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Final Report

Office of Naval Research Contract 401(05)-NR356-294

"Aggregation Reactions of Phosphates In Ansolvous Media"

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Cornell University  
1954

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## II. Introduction

### A. Project History

Office of Naval Research Contract 401(05)-NR356-294, "Aggregation Reactions of Phosphates in Ansolvous Media," covered the period October 1, 1951 through September 30, 1953. Personnel of the project were as follows:

Meyer M. Markowitz, one-half time research assistant, employed October 1, 1951 through December 31, 1952. Principal responsibility: Thermal aggregation of alkali metal hydrogen phosphates.

Robert P. Langguth, one-half time research assistant, employed June 16, 1952 through August 31, 1952. Principal responsibility: Thermal aggregation of divalent metal hydrogen phosphates (only a portion of the work on this subject contained in this report was actually supported by this project).

Robert G. Fessler, one-half time research assistant, employed February 1, 1952 through July 20, 1952. Principal responsibility: Effect of humidity on the thermal aggregation of hydrogen phosphates.

Steven Fitch, one-half time research assistant, employed September 20, 1952 through September 30, 1953. Principal responsibility: Effect of humidity on the thermal aggregation of hydrogen phosphates.

This project was under the direction of Dr. R. K. Osterheld.

### B. Scope of the Project

The large scale use of high temperature reactions in essentially ansolvous media is an important part of the phosphate industry, particularly for the preparation of aggregated species. In spite of this, relatively little has been learned about the course or mechanism of even the most common reactions. Although it has long been clear that the behavior of phosphates at elevated temperatures depends upon the cation present a systematic investigation of the aggregation reactions in systems employing a variety of cations has been lacking. To provide a basis for a better understanding of phosphate aggregation reactions the present project undertook to augment available data pertaining to the thermal aggregation (thermal decomposition) of sodium and potassium hydrogen phosphates with comparable data for other alkali metal systems (specifically, for lithium and cesium hydrogen phosphates) and for divalent metal systems (specifically, for barium and lead hydrogen phosphates).

Inasmuch as there was evidence that the course and product of the thermal aggregation of hydrogen phosphates depends upon the humidity of the atmosphere surrounding the sample, this phenomenon was also investigated.

### III. Technical Reports on the Several Phases of the Work

#### A. Experimental Techniques

##### 1. Differential thermal analysis.

The method of differential thermal analysis served to determine the temperatures at which dehydrations, transitions, and reactions of the materials under investigation occurred or became appreciable in rate. For differential thermal analysis a ten gram sample in a platinum crucible was heated at a controlled rate in a small muffle furnace along with ten grams of similarly placed ignited aluminum oxide. Pt-90Pt10Rh thermocouples in conjunction with Brown Elektronik recorders produced continuous, simultaneous records of the sample temperature and of the difference in temperature between the sample under investigation and the aluminum oxide. The thermal analysis apparatus was calibrated periodically against the following standards:

Benzoic acid	M.p.	122°C
Potassium dichromate	M.p.	398°
Potassium sulfate	Trans.	583°
Sodium chloride	M.p.	800°

The corrections required were from 0 to 4 degrees Centigrade. Temperatures listed throughout this report were obtained by considering the two graphs and have been corrected as required. The temperature measurements were considered reliable to within 3°. It must be realized that reaction temperatures given in this report are the temperatures at which the reactions become appreciable in rate and are generally not the minimum temperatures at which the reactions will occur.

##### 2. X-ray analysis.

X-ray diffraction powder photographs were obtained using nickel filtered Cu-K $\alpha$  radiation. These photographs were used for qualitative identification of the crystalline phases present in samples. However, since the data may prove useful to others, in Section V the x-ray diffraction patterns are listed for many of the materials encountered in this work.

##### 3. Chemical analysis.

Unless otherwise noted in later sections analyses were performed as indicated below.

a. Orthophosphate was determined by the Jones volumetric procedure (1). After interfering polyphosphates had been removed by precipitation with barium ion the orthophosphate was precipitated as ammonium phosphomolybdate which was then determined volumetrically.

b. Pyrophosphate and triphosphate were determined by the Bell method (2). Briefly, the method consisted of adjusting the pH of the unknown solution to 3.80 and adding a zinc sulfate solution also at pH 3.80. Under uniform conditions titration with standard sodium hydroxide solution back to pH 3.80 was a measure of the total pyrophosphate content plus an empirical fraction of the triphosphate content. During the titration zinc pyrophosphate precipitated. The weight of the zinc pyrophosphate after reprecipitation and ignition served as an independent measure of the pyrophosphate content of the sample and permitted calculation of the triphosphate content.

c. Long-chain metaphosphates were precipitated as barium salts after adjusting the acidity according to the method of Jones (1). The precipitated metaphosphates were converted to orthophosphate by boiling with nitric acid and determined as orthophosphate by the method outlined in a, above.

d. Cyclic metaphosphates alone remained in solution when a barium chloride solution was added to the unknown solution and the mixture made alkaline to phenolphthalein (1). After filtration, the cyclic metaphosphates were converted to orthophosphate by boiling with nitric acid and were determined as orthophosphate by the method outlined in a, above.

e. Total phosphorus content of a sample was determined by converting all phosphates present to orthophosphate by boiling the sample with nitric acid (1) and performing an orthophosphate analysis as outlined in a, above.

f. Lead and barium analyses were performed in standard fashion (3).

g. Acid equivalents of the acid orthophosphates were determined by the titration of the dihydrogen orthophosphates with standard sodium hydroxide to the phenolphthalein end-point and titration of the monohydrogen orthophosphates with standard hydrochloric acid to the methyl orange end-point.

h. The length of long-chain metaphosphates was estimated by the method of end-group titration (4), making use of the observation that there is a relatively weakly dissociated hydrogen ion for each end of a polyphosphoric acid.

## B. Thermal Aggregation of Alkali Metal Hydrogen Phosphates

### 1. Introduction.

The extensive literature of the phosphates is largely concerned with the sodium and potassium phosphates, the sodium phosphates having acquired considerable commercial importance in recent years. It is clear from published studies that the high temperature chemistry of hydrogen phosphate anions is dependent upon the cation

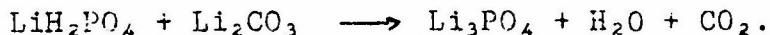
in conjunction with which they are studied. Thus, at moderate temperatures sodium dihydrogen orthophosphate may be readily converted to sodium dihydrogen pyrophosphate, whereas the analogous reaction with the potassium salt does not stop at the dihydrogen pyrophosphate but proceeds to the formation of potassium metaphosphate. Also, suitable thermal treatment of sodium dihydrogen orthophosphate produces several different crystalline sodium metaphosphates; only one crystalline potassium metaphosphate has been obtained by such means. Furthermore, sodium metaphosphate forms a clear glass readily, but potassium metaphosphate glass preparations are invariably clouded by partial crystallization of the material.

To evaluate the effect of different cations on the behavior of the hydrogen phosphate anions data must be available for a wider variety of hydrogen phosphates. Only a few, relatively superficial, studies have been reported dealing with the thermal aggregation of other than sodium and potassium hydrogen phosphates. As a part of this project systematic studies of the thermal behavior of lithium and cesium hydrogen phosphates were carried out, interesting in themselves as extensions of available information concerning the alkali metal phosphates and interesting in that the availability of data for a greater variety of cations makes possible some discussion of the factors influencing the temperature and course of these reactions.

