. of Li by the voluminous nature of the precipitate and the washing requirements, the transfer and washing operations during filtration being carried out with only four 2 ml. portions of 4 N KOH. Obviously the washing operation must be effective to prevent interference by the excess precipitating agent with its high periodate content. Actually the washing action is much more effective than would be expected, provided the wash solution is applied with a pipette in a careful and systematic manner.

The errors inherent in such an empirical method are apparent. Rogers and Caley indicated that, in general, 1 to 2 percent error might be expected. This was confirmed in this work. It was found that a given set of replicate samples might give results differing by no more than 1%. Another set of the same samples run on a subsequent occasion might differ by 2% from the first results, although again differing by no more than 1% among the set. Consequently, for these analyses, numerous aliquots were taken on at least two different occasions for each sample in order to partially overcome this difficulty. For the standardizations a large number of checks were made whenever these analyses were performed. The titer was usually determined to an average value subject to probably less than 1% error. The actual lithium analyses were subject to possible errors of at least 1%. This represented a serious difficulty in the region of the Li_2BeF_4 point where the corresponding error in the calculated composition amounted to about 0.3 mole percent.

APPENDIX 15

APPENDIX 15

ANALYTICAL RESULTS

PART A

ANALYSIS OF CALCIUM FLUORIDE

Methods generally were based on the National Bureau of Standards method (103) for lower grade types of fluorspar. Typical results for the material used in this work were as follows:

1) Carbonate by Evolution and Absorption. (71)

   Sample 5.000 g., Gain in wt. due to CO_2 = 0.0005 g.

   % $CaCO_3$ = 0.02.

2) Acid soluble "carbonate" from acetic acid extraction.

   Based on calcium content of extract, % extractable "$CaCO_3$" = ca. 1.0.

   When the method was modified by adding some LiF to the acetic acid prior to extraction to reduce solubility of CaF_2, the following result was obtained. Based on calcium content of extract, % extractable "$CaCO_3$" = 0.1

3) Silica by HF Evolution Method.

   Results -- Unmeasurable, or slightly negative, silica

4) Heavy Metals by H_2S Precipitation in Acid and Alkaline Solution.

   Unweighable traces, estimated 0.003%.

5) Calcium by precipitation as oxalate and titration with standard potassium permanganate.

Date of Analysis	Sample Wt., g.	Vol. $KMnO_4$, ml.	$KMnO_4$ Soln. No.	Wt. Percent CaF_2	See Note No.
12/18/49	0.4900	46.38	2	97.8	1
12/20/49	0.5000	47.52	2	100.4	2
12/22/49	0.5000	47.51	2	100.4	3
12/22/49	0.5000	47.47	2	100.2	3
3/18/50	0.1000	49.55	4	99.8	3, 4
5/29/50	0.0950	47.23	4	100.5	3, 4

Notes (1) Sample extracted with acetic acid. Volume shown consisted of 45.94 ml. in regular titration and 0.44 ml. in titration of CaC_2O_4 precipitated from the extract. Total = 46.38 ml.

(2) Same comment, except 47.01 + 0.51 = 47.52 ml.

(3) These samples were not extracted with acetic acid.

(4) The sample used was "CaF_2, Batch 3/10/50", which was used for all subsequent requirements for calcium fluoride.

(5) Standardization of $KMnO_4$ Titers.
Soln. #2 -- 0.01055 g. CaF_2/ml. -- See part G for details.
Soln. #4 -- On 3/18/50, 0.002016 g. CaF_2/ml. See Part H
-- On 5/29/50, 0.002020 g. CaF_2/ml. for details.

It is believed in view of the "Carbonate by Evolution" results, that most of the calcium in the acetic acid extract was derived from CaF_2 rather than $CaCO_3$ impurity. See Lundell (103) for data in this respect.

The general accuracy of the method for calcium is no better than ± 0.2% at best when the sample must be treated by perchloric acid evaporation with possible attendant losses.

PART B

ANALYSIS OF BERYLLIUM FLUORIDE AND "BERYLLIUM CARBONATE"

Analysis of Beryllium Fluoride. (Brush Beryllium Corp. product.)

Method - Perchloric acid evolution of fluorine using platinum dish and precipitation of $Be(OH)_2$ by ammonium hydroxide. Hydroxide filtered, washed and ignited and weighed as BeO with precautions noted under section on general analytical methods. Precipitation of iron and aluminum by 8-hydroxyquinoline prior to precipitation of the hydroxide gave only a negligible trace of colored precipitate when filtered.

Sample Wt., g.	Wt. BeO, g.	% Purity of BeF_2
0.2903	0.1530	99.0
0.2077	0.1112	100.5

Analysis of "Beryllium Carbonate" (Kahlbaum)

Method - 8-hydroxyquinoline precipitation to primarily separate iron and aluminum; then beryllium precipitated as $Be(OH)_2$ and ignited and weighed as BeO.

Sample Wt.,g.	Wt. of Oxine Ppt., g.	Wt. BeO, g.	Wt. % Fe	Wt. % $BeCO_3$
1.000	0.0152	0.3582	0.19	99.0
1.000	0.0173	0.3551	0.21	98.0

Notes - Sample oven dried at 120°. Oxine precipitate largely due to Fe. Results calculated as percent Fe and percent $BeCO_3$, although latter compound probably does not exist, but is really a basic salt.

The results of analyses of three samples of BeF_2 prepared by evolution of NH_4F from $(NH_4)_2BeF_4$ (without adding another fluoride) are given in Part H of this Appendix. The values obtained (99.3%, 101.3%, 99.2% and 98.5%) probably were controlled somewhat by the presence of carbon as an impurity from contact with the carbon crucibles used for the evolution process. This carbon was either destroyed by using added nitric acid (during the perchloric acid treatment), or was removed by filtration, so that slightly low results would be expected unless its ash content was unusually high.

PART C

ANALYSIS OF AMMONIUM FLUOBERYLLATE PREPARATIONS

Method -- The procedure, as given in Appendix 14, consisted of volatilizing fluorine by perchloric acid evaporation, precipitation as the hydrated beryllium oxide, and ignition to BeO. Weighings were made with suitable precautions.

These samples were analyzed in conjunction with the melt samples and the details are reported in the part dealing with those samples. The data tabulated below summarize the results obtained.

Sample Designation	Average Percent Purity	For Details See--
$(NH_4)_2BeF_4$ Lot L-1	75.	Table C, Part I.
$(NH_4)_2BeF_4$ Lot L-2,3	65.	" "
$(NH_4)_2BeF_4$ 1/19/51 First fraction	98.	" "
$(NH_4)_2BeF_4$ 1/19/51 Last fraction	76.	" "
$(NH_4)_2BeF_4$ Lot M	99.5	" "
$(NH_4)_2BeF_4$ Lot J-2	98.8	" "

PART D

ANALYSIS OF BERYLLIUM BASIC ACETATE PREPARATIONS

Method -- Since these samples contained no fluorine, the fluorine volatilization step was omitted. The material was converted to the nitrate by boiling with nitric acid. Then, to make the situation comparable with the other beryllium analyses, the nitrate was converted to perchlorate by boiling with 80% perchloric acid. The usual method of precipitation of beryllium hydroxide and ignition to BeO followed.

Comments -- On many of the early analyses the purity was low apparently because of entrapped acetic acid. Unless dried at higher temperatures than 110° there seems to be incomplete removal of the acid as may be seen from the example shown below.

That there may have been interference due to other causes would appear from a comparison of the last two analyses for which the samples differed only by two additional recrystallizations.

Date of Analysis	Sample Designation	Sample Drying Temp., °C.	Sample Wt., g.	Wt. BeO, g.	% Purity	See Note No.
2/27/51	Mixture	110	0.4000	0.0858	87.3	1
	Prod. 1/2/51	110	0.4000	0.0841	85.5	2
3/21/51	Prod. 3/21/51	110	1.000	0.2225	90.3	
4/24/51	Redried	180	0.4000	0.0921	93.5	3
	Recryst.	180	0.4000	0.0990	100.5	4

Notes -- (1) The starting material was a mixture of the following composition, which was treated to convert to perchlorate form and subjected to the regular analytical scheme.

	0.1000 g. $CaCO_3$
Mixture	1.000 g. Li_2CO_3
	0.4000 g. Beryllium basic acetate, Prod. 1/2/51.

(2) The treatment was the same as (1) except no other metal ions were present.

(3) The same material as Prod. 3/21/51, except dried at a higher temperature.

(4) Same as (3) except with two additional recrystallizations of the Prod. 3/21/51 and dried at higher temperature.

