THERMAL ANALYSIS OF THE SYSTEM
POTASSIUM FLUORIDE-POTASSIUM METAPHOSPHATE

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By

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TABLE OF CONTENTS

I. INTRODUCTION

The system potassium fluoride-potassium metaphosphate has been studied by the method of thermal analysis to determine what compounds may be formed and the conditions under which these compounds are stable.

For such a condensed system the phase rule as deduced by J. Willard Gibbs may be stated as $F = C - P + 1$, where F is the number of degrees of freedom, C the number of components, and P the number of phases in the system. In this case, for a two component system, both temperature and composition must be specified to fix the system if there is only a single phase present. If there are two phases in equilibrium, specification of either temperature or composition will serve to fix the system, while if there are three phases in equilibrium the system is invariant and both temperature and composition are fixed.

Advantage is taken of these phase relations by use of the method of thermal analysis as applied to systems in phase equilibrium. In this method a mixture of the two components is made and heated until a homogeneous liquid phase is obtained. The melt is then cooled at a uniform rate, with temperature versus time measurements being recorded as the cooling proceeds. The cooling curve plotted from these measurements will show an inflection at the temperature at which solid first begins to separate from the melt. The condensed system will then be univariant, and the temperature will continue to fall as the solid separates. The point of inflection in the cooling curve results from a change in

the rate of cooling of the mixture which is brought about by the release of heat of crystallisation by the separating solid. The temperature of initial crystallisation varies with the composition of the mixture.

A second point of inflection, which in favorable cases will be an almost horizontal flat, will be found on the cooling curve at the temperature at which a second solid phase begins to separate. This temperature is invariant since two solid phases are in equilibrium with a liquid phase so that $F = 2 - 3 + 1 = 0$. The resulting mixture of two solid phases is known as an eutectic mixture and the temperature at which they are in equilibrium with the liquid phase is the eutectic temperature.

A graph of temperature against composition on which the dependence of the temperature of initial crystallisation with composition and the eutectic temperature are shown constitutes the phase diagram of the system.

In certain two component systems compound formation between the components occurs. The cooling curve of the mixture whose composition corresponds with that of the compound will be that of a one component system. The system will be invariant at the freezing point of the compound, which is said to have a congruent melting point. The phase diagram has a characteristic maximum in the curve of initial crystallisation versus composition at the composition corresponding with that of the compound.

In other systems, or in the same system, a compound may be formed between the two components which dissociates at or below its melting point. For such a system there will be a point of in-

flection in the curve of initial crystallization at the temperature above which the compound is not stable. This type of compound is said to have an incongruent melting point at the temperature at which it dissociates.

A compound with an incongruent melting point will form a simple eutectic with one component of the system. If the other component is in excess it will separate as a solid at a temperature above that at which dissociation occurs. At the temperature of the incongruent melting point this solid will react with the melt so as to form the unstable compound. This invariant temperature (two solid and one liquid phase) is known as the peritectic temperature and the reaction which occurs is known as the peritectic reaction. Cooling curves of this type of mixture will show an inflection at the initiation of crystallization and a halt at the peritectic temperature.

Solid phase transitions between two crystalline forms of a single compound can be detected by thermal analysis if the equilibrium between the two forms is readily attained. Cooling curves will show an inflection at the transition temperature, which is invariant.

This sketch of the phase rule and its application has included only that which is pertinent to the system which was studied. More complete discussions can be found in any good text of general physical chemistry, while good discussions of the methods of thermal analysis can be found in most metallurgical works.

Mario Amadori (1) has studied the system potassium fluoride-

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(1) Amadori Atti. accad. Lincei <u>21</u>, 688-95 (1912)

potassium metaphosphate by the methods of thermal analysis. He
presented evidence which he interpreted as indicating the formation
of a compound with an incongruent melting point at 33.3 mole %
KPO_3, which he gave the empirical formula $KPO_3.2KF$. Evidence was
also found for the formation of a compound with a congruent melt-
ing point at 50.0 mole % KPO_3, to which he ascribed the formula
$KPO_3.KF$. Two solid phase transitions were found in the system,
one of which he believed to be in KPO_3, the other in $KPO_3.2KF$.

The results of the present study indicate that the compound
formed at 33.3 mole % KPO_3 is fairly stable at its melting point
and that it forms an eutectic with the compound formed at 50.0
mole % KPO_3. Evidence for a region of liquid immiscibility, and
for a solid phase transition in the compound formed at 50.0 mole %
KPO_3 were also found. Amadori did not report either of these
phenomena.

II. EXPERIMENTAL METHODS and EQUIPMENT

A tubular furnace, wound with nichrome wire, $1\frac{1}{2}$" inside diameter and 9" deep was used to heat the mixtures throughout this investigation. A Variac (model V5MT) was used to control the rates of heating and cooling the furnace. The furnace would heat to 900° in about 25 to 30 minutes with a $4\frac{1}{2}$ ampere current. The furnace was satisfactory in all respects except one; that is, there was a temperature gradient in the bore of the furnace so that the top of a crucible was at a somewhat lower temperature than was the bottom.

A platinum-platinum, 13% rhodium thermocouple was used to follow the temperature of the mixtures. This couple was calibrated at the freezing points of copper and aluminum. These metals were obtained from and their melting points were certified by the National Bureau of Standards. In addition, the freezing points of silver and of sodium chloride were used in the calibration. All four points fell on a straight line. The procedure used in calibrating was that recommended by Roeser and Wensel. (1) Temperatures were determined by comparison with standard tables prepared by Roeser and Wensel. (2)

A Leeds and Northrup type K-1 potentiometer, No. 316493, was

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(1) Roeser and Wensel, Methods of Testing Thermocouples and Thermocouple Materials National Bureau of Standards, Research Paper RP768

(2) Roeser and Wensel, Reference Tables for Platinum to Platinum-Rhodium Thermocouples National Bureau of Standards, Research Paper No. 530

used for most of the measurements. This potentiometer could be easily read to $\pm$ 1 microvolt; we consider, however, that the precision of the instrument is no better than $\pm$ 5 microvolts or about 0.5°C. A Leeds and Northrup wall galvanometer was used in balancing the potentiometer. This galvanometer had a period of 8 seconds, somewhat greater than desirable, and a sensitivity of about 1.1 microvolts per millimeter deflection, which was adequate.

A Brown Electronic recording potentiometer was also used to follow the cooling curves. This instrument could be read to $\pm$ 5 microvolts, and we consider that the precision was about $\pm$ 1.0°C. The Brown instrument was especially useful for the first cooling curve of a mixture, since with it we could readily determine the approximate temperature at which an inflection in the cooling curve occurred, which expedited subsequent measurements with the type K potentiometer. The Brown potentiometer was calibrated against the type K potentiometer.

An electric kitchen clock with a large sweep second hand was used to measure time intervals. This clock could be easily and quickly read, and was much more satisfactory than a stop watch.

The uncertainty in temperature is believed to be of the order of one degree centigrade.

A platinum crucible was used as a container for the first few mixtures which were run. The crucible was supported in a loop in a platinum wire which was hung from the thermocouple support. These crucibles were found to be unsatisfactory, as there was creeping of the melt from the crucible. This creeping is believed to have resulted in a change of composition of the mixture so that

the measurements were unreliable.

All of the mixtures from which data was taken for the phase diagram were run in crucibles of Acheson graphite. These crucibles were turned down on a lathe to outside dimensions of 50mm in height and 22mm in diameter, and inside dimensions of 45mm in depth and 11mm in diameter. They were found to fulfill their purpose very well.