## 2. Preparation of alkali metal hydrogen phosphates.

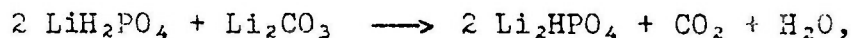
a. Lithium dihydrogen orthophosphate. To a slurry of lithium carbonate in water was added a 50% excess of orthophosphoric acid. The resulting solution was evaporated until it became viscous and was allowed to cool. Lithium dihydrogen orthophosphate was precipitated by the addition of acetone. To insure that the product was dihydrogen orthophosphate, this initial material was heated with glacial acetic acid on a water bath for two hours. The product was recovered by filtration. A fine, free-flowing powder was obtained by washing out the traces of acetic acid with acetone. The lithium dihydrogen orthophosphate was dried at 150°; no decomposition was analytically detectable at that temperature. Analysis for  $\text{PO}_4^{-3}$ : Found 90.6%, calculated 91.4% (corresponds to 99.1%  $\text{LiH}_2\text{PO}_4$ ). Titration of the product to the phenolphthalein end-point required only 94.8% of the theoretical quantity of strong base. This phenomenon has been previously reported for this material (5).

b. Lithium monohydrogen orthophosphate. The successful preparation of lithium monohydrogen orthophosphate has never been reported. Attempts to crystallize this compound from aqueous solutions of appropriate composition produce instead a highly insoluble trilithium orthophosphate, which is believed not to be a true trilithium orthophosphate but to contain hydroxide ions as well. True trilithium orthophosphate can be prepared by the high temperature reaction:



An intimately ground mixture of stoichiometric quantities of the reactants reached constant weight when heated for three two-hour periods at 900°, the sample having been ground between heating periods. Analysis for  $\text{PO}_4^{-3}$  calculated as  $\text{P}_2\text{O}_5$ : Found 60.6%, calculated for  $\text{Li}_3\text{PO}_4$  61.3% (corresponds to 98.8%  $\text{Li}_2\text{PO}_4$ ).

Lack of success of attempts to prepare lithium dihydrogen orthophosphate from aqueous solution caused us to consider methods of preparation in anhydrous media. The following reactions between solids were attempted:



Neither approach proved successful.

c. Cesium dihydrogen orthophosphate. Dilute (3N) orthophosphoric acid was added to a solution of 55 g. of cesium hydroxide in 200 ml. of water until the methyl orange end-point was reached. The solution was evaporated to about one-half its original volume and allowed to cool to room temperature. Addition of 400 ml. of 95% ethanol caused precipitation of the product as a white, crystalline material. This was recovered by filtration, washed with 95% ethanol and dried at 150° for two hours. Yield: 94.9% based on cesium. Analysis for  $\text{PO}_4^{-3}$ : Found 41.0%, calculated 41.3% (corresponds to 99.3%  $\text{CsH}_2\text{PO}_4$ ). Titration with standard base to the phenolphthalein end-point gave a value of 99.9%  $\text{CsH}_2\text{PO}_4$ .

d. Cesium monohydrogen orthophosphate. Dilute (3N) orthophosphoric acid was added to a solution of 100 g. of cesium hydroxide in 300 ml. of water to the phenolphthalein end-point. Evaporation of the resulting solution to the appearance of a film of crystals on the surface of the liquid, followed by the addition of absolute ethanol to the vigorously stirred cooled solution gave an oily layer of product. Additional heating and stirring of the product with absolute ethanol brought about crystallization. The final product when dried at 100° for eight hours was the monohydrate. Yield: 118 g., 93.1% of theoretical based on cesium. Analysis: 100.1%  $\text{Cs}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$  (on the basis of  $\text{PO}_4^{-3}$ ). Titration with standard hydrochloric acid to the methyl orange end-point gave a value of 100.3%  $\text{Cs}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ .

Thermal analysis showed the dehydration of the monohydrate became appreciable in rate near 115°. The total weight loss experienced by the monohydrate in reaching constant weight at 145° corresponded to the loss of 1.01 moles of water per formula weight of  $\text{Cs}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ . The product thus obtained analyzed as 100.1%  $\text{Cs}_2\text{HPO}_4$  (on the basis of  $\text{PO}_4^{-3}$ ). Anhydrous cesium monohydrogen orthophosphate and the monohydrate were highly deliquescent substances.

e. Cesium dihydrogen pyrophosphate. Eighty grams of cesium pyrophosphate (produced by igniting cesium monohydrogen orthophosphate) were dissolved in a solution of 270 ml. of glacial acetic

acid in 250 ml. of water (Cf. ref. 6). The solution was heated, with continuous stirring, for two hours at 50°, cooled, and the product precipitated by the addition of 1800 ml. of 95% ethanol, while stirring. The product was recovered by filtration, washed with 300 ml. of ether and dried for three hours at 60°. Yield: 41.0 g., 81.9% of theoretical. Analysis for  $P_2O_7^{4-}$ : Found 38.5%, calculated 39.4% (corresponds to 97.7%  $Cs_2H_2P_2O_7$ ). Analysis for total  $P_2O_5$ : Found 31.7%, calculated 32.1% (corresponds to 98.6%  $Cs_2H_2P_2O_7$ ).

Since in this preparation only half of the cesium is recovered as the dihydrogen pyrophosphate, the combined filtrates, from the precipitation and washings, were treated with a 10% excess of orthophosphoric acid. The solution was evaporated to the appearance of crystals. After cooling the solution 95% ethanol was added to cause precipitation. Yield: 33.0 g. of  $CsH_2PO_4$  of 98.0% purity (based on  $PO_4^{3-}$ ).

### 3. Modification of the differential thermal analysis method.

In our first thermal analyses of lithium dihydrogen orthophosphate the irregular appearance of an exothermic break in the temperature range 331-403° was noted. It was found on further investigation that the exothermic process was reproducibly absent from thermal analysis curves when care was taken to maintain a low humidity level in the atmosphere surrounding the sample. On the other hand, the presence of a crucible of water in the furnace caused the regular appearance of the exothermic process when the thermal analysis was run. Consequently, the thermal analysis apparatus was modified to permit the continuous sweeping out of the furnace cavity (volume about 1000 ml.) with preheated dry air (flow rate about 85 ml. per minute). All data relative to the thermal behavior of lithium and cesium hydrogen phosphates presented in this report was obtained under the low-humidity conditions afforded by the modified apparatus.

### 4. Thermal decomposition of lithium dihydrogen orthophosphate.

Differential thermal analyses of lithium dihydrogen orthophosphate carried out under low-humidity conditions exhibited just three breaks, all endothermic, at 189°, 277°, and 656°.

a. The endothermic process at 189°. In order to determine the nature of this process, samples of lithium dihydrogen orthophosphate were heated at four temperatures in the vicinity of 189°. The samples were heated for regular periods and ground between periods; heating and grinding were continued until essentially constant weight was obtained. Samples were withdrawn for chemical analysis after each period. Table 1 lists the treatment required to reach constant weight at the several temperatures and the compositions of the constant weight products. Tables 2 and 3 show the progress of the isothermal decomposition at 189° and 230°.