(5) The calculated purity is based on the formula $BeO(CH_3COO)_6$ for beryllium basic acetate.

PART E

ANALYSIS OF Li_2BeF_4:$1H_2O$ PREPARATION AND DETERMINATION OF SOLUBILITY OF Li_2BeF_4

The starting material was prepared from a relatively pure first crop of $(NH_4)_2BeF_4$ with an analysis of 98.4% purity. A known weight of LiF was added to a weighed quantity of $(NH_4)_2BeF_4$, and the NH_4F was volatilized by heating. During preparation of the Li_2BeF_4 it was found necessary to use 1.8% excess of the $(NH_4)_2BeF_4$ (assuming 100% purity) to obtain the theoretical weight of product, which checks well, within the accuracy of the analysis. This product, called Li_2BeF_4, 1/19/51, was analyzed to contain 33.4 mole percent BeF_2. (See Sample S in this Appendix, Part J). This material, therefore, was checked in three ways as being very close to Li_2BeF_4 in composition.

A sample of 39.0 g. of the above material was dissolved in approximately 3 liters of water at room temperature with negligible residue on filtration. On evaporation at reduced pressure no deposition of material was observed until the volume reached about 1500 ml. The approximate solubility of Li_2BeF_4 at room temperature was therefore about 26 g/liter.

After about 3 weeks additional evaporation, the crystals and mother liquor were allowed to stand at room temperature for about 5 weeks before filtration, washing and air drying. This hydrated product was marked Li_2BeF_4:$1H_2O$, 3/20/51. A 20 ml. sample of the undiluted mother liquor was also taken with a pipette after filtration. The analyses of these samples are indicated below, the procedure used being that described in Appendix 14.

$Li_2BeF_4:1H_2O$

Wt. sample (air dried) 1.1000 g. Wt. after drying (180°) 0.9470 g.

(Note-about 2% of water was evolved between 110 and 180°.)

Wt. water lost = 0.1530 g.

Wt. BeO residue = 0.2323 g.

Vol. $Na_2S_2O_3$ "B" = 47.81 ml. (for 10 ml. aliquot of 100 ml.)

Titer of $Na_2S_2O_3$ "B" = 0.00106 g. LiF/ml. on 3/21/51

(See Part J of this appendix.)

Calculated on anhydrous and hydrated bases:

	Wt. Percent			Sum of Wt. Percent	Mole Percent		
	H_2O	LiF	BeF_2		H_2O	LiF	BeF_2
Hydrated	13.9	46.1	39.7	99.7	23.0	52.2	24.8
Anhydrous	---	53.5	46.1	99.6	---	67.8	32.2

Despite the good recovery values, the results differ from theory by about 1% with a probable error of about 0.5%. The difference in the case of the hydrated material can only be partially explained by some dehydration during the separation and air drying operations.

Subsequently the balance of the hydrated product was used to prepare Melt d and after thermal analysis, this material was sampled. The results (See Part I of this appendix) were as follows:

Wt. Percent		Sum of Wt. Percent	Mole Percent	
LiF	BeF_2		LiF	BeF_2
53.7	47.1	100.8	67.5	32.5

The agreement was reasonably good with the preceding analysis, but still showed disagreement with theory beyond the probable error of about ± 0.5 mole percent.

The results obtained on the solubility determination by analysis of the mother liquor sample are shown below.

Mother Liquor Sample (20 ml.).

On drying this material prior to perchloric acid treatment, oxyfluoride formation occurred and hence the weight obtained was meaningless as an indication of solubility. The usual Be and Li analyses were carried out to obtain the following results.

Wt. BeO residue = 0.1752 g.

Vol. $Na_2S_2O_3$ "B" used -- 22.42 ml. for 10 ml. aliquot of 100 ml. volume.

44.90 ml. for 20 ml. aliquot of 100 ml. volume.

Titer of $Na_2S_2O_3$ = 0.00106 g. LiF/ml. on 4/24/51.

(See Part J of this appendix.)

Calculating the moles of LiF and BeF_2 present in the sample volume and converting to the basis of a liter of sample, the following results were obtained.

	In 20 ml. Sample		Mole Ratio LiF/BeF_2		Per liter,
	g.	moles			g.
LiF	0.238	0.00918	1.31/1		11.9
BeF_2	0.3292	0.00700			16.5
				Total	28.4

Assuming a 2 to 1 molal ratio and a solubility of 0.00918 moles of LiF per 20 ml., the total weight of LiF + BeF_2 should be 22.7 g./liter.

If the starting material (Li_2BeF_4, 1/19/51) contained a slight excess of BeF_2, this would explain the failure of the mother liquor to have the proper 2 to 1 molal ratio of LiF to BeF_2. On this basis a solubility of

Li_2BeF_4 in water of approximately 23 g./liter at room temperature is obtained in fairly good agreement with the roughly estimated value of about 26 g./liter obtained during evaporation.

This value is about twice the value given by Ray (128) in the original report on the preparation of the compound, namely 13.2 g./liter.

PART F

DISCUSSION OF ANALYTICAL ACCURACY AND CORRECTION OF CALCULATED COMPOSITIONS

The inaccuracies of the analyses for the determination of Be, Ca and Li have been estimated in Appendix 14 in connection with the discussion of the methods. The errors are dependent to some extent on the amount of the constituent present, but as a general rule the following possible errors may be given.

CaF_2, ± 0.2 to 0.3 wt. percent.
BeF_2, ± 0.3 to 0.5 wt. percent.
LiF, ± 0.5 to 1.0 wt. percent.

The effect of these errors in weight percent is different when the over-all compositions are expressed in mole percentages, and is dependent also upon the region of the ternary system under consideration. In the regions of most critical interest, near the composition points of $CaBeF_4$ and Li_2BeF_4, the resultant possible errors are estimated as being at least ± 0.3 to 0.4 mole percent with ± 0.5 mole percent as a conservative estimate.

For a few cases of very critical nature, in which undegraded samples were available, and on which a number of check determinations were made, it is believed the probable error was no greater than ± 0.25 mole percent.

In view of these analytical uncertainties, the correction of melt compositions was made only when the calculated compositions differed from the analytical compositions by more than the estimated analytical error.

In general the calculated compositions were considered more reliable, unless a confirmatory series of analyses indicated a uniform deviation of the compositions. In a few such cases, the compositions were then recalculated to obtain agreement with the analyses. Usually an average value was used in the few cases of deviations of 1 to 1.5 mole percent, rather than accepting the analytical value. Most analyses agreed within 1 mole percent with the calculated compositions, so that the analyses primarily served to check the composition, rather than to determine it.

In the tabulations of the analyses of melt samples the calculated composition is shown for comparison with the analytical results. Many of the results are given to the nearest 0.1 mole percent, but as noted above, this implied general accuracy was not obtained. In some cases, however, where only a small amount of a component had been added, the composition with respect to this component was actually known to ± 0.01 mole percent. It has, therefore, been generally necessary to retain at least one uncertain figure in presenting the results. The uncertainty in relative compositions is quite often smaller than 0.1 mole percent, so that from this standpoint, the number of "significant" figures is justified.

PART G

SYSTEM CaF_2-LiF ANALYSES

The analytical results shown in the following tabulation require the following explanatory notes.

Samples EA, EB and EG were obtained by dipping samples of the eutectic liquid from the solidifying melt during the invariant reation at the eutectic point. Naturally such samples might have contained some previously deposited solid. The melts in question were A, B and G.

Sample PE consisted of CaF_2 crystals collected from the stirring rod prior to the eutectic reaction on melt E.

The other samples were representative of the solidified melts as a whole.

The "theoretical composition" indicated is the calculated composition based on the weights of CaF_2 and LiF used in preparing the melts.

Information on the standardization of the potassium permanganate follows the tabulation.

The analytical methods were as described in Appendix 14, except that lithium determinations were made only on the samples marked CL.