The graphite crucibles containing the charge to be examined were placed in a fused quartz tube which was then lowered into the furnace. This method worked very well until part of one mixture was accidentally spilled and reacted with the quartz, destroying the tube. Since no other quartz tubes of the proper size were available, a fire clay support was prepared. The crucibles were lowered onto it with a pair of tongs. The principle objection to this method was that it exposed the crucible to excessive oxidation so that the crucible became worthless for further use.

The bare junction was inserted in the mixtures. This was considered necessary because any protecting tube containing silica would react with the melts while metal tubes might have changed the characteristics of the couple. Graphite protecting tubes should have served quite well, but the bare couple gave satisfactory results and we felt that nothing would be gained by preparing such tubes. The use of the bare junction had one very important advantage in that it quickly adjusted itself to the temperature of mixture.

The mixtures of about three grams each, were prepared by weighing out the appropriate amounts of KF and KPO_3 and mixing them

with a mortar and pestle. Since it has been proposed that KF and H_2O react at high temperatures to give HF and KOH, precautions were taken to prevent the inclusion of water in the mixtures. Both components had previously been dried in an oven at 180-200°C. The mixture and crucible were also dried for several hours before the crucible was filled, while the filled crucible was kept in the oven until time for its use. Some water was absorbed by the KF in the process of weighing, which introduced a slight error in the composition variable.

Two different lots of potassium fluoride were used in this investigation. These were Ozark-Mahoning lot No. W-5-28, 99.4% KF and Baker and Adamson lot No. 52, reagent grade, 99.67% KF. The potassium metaphosphate used was Ozark-Mahoning lot No. W-5-27, 99.9% KPO_3.

III. THE PHASE DIAGRAM

TABLE I

PHENOMENA ENCOUNTERED IN THE SYSTEM

Phenomenon	Temperature	
	This study	Observations of Amadori
Eutectic at 20 mole% KPO_3	698°	742°
Invariant (two liquid and one solid phase)	729°	not observed
Maximum at 33.3 mole% KPO_3	800°	not observed
Incongruent melting point at 33.3 mole% KPO_3	not observed	793°
Eutectic at 41 mole % KPO_3	752°	not observed
Maximum at 50 mole % KPO_3	886°	880°
Eutectic at 84 mole % KPO_3	612°	604°
Transition in solid KPO_3	443°	450°
Transition in solid $KPO_3.KF$	800°	not observed
Transition in solid $KPO_3.2KF$	540°	540°
Freezing point, KF	859.3°	855°
Freezing point, KPO_3	804.4°	798°

A. General Description. The most important temperatures found from this study are compared with the observations of Amadori in Table I.

Addition of KPO_3 to KF lowers the freezing point until an

SYSTEM KF-KPO₃
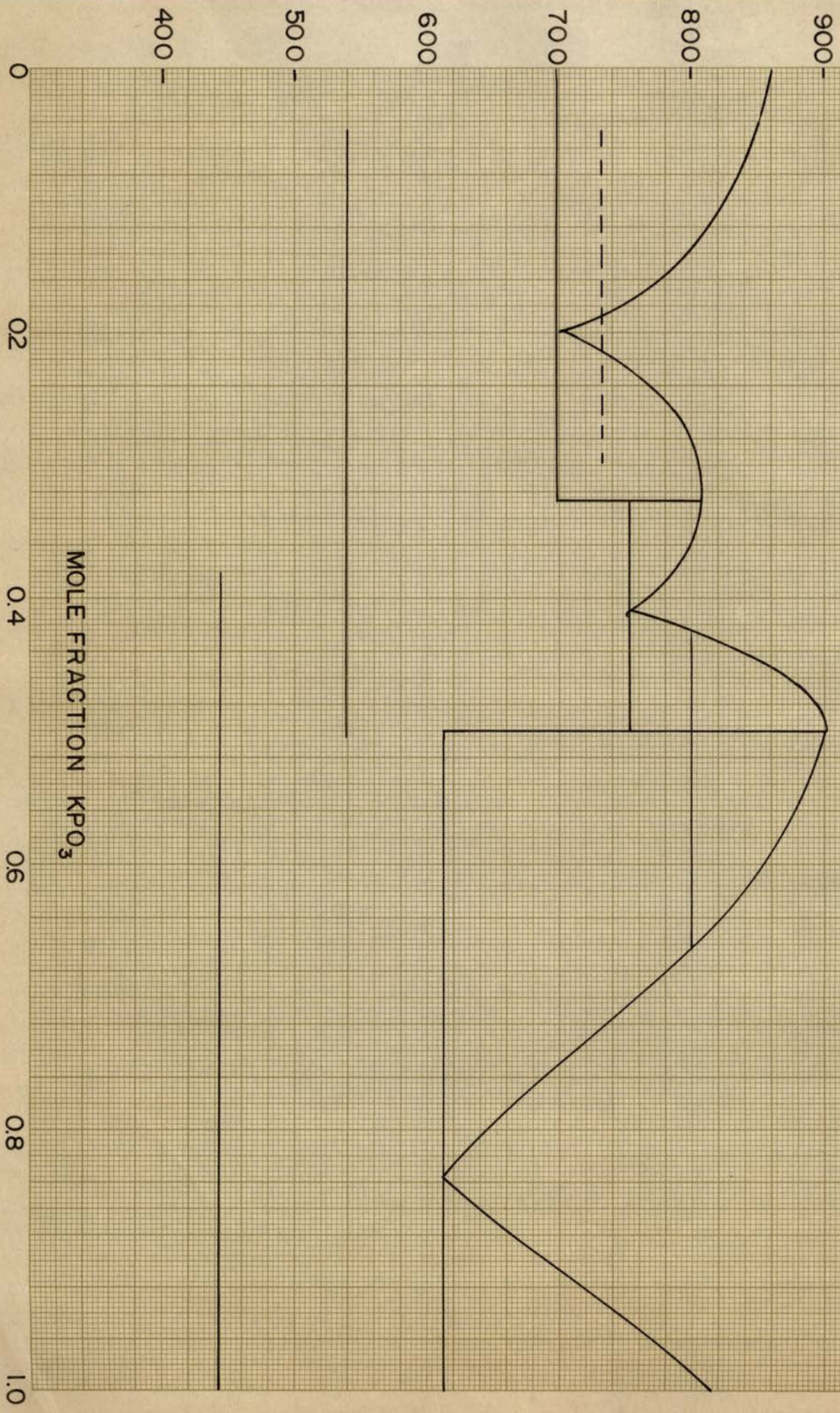
MOLE FRACTION KPO₃

eutectic is reached at 20 mole% KPO_3 at a temperature of 698°.
Further addition of KPO_3 then results in an increase in the temper-
ature of initial crystallization until a broad, flat maximum is
reached at 800° at a composition of 33.3 mole% KPO_3. The eutectic
at 698° continues in the system up to this concentration, but at
higher concentrations of KPO_3 an eutectic is found at 752°. The
temperature of initial crystallization falls rather sharply be-
tween 37.5 mole%KPO_3 and the eutectic composition, 41 mole% KPO_3.
As the system becomes still more rich in KPO_3, the temperature of
initial crystallization rises sharply to 886° at 50.0 mole% KPO_3.
The eutectic at 752° persists through this range. There is some
indication of a phase transition at 540°; those mixtures for which
cooling curves were taken in this range gave very slight inflections
near this temperature. Amadori believed this transition to be an
equilibrium between two crystalline forms of $KPO_3.2KF$. Such evi-
dence as can be gained from the present study supports this view-
point; this evidence is not, however, sufficient to fully establish
this transition.