Table 1

Thermal Decomposition of Lithium Dihydrogen Orthophosphate.

Temp.	Heating periods	% of total P as:			
		$\text{PO}_4^{-3}$	$\text{P}_2\text{O}_7^{-4}$	$\text{P}_3\text{O}_{10}^{-5}$	$(\text{PO}_3^-)^{\text{a}}$
189°	7-2 hr.	2.5	86.4	0.0	11.1
205°	6-2 hr.	1.6	82.4	0.0	16.0
225°	3-1 hr.	0.9	91.8	0.0	7.3
230°	3-2 hr.	0.7	89.2	0.0	10.1

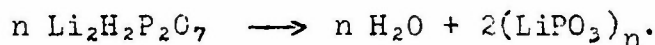
<sup>a</sup> By difference.

It was evident that the primary reaction at or slightly above 189° was:



However, a side reaction to produce lithium metaphosphate must also have occurred. It is significant that most of the lithium metaphosphate formed during the period when the conversion of orthophosphate to pyrophosphate was proceeding most rapidly (cf. Tables 2 and 3). A picture that accounts for this will be presented in a later section of the report. Thermal analyses of the products described in Table 1 showed complete absence of the 189° break. The new lines appearing in the x-ray patterns of samples taken during the reaction were attributed to lithium dihydrogen pyrophosphate.

b. The endothermic process at 277°. The investigation of the process that became rapid at 277° was carried out on samples obtained by heating lithium dihydrogen orthophosphate to constant weight at about 230°. From Table 1 it can be seen these samples were principally lithium dihydrogen pyrophosphate but were contaminated with lithium metaphosphate. The behavior of these samples at 275° and 285° is shown by Tables 4 and 5. X-ray examination of the samples of the 275° series showed a steady disappearance of the lines characteristic of lithium dihydrogen pyrophosphate and a regular increase in the strength of a new set of lines, taken to be those of lithium metaphosphate. These data showed that the reaction becoming rapid at 277 was:



c. The endothermic process at 656°. Thermal analysis of the lithium metaphosphate gave only an endothermic break at 656°, at which point the lithium metaphosphate fused. Slow cooling of the fused material permitted recrystallization to give the original metaphosphate. The white, crystalline metaphosphate originally obtained or recrystallized from the melt was insoluble in water

Table 2

Progress of Lithium Dihydrogen Orthophosphate  
Decomposition at 189°C

Cumulative time	% of total P as:			
	$\text{PO}_4^{-3}$	$\text{P}_2\text{O}_7^{-4}$	$\text{P}_3\text{O}_{10}^{-5}$	$(\text{PO}_3^-)$
0 hrs.	100	0	0	0
2	75	24	0	1
4	36	61	0	4
6	8	84	0	10
8	4	85	0	11
10	3	85	0	13
12	3	86	0	13
14	3	86	0	13

Table 3

Progress of Lithium Dihydrogen Orthophosphate  
Decomposition at 225°C

Cumulative time	% of total P as:			
	$\text{PO}_4^{-3}$	$\text{P}_2\text{O}_7^{-4}$	$\text{P}_3\text{O}_{10}^{-5}$	$(\text{PO}_3^-)$
0 hrs.	100	0	0	0
1	5	90	0	7
2	2	92	0	8
3	2	92	0	9

Table 4

Progress of Lithium Dihydrogen Pyrophosphate Decomposition  
at 275°C

Cumulative time	% of total P as:		
	$P_2O_7^{-4}$	$P_3O_{10}^{-5}$	$(PO_3^-)$
0 hrs.	94	0	6
2	72	0	29
4	39	0	61
6	20	0	81
8	14	0	87
10	10	0	93

Table 5

Progress of Lithium Dihydrogen Pyrophosphate Decomposition  
at 285°C

Cumulative time	% of total P as:		
	$P_2O_7^{-4}$	$P_3O_{10}^{-5}$	$(PO_3^-)$
0 hrs.	89	0	11
2	33	0	67
4	16	0	84
6	4	0	95
8	3	0	97
10	2	0	97

(but somewhat soluble in the presence of much pyrophosphate). The lithium metaphosphate is probably of a highly polymeric nature. Rapid quenching of fused lithium metaphosphate produced a clear, water-soluble glass that gave a diffuse x-ray pattern. An aqueous solution of the glass formed a precipitate with silver ion that was soluble in excess metaphosphate. This indicated the glass was of a long-chain, polyphosphate character. Thermal analysis of the powdered glassy material produced two breaks. The first, an exothermic break at  $359^{\circ}$ , corresponded to crystallization of the glass to give the original crystalline metaphosphate, verified by an x-ray diffraction pattern of a product obtained by heating a glass sample slightly past  $359^{\circ}$ . The second break was endothermic, occurred at  $656^{\circ}$ , and was the melting point of the crystallized lithium metaphosphate.

#### 5. Thermal decomposition of cesium dihydrogen orthophosphate.

Differential thermal analyses of cesium dihydrogen orthophosphate carried out under low-humidity conditions showed endothermic processes became appreciable in rate at or near  $233^{\circ}$ ,  $263^{\circ}$ ,  $330^{\circ}$ ,  $480^{\circ}$ , and  $735^{\circ}$ .

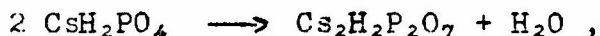
a. The endothermic process at  $233^{\circ}$ . Samples of cesium dihydrogen orthophosphate heated to constant weight at  $234^{\circ}$  and  $250^{\circ}$  (i.e., at or slightly above the first thermal analysis break) experienced weight losses corresponding to complete conversion to cesium metaphosphate. Thermal analyses of the constant weight materials did not show the first three breaks, which indicated these were connected with the overall process of the conversion of the orthophosphate to metaphosphate. The results of chemical analyses of samples withdrawn after each heating period during the conversion at  $234^{\circ}$  are presented in Table 6. It was evident that cesium dihydrogen pyrophosphate was an intermediate in the reaction.

Table 6

Progress of Cesium Dihydrogen Orthophosphate Decomposition at  $234^{\circ}\text{C}$

Cumulative time	% of total P as:		
	$\text{PO}_4^{-3}$	$\text{P}_2\text{O}_7^{-4}$	$(\text{PO}_3^-)$
0	100	0	0
2	72	30	2
4	40	58	2
6	13	83	2
8	3	86	11
10	0	71	30
12	0	51	49
14	0	29	70
16	0	7	94

Cesium dihydrogen pyrophosphate prepared by the acetic acid method described in an earlier section (III B 2e) was subjected to thermal analysis. The 233° break did not appear; the four higher breaks did occur. Thus the 233° break was associated with the process:



and marked the temperature at which that process became appreciable in rate.

b. The endothermic processes at 263° and 330°. The breaks at 263° and 330° in the thermal analyses of cesium dihydrogen pyrophosphate (and which were absent from thermal analyses of metaphosphate prepared at 234° and 250°) must have been connected with the conversion of the dihydrogen pyrophosphate to metaphosphate. The fact that two breaks were connected with this conversion suggested: 1) that two cesium metaphosphates differing in molecular or crystal structure were involved and that as the temperature was raised the first formed metaphosphate was converted to the second, or 2) that there was formation of an intermediate polyphosphate (e.g., a triphosphate or tetraphosphate).