Sample, No.	Date	Sample Wt., g.	$KMnO_4$ Vol., ml.	Analytical Composition, Mole % CaF_2	Theoretical Composition, Mole % CaF_2	Date of Analysis
EA	11/17/49	1.000	40.61	19.5	--	12/20/49
		1.200	44.38	17.7	Poor Result.	"
EB	11/17/49	1.000	40.40	19.9	--	12/20/49
		1.200	48.45	19.9	--	12/22/49
EG	11/13/49	1.000	41.12	20.3	--	12/20/49
		1.200	49.28	20.3	--	12/22/49
PE	11/15/49	0.5000	48.51	102.	--	12/22/49
G	11/13/49	0.8500	47.10	32.1	33.3	"
"23.3"	11/17/49	1.000	44.60	22.8	23.3	12/27/49
		1.000	44.50	22.8		"
"24"	11/17/49	1.000	46.22	24.05	24.0	"
		1.000	46.13	24.0		"
"29"	11/14/49	0.9000	47.36	29.3	29.0	"
		0.9000	47.22	29.2		"
"50"	11/14/49	0.6500	46.50	50.6	50.0	"
		0.6500	46.57	50.7		"
"70"	11/15/49	0.5500	45.79	70.6	70.0	"
		0.5500	45.72	70.4		"
1CL	6/6/51	1.000	45.62	22.0	22.0	9/19/51
4CL	6/6/51	1.000	51.04	26.3	25.9	"
10CL	6/6/51	1.000	39.96	18.4	18.3	"

$KMnO_4$ Standardizations

Standard $KMnO_4$ Solution #2 used on all samples. Standardized against CaC_2O_4 obtained from primary standard $CaCO_3$, 99.97% purity, Baker Special Grade.

Solution No.	Wt. $CaCO_3$, g.	Vol. $KMnO_4$, ml.	CaF_2 Titer, g./ml.	Ave. CaF_2 Titer, g./ml.	Date
2	0.6200	45.76 avg.	0.01054	0.01055	12/11/49
2	0.6200	45.77 avg.	0.01054		12/18/49
2	0.6200	45.71 avg.	0.01056		12/22/49
2	0.6200	45.73 avg.	0.01055		12/27/49
2	0.6000	46.22	0.01012	0.01012	9/19/51
2	0.6000	46.21	0.01012		

PART H

SYSTEM CaF_2-BeF_2 ANALYSES

The following comments apply to the tabulated analytical results for this system. The methods used were those described in Appendix 14.

In the calculation of the compositions from the analytical results it was frequently found that the sum of the weight percentages did not closely equal 100%. In some cases this was apparently due to impurities originating in the use of carbon crucibles and in other cases hydrolysis product contamination seemed to be the cause. Calculations of mole percentages were therefore made in the following ways.

For the analyses dated 2/23/50 and 2/27/51 the results were calculated as if the sums of the weight percents were equal to 100.

For the analyses of 3/18/50 and 5/29/50 the deviation from 100% was too great, so the compositions were calculated assuming the weight percent of CaF_2 to be correct and obtaining the weight percent of BeF_2 by difference. This is justified by the generally better accuracy of the Ca determination, and the fact that CaF_2 seems less subject to hydrolysis effects.

The accuracy of the results is definitely less than is implied by the number of significant figures retained in the calculations. The CaF_2 analyses are probably precise to no better than 1 or 2 parts per thousand. The probable error on the BeF_2 analyses is dependent to a large extent on the size of the residue of BeO weighed. For practical reasons connected with the filtration and washing of the $Be(OH)_2$ precipitate this residue has to be kept small. Probable error should not be worse than 5 parts per

1000 on the weighing operations, but the presence of BeO in the original sample together with other impurities apparently greatly increased the total error in many cases.

Some of the samples in the tabulation were special samples, not representative of the whole melt, as indicated in the footnotes. Some representative analyses of BeF_2 products are included. These materials were produced in the early stages of the work when the NH_4F evolution from the $(NH_4)_2BeF_4$ was carried out without addition of the other fluoride components.

The column headed "Theoretical Comp." lists the calculated compositions based on inputs to the melts. Particularly in the earlier work this value was uncertain because of inability to accurately weigh the BeF_2 products which were used.

The column headed "Sum of Wt. Percents" gives a fairly good indication of the reliability of the analyses and the extent of degradation of the samples. Some of the high results on the samples marked with an asterisk are purely due to the assumption that fluorides were present, whereas such was not the case, BeO being obviously present.

Date of Analysis	Sample	Sample Wt., g.	Wt. BeO, g.	Wt. % BeF$_2$	Vol. KMnO$_4$, ml. **	Wt. % CaF$_2$	Sum of Wt. Percents	Analyt. Mole % CaF$_2$	Theoret. Comp., Mole % CaF$_2$
2/23/50	BeF$_2$,2/8/	0.1505	0.0795	99.3	--	--			
"	BeF$_2$,2/19/	0.1500	0.0809	101.3	--	--			
"	A	0.2000	0.0956	89.8	9.41	9.3	99.1	6.0	7.2
"	B	0.2000	0.0868	81.55	18.47	18.25	99.9	11.9	11.8
"	C	0.2000	0.0685	64.35	36.26	35.83	100.1	25.2	25.
"	D	0.2000	0.0970	91.1	5.55	5.50	96.6	3.8	3.5
"	E	0.2500	0.1107	83.2	19.55	15.44	98.6	10.1	--
"	F*	1.000	0.3995	75.0	128.50	25.40	100.4	16.9	ca.20.3
"	G	0.3000	0.1108	69.3	46.05	30.30	99.6	20.8	
3/18/50	BeF$_2$,2/19/	0.1800	0.0950	99.2	--				
"	BeF$_2$,2/10/	0.1800	0.0943	98.5	--				
"	D	0.2000	0.1001	94.1	5.75	5.8	99.9	2.8	3.5
"	H*	0.3000	0.0863	54.0	77.30	51.9	105.9	39.4	44.1
"	J	0.3000	0.0638	40.0	90.20	60.6	100.6	48.1	
"	J'*	0.0260	0.0048	32.8	7.65	59.2	92.0	46.6	
"	K*	0.1500	0.0169	21.2	60.88	81.9	103.1	73.1	ca.78.
"	L*	0.1500	0.0199	24.9	59.90	80.5	105.4	71.3	
"	M	0.1500	0.0136	17.0	63.40	85.2	102.2	77.6	
"	N	0.1500	0.0267	33.4	51.00	68.5	101.9	56.7	57.
"	O*	0.2000	0.0223	21.0	79.85	80.5	101.5	71.3	75.
"	P	0.2500	0.0261	19.6	103.6	83.6	103.2	75.4	
"	Q*	0.2000	0.0150	14.1	84.37	85.1	99.2	77.5	
5/29/50	R	0.4000	0.1050	49.3	104.7	52.8	102.1	40.3	40.
"	S*	0.4000	0.1162	54.5	120.1	60.7	115.2	48.2	
"	T	0.4000	0.0992	46.6	124.5	62.9	109.5	50.5	50.5
"	X	0.4000	0.0835	39.2	122.9	62.1	101.3	49.7	50.
"	Y*	0.4000	0.0950	44.6	118.8	60.1	104.7	47.6	
"	Z*	0.5000	0.0778	29.2	189.9	76.8	105.9	66.5	64.5
"	AA	0.5000	0.0807	30.3	186.3	75.3	105.5	64.6	

Continued next page

Date of Analysis	Sample	Sample Wt., g.	Wt. BeO, g.	Wt. % BeF_2	Vol. $KMnO_4$, ml. **	Wt. % CaF_2	Sum of Wt. Percents	Analyt. Mole % CaF_2	Theoret. Comp., Mole % CaF_2
5/29/50	BB*	0.6000	0.1362	42.6	174.4	58.8	101.3	46.2	53.5
"	CC	0.6000	0.1160	36.3	194.9	65.7	101.9	53.5	
"	DD	0.7000	0.1235	33.2	245.1	70.7	103.9	59.3	59.3
2/25/51	a	0.4595	--	--	119.5	52.5	--	ca. 40.	40.
	a-6	0.8000	0.1592	37.4	51.55	65.1	102.5	51.2	50.
	a-10	0.5000	0.0976	36.7	31.80	64.3	101.0	51.4	50.
	a-12	0.6000	0.1052	32.9	40.68	68.4	101.3	55.6	54.8

Notes -- * Samples taken from the walls of the crucible or non-representative parts of the melt.

F, sample from walls on Melt G.
H, " " " " " J.
L, " " " " " M.
Q, " " " " " P.
S, " " " " " R.
Y, " " " " " X.
Z, " " " " " AA.
BB, " " " " " CC.
J', single crystal of $CaBeF_4$ (probably not pure) taken from Melt J.
K, crystal sample from stirrer on Melt L, <u>prior</u> to eutectic reaction.
O, sample obtained from melt P by dipping with cold rod (impure).