There is a transition in the KF rich part of the region and
another at 50 mole% KPO_3 which are difficult to explain. Some of
the ideas which have been entertained concerning these transitions
will be presented later.

The KPO_3 rich part of the system forms a simple eutectic be-
tween 50 mole% KPO_3 and pure KPO_3. The eutectic composition is
about 84% KPO_3, while the eutectic temperature is 612°. The eutectic
temperature falls off sharply on both sides of the eutectic compo-
sition.

TABLE II

PURE KF TO 33.3 MOLE% KPO$_3$

*No.	Mole% KPO$_3$	Initial Crystallization	Length of Halt	Invariant (two liquid and one solid phase)	Length of Halt	Eutectic	Length of Halt	Transition in KPO$_3$.2KF	Length of Halt
	0.0	859.3°C		None		None		None	
27	5.06	841.0	150"	709.2°C	5"	697.8°C	25"	550°	10"
35	9.98	817.7	50	714.7	55	694.0	55	527°	10
28	14.9	780.7	40	723.1	60	697.0	60	527°	15
	17.19	758.5	30	723.1	60	697.5	70	540°	10
11	19.61	None		729.5	55	692.5	45	Not run	
12	24.73	770.6	20	729.6	35	700.3	25	Not run	
13	29.66	785.2	75	723.7	5	700.1	80	Not run	
19	32.71	793.9	120	740.1	5	688.0	40	Not run	
14	34.73	797.0	120	None		752.7	40	Not run	

*No. refers to the order in which the mixtures were run. Those mixtures numbered 26 and smaller were made with the Ozark-Mahoning KF, while those numbered 27 and larger were made with the Baker and Adamson KF.

A solid phase transition is found in KPO_3 at 443°. This transition persists through the system to about 37 mole% KPO_3.

B. The System from Pure KF to 33.3 Mole% KPO_3. The freezing point of potassium fluoride, Ozark Mahoning lot No. W-5-28 was found to be 854.0°, while that of the Baker and Adamson lot No. 52 was found to be 859.3°. This difference can be readily explained as resulting from differences in the purity of the two lots. There is considerable discrepancy in the literature values for the freezing point of potassium fluoride. As an example, the International Critical Tables (1) give values ranging from 851° to 885° for the freezing point of this compound.

Throughout most of this composition range the initiation of crystallization manifests itself by good flats, sometimes accompanied by slight supercooling, in the cooling curves. As a result, these temperatures can be determined with considerable accuracy. There is a tendency for the temperature of initial crystallization to become somewhat lower with successive coolings of a particular mixture.

There are three well defined halts in the cooling curves of all mixtures between 10 and 25 mole% KPO_3; at 5 and 30 mole% KPO_3 the second of these gives only a very slight inflection, as can be seen from an examination of table 2. The second of these halts has considerable tendency to drift downward with successive runs on the same sample; it may eventually coincide with the third point if the

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(1) International Critical Tables 4, 70
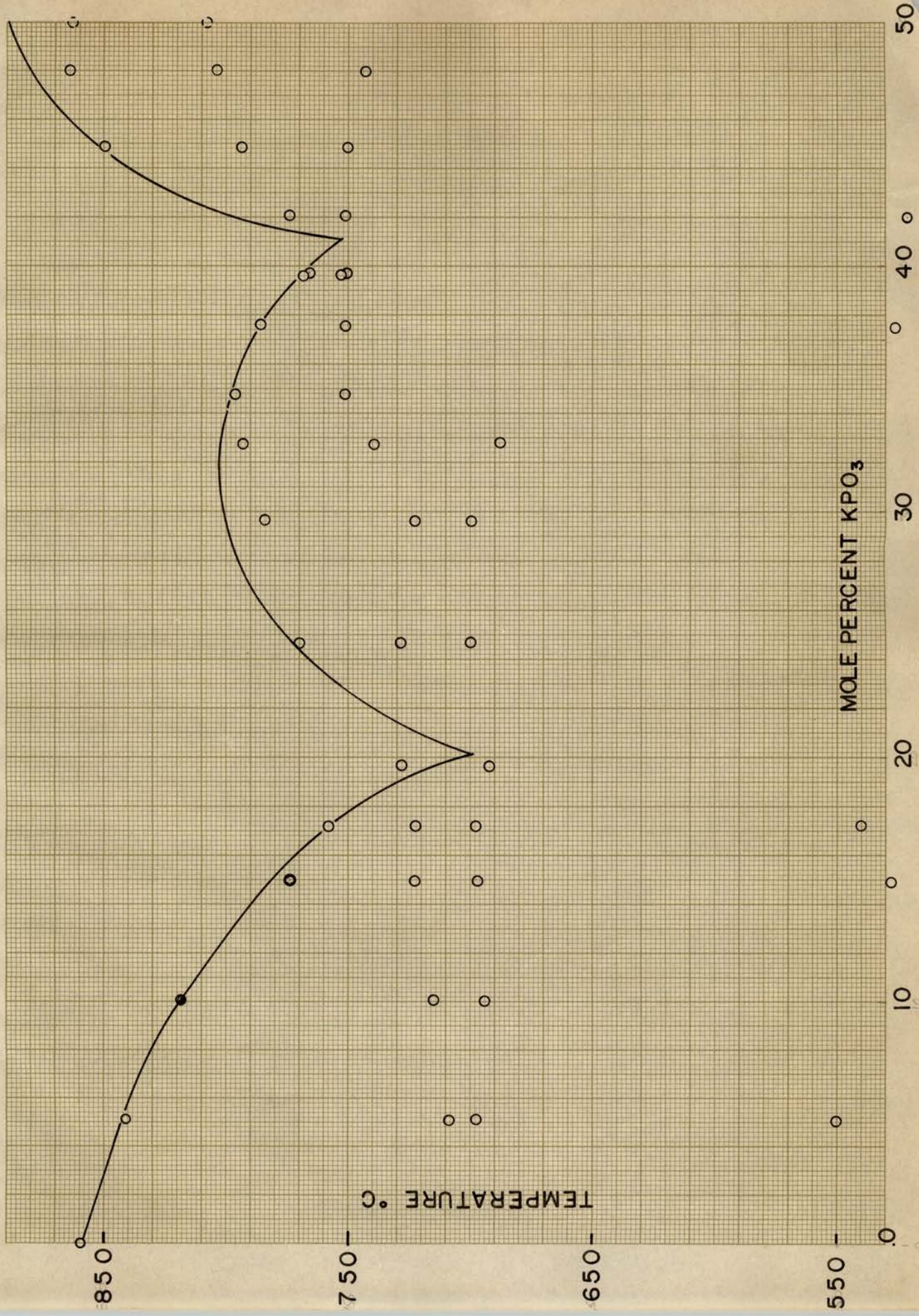
mixture were kept molten for a long enough time. The third point
seems to be independent of the time of heating. The first of these
inflections is that of initial crystallization, and is variable
with composition, while the second and third are invariant, at
729° and 698°, respectively, although they both have a tendency to
fall off on either side of the eutectic.

A possible explanation for these two invariant points is that
the one at the higher temperature is the eutectic for the system
while the lower represents a solid phase transition in one of the
components. The arguments against this seem to be overwhelming.
If the transition occurred in either potassium fluoride or the com-
pound formed at 33.3 mole% KPO_3, the length of the halt in the cool-
ing curve should increase as the composition of the mixture approach-
ed that of the pure component. Instead, the length of the halt is
greatest at the eutectic composition, and no halt is found in the
cooling curve of either pure component.