The first interpretation, that two metaphosphates were involved, was discarded in that cesium metaphosphate samples prepared at lower temperatures did not show either the 263° or 330° breaks. Also, insofar as metaphosphates differing in molecular structure were concerned, only long-chain cesium metaphosphate was encountered; no cyclic metaphosphates were analytically detected in any of the samples obtained during the course of heating cesium dihydrogen orthophosphate or cesium dihydrogen pyrophosphate.

The second interpretation, that an intermediate polyphosphate (besides the pyrophosphate) was formed, is more difficult to assess. Analytical data for samples taken at intervals during the conversion of cesium dihydrogen pyrophosphate to cesium metaphosphate at 250° and at 275° appear in Table 7. Since appreciable coprecipitation of metaphosphate prevented the independent gravimetric determination of pyrophosphate in samples that contained more than 15 wt. % cesium metaphosphate the analytical data for pyrophosphate in Table 7 were based on the volumetric determination only; the calculation in effect assumed that triphosphate and higher polyphosphates were absent. The fact that in a number of cases the analyses for pyrophosphate and metaphosphate did not account for 100% of the phosphorus content was an indication that triphosphate and/or higher phosphates were present during the course of the reaction. However, the usually close approach of the analyses to accounting for 100% of the phosphorus served to show that any intermediate was present in relatively small amounts. Furthermore, although possibly the intermediate was non-crystalline, none of the x-ray pictures for samples taken during the conversion of cesium dihydrogen orthophosphate at 234° or of cesium dihydrogen pyrophosphate at 275° showed any lines attributable to other than cesium dihydrogen orthophosphate, dihydrogen pyrophosphate, or metaphosphate. It was clear that conversion of the dihydrogen pyrophosphate

Table 7

Progress of Cesium Dihydrogen Pyrophosphate  
Thermal Decomposition

Hours at 250°	% of total P as: $P_2O_7^{-4}$ *	P as: $PO_3^{-n}$	Hours at 275°	% of total P as: $P_2O_7^{-4}$ *	P as: $PO_3^{-n}$
0	100	0	0	100	0
2	84	16	1	51	49
4	70	30	2	17	84
6	52	42	3	5	92
8	42	-	4	4	95
10	32	68	5	3	97
12	23	75	6	2	98
14	15	84			

\*

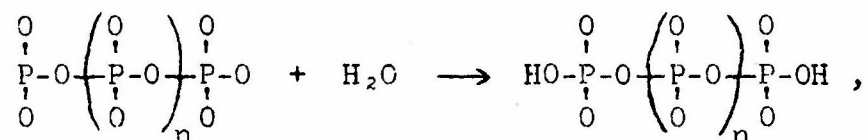
Based on volumetric method only. See text. No cyclic metaphosphate detected in any sample.

to metaphosphate might have proceeded through an intermediate polyphosphate but that the quantity of the intermediate present at any time must have been small, in fact, small enough that it was difficult to attribute the 330° break to its presence.

A third interpretation was possible. The 263° break could be attributed to the conversion of cesium dihydrogen pyrophosphate to metaphosphate (the process perhaps involving transitory intermediates), and the 330° break then attributed to a change in the rate-controlling step of the above process or some more fundamental change in reaction mechanism. A specific suggestion can be made along these lines. On the basis of other studies it appears likely that the kinetics of most hydrogen phosphate thermal decomposition reactions are diffusion-controlled, the rate-controlling process being the transfer of water molecules from the reaction zone in the interior of each particle to the surface of the particle through a layer of reaction product. The break at 263° would, on this basis, be attributed to the rate of conversion of cesium dihydrogen pyrophosphate to cesium metaphosphate becoming appreciable, the rate being determined by the diffusion process, particularly after an adherent surface layer of product had built up. The 330° break might then mark a temperature at which the diffusion difficulty is removed or greatly lessened. Unfortunately, evaluation of this interpretation must wait upon the development of adequate treatments of the kinetics of thermal decomposition of solids based on study of simpler systems.

c. The endothermic process at 430°. The process at 480° proved to be reversible and marks a crystallographic transition characteristic of the cesium metaphosphate.

d. The endothermic process at 735°. The cesium metaphosphate fused at 735°. Products obtained by slow cooling of the melt or quenching in chloroform at -70°C gave identical x-ray patterns. The quenched material dissolved readily in water; the slowly cooled material gelled in water, slowly dissolving to form a viscous solution. Aqueous solutions of both materials gave precipitates with silver ion which dissolved in excess of the phosphate, which indicated the metaphosphate was of the long-chain polyphosphate variety. Aqueous solutions of the slowly crystallized metaphosphate caused immediate and abundant precipitation of solutions of albumen in dilute acetic acid, whereas solutions of the quenched product gave only a slight turbidity, which indicated the quenched material was of distinctly lower molecular weight. To check the latter observation, cesium metaphosphate was heated to 1000°. One portion was cooled slowly to room temperature, the other was quenched in chloroform at about -70°. Chemical analyses showed the quenched material contained 5.4 wt. % of cyclic metaphosphates; the other product had none. End-group titrations (corrected for cyclic metaphosphate content) showed that the number average chain lengths of the slowly cooled and of the quenched metaphosphates were 112 and 40  $\text{PO}_3^-$  units, respectively. The pH's of 1% aqueous solutions of the slowly cooled and quenched products were 5.54 and 4.70, respectively. The greater acidity of the quenched material was attributed to reaction of the shorter, broken chains with water:



and the ionization of the weakly acidic terminal hydrogen ions.

#### 6. Thermal decomposition of cesium monohydrogen orthophosphate.

Two endothermic breaks appeared at 339° and 965° in the differential thermal analyses of cesium monohydrogen orthophosphate. Analyses of products showed the 339° break to mark the temperature at which the conversion of cesium monohydrogen orthophosphate to cesium pyrophosphate became appreciable in rate:



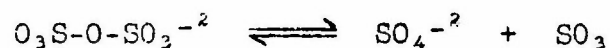
The cesium pyrophosphate fused at 965°. Cooling and heating curves for cesium pyrophosphate showed a reversible crystallographic transition at 238°.

#### 7. Comparative thermal stability of alkali metal pyrophosphates.

According to the Lux-Flood (7) adaptation for high temperature oxygen-containing systems of the Lewis acid-base theory an acid-base reaction involves the combination of an oxide ion (the Lux-Flood base) with an acid, the transfer of an oxide ion from base to

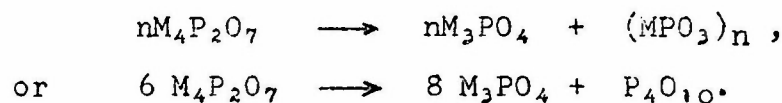
acid, or the passage of an oxide ion from one state of polarization to another.