** See following tabulation for titers of the different standard solutions of $KMnO_4$ used.

Standardization of Different $KMnO_4$ Solutions

Date of Use and Standardization	Wt. $CaCO_3$, g.	$KMnO_4$ Vol., ml.	Solution No.	Average Titer, g. CaF_2/ml.
2/23/50	0.2500	98.70	#3	0.001976
2/23/50	0.2500	98.60	#3	
3/18/50	0.1200	46.37	#4	0.002016
3/18/50	0.1200	46.30	#4	
5/29/50	0.1200	46.40	#4	0.002020
5/29/50	0.1200	46.20	#4	
2/22/51	0.6000	ca.235.0	#4	ca. 0.00200
2/27/51	0.6000	46.19	#2	0.01011
2/27/51	0.6000	46.33	#2	

PART I

SYSTEM LiF-BeF_2 ANALYSES

The compositions of some of the samples of the above binary system were checked by the analysis of derived ternary samples, using graphical extrapolation to determine the original composition of the melt in the binary system. The values obtained in this manner are given in Table A.

In addition certain binary samples were analyzed, particularly those related to series of melts in the vicinity of 33.3 mole percent BeF_2. These samples were analyzed for beryllium and lithium contents and the analytical data and results are tabulated in Table B.

In Table C results are tabulated for materials such as BeF_2 and $(NH_4)_2BeF_4$ used in preparing the melts of the LiF-BeF_2 system.

The analyses followed the procedure described in Appendix 14. As noted there, all lithium sample solutions were diluted to 100 ml. volume before taking aliquots.

The accuracy of the analyses is less than is implied by the number of significant figures retained in the calculations. The possible analytical error is as great as 0.5 mole percent for samples of melts which were used for a series of thermal analyses. For a few cases, where the melts were sampled before use, or where the conditions of use were less severe, the accuracy is better, but in no case is the possible error less than 0.25 mole percent.

The column headed "Sum of Wt. Percents" gives an indication of the relative reliability of the results, or the extent of melt degradation.

In Tables D and E the results and data have been tabulated with reference to the determination of the titers of the different standard solutions used.

TABLE A

COMPOSITIONS OBTAINED BY GRAPHICAL EXTRAPOLATION FROM ANALYZED TERNARY SAMPLES

Binary Melt	Calc'd Comp. Based on Wt. of Input, Mole % BeF_2	Calc'd Comp. Based on Analysis of Input, Mole % BeF_2	Extrapolated Analytical Composition, Mole % BeF_2	Based on Analysis of Ternary Sample Number (See Part J)
A	3.3	4.2	4.0	A-8
B	7.9	8.1	8.1	B-7
C	11.8	12.0	12.0	C-7
D	13.8	15.4	15.0	D-7
E	18.8	19.0	19.0	E-5
F	22.0	22.3	22.0	F-4
FF	23.0	23.0	23.0	FF-5
G	24.3	23.8	25.0	G-6
H	27.5	26.9	28.0	H-5
I	29.5	28.7	30.5	I-5
J	32.5	31.7	33.2	J-5

TABLE B

ANALYSES OF MELT SAMPLES, LiF-BeF_2 SYSTEM

Melt No.	Sample Wt., g.	Wt. BeO, g.	Vol. Aliquot Li Detn., ml.	Vol. Std. Reduc'g Agent, ml.	Reducing Agent Soln. Used (*See note)	Sum of Wt. Percents	Analyt. Comp., Mole % BeF_2	Calc'd Comp. Based on Input, Mole % BeF_2
7II	1.000	0.2574	10	35.27	AsO_2^- (a)	100.1	34.1	ca. 33.6
5KK	1.000	0.2499	10	51.12	Thio. (a)	101.2	32.3	ca. 32.5
19R	1.000	0.2482	10	50.92	Thio. (a)	100.7	32.3	31.8
8R	1.000	0.2428	10	49.38				
				50.37				
				51.86				
				50.5 Avg.	Thio. (b)	99.2	32.0	32.4
d	1.000	0.2503	5	24.88				
				25.30				
				25.27				
				25.25 Avg.	Thio. (c)	100.8	32.5	
2d	1.000	0.2605	5	23.73				
				23.94				
				23.85 Avg.	Thio. (c)	99.8	34.7	
4d	0.7500	0.2028	5	17.62				
				17.50				
				17.55 Avg.	Thio. (c)	100.8	36.0	
7d	1.000	0.2441	5	25.85				
				25.70				
				25.80 Avg.	Thio. (c)	100.8	31.5	
10d	1.000	0.2259	5	27.45				
				27.34				
				27.40 Avg.	Thio. (c)	100.9	28.7	
n	1.000	0.3917	5	12.93				
				12.67				
				12.8 Avg.	Thio. (d)	100.3	60.3	60.

Continued next page

Melt No.	Sample Wt., g.	Wt. BeO, g.	Vol. Aliquot Li Detn., ml.	Vol. Std. Reduc'g Agent, ml.	Reducing Agent Soln. Used (*See note)	Sum of Wt. Percents	Analyt. Comp., Mole % BeF_2	Calc'd Comp. Based on Input, Mole % BeF_2
3n	1.000	0.3480	5	16.60				
				16.50				
				16.55 Avg.	Thio. (d)	100.0	51.1	50.9
p	1.000	0.3443	5	16.53				
				16.56				
				16.55 Avg.	Thio. (d)	99.3	50.9	50.
3p	1.000	0.2916	5	21.10				
				20.93				
				21.0 Avg.	Thio. (d)	98.6	40.9	40.
S	0.6000	0.1516	10	21.01				
			20	42.41				
			Avg. for 10 =	21.1	AsO_2^- (e)	99.5	33.4	33.3
LiF-BeF_2	0.6000	0.1997	10	14.97				
2/18/51			10	14.8				
				14.9 Avg.	AsO_2^- (f)	99.3	48.5	
Li_2BeF_4	0.6000	0.1516	10	21.01				
1/19/51			20	42.41				
			Avg. for 10 =	21.1	AsO_2^- (e)	99.5	33.4	33.3

* The letter following the reagent solution identifies its titer value as of a particular date of use. See Table D.

TABLE C

MATERIALS USED IN MELT PREPARATION, LiF-BeF_2 SYSTEM

Sample Designation	Sample Wt., (*See note) g.	Wt. BeO, g.	% Purity BeF_2 or $(NH_4)_2BeF_4$	Avg. % Purity
$(NH_4)_2BeF_4$, L-1	Mixt. A 0.7500 Mixt. B	0.1165 0.1138 0.1160	75.2 73.4 74.9	75.
$(NH_4)_2BeF_4$, L-2,3	0.7500 Mixt. C	0.0980 0.1030	63.3 66.5	65.
$(NH_4)_2BeF_4$, 1/19/51 First Fraction	Mixt. D Mixt. E	0.2031 0.2010	98.4 97.4	98.
Same, except Last Fraction	1.000	0.1576	76.2	76.
$(NH_4)_2BeF_4$ J-2	0.5000	0.1021	98.8	99.
$(NH_4)_2BeF_4$, M	0.7500 0.7500	0.1108 0.1097	71.5 70.7	71.
BeF_2, Brush Beryllium Corp. Product.	0.2903 0.2077	0.1530 0.1112	99.0 100.5	99.5

* Mixtures referred to above were control samples (for standardizations) into which $(NH_4)_2BeF_4$ was introduced to check on interferences. See Table E for details of mixtures.

TABLE D

SUMMARY OF TITER VALUES OF STANDARD SOLUTIONS

Date Used	Std. $KMnO_4$ Soln. #2, g. CaF_2/ml.	Std. Arsenite Soln., g. LiF/ml.	Std. $Na_2S_2O_3$ Soln., g. LiF/ml.
7/12/50	0.01056	0.001503	---
7/27/51	0.01011	0.001477 (f)	---
3/10/51	0.01012	0.00148 (e)	---
3/21/51	0.01012	0.001465 (a)	0.00106 (a)
4/24/51	0.01012	---	0.00106 (b)
5/15/51	0.01010	---	0.001065 (c)
9/12/51	0.01012	---	0.00104 (d)

Note -- The letters (a), (b), etc identify the titer values to be used with results given in Table B.

TABLE E

STANDARDIZATION AND CONTROL SAMPLES FOR LiF-BeF_2 SYSTEM ANALYSES

	Sample or Mixture	Sample Wt., g.	Vol. $KMnO_4$, ml.	Aliquot Vol. Li Detn., ml.	Type Reducing Agent	Vol. Reducing Agent Used, ml.	Avg. Vol. Equivalent to 0.1 g. of Li_2CO_3, ml.
A	$CaCO_3$	0.1500	Spoiled				
	Li_2CO_3	0.4000	Spoiled				
	$(NH_4)_2BeF_4$	0.7500	See Table C				
B	$CaCO_3$	0.3000	24.22				
	Li_2CO_3	0.6000		15 15	AsO_2^-	42.08 42.50	47.0
	$(NH_4)_2BeF_4$	0.7500	See Table C				
C	$CaCO_3$	0.1200	Spoiled				
	Li_2CO_3	0.4000		20 20	AsO_2^-	38.47 38.47	47.4
	$(NH_4)_2BeF_4$						
CC	$CaCO_3$	0.6000	44.17				
	Li_2CO_3	1.000		20 10	AsO_2^-	92.8 46.83	46.7
	$CaCO_3$	0.6000	44.37				
	Li_2CO_3	1.000		20 10	AsO_2^-	92.08 46.45	46.3
	Li_2CO_3	1.000	Fifteen trials with AsO_2^-		Avg. value	46.8	
	Avg. of Results on 7/12/50	Titer $KMnO_4$ = 0.01056 g. CaF_2/ml. Titer AsO_2^- = 0.001503 g. LiF/ml.					