Separation of the melt into two liquid phases at compositions
near that of the eutectic might also account for three halts.
Glasstone (2) gives a very good account of a system which separates
into two liquid phases. A mixture whose composition lay in the
range in which immiscibility in the liquid phase occurred would
probably show no inflection when the liquid separated into two phases,
since such a transition would be accompanied by a very small heat
effect. If cooling of this mixture were continued, separation of
solid KF, or of the other component, would occur when the temper-

(2) Glasstone, S. Textbook of Physical Chemistry, 2nd Edition
753-54

ature had been reduced sufficiently. This temperature would be invariant, since two liquid phases would be in equilibrium with one solid phase. As the solid continued to separate, the two liquid phases would adjust their relative volumes so as to maintain the equilibrium until such time as they became identical and formed a single liquid phase. The system would then become univariant, and the temperature would fall until the eutectic temperature was reached, at which time both solids would separate as an eutectic mixture. Two solid phases would then be in equilibrium with one liquid phase, and the system would be invariant. There would thus be two points of inflection in the cooling curve of such a mixture. This is what was found in the case of a mixture containing 19.6 mole% KPO_3.

If a mixture whose composition lay outside the range of limited miscibility were cooled, the system would become univariant at the temperature of initial crystallization. If this mixture were rich in KF, KF would begin to separate. As the temperature fell, the composition of the liquid would adjust itself so as to maintain equilibrium, becoming increasingly rich in $KPO_3.2KF$, until the liquid separated into two phases. The behavior of the system would then be similar to that described in the preceeding paragraph. That is, it would be invariant as long as there were two liquid phases. As soon as there was only one liquid phase, the temperature of the univariant system would fall until the eutectic mixture began to separate, at which time the system would again be invariant. This type of mixture would result in three halts in the cooling curve; one at the temperature of initial crystallization, one at the in- variant point with two liquid and one solid phase, and one at the

invariant point with two solid and one liquid phase.

This explanation requires the existence of two regions of partial miscibility, one small region on the KF rich side of the eutectic and another small region on the 33 mole% compound rich side of the eutectic. Such a phenomena is not common. More powerful methods of investigation then thermal analysis would be required to resolve this problem.

C. The System from 30 to 37 Mole % KPO_3. A poorly defined maximum in the curve of initial crystallization is found in this region. Supercooling is excessive for all mixtures, and it is probable that the curve should lie several degrees higher than is shown. A mixture containing 32.7 mole% KPO_3 gives an eutectic at 698°, as do all mixtures less rich in KPO_3 than this, while a mixture containing 34.7 mole% KPO_3 has an eutectic at 752°, as do all mixtures more rich than this in KPO_3 (up to 50 mole%). This is an excellent indication that compound formation occurs at a composition lying between these two compositions, whose empirical formula would be given by $KPO_3.2KF$. Amadori reported this same compound as being formed by a peritectic reaction. In view of the extreme flatness of the maximum in the curve, which is commonly taken as indication of a high degree of dissociation in the liquid state, it may well be that under different experimental conditions an incongruent melting point would be found for this compound rather than the congruent melting point which was obtained in the present study. It should be mentioned that the cooling curves of mixtures which were run in platinum crucibles support the contention of a compound with a congruent melting point. Eutectics were found on both sides of the

TABLE III

30 to 37 Mole% KPO_3

No.	Mole% KPO_3	Initial crystal-lization	Length of Halt	Eu-tectic	Length of Halt
13	29.66	785.2°C	75"	700.1°C	80"
19	32.71	793.9	120	688.0	40
14	34.73	797.0	120	752.7	40
36	37.57	786.4	110	751.1	90
17	39.62	769.0	20	752.8	130

maximum at the same temperatures at which they were found with the graphite crucibles, while the temperature of initial crystallization of mixtures containing about 40 mole% KPO_3 was found to be considerably lower than was that found at about 35 mole% KPO_3.

No mention has been found in the literature of a compound of the composition $KPO_3.2KF$ other than that of Amadori (the data found in the International Critical Tables was taken from Amadori's work). However, Willy Lange (3) has reported the compound KPO_2F_2, potassium difluophosphate. This compound may be formed by the dissociation of $KPO_3.2KF$ according to the equation:

$$KPO_3.2KF = KPO_2F_2 + K_2O$$

The free basic oxide might then react with excess KPO_3 or with $KPO_3.2KF$:

$$3KPO_3.2KF + 2K_2O = K_4P_2O_7 + K_3PO_4 + 6KF$$

The stoichiometric equation can be altered to give almost any ratio of pyro-to orthophosphate.

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(3) Lange, Willy Ber **62B**, 793-801 (1929)

Water solutions of the mixtures which have been subjected to thermal analysis all have a pH of about 8.5, that is, they are either barely acidic or barely basic to phenolphthalein. They exert a considerable buffer effect. Addition of silver ion to the solutions results in a white precipitate in all cases. This precipitate could be due to either or both the fluophosphate or the pyrophosphate ion; orthophosphate would have given a yellow precipitate of silver orthophosphate if it had been present.

We believe that the presence of potassium phrophosphate in the mixtures is indicated. Other reactions than the one indicated may be reponsible for the formation of pyrophosphate, however. This subject will be expanded in the section of miscellaneous observations.

The work of Schmitz-Dumont and Schmitz (4) with systems of alkali halides and the corresponding alkali metavanadates established the formation of compounds of the type formula $MVO_3.2MF$ for the potassium, rubidium, and cesium systems, while there was no compound formation in the lithium and sodium systems. Comparison of the alkali metaphosphates with the alkali metavanadates indicates that compounds of the type $MPO_3.2MF$ might also be stable, where M refers to the heavier alkali metals.

The phase diagram shows that compound formation occurs in the system potassium fluoride-potassium metaphosphate at 33.3 mole% KPO_3, and indicates that this compound has the formula $KPO_3.2KF$. Other methods of investigation would be required to establish the correct formula for this compound.

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(4) Schmitz-Dumont and Schmitz Z. Anorg. Chem. <u>252</u>, 329-53 (1944)

TABLE IV

33.3 to 50 Mole% KPO$_3$

No.	Mole% KPO$_3$	Initial Crystallization	Length of Halt	Eutectic	Length of Halt	Transition in KPO$_3$.2KF	Length of Halt	Transition in KPO$_3$	Length of Halt
19	32.71	793.9°C	120"	688.0°C	40"	not run		not run	
14	34.73	797.0	120	752.7	40	not run		not run	
36	37.57	786.4	110	751.1	90	530°C	25"	443°C	5"
17	39.62	769.0	20	752.8	130	not run		not run	
15	39.68	766.0	20	749.8	90	not run		not run	
29	42.00	774.9	25	751.9	55	523	5	443	5
16	44.81	850.1	55	750.8	70	not run		not run	
20	48.07	880.8*	50	743.4	45	none		443	15
30	50.00?	864.7?	20	none		none		454	20
21	51.92	885.4*	80	none		none		443	50

*The temperature of initial crystallization or mixture 20, 48.07 mole% KPO$_3$ and mixture 21, 51.92 mole% KPO$_3$ here tabulated has been extrapolated to zero time of heating. ?Mixture 30, 50.0 mole% KPO$_3$ was contaminated with silica and the data from this mixture is not considered reliable.