Reactions involving a change in degree of aggregation in oxyacid systems, such as:



are regarded as being of an acid base nature. A number of these have been investigated by Flood and coworkers (8). They concluded that the instability of the oxygen bridges in the condensed species was a function of the polarizing power of the cation associated with the decomposing anion. For pyrosulfates, instability increased in the sequence  $\text{K} < \text{Na} < \text{Tl}^{\text{I}} < \text{Li} < \text{Ag}$ ; for dichromates the sequence was  $\text{K} < \text{Na} < \text{Tl}^{\text{I}}$ .

A brief study of the thermal stability of alkali metal pyrophosphates was undertaken for comparison. Thermal decomposition of alkali metal pyrophosphates may proceed in two ways:



In either case P-O-P bonds are broken. If the first reaction occurs it would be expected that annealing at lower temperatures might bring about recombination to pyrophosphate. If the second reaction occurs loss of the phosphorus pentoxide from the sample would be expected to preclude recombination on annealing.

Analyses (reported here as weight % of alkali metal pyrophosphate in the sample) were performed on four types of samples. Experimental details and analyses appear in Table 8. The variations in pyrophosphate content were not those which would have been expected on the basis of Lux-Flood considerations. The fact that in all cases the pyrophosphate content rose after the tempering period was evidence that the disproportionation into orthophosphate and metaphosphate was responsible for at least part of the disappearance of pyrophosphate.

This work only explored the question of thermal stability of the condensed phosphates. Additional study, particularly truly equilibrium study, for which we did not have time, is clearly desirable.

Table 8

## Thermal Stability of Alkali Metal Pyrophosphates

Compound	Melting point	Analyses of samples of type <sup>a/</sup>			
		<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
$\text{Li}_4\text{P}_2\text{O}_7$	875°C	98.8	97.2	95.3	96.4
$\text{Na}_4\text{P}_2\text{O}_7$	985°	99.0	98.5	98.2	99.1
$\text{K}_4\text{P}_2\text{O}_7$	1090°	98.5	96.9	90.9	92.9
$\text{Cs}_4\text{P}_2\text{O}_7$	965°	99.0	96.8	93.5	95.1

% loss in $\text{P}_2\text{O}_7^{-4}$ content				
	<u>II</u>	<u>III</u>	<u>IV</u>	
$\text{Li}_4\text{P}_2\text{O}_7$	1.7	3.5	2.4	
$\text{Na}_4\text{P}_2\text{O}_7$	0.5	0.8	-0.1	
$\text{K}_4\text{P}_2\text{O}_7$	1.6	7.7	5.7	
$\text{Cs}_4\text{P}_2\text{O}_7$	2.2	5.6	3.9	

<sup>a/</sup>

- I. Original sample.
- II. Heated for two hours at 1000° and slowly cooled.
- III. Heated at 1000° for five minutes and quenched in 0° carbon tetrachloride.
- IV. Material from III annealed for two hours at 700°.

## C. Thermal Aggregation of Divalent Metal Hydrogen Phosphates

## 1. Introduction.

Relatively few studies have been made of the aggregation reactions occurring when solid divalent metal hydrogen phosphates are heated although the reactions might be expected to be analogous to those in the classical method for preparation of tetrametaphosphate compounds (9). The classical method calls for heating copper oxide, lead oxide, or another heavy metal oxide with a slight excess of phosphoric acid to a temperature not to exceed 450°C. Reactions occurring when crystalline divalent metal dihydrogen orthophosphates are heated might be expected to proceed in better defined fashion. In our program of studying hydrogen phosphate thermal aggregation reactions in conjunction with various cations, barium dihydrogen orthophosphate and lead dihydrogen orthophosphate were chosen as representative divalent metal systems for study.

## 2. Preparation of barium and lead hydrogen phosphates.

a. Barium dihydrogen orthophosphate. Powdered barium hydroxide was added to a 50% solution of orthophosphoric acid until precipitation began. After discarding the precipitate slow evaporation of the filtrate on a steam bath produced anhydrous crystals of barium dihydrogen orthophosphate. Analyses of product: Ba 41.30%, P present as  $\text{PO}_4^{-3}$  18.75%; calculated for  $\text{Ba}(\text{H}_2\text{PO}_4)_2$ : Ba 41.44%, P 18.69% (corresponds to 99.7% and 100.3%  $\text{Ba}(\text{H}_2\text{PO}_4)_2$ , respectively).

b. Lead monohydrogen orthophosphate. Lead monohydrogen orthophosphate precipitated when a hot solution of orthophosphoric acid (5% excess in 500 ml. of water) was added to a boiling solution of 100 g. of lead nitrate in 300 ml. of water. Analysis of the product: P present as  $\text{PO}_4^{-3}$  10.21%, calculated for  $\text{PbHPO}_4$  10.22% (corresponds to 99.9%  $\text{PbHPO}_4$ ).

c. Lead dihydrogen orthophosphate. The lead monohydrogen orthophosphate was dissolved in warm concentrated orthophosphoric acid. Lead dihydrogen orthophosphate precipitated on cooling the solution. The crystals were washed with diethyl ether. Analyses of product: Pb 51.21%, P present as  $\text{PO}_4^{-3}$  15.54%; calculated for  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ : 51.65% and 15.44%, respectively (corresponds to 99.2% and 100.6%  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ , respectively).

## 3. Thermal decomposition of barium dihydrogen orthophosphate.

Differential thermal analyses of barium dihydrogen orthophosphate showed that endothermic processes became appreciable in rate at 243°, somewhat above 300° (very weak), and 875°.

a. The endothermic process at 243°. Weight losses for barium dihydrogen orthophosphate samples heated to constant weight at 245° and 270° (i.e., at or somewhat above the temperature of the first break) corresponded to the conversion of the samples to barium metaphosphate. Analytical data, presented in Table 9, for samples withdrawn during the thermal decomposition of barium dihydrogen orthophosphate at 245° showed barium dihydrogen pyrophosphate to be a reaction intermediate, but there was no evidence for any higher polyphosphate intermediate. An interesting feature of the reaction at 245° was that the x-ray diffraction pattern characteristic of barium dihydrogen orthophosphate was retained by the samples through 1.5 hours of heating. That is, it persisted through the decomposition of 84% of the dihydrogen orthophosphate groups, about 72% going to dihydrogen pyrophosphate and 12% to metaphosphate. On further heating the dihydrogen orthophosphate pattern was replaced by that of barium metaphosphate. Although no new lines appeared through the first half of the reaction a systematic decrease in the barium dihydrogen orthophosphate interplanar spacings was noted (an increase in line spacings) with each heating. The contraction was attributed to the replacement of pairs of dihydrogen orthophosphate ions by dihydrogen pyrophosphate ions, the temperature being insufficient to permit major recrystallization. The x-ray pattern, of course, was largely due to reflections from planes of barium ions.