Continued next page

TABLE E - Continued

Sample or Mixture	Sample Wt., g.	Vol. $KMnO_4$, ml.	Aliquot Vol. Li Detn., ml.	Type Reducing Agent	Vol. Reducing Agent Used, ml.	Avg. Vol. Equivalent to 0.1 g. of Li_2CO_3, ml.
D { $CaCO_3$	0.6000	46.19				
D { Li_2CO_3	1.000		10 10	AsO_2^-	46.73 46.26	46.5
D { $(NH_4)_2BeF_4$	1.000	See Table C				
E { $CaCO_3$	0.6000	46.33				
E { Li_2CO_3	1.000		10	AsO_2^-	46.3	46.3
E { $(NH_4)_2BeF_4$	1.000	See Table C.				
Li_2CO_3	1.000		10	AsO_2^-	47.46 47.64 47.42 47.73 47.02 47.40 47.82 47.53 47.40 47.21 47.60	47.5
Avg. of Results on 2/27/51	Titer $KMnO_4$ = 0.01011 g. CaF_2/ml. Titer AsO_2^- = 0.001477 g. LiF/ml.					
$CaCO_3$	0.6000	46.25				
$CaCO_3$	0.6000	46.20				
Li_2CO_3	1.000		10	AsO_2^-	47.40 47.40 47.56 47.40 47.50	47.4
Avg. of Results on 3/10/51	Titer $KMnO_4$ = 0.01012 g. CaF_2/ml. Titer AsO_2^- = 0.00148 g. LiF/ml.					

Continued next page

TABLE E - Continued

Sample or Mixture	Sample Wt., g.	Vol. $KMnO_4$, ml.	Aliquot Vol. Li Detn., ml.	Type Reducing Agent	Vol. Reducing Agent Used, ml.	Avg. Vol. Equivalent to 0.1 g. of Li_2CO_3, ml.
Li_2CO_3	1.000		10	AsO_2^-	47.80 48.00 48.47 47.68 47.60	47.9
$CaCO_3$	0.6000	46.21				
$CaCO_3$	0.6000	46.25				
Li_2CO_3	1.000		5	Thio.	33.10 33.10	
			10	Thio	65.90 67.00 66.10 66.60 66.50 66.60	66.2
Avg. of Results on 3/21/51	Titer $KMnO_4$ = 0.01012 g. CaF_2/ml. Titer AsO_2^- = 0.001465 g. LiF/ml. Titer $Na_2S_2O_3$ = 0.00106 g. LiF/ml.					
$CaCO_3$	0.6000	46.32				
$CaCO_3$	0.6000	46.28				
Li_2CO_3	1.000		5	Thio	33.00 33.00 33.00 32.90 32.86 33.00 32.85	65.9
Avg. of Results on 5/15/51	Titer $KMnO_4$ = 0.01010 g. CaF_2/ml. Titer $Na_2S_2O_3$ = 0.001065 g. LiF/ml.					

Continued next page

TABLE E - Continued

Sample or Mixture	Sample Wt., g.	Vol. $KMnO_4$, ml.	Aliquot Vol. Li Detn., ml.	Type Reducing Agent	Vol. Reducing Agent Used, ml.		Avg. Vol. Equivalent to 0.1 g. of Li_2CO_3, ml.
$CaCO_3$	0.6000	46.25					
$CaCO_3$	0.6000	46.20					
Li_2CO_3	1.000		10	Thio	65.90 66.10 66.60	66.50 66.60 67.00	66.2
			5	Thio	33.10 33.10 33.05	32.95 32.91	
Avg. of Results on 4/24/51	Titer $KMnO_4$ = 0.01012 g. CaF_2/ml. Titer $Na_2S_2O_3$ = 0.00104 g. LiF/ml.						
Mixt. $CaCO_3$	0.6000	46.22					33.7
Mixt. Li_2CO_3	1.000		5	Thio.	33.67		
Mixt. $CaCO_3$	0.6000	46.21					
Mixt. Li_2CO_3	1.000		5	Thio.	33.67		
Li_2CO_3	0.7500		10	Thio.	51.00 51.30	51.08 51.34	33.7
			5	Thio.	25.20 25.05	24.97	
Avg. of Results on 9/12/51	Titer $KMnO_4$ = 0.01012 g. CaF_2/ml. Titer $Na_2S_2O_3$ = 0.00104 g. LiF/ml.						

PART J

SYSTEM CaF_2-LiF-BeF_2 ANALYSES

The analytical methods used were those described in Appendix 14.

In tabulating the data, condensation was necessary, so that the following notes explain certain features of the tabulations.

Table A is sectionalized according to the date of analysis, so that the titers of the standard solutions (as of that date) may be obtained from the summary table (B) at the end of this part of the appendix.

In the column headed "Vol. Reducing Agent", the symbol "T" or "R" signifies use of sodium thiosulfate or arsenite solution.

In the columns under "Composition, Wt. Percent", the value for lithium fluoride has been omitted, it being understood that it is obtainable by deduction of the weight percents of calcium and beryllium fluorides from the "Sum Wt. Percent" value.

Similarly in the columns of "Composition, Mole Percent", the value for lithium fluoride is obtainable by difference from 100.

The aliquot values in the lithium determination are not shown, usually a volume between 1 and 20 ml. being taken to adjust the amount of precipitate to a convenient titration value. The value shown in the column "Vol. Reducing Agent" is given on the basis of using 10 ml. aliquots in all cases, based on several titrations.

For the results on 7/12/50 only, the calculation of the mole percentages was made after first adjusting the weight percentages to a total of 100. On the other dates, the mole percentages were calculated as if the sums of the weight percentages were equal to 100, without adjustment.

TABLE A

ANALYTICAL RESULTS FOR TERNARY SYSTEM SAMPLES

Sample	Sample Wt., g.	Wt. BeO, g.	Vol. $KMnO_4$, ml.	Vol. Reducing Agent, ml.	Composition Wt. Percent, BeF_2	Composition Wt. Percent, CaF_2	Sum Wt. Percents	Analytical Composition, Mole Percent BeF_2	Analytical Composition, Mole Percent CaF_2	Theoretical Composition, Mole Percent BeF_2	Theoretical Composition, Mole Percent CaF_2
7/12/50				"R"							
A-8	3.000	0.0630	128.1	101.3	3.94	45.15	99.7	3.2	22.1	2.6	22.0
B-7	2.000	0.0638	96.07	58.2	5.99	50.75	100.5	5.2	26.4	5.8	26.6
C-7	2.000	0.1180	79.45	64.7	11.08	41.9	101.6	8.9	20.3	9.3	20.8
D-7	2.000	0.1445	85.40	59.4	13.57	45.1	103.4	11.1	22.3	10.9	22.4
E-5	1.500	0.1675	43.98	51.0	20.96	30.94	103.0	15.9	14.2	16.2	13.6
F-4	1.500	0.2735	39.88	44.6	34.20	28.1	108.*	25.5?	12.6?	19.?	14.?
FF-5	1.500	0.2180	41.78	46.8	27.27	29.4	103.6	21.0	13.6	19.8	14.0
G-6	1.250	0.1810	39.37	33.9	27.18	33.3	101.2	22.5	16.6	20.3	16.4
H-5	1.250	0.1965	34.38	35.0	29.50	29.05	100.8	24.9	14.2	23.7	14.0
I-5	1.000	0.1890	21.98	26.8	35.50	23.2	99.1	28.9	11.4	26.?	11.5
J-5	1.000	0.1775	24.67	26.3	33.34	26.1	99.0	27.6	13.0	28.?	12.9
* F-4 contaminated with considerable BeO											
2/27/51				"R"							
g-6	1.000	0.2552	37.30	12.1	47.95	37.7	103.6	46.5*	22.1	47.2	21.4
g-9	0.7500	0.2128	17.97	12.3	53.35	24.2	101.9	47.6*	13.0	47.8	11.7
g-11	0.5000	0.1491	8.44	9.4	56.04	17.1	100.9	48.0*	8.8	48.0	7.8
g-14	1.000	0.3222	8.84	21.6	60.6	8.9	101.4	49.0*	4.3	48.2	3.5
*See subsequent repeat analyses.											
3/10/51				"R"							
g-6	1.000	0.2447	Lost	Lost	46.05	--	--	* --	* --	--	--
g-9	1.000	0.2828	24.05	17.1	53.2	24.3	102.8	47.8	12.9	47.8	11.7
g-11	0.4058	0.1210	7.03	7.8	56.1	17.5	102.2	47.4	8.9	48.0	7.8
g-14	1.000	0.3211	9.10	22.0	60.4	9.2	102.2	48.3	4.5	48.2	3.5
CB' **	1.000	0.2029	62.00	None	38.2	62.7	100.9	50.3	49.7	50.0	50.0
X-8	1.000	0.1672	62.53	5.0	31.4	63.2	102.0	37.9	45.9	38.5	45.0
Z-9	1.000	0.1820	64.75	1.6	34.2	65.5	102.1	43.7	50.7	46.8	48.0
V-8	1.000	0.1556	61.94	7.0	29.3	62.6	102.3	34.1	43.9	35.8	40.4
Y-7	1.000	0.1835	62.63	3.0	34.5	63.3	102.2	42.8	47.3	42.9	46.4