D. <u>The system from 33.3 to 50.0 mole% KPO$_3$</u>. Mixtures in this composition range have an eutectic at 752° at about 41 mole% KPO$_3$. The temperature of initial crystallization rises sharply from the eutectic to a maximum of 886° at 50 mole% KPO$_3$. Except for the mixtures whose composition is near 33.3 mole% KPO$_3$, which super- cool excessively at the initiation of crystallization, both initial and eutectic crystallization are represented by either good halts or well defined inflections in the cooling curves.

As can be seen from table 4, the transition at about 540° was found for two mixtures in this range. The length of halt is greatest at 37.6 mole% KPO$_3$. This is the transition which is be- lieved to occur in the compound formed at 33.3 mole% KPO$_3$.

A transition at 443° was found for all mixtures more rich than 37% KPO$_3$.

E. <u>The Maximum at 50.0 Mole% KPO$_3$</u>. A very well defined, sharp maximum is obtained in the initial crystallization curve at 50.0 mole% KPO$_3$. Cooling curves of mixtures whose composition lies near this maximum give very good flat halts at the initiation of crystal- lization. The temperature of initial crystallization declines rapidly with each run, however, so that extrapolation to zero time of heating was required. From this extrapolation, the melting point of the compound KPO$_3$.KF is estimated to be 886°C.

Mixtures less rich than 50.0 mole% KPO$_3$ show an eutectic halt in their cooling curves at 752°, while those more rich than 50.0 mole% KPO$_3$ show an eutectic halt at 612°. These different eutectics, combined with the maximum in the curve show that a reaction occurs between KF and KPO$_3$ to form the compound KPO$_3$.KF. This compound

TABLE V

THE SYSTEM NEAR 50.0 MOLE% KPO_3

No.	Mole% KPO_3	Initial crystal- lization	Length of Halt	Eu- tectic	Length of Halt	Transition in $KPO_3 \cdot KF$	Length of Halt
29	42.00	774.9°C	25"	751.9°C	55"	none	
16	44.81	850.1	55	750.8	70	795.4°C	5"
20	48.07	880.8	50	743.4	45	803.6	55
30	50.00?	864.7	20	none		799.4	30
21	51.92	885.4	80	none		791.7	40
22	55.03	864.3	45	526	20	799.4	10
31	60.04	818.6	20	545	30	790.5	5
23	65.01	790	?	581	20	none	

has been reported in the literature as $K_2PO_3F_2$ by W. Lange (5) and others. The monofluophosphate ion is reported to form salts with other alkali and alkaline earth metals, as well as with certain organic bases, to form the monofluophosphates. The phase diagram thus serves to confirm the existence of potassium monofluophosphate and to show that it is stable at high temperatures.

Halts are found in cooling curves of mixtures in this region at about 800°. These halts are well defined flats at compositions near 50 mole% KPO_3, but become very poor inflections at 42 and 60 mole% KPO_3. This halt is believed to result from a phase tran- sition in $KPO_3 \cdot KF$. The temperature at which we found this tran- sition to occur is the same as the temperature we found for the maximum at 33.3 mole% KPO_3, 800°C. Amadori reported halts at

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(5) Lange, Willy (loc. cit.)

about the same temperature, 793°, for mixtures which contained less than 50 mole% KPO_3, but did not report such halts in mixtures more rich than this in KPO_3. He believed this halt was caused by a peritectic reaction between solid $KPO_3 \cdot KF$ and molten KF to give solid $KPO_3 \cdot 2KF$. We believe that a solid phase transition as here postulated is a better explanation of the experimental data.

F. The Reaction at 50 Mole% KPO_3. We have found that when a physical mixture of the two salts potassium fluoride and potassium metaphosphate of about the same number of moles of each is heated for the first time, the mixture first begins to melt at about 650°. The temperature then continues to rise at a uniform rate to about 735°, from which it rises more slowly to about 756°. The temperature then rises rapidly to a sharp maximum, from which it falls off slowly to a minimum. Before the sharp temperature rise occurs, the mixture is almost completely molten, while it is almost completely solid after the temperature rise. As heating of the mixture is continued, the temperature rises from the minimum until the melting point is reached, at which time the usual flattening of the heating curve at melting points is found.

The sharp rise in the heating curve, accompanied by solidification of the melt, indicates that a highly exothermic reaction occurs. The temperature at which it occurs (756°), is invariant, which indicates that this reaction occurs slowly if at all below this temperature. The reaction is believed to be that between potassium fluoride and potassium metaphosphate to form potassium monofluophosphate. Lange (6) reports a similar phenomenon for the

(6) Lange, Willy Inorganic Syntheses Vol. II, 157-8

TABLE VI

THERMAL EVIDENCE for REACTION at 50MOLE% KPO$_3$

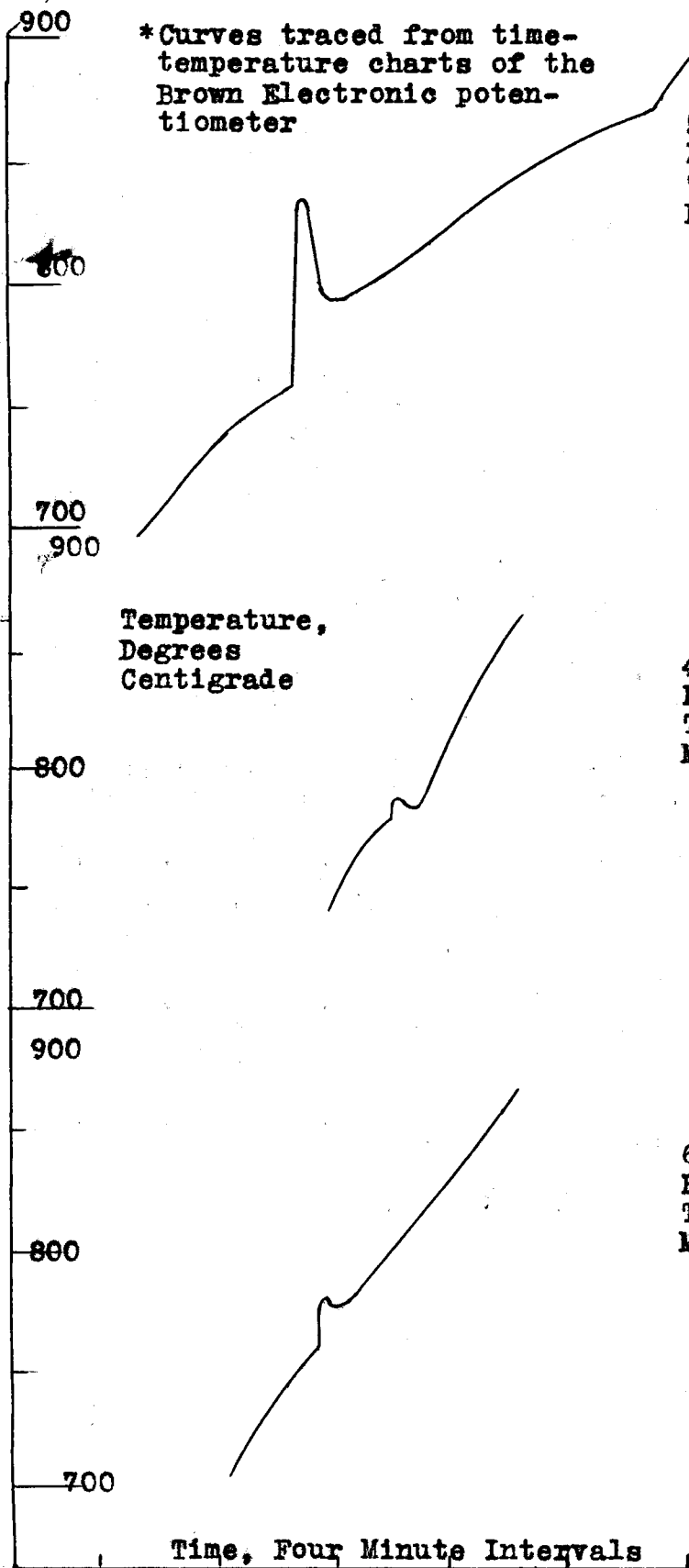| Mole% KPO$_3$	First Melting	Reaction Temperatures		Time elapsed	Low temperature reached after reaction	Time elapsed	Melting Point
		Low	high				
42.00	724°C	778°C	786°C	2 sec.	782°C	45 sec	molten
51.92	662	754	833	3	789	65	885
55.03	660	756	809	3	781	30	859
60.04	651	756	795	4	792	30	838
65.01	649	754	777	10	773	15	805
70.02	651	753	760	10	did not decline		molten
75.02	698	755		inflection only in heating curve			molten