Table 9

Progress of Barium Dihydrogen Orthophosphate  
Decomposition at 245°

Cumulative time	% of total P as: <sup>a</sup>		
	$\text{PO}_4^{-3}$	$\text{P}_2\text{O}_7^{-4}$	$(\text{PO}_3^-)$
0.0 hrs.	100.0	0.0	0.0
0.5	82.2	17.9	0.0
1.0	50.1	49.3	0.0
1.5	15.9	72.0	11.6
2.0	8.4	20.8	69.5
2.5	1.4	4.0	93.5
3.0	0.8	1.0	98.0

<sup>a</sup> No triphosphate found. With the Bell method this implied absence of higher polyphosphates as well.

b. The endothermic process slightly above 300°. This endothermic process was very weak. It occurred in the thermal analysis curves for samples of barium dihydrogen orthophosphate or of barium metaphosphate, passing the temperature for the first time, but was absent from cooling or subsequent heating curves. There was no detectable weight loss or change in x-ray diffraction pattern associated with the break. It should probably be attributed to a small amount of impurity, perhaps some previously unconverted dihydrogen pyrophosphate or the product of a side reaction.

c. The endothermic process at 875°. The barium metaphosphate fused at 875°. On moderately slow cooling the melt appeared to recrystallize completely to give the original metaphosphate. The x-ray pattern was unchanged by fusion and recrystallization, and subsequent heating curves showed no break other than the 875° melting point.

d. The identity of the barium metaphosphate. The barium metaphosphate produced by the thermal decomposition of barium dihydrogen orthophosphate was treated as an aqueous suspension with 50% of the calculated amount of sodium sulfate. The resulting suspension was filtered and the soluble metathetical product recovered by adding acetone to the filtrate until no further precipitation occurred. The precipitate was recovered by filtration and dried at 80°. The x-ray pattern of this soluble material was principally that reported by Bell, et al. (10), for the high temperature form of sodium tetrametaphosphate four-hydrate but also contained strong lines of anhydrous sodium tetrametaphosphate and sodium sulfate. It was concluded that the barium metaphosphate was the cyclic tetrametaphosphate.

Furthermore, the x-ray diffraction pattern (see Section V) and melting point for our product were identical with those for barium tetrametaphosphate prepared by the Warschauer method according to the directions of Andress, et al. (11).

#### 4. Thermal decomposition of lead dihydrogen orthophosphate.

Differential thermal analyses of lead dihydrogen orthophosphate showed endothermic processes became appreciable in rate near 208°, 320° (weak), 338° (weak), and 667°.

a. The endothermic process at 208°. Weight losses for samples of lead dihydrogen orthophosphate heated to constant weight at 195° and at 210° (i.e., in the vicinity of the temperature of the first thermal analysis break) corresponded to conversion of the samples to lead metaphosphate.

An investigation of the course of this conversion was hampered by inability to devise a satisfactory analytical scheme. It was observed, however, in a thermal analysis of a sample that had lost three-fourths of its "constitutional water" (1.5 moles out of 2.0 moles per formula weight of  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ ) that the sample still underwent further reaction starting at temperatures as low as originally. On the other hand, by the time half the constitutional water had been lost samples exhibited a new x-ray pattern, the lines characteristic of lead dihydrogen orthophosphate being completely absent. On this basis it was postulated that lead dihydrogen pyrophosphate was an unstable intermediate. The 208° break would then mark the temperature at which the following reaction became appreciable in rate:



b. The endothermic processes at 320° and 338°. Although thermal analyses of lead dihydrogen orthophosphate showed endothermic processes occurred near 320° and 338°, lead dihydrogen orthophosphate was completely converted to lead metaphosphate by extended heating (about 20 hours) at temperatures as low as 195°, and thermal analyses of the lead metaphosphate so produced did not exhibit the 320° and 338° breaks. These breaks may have corresponded to temperatures at which steps in the overall process abruptly increased in rate although all steps must have been rapid enough to readily effect conversion at much lower temperatures.

c. The endothermic process at 667°. The lead metaphosphate fused at 667°C. Even on moderately slow cooling of the melt a clear, glassy product was obtained. The powdered glass crystallized when heated to 375° to give a material having the same x-ray pattern as the original metaphosphate.

d. Identification of the lead metaphosphate. A stoichiometric amount of the lead metaphosphate was added to a well stirred solution of sodium sulfide. After filtering the resulting suspension, the soluble product of the metathesis was recovered from the fil-

trate by adding acetone until there was no further precipitation. The product was dried at 120°. The x-ray pattern of the dried material was principally that of anhydrous sodium tetrametaphosphate but included lines of the high temperature form of sodium tetrametaphosphate four-hydrate. It was concluded that the lead metaphosphate was the tetrametaphosphate.

This conclusion was supported by the fact that the x-ray diffraction pattern and thermal analysis curve (m.p. 667°) for the lead metaphosphate produced by the thermal decomposition of crystalline lead dihydrogen orthophosphate were the same as those for lead metaphosphate obtained in the classical Warschauer preparation. Warschauer (9) presented evidence for the tetrameric nature of the product of this preparation using lead oxide and phosphoric acid, and for the identity of the anionic species with that of the metaphosphate produced when copper oxide is used (the latter being generally accepted as copper tetrametaphosphate).

It must be noted, however, that Andress and Fischer (12) in recently reported work concluded that a lead metaphosphate also prepared by the thermal decomposition of lead dihydrogen orthophosphate and having an x-ray pattern identical with ours but melting at a lower temperature (600-650° compared to 667°) was not a tetrametaphosphate but was a long-chain metaphosphate. Some of their evidence for its long-chain nature is based on properties of the solution prepared from the lead metaphosphate by metathesis with sodium sulfide: The sodium salt solution was highly viscous, had marked complexing ability, gave a deep orange-red silver complex, and could not be crystallized. Our solutions were not viscous and readily yielded a crystalline product. The metathetical cycle used by them to specifically demonstrate the thermal instability of lead tetrametaphosphate in the temperature range involved in these preparations serves equally well, using their reported results, to demonstrate that lead tetrametaphosphate is stable at the temperatures involved. Thus one piece of evidence presented by them for the thermal instability of lead tetrametaphosphate was the fact that the x-ray pattern of a sample prepared by dehydrating lead tetrametaphosphate four-hydrate at 215° showed the lines of the long-chain metaphosphate. These lines are the ones we have assigned to the tetrametaphosphate.

Our work supports the older work of Warschauer (although he employed lead oxide-orthophosphoric acid mixtures and we employed crystalline lead dihydrogen orthophosphate) which concluded that the product at temperatures short of fusion was lead tetrametaphosphate, the product after fusion being a different chemical entity, probably long-chain metaphosphate. Parts of Warschauer's observations have been criticized by some on the basis of a misquote to the effect that heating the lead tetrametaphosphate first produced past 400° converts it to another modification. His statement was that heating the lead metaphosphate past 400° until a completely clear melt results converts it to another modification.

## D. Pyrophosphate-Metaphosphate Phase Diagrams

### 1. Introduction.

In view of the differences in thermal behavior of the divalent metal dihydrogen phosphate systems as compared to the alkali metal dihydrogen phosphate systems - specifically the formation of barium and lead tetrametaphosphates whereas trimetaphosphate and long-chain metaphosphate form in the alkali metal systems, an investigation of reactions in dihydrogen phosphate-monohydrogen phosphate mixtures designed to produce polyphosphates was undertaken. It was already known that triphosphate was the only polyphosphate, other than pyrophosphate, that could be detected when sodium or potassium dihydrogen-monohydrogen orthophosphate mixtures were heated.