Continued next page

TABLE A - Continued

Sample	Sample Wt., g.	Wt. BeO, g.	Vol. $KMnO_4$, ml.	Vol. Reducing Agent, ml.	Composition, Wt. Percent		Sum Wt. Percents	Analytical Composition, Mole Percent		Theoretical Composition, Mole Percent	
					BeF_2	CaF_2		BeF_2	CaF_2	BeF_2	CaF_2
3/10/51				"R"							
ZZ-11	1.000	0.1891	65.71	1.4	35.6	66.4	104.1	44.9	50.3	48.5	49.2
b-6	1.000	0.1502	50.60	18.1	28.2	51.1	106.1	26.2	28.6*	26.5?	26.5?
U-8	1.000	0.1354	59.83	10.6	25.5	60.5	101.7	28.2	40.3	35.4?	35.7?
W-10	1.000	0.1641	62.83	5.87	30.9	63.5	103.1	36.4	45.0	37.4	42.5
* See subsequent repeat analysis. ** Binary melt used to shift ternary melts.											
3/21/51											
K-5	1.000	0.1751	30.77	25.05R	32.9	31.1	100.6	27.8	15.9	28.1	15.7
L-5	1.000	0.1833	31.11	24.22"	34.5	31.45	101.2	29.4	16.2	30.2	15.7
LL-14	0.8000	0.2034	9.23	22.70"	47.8	11.66	101.1	36.7	5.4	35.8	5.4
M-4	1.000	0.2286	22.10	34.27T	43.0	22.35	101.6	35.2	11.0	35.6	10.8
MM-14	0.8000	0.2238	7.43	22.20R	52.6	9.4	102.3	40.1	4.3	40.1	4.4
				30.57T	52.6	9.4	102.5	40.0	4.3		
N-4	1.000	0.2378	27.31	21.08R	44.7	27.6	102.7	38.4	14.2	38.5	14.5
				28.90T	44.7	27.6	102.9	38.2	14.3		
O-4	1.000	0.3152	7.70	22.72R	59.3	7.78	100.7	47.5	3.8	46.4	3.7
P-5	0.9000	0.2889	8.90	18.96"	60.4	9.9	101.4	49.2	4.9	48.6	4.7
2Q-7	0.7900	0.1882	3.23	27.86"	44.75	4.14	100.0	32.0	1.8	31.0	1.7
3Q-6	1.000	0.2401	6.80	33.15"	45.1	6.88	100.5	32.9	3.0	31.8	2.8
6Q-9	1.000	0.2147	8.58	48.57T	40.4	8.68	100.6	29.1	3.8	28.8	3.7
7Q-10	1.000	0.2438	9.38	30.64R	45.8	9.49	100.2	34.4	4.3	32.7	4.2
8Q-9	1.000	0.2439	10.57	29.90R	45.9	10.69	100.4	34.8	4.9	33.4	4.6
9Q-7	1.000	0.2303	5.79	35.15R	43.3	5.86	100.7	30.9	2.5	29.9	2.5
				48.90T	43.3	5.86	101.1	30.7	2.5		
10Q-11	1.000	0.2448	13.67	28.70R	46.0	13.83	101.7	35.4	6.4	34.5	5.8
12Q-11	1.000	0.2472	13.85	27.60"	46.5	14.01	101.0	36.2	6.6	35.3	6.6
13Q-16	1.000	0.2452	15.78	25.85"	47.0	15.96	100.6	37.7	7.7	36.5	7.7
S-4	1.000	0.1414	44.60	19.70"	26.6	45.1	100.5	25.1	25.7	25.0	25.0

Continued next page

TABLE A - Continued

Sample	Sample Wt., g.	Wt. BeO, g.	Vol. $KMnO_4$, ml.	Vol. Reducing Agent, ml.	Composition, Wt. Percent BeF_2	Composition, Wt. Percent CaF_2	Sum Wt. Percents	Analytical Composition, Mole Percent BeF_2	Analytical Composition, Mole Percent CaF_2	Theoretical Composition, Mole Percent BeF_2	Theoretical Composition, Mole Percent CaF_2
4/24/51				"T"							
g-6	1.000	0.2509	37.63	16.85	47.15	38.1	103.1	46.0	22.4	47.2	21.4
b-6	1.000	0.1545	49.85	24.85	29.04	50.4	105.8	27.1	28.3	26.5?	26.5?
LL-7	0.8400	0.2304	3.42	35.70	51.6	4.12	100.7	38.0	1.8	37.3	1.8
MM-6	0.7100	0.2110	2.32	27.86	55.9	3.31	100.9	41.9	1.5	41.4	1.4
1Q-8	0.8300	0.2092	4.78	38.40	47.3	5.83	102.3	33.8	2.5	33.5	2.4
4Q-7	0.9500	0.2264	6.42	43.85	44.8	6.84	100.6	32.5	3.0	31.2	3.1
11Q-8	1.000	0.2377	6.24	46.50	44.7	6.31	100.3	32.4	2.8	30.8	2.8
S-6	1.000	0.1550	51.77	18.3	29.2	52.4	101.0	30.4	32.9	30.7	30.7
5/15/51				"T"							
e-1	0.6350	0.1456	5.04	29.2	43.15	8.02	100.2	31.5	3.5	31.3	3.5
e-2	0.4800	0.1146	1.96	23.2	44.9	4.13	100.5	32.0	1.7	31.9	1.7
e-6	0.5200	0.1082	3.75	26.0	39.0	7.29	99.6	27.8	3.2	27.4	3.1
e-10	0.8000	0.1710	2.89	42.4	40.2	3.65	100.4	27.95	1.55	27.6	1.55
e-19	1.000	0.1951	16.44	44.6	36.7	16.60	100.8	27.6	7.5	27.2	7.5
e-20	1.000	0.2016	12.31	47.1	37.9	12.43	100.5	27.8	5.5	27.6	5.6
t-6	1.000	0.1878	17.23	44.8	35.3	17.40	100.5	26.6	7.9	26.0	8.1

TABLE B

TITERS OF STANDARD SOLUTIONS

Date of Analysis	Std. $KMnO_4$ #2, g. CaF_2/ml.	Std. Arsenite Soln., g. LiF/ml.	Std. $Na_2S_2O_3$, g. LiF/ml.
7/12/50	0.01056	0.001503	---
2/27/51	0.01011	0.001477	---
3/10/51	0.01012	0.00148	---
3/21/51	0.01012	0.001465	0.00106
4/24/51	0.01012	---	0.00106
5/15/51	0.01010	---	0.001065

Source of Standardization values -- Table E of Part I of this appendix.

PART K

ANALYSIS OF ELECTROLYTIC SAMPLES

As a means of determining the composition of the solidified lead cathodes from the electrolysis samples the following analytical scheme was used. The objective was to completely remove all lead by appropriate separations in order to prevent interference with subsequent beryllium, calcium and lithium analyses.