reaction between phosphorus pentoxide and ammonium fluoride. The products of this reaction are ammonium monofluophosphate and ammonium difluophosphate.

G. The System from 50 to 100 Mole% KPO$_3$. A simple eutectic is formed between potassium monofluophosphate and potassium metaphosphate at a temperature of about 612° at a composition of about 84 mole% KPO$_3$. Very good halts at the eutectic are found in the cooling curves of mixtures near to the eutectic in composition, but mixtures which differ much from the eutectic in composition give only slight inflections in their cooling curves. The eutectic temperature declines considerably in mixtures far removed from the eutectic in composition.

The curve of initial crystallization is poorly defined throughout most of this region. Initiation of crystallization manifested itself by slight changes of slope in the cooling curves which were difficult to read. Some of these were so poor that we would

HEATING CURVES OBTAINED AT ABOUT 50 MOLE% KPO$_3$*

*Curves traced from time-
temperature charts of the
Brown Electronic poten-
tiometer

51.9 mole% KPO$_3$
Reaction Temperature: 754°
Temperature rise: 69°
Melting Point: 885°

900

800

700

900

Temperature,
Degrees
Centigrade

42.0 mole% KPO$_3$
Reaction Temperature: 778°
Temperature rise: 8°
Melting Point: molten at re-
          acti on temperature

800

700

900

65.0 mole% KPO$_3$
Reaction Temperature: 753°
Temperature rise: 7°
Melting Point: molten at
          reaction temperature

800

700

Time, Four Minute Intervals

TABLE VII

50 to 100 MOLE% KPO_3

No.	Mole% KPO_3	Initial Crystal- lization	Length of Halt	Eu- tectic	Length of Halt	Transition KPO_3	Length of Halt
21	51.92	885.4°C	80"	none		443°C	60"
22	55.03	864.3	45	526°C	20"	443	35
31	60.04	818	20	545	30	445	20
23	65.01	804	?	581	20	447	30
32	70.02	726	20	591	60	443	5
24	75.02	708	?	611.4	120	443	25
33	80.00	?		612.2	80	443	30
25	84.93	?		616.5	45	439	20
34	89.97	679	60	617.8	40	443	35
26	95.00	734.3	80	599	15	440	35
	100.0	804.4	115	none		443	35

seriously question their existence if physical observation had not verified that solidification was occurring.