Reaction products were obtained in several metal systems (lead, barium, cesium) by heating mixtures of the dihydrogen and monohydrogen orthophosphates of the metals at as high a temperature as could be used without causing the appearance of a liquid phase. The reaction products were evaluated by subjecting them to differential thermal analysis and constructing a phase diagram from the thermal analysis data.

### 2. The system: lead pyrophosphate-lead metaphosphate.

Samples corresponding to various compositions in the lead pyrophosphate-lead metaphosphate system were prepared by heating appropriate mixtures of lead dihydrogen and monohydrogen orthophosphates to constant weight at 550°, a temperature at which the individual reactants are converted to lead tetrametaphosphate and lead pyrophosphate, respectively, but below the temperature of appearance of any liquid phase. The products were ground thoroughly using an agate mortar and reheated at 550° for twelve hours to insure complete reaction.

Data from the differential thermal analysis curves of these samples appears in Table 10 and Figure 1. The temperatures and strengths of the various arrests made it evident that a new species corresponding to  $1P_2O_7^{2-}:2PO_3^-$  was present in the system. This was the composition of lead tetrphosphate,  $Pb_3P_4O_{13}$ . The x-ray diffraction pattern for the lead tetrphosphate sample was distinct from that of lead tetrametaphosphate and that of lead pyrophosphate (see Section V). X-ray patterns for the other samples were those of lead tetrphosphate and lead tetrametaphosphate or lead pyrophosphate, which supported the thermal evidence that no polyphosphate other than tetrphosphate occurred intermediate between lead pyrophosphate and lead tetrametaphosphate in samples prepared at 550°. Lead tetrphosphate melted incongruently at 700°.

Table 10

The System: Lead Pyrophosphate-Lead Metaphosphate

Mole Per Cent <sup>a/</sup>		$Pb_3P_4O_{13}$ - $Pb_2(PO_3)_4$		$Pb_3P_4O_{13}$		Liquidus Temp.
$P_2O_7^{4-}$	$PO_3^-$	Eutectic Temp.	Strength	Incongruent m.p. Temp.	Strength	
0.0	100.0	---	--	---	--	667
5.0	95.0	645	b	---	--	663
10.0	90.0	645	b	---	--	652
15.0	85.0	645	b	---	--	648
20.0	80.0	645	8	---	--	675
25.0	75.0	645	4	---	--	695
30.0	70.0	645	2	703°	10	700
33.3	66.7	---	0	700	17	733
40.0	60.0	---	--	700	11	770
45.0	55.0	---	--	700	8	780
50.0	50.0	---	--	700	6	790
55.0	45.0	---	--	700	5	794
60.0	40.0	---	--	701°	3	798

<sup>a/</sup> Molar compositions are calculated in terms of the species  $PO_3^-$  and  $P_2O_7^{4-}$  and not in terms of their lead salts.

<sup>b/</sup> Rate control not in use.

### 3. The system: barium pyrophosphate-barium metaphosphate.

A phase study similar to the one just described was attempted for the system barium pyrophosphate-barium metaphosphate. Samples corresponding to various compositions in the system were prepared by heating appropriate mixtures of barium dihydrogen and mono-hydrogen orthophosphates to constant weight at 550°. The products were ground thoroughly using an agate mortar and reheated at 650° for twelve hours to insure complete reaction.

Data from the differential thermal analysis curves for these samples appears in Table 11. However, the liquidus for these samples lay above 1050°, above the range of our equipment.

No conclusions could be drawn from the available thermal data.

X-ray diffraction patterns of the samples indicated that all the samples contained a compound other than barium pyrophosphate or barium metaphosphate. The x-ray pattern for this material is listed in Section V as "barium polyphosphate." There were no discernible trends in the strengths of the x-ray lines to permit assigning a composition to the compound.

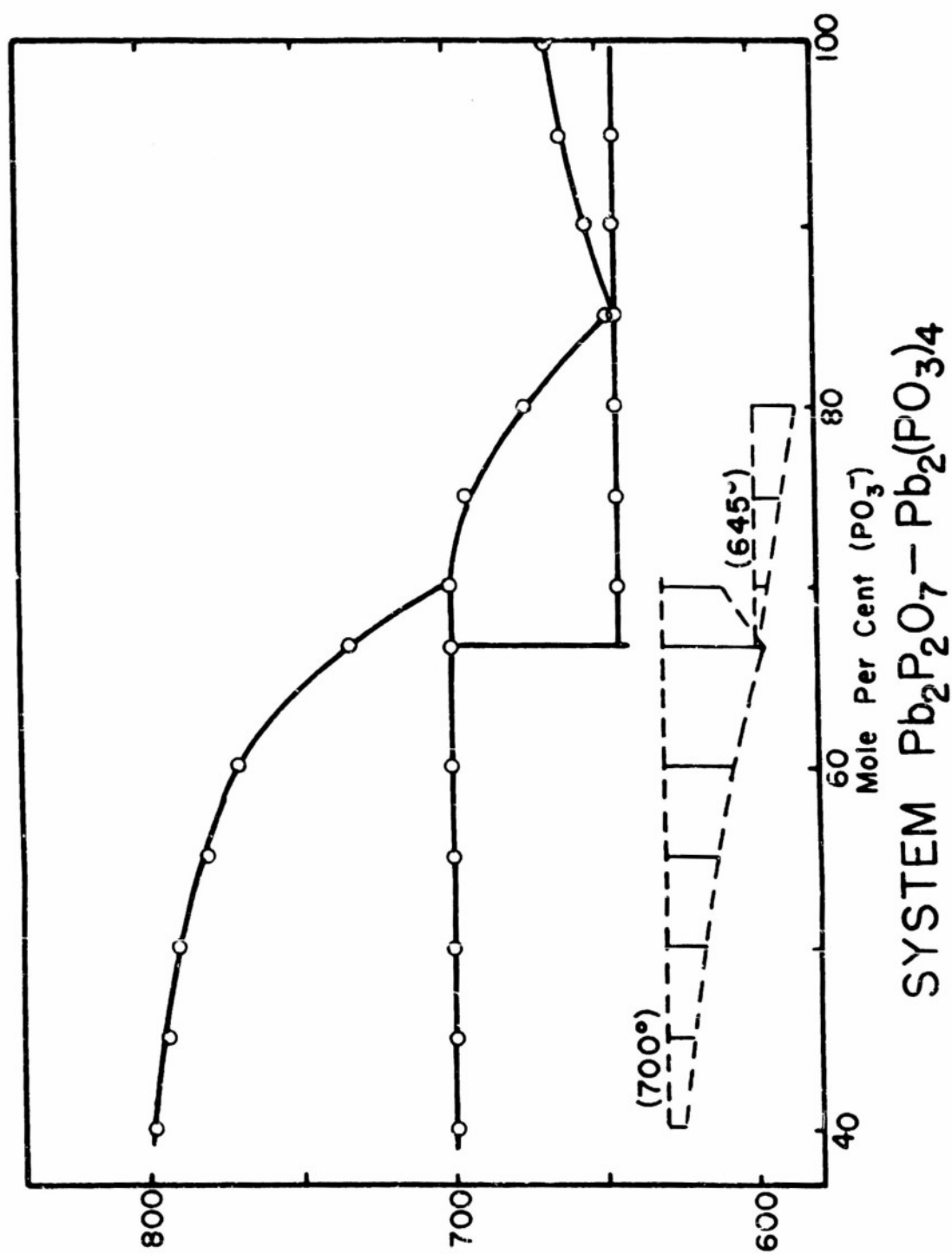


Table 11

The System: Barium Pyrophosphate-Barium Metaphosphate

Mole per cent <sup>a</sup>		Breaks in heating curves					
$P_2O_7^{-4}$	$PO_3^-$	Temp.	Strength	Temp.	Strength	Temp.	Strength
20.0	80.0	850	5	895	1	-	-
25.0	75.0	850	6	895	2	994	1
30.0	70.0	850	5	895	3	990	1
33.3	66.7	850	4	895	4	986	1
40.0	60.0	850	3	895	5	986	2
45.0	55.0	850	1	895	7	986	2

<sup>a</sup> Molar compositions are calculated in terms of the species  $PO_3^-$  and  $P_2O_7^{-4}$ , not in terms of their barium salts.