After removing all traces of solidified melt by scraping the samples, shavings of the cathode samples were prepared. One gram samples were dissolved in mixed nitric and hydrochloric acids at steam bath temperature and were evaporated just to dryness three times with subsequent addition of hydrochloric acid. The residue was taken into solution in dilute hydrochloric acid and allowed to slowly evaporate (under a watch glass) on the steam bath until lead chloride crystals commenced to form. The solution was allowed to cool and the major portion of the lead was removed by filtration, as lead chloride, using cold dilute hydrochloric acid as a wash liquid. The lead chloride was retained for subsequent combination with the small amount of lead remaining in the filtrate.

The filtrate was converted to the nitrate form, was taken to dryness, and sufficient nitric acid was added to bring the acid concentration to about 10 ml. of dilute nitric acid per 100 ml. of solution. This solution was electrolyzed at low current density with stirring, using platinum electrodes, to anodically deposit PbO_2.

The solution that remained was converted to the perchlorate form and (omitting the fluoride decomposition step) beryllium, calcium and lithium analyses were performed. Much smaller volumes were used in line with the low values anticipated for the "impurities" in the lead cathode. A sample of the original chemically pure lead was used as a parallel control sample.

The deposit of PbO_2 was converted to chloride form and was combined with the previously separated $PbCl_2$ to form a solution which was taken to dryness to remove excess HCl. The residue was redissolved and the lead was precipitated and recovered as $PbSO_4$ using Gooch filtering crucibles. The crucible and precipitate were ignited at 550° and weighed as $PbSO_4$.

The results are tabulated below:

Samples	Orig. Lead	"After 1EL-1"	"After 2EL-1"	"After 4EL-1"	"After 5EL-1"
Sample weight, g.	1.0012	1.0042	1.0034	1.0033	1.0024
Vol. $KMnO_4$, ml.	<0.05	<0.05	<0.05	<0.05	<0.05
Wt. BeO, g.	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Vol. $Na_2S_2O_3$, ml.*	0.10 avg.	0.15 avg.	0.14 avg.	0.15 avg.	0.10 avg.
Wt. % Ca	<0.02	<0.02	<0.02	<0.02	<0.02
Wt. % Be	<0.03	<0.03	<0.03	<0.03	<0.03
Wt. % Li	0.03	0.04	0.04	0.04	0.03
Wt Xbl. + $PbSO_4$	16.6198	19.2504	18.8366	19.2420	15.9949
Wt. MT Xbl.	15.1648	17.7994	17.3833	17.7916	14.5403
Wt. $PbSO_4$	1.4550	1.4510	1.4533	1.4504	1.4546
Wt. % Pb	99.3	98.8	99.0	98.8	99.3

Notes: Solutions -- $KMnO_4$ = 0.01012 g. CaF_2/ml.
$Na_2S_2O_3$ = 0.02083 g. LiF/ml.
* 10 ml. aliquots of 100 ml. volume.

In view of the fact that the analytical samples did not differ significantly from the control sample, it was concluded that no appreciable Ca, Be or Li content was present in the samples. The over-all recovery was reasonably high considering all the manipulations. Other samples, containing the three elements, which were run at the same time gave satisfactory results.

APPENDIX 16

APPENDIX 16

CONDUCTANCE MEASUREMENTS

Rough conductivity determinations were made on several ternary melt mixtures prior to electrolytic work. Primarily this information was desired only in order that the cause of any high cell resistance during electrolysis could be properly attributed to either a conductance effect or a result of electrode polarization. The equipment and general accuracy have been discussed in the section dealing with the electrolytic study of the ternary system.

In the results that follow showing resistance of the cell as a function of temperature and composition, there is some obvious discordance in that reproducible results were not obtained as a melt was heated and cooled. This may have been the result of unknown film resistance on the electrodes, or conceivably could be due to a change in the molecular complexity of the melt in a time dependent manner.

The results tabulated show the resistance of pairs of melts differing in composition by only a slight amount of added CaF_2. Some of the values refer to the solid form, as the melts were heated and cooled (in some cases) through the melting point.

Melt 1 EL

Temp., °C.	Resist., ohms	Temp., °C.	Resist., ohms
430	36.0	469	2.0
443	23.0	476	1.0
448	16.0	486	0.4
451	13.5	505	0.4
453	9.0	509	0.4
454	7.0	482	0.4
455	5.8	465	0.5
455	5.1	455	0.5
456	4.2	444	0.6
456	4.0	433	1.5
457	3.8	428	5.0
463	3.0		

Melt 1EL-1

Temp., °C.	Resist., ohms
450	3.6
456	3.0
463	2.4
472	1.7
481	1.1
490	0.5
502	0.4
521	0.3
534	0.3

Melt 2EL
(Heated to 600° and
allowed to cool)

Temp., °C.	Resist., ohms
600	0.3
510	0.5
470	0.5
448	0.6
440	0.7
435	0.8

Melt 2EL-1

Temp., °C.	Resist., ohms	Temp., °C.	Resist., ohms
452	9.0	520	2.1
473	6.5	489	2.2
490	5.4	466	2.5
506	3.8	446	2.8
520	2.8	435	3.2
560	2.2	430	3.9
580	1.8	420	5.5
580	1.6	410	7.8
560	1.7	400	12.0
550	1.8	390	27.5
540	1.8	385	57.0
		375	112.0

Continued next page

Melt 3EL		Melt 3EL-1	
Temp., °C.	Resist., ohms	Temp., °C.	Resist., ohms
464	3.4	335	4.0
490	2.8	340	3.7
521	2.3	375	4.5
510	2.2	420	1.4
495	2.4	475	0.9
452	2.4	510	0.7
403	2.6	480	0.8
320	22.0	430	1.4
		365	1.6

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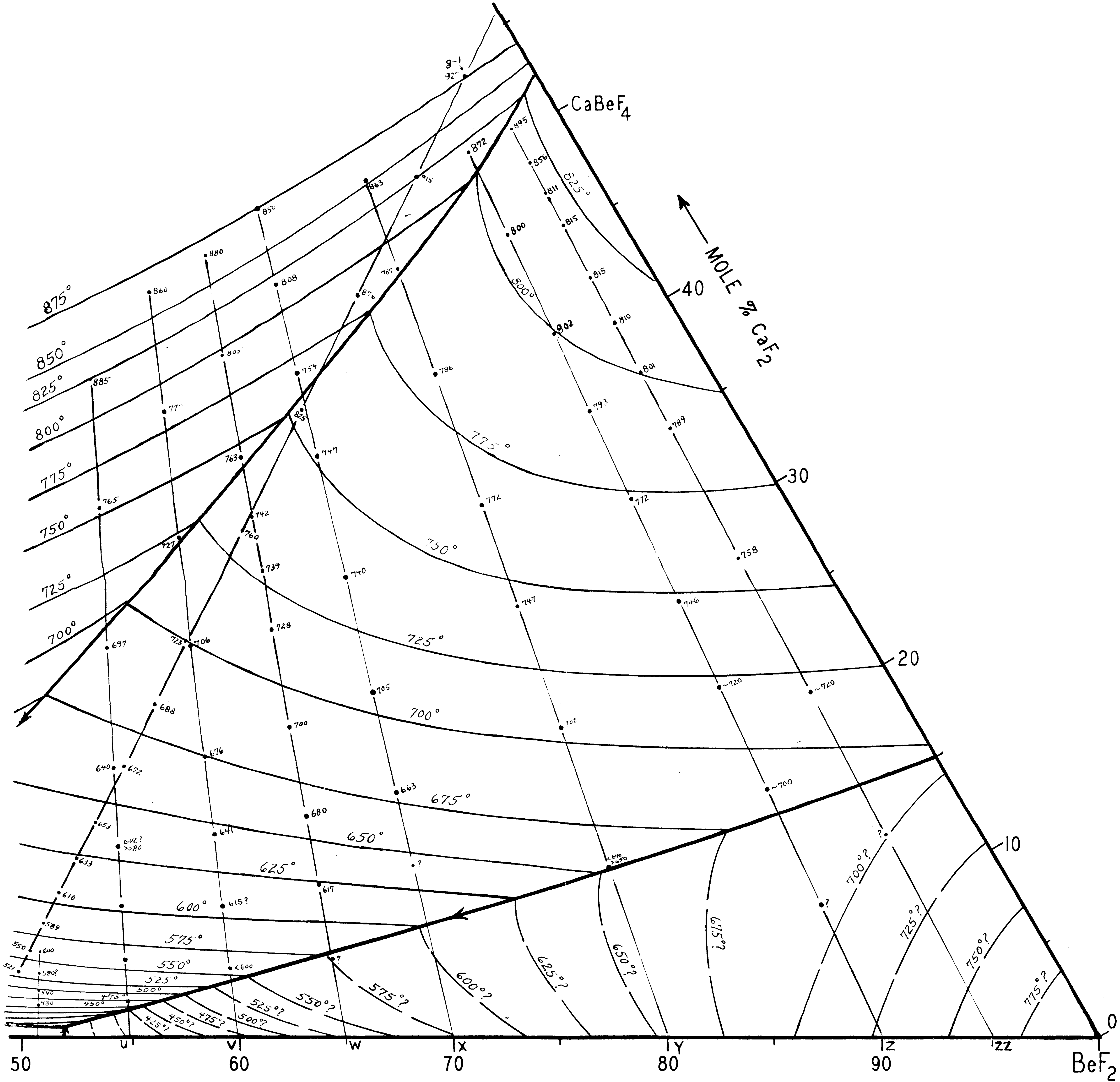

FIGURE 12
BeF$_2$-RICH REGION

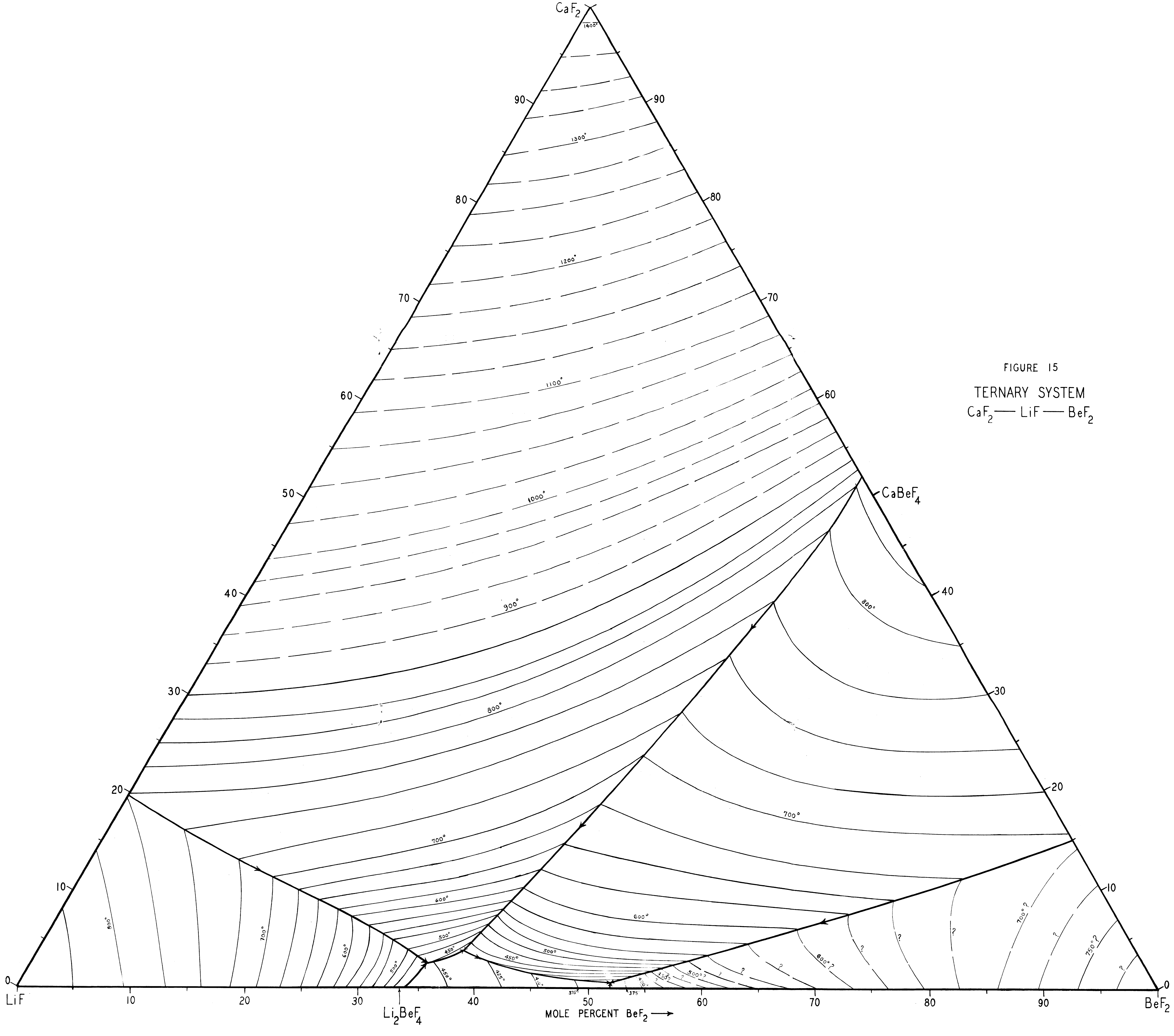

FIGURE 15

TERNARY SYSTEM

CaF$_2$ — LiF — BeF$_2$

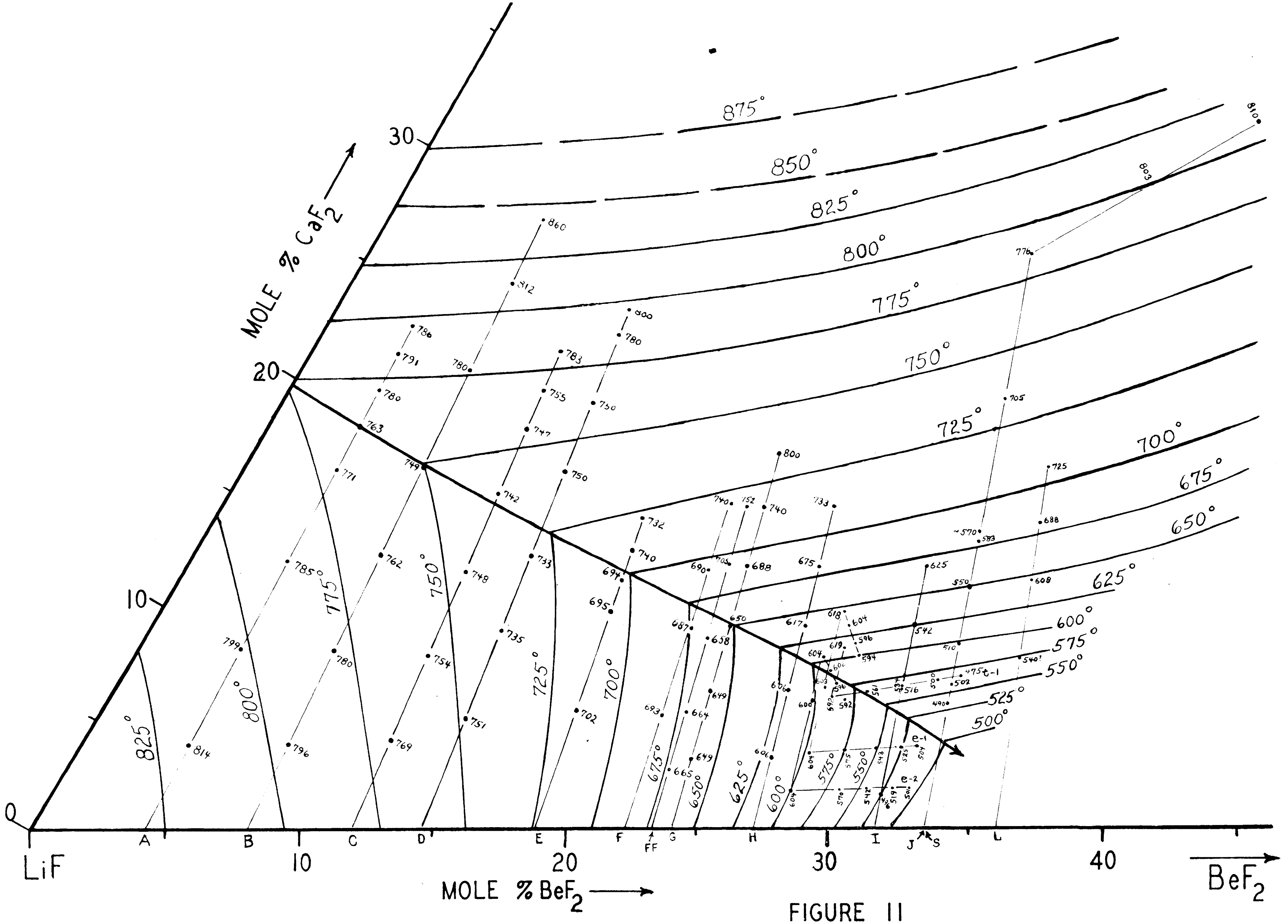

FIGURE 11

LiF-RICH REGION

FIGURE 13
Li_2BeF_4—RICH REGION