Cooling curves of all mixtures more rich than 37 mole% KPO_3 show inflections in their cooling curves at 443°, as well as in the heating curves, including the first heating of the physical mixture. Although the length of the halt in the cooling curve varies from mixture to mixture, it seems to be independent of composition, as is shown in table 7. Amadori also reported this transition persisted throughout this temperature range, although he found the length of the halt to become less as the concentration of KF was increased. He believed the presence of this halt in mixtures less rich than 50 mole% KPO_3 to indicate the dissociation of $KPO_3 \cdot KF$, re-
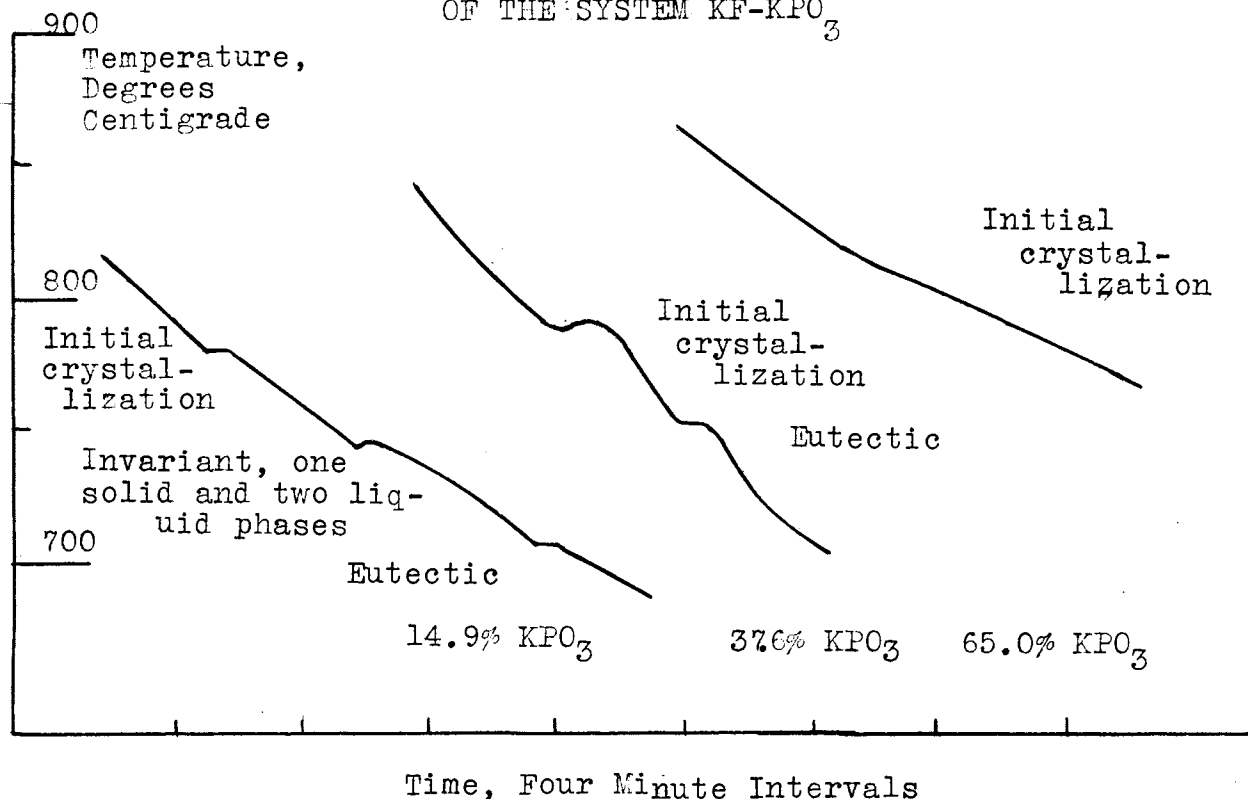
sulting in the formation of $KPO_3 \cdot 2KF$ and KPO_3. The KPO_3 then underwent a solid phase transition at $450°$ (According to Amadori). This explanation does not seem wholly satisfactory when applied to the results of the present study. The most pronounced halt found in any cooling curve was that in the curve for 51.92 mole% KPO_3; this explanation would require complete dissociation of $KPO_3 \cdot KF$. All other evidence available indicates that the compound formed at 50 mole% KPO_3 is more stable than is that formed at 33.3 mole% KPO_3. The only alternative to Amadori's proposal is that KPO_3 and $KPO_3 \cdot KF$ undergo the same change in crystalline structure at the same temperature, and with comparable heat effects. Neither explanation is satisfactory. It is evident that thermal analysis is not sufficient to resolve this problem; indeed, all that thermal analysis has accomplished is to pose the problem.
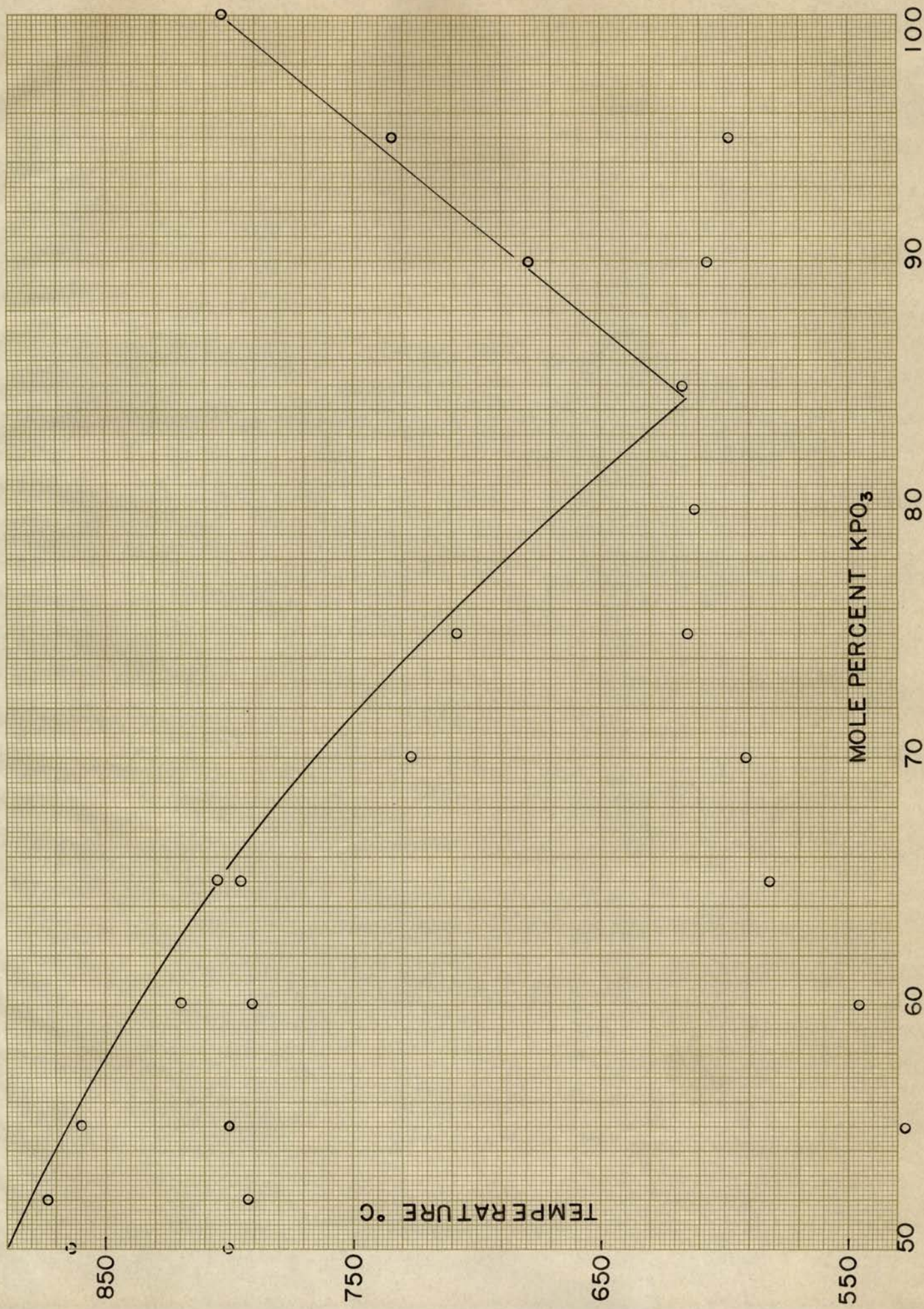
The freezing point of pure KPO_3 was found to be $804.4°C$. This compares favorably with the value of $806.8°C$ found by Madorsky and Clark (7). These investigators obtained this value from heating curves; that is, it is for the melting point. KPO_3 is subject to extensive supercooling, so that freezing point values are not reliable. We succeeded in "seeding" the melt by the insertion of a small platinum wire upon which a tiny crystal of KPO_3 had crystallized. Good flats were obtained at the freezing point by use of this method. This same technique was attempted at that part of the phase diagram in which supercooling was pronounced; that is, at 30 to 37 mole% KPO_3. We failed to obtain satisfactory results at

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(7) Madorsky and Clark Ind. Eng. Chem. 32, 248 (1940)

TYPES OF COOLING CURVES OBTAINED IN THE STUDY*
OF THE SYSTEM KF-KPO$_3$

900

Temperature,
Degrees
Centigrade

800

Initial
crystal-
lization

Invariant, one
solid and two liq-
uid phases

700

Eutectic

Initial
crystal-
lization

Eutectic

Initial
crystal-
lization

14.9% KPO$_3$

37.6% KPO$_3$ 65.0% KPO$_3$

Time, Four Minute Intervals

*These curves were traced from the time-temperature charts of the Brown Electronic Potentiometer.

1. 14.9% KPO$_3$.
    The curve shown clearly demonstrates the three halts found in the cooling curves of mixtures in the region from 5 to 30 mole% KPO$_3$.

2. 37.6% KPO$_3$.
    The curve shown demonstrates the excessive supercooling of mixtures of composition near 33.3 mole% KPO$_3$.

3. 65.0 % KPO$_3$.
    The curve shown demonstrates the difficulty with which temperatures of initial crystallization could be ascertained in the region from 60 to 90 mole% KPO$_3$.

these concentrations.

Mixtures made with the Ozark Mahoning KF were found to have consistently higher temperatures of initial crystallization than were mixtures made with Baker and Adamson KF in the region from 50 to 100 % mole% KPO_3. Throughout the other half of the phase diagram, however, there was no apparent difference between the results obtained with the two lots of potassium fluoride.

IV.   MISCELLANEOUS OBSERVATIONS

A. **The Gaseous Phase.** The system $KPO_3 \cdot KF$ was considered to
be a two component, condensed system throughout this investiga-
tion. Unfortunately, this was not strictly true.

Some of the mixtures of KPO_3 and KF could be removed from the
graphite crucibles without damage. These were weighed and in each
instance the charge was found to have lost weight. This loss in
weight was dependent on time of heating and was of the order of 1%
by weight per hour that the mixture was kept molten. Gases could
be seen in the furnace; it was also noted that silicious materials
above the melt were moderately attacked by these gases. Universal
indicator paper, dampened and held at the top of the furnace,
rapidly took on the color which it assumed in solutions of pH less
than two.

These observations showed that an acidic gaseous phase existed
in the system at sufficiently high temperatures. The loss of
these acidic gases undoubtedly changed the composition of a mix-
ture being studied and at the same time introduced impurities into
the charge. It is believed that in most cases the change in com-
position was not great enough to interfere with the study; the
introduction of impurities, however, caused the temperature of
initial crystallization to be lowered. It was noted that through-
out the system the temperature of initial crystallization fell with
successive runs on a specific mixture; at 50 moles% KPO_3 this decline
was so large as to necessitate an extrapolation to zero time of
heating.