4. The system: cesium pyrophosphate-cesium metaphosphate.

Samples corresponding to various compositions in the cesium pyrophosphate-cesium metaphosphate system were prepared by heating appropriate mixtures of cesium dihydrogen orthophosphate and cesium monohydrogen orthophosphate-monohydrate at 250-300° and annealing the products at 415° for 15 hours. Data from the differential thermal analyses for these samples appear in Table 12. The data were characteristic of a simple eutectic system.

Table 12

The System: Cesium Pyrophosphate-Cesium Metaphosphate

Mole per cent <sup>a</sup>		Eutectic arrest		Liquidus
$P_2O_7^{-4}$	$PO_3^-$	Temp.	Strength	temp.
0	100	-	-	735°
5	95	513°	5.0	708
10	90	528	6.3	676
15	85	528	7.0	628
20	80	528	8.6	588
25	75	528	9.0	603
30	70	528	8.0	643
35	65	528	6.5	693
40	60	528	6.0	728
45	55	533	5.7	769
50	50	530	5.0	805
55	45	528	4.5	852
60	40	533	3.8	877
100	0	-	-	965

<sup>a</sup> In terms of the species  $PO_3^-$  and  $P_2O_7^{-4}$ .

However, when samples of all the intermediate compositions were annealed at temperatures lower than  $415^\circ$ , specifically when annealed for 24 hours at  $330^\circ$  or 36 hours, 72 hours, or 2 weeks at  $385^\circ$ , thermal analyses showed breaks at  $445^\circ$ . Unfortunately, the strength of the  $445^\circ$  breaks varied in erratic fashion with composition and with manner of annealing. While no firm conclusion could be drawn, the observations pointed to the presence of a cesium polyphosphate, the composition of which could not be adduced. A sample that exhibited a moderately strong break at  $445^\circ$  and that should have had 73.9% of its phosphorus content as metaphosphate and 26.1% as pyrophosphate if those were the only phosphate species present, was actually found by chemical analysis to have 70.6% of its phosphorus content as metaphosphate and 20.8% as pyrophosphate. No cyclic metaphosphates were found. The discrepancy of 3.6% of the phosphorus being unaccounted for supported the presence of an analytically undetectable polyphosphate in the system.

#### E. Effect of Humidity on the Thermal Aggregation of Hydrogen Phosphates

##### 1. Introduction.

For some years it has been evident that the thermal aggregation reactions undergone by hydrogen phosphates are affected by the humidity of the atmosphere in which the samples are heated. Since the reactions we are concerned with here involve water as a gaseous phase, e.g.:



one might expect that variations in the humidity of the atmosphere would affect the temperature at which aggregation occurs. One can say, a priori, that the hydrogen phosphate must be heated to a temperature at which its dissociation pressure exceeds the water vapor pressure of the atmosphere before conversion will occur.

In addition to the above, more or less obvious, effect of water vapor another, more subtle, effect has been noted. A change in the humidity of the atmosphere in which a hydrogen phosphate is heated may cause a change in reaction product. Thus, the use of humid conditions is involved in the preparation of a sodium metaphosphate (13). In a previous section (III B 3) we pointed out a difference in behavior of lithium dihydrogen orthophosphate when heated under humid or non-humid conditions. Additional examples have appeared in the literature but no serious attempts to elucidate the nature of this effect have been reported. At the termination of this project our investigation of this problem had not been completed. Our observations and preliminary conclusions follow.

## 2. Special differential thermal analysis apparatus.

Although the differential thermal analysis apparatus employed in the studies described in the earlier sections of this report provided for continuous sweeping of the furnace cavity with preheated dry air it was necessary to design and construct a new apparatus adapted to the task of performing differential thermal analyses under controlled levels of humidity and for carrying out reactions at controlled temperatures and humidity.

A 2.5 cm. diameter tube furnace, with a heated zone about 67 cm. in length, was the foundation of the apparatus. Humidity control was effected by sweeping the tube with a continuous flow of an air-water vapor mixture at a lineal rate of about 25 cm. per minute measured at room temperature, or about 50 cm. per minute at 300°, a more significant temperature. A constant head device supplied water at a constant and measured rate to a flash boiler located within the tube at the entrance to the tube furnace. A constant and measured flow of dry air was introduced at the same point. The air and water vapor were mixed and preheated by passage through 40 cm. of the tube furnace before coming in contact with the sample. A removable rack inserted through the exit end of the tube furnace facilitated introduction of the sample, a similar amount of aluminum oxide, and the several thermocouples. Pt-90 Pt 10 Rh thermocouples were used. Temperatures were recorded and the apparatus calibrated as described in Section III A 1 of this report. Possible humidity variations from the recorded values were estimated to be 5%.

## 3. The thermal decomposition of sodium monohydrogen orthophosphate.

The thermal decomposition of sodium monohydrogen orthophosphate



was chosen as a relatively simple process on which to commence a study of the effect of humidity. Differential thermal analyses were run on sodium monohydrogen orthophosphate in a dry atmosphere and in atmospheres containing various mole fractions of water vapor. The samples used were the reagent grade anhydrous salt. It is to be expected that other preparations than the one we used will give somewhat different results. Reaction was detectable at 232°C in the thermal analysis run in a dry atmosphere. The reaction appeared to continue at moderate rate up to 321°C, at which point there appeared to be a sudden marked increase in rate. Comparison with the thermal analyses carried out in humid atmospheres showed the temperature at which reaction could first be detected in thermal analyses to be sensitive to humidity, whereas the temperature at which the marked increase in rate was observed was relatively insensitive (see Table 13).

Table 13

Thermal Analyses of Sodium Monohydrogen Orthophosphate  
at Controlled Humidities <sup>a/</sup>

Mole fraction H <sub>2</sub> O in atmos.	0.00	0.46	0.85	1.00
Reaction detected (°C)	282°	287°	302°	317°
Reaction became rapid (°C)	322°	318°	320°	322°

<sup>a/</sup> The temperatures listed here differ from some previously reported in that thermocouple corrections were not applied to values in preliminary reports.

The variation with humidity of the temperature at which reaction could first be detected suggested that each increase in humidity required that the reactant reach a higher temperature before its dissociation pressure exceeded the water vapor pressure