It has been proposed that at high temperatures the alkali

fluophosphates are hydrolytically decomposed to hydrogen fluoride and alkali hydroxides. This is in agreement with the observations of W. Lange (1). The precautions taken with the mixtures used in this study should have been sufficient to exclude the possibility of occluded water, so that hydrolysis would necessitate a surface reaction with atmospheric water. We believe that this reaction was unlikely to have occurred.

Thermal decomposition would also account for the observations which were made, as is shown by the hypothetical equation:

$$3K_2PO_3F = POF_3 + K_2O + K_4P_2O_7$$

Equations can also be proposed which would result in the formation of orthophosphate, but as has been previously mentioned, analysis indicated that no orthophosphate was present. Lange (2) has reported that POF_3 is hydrolysed to monofluophosphoric and difluophosphoric acids, both of which are strong acids and would account for the acidity of the gaseous phase.

On the basis of these rather casual studies we believe that thermal decomposition of potassium monofluophosphate occurs slowly at temperatures above its melting point; the primary products of this decomposition being potassium pyrophosphate and phosphorous oxyfluoride. A thorough investigation of this decomposition should make an interesting study.

The decomposition of $KPO_3 \cdot 2KF$, the hydrolytic and thermal

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(1) Lange, Willy Ber. 62B, 786-92 (1929)

(2) Lange, Willy (loc. cit.)

decomposition of $KPO_3 \cdot KF$ as postulated in this thesis all result in the formation of potassium oxide, and of potassium pyrophosphate. Thermal analysis of systems of equimolar quantities of KPO_3 and KF and of systems of two moles of KF to one mole of KPO_3 to which were added small quantities of K_2O or $K_4P_2O_7$ should be interesting and informative.

B. **Chemical Analysis**. The first mixtures which were subjected to thermal analysis gave very poor results. In one of these, of about 50 mole% KPO_3, the temperature of initial crystallization rose rapidly with successive heatings and seemed to be approaching a maximum of about 1100 or 1200°C. Other mixtures also gave results which were, to say the least, peculiar. As an example, a micture containing 33 mole% KPO_3 had a temperature of initial crystallization well below that obtained with either a 30 or 35 mole% KPO_3 mixture. It was decided that analysis of selected mixtures for fluorine and phosphorus would be of aid in the study of the system.

The Ozark Mahoning Company very kindly sent outlines of the procedure used by them for these analyses. The procedure followed in the fluorine analysis was essentially the Churchill (3) modification of the Willard-Winter (4) procedure. It involved the steam distillation of fluosilicic acid from either sulfuric or perchloric acid. Titration of the distillate with standard

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(3) Churchill, H. V. Ind. Eng. Chem., Anal. Ed. 17, 720-21 (1945)

(4) Willard, I. H. and Winter, O. B. Ind. Eng. Chem., Anal. Ed. 5, 7 (1933).

thorium nitrate, using sodium alizarin sulphonate as indicator, then resulted in the quantitative precipitation of thorium flouride.

The analysis for phosphorus was conducted by first hydrolyzing all of the phosphates present to orthophosphate with dilute nitric acid. Silver nitrate was then used to precipitate silver orthophosphate from the solution, the pH of which was carefully controlled to prevent the precipitation of silver oxide or the solution of the orthophosphate. The excess of silver was then titrated with standard potassium thiocyanate (to a ferrous ammonium sulphate end point) and the amount of phosphorus calculated from this titer.

In all cases, the mixtures analysed were found to have a very low fluorine content, and to have an approximately theoretical phosphorus content. It was thought at first that the method of analysis might be at fault, but analysis of a sample of silver monofluophosphate gave virtually theoretical results for fluorine as well as for phosphorus and silver. We selected those mixtures for analysis which had given anomolous results, which was perhaps an unfortunate choice, in the hope that we could determine their proper place on the phase diagram. We succeeded only in showing that these mixtures had an extremely low fluorine content, and no longer could be considered as being of the system under investigation.

The precision obtained in the fluorine analysis was poor, so that it seemed undesirable to put more time into work of doubtful value.

V. CONCLUSIONS

The system potassium fluoride-potassium metaphosphate has been studied by the methods of thermal analysis. The data obtained by this study has been used to construct the phase diagram of the system.

A maximum occurs in the phase diagram at 33.3 mole per cent potassium metaphosphate, which indicates the formation of the stable compound $KPO_3 \cdot 2KF$, which melts at 800°C. The work of W. Lange with the fluophosphates indicates that this compound may dissociate into potassium difluophosphate, KPO_2F_2, and potassium oxide. The compound forms an eutectic with potassium fluoride at 20 mole per cent potassium metaphosphate, which melts at 698°C. This compound appears to undergo a change in crystalline form at about 540°.

Another maximum is found at 50.0 mole per cent potassium metaphosphate. This indicates that a stable compound, $KPO_3 \cdot KF$, is formed at this concentration. The work of W. Lange supports the contention that this compound is potassium monofluophosphate, K_2PO_3F. It forms eutectics with the compound formed at 33.3 mole per cent potassium metaphosphate at 41 mole per cent potassium metaphosphate which melts at 752°C and with potassium metaphosphate at 84 mole per cent potassium metaphosphate which melts at 612°C. Potassium monofluophosphate undergoes a change in crystalline form at 800°C.

Potassium monofluophosphate is formed by a highly exothermic reaction between equimolar quantities of potassium fluoride and potassium metaphosphate at 756°C.

Potassium metaphosphate undergoes a change in crystalline form at 443°C. There are indications that potassium monofluophosphate undergoes the same transition at the same temperature.

Evidence, which was far from conclusive, was found for the existence of a region or regions of partial miscibility in the melt in compositions near the eutectic found at 20 mole per cent potassium metaphosphate.

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5, 7 (1933).

BIOGRAPHY

Robert Shoop Munger was born in Perry, Oklahoma, on March 17, 1921. He grew up in Perry and was educated in the public schools of that town, graduating from the Perry High School in May, 1939. He entered the Oklahoma Agricultural and Mechanical College in September, 1939.

In September, 1940, he was called into Federal Service with Battery C, 158th Field Artillery, 45th Infantry division, Oklahoma National Guard. He remained with this organization until his transfer to the Field Artillery School, Officer's Candidate School, Fort Sill, Oklahoma, in September, 1942. He was commissioned as Second Lieutenant, Field Artillery, Army of the United States, on December 24, 1942, and was assigned to the 88th Infantry Division, Camp Gruber, Oklahoma. He served with the 337th Field Artillery Battalion, 88th Infantry Division in the United States and in the Mediterranean Theatre of Operations until the time of his separation from the service, December 25, 1945.

He reentered the Oklahoma Agricultural and Mechanical College in February, 1946, and received the Bachelor of Science Degree in May, 1948. He became a member of Phi Eta Sigma, Phi Lambda Upsilon, and Phi Kappa Phi as an undergraduate.

He entered the Graduate School of the Oklahoma Agricultural and Mechanical College in June, 1948. In September, 1948, he was granted a research fellowship by the college. This fellowship was sponsored by the Ozark Mahoning Company of Tulsa, Oklahoma. The results which were found during the course of the fellowship are the subject of this paper.

On August 2, 1947, he was married to Dorothy Wade, of Glen Burnie, Maryland. They have one child, a son, Thomas Wade Munger, who was born June 19, 1948.

Typed By:

<u>Mrs. Ann McCaslin</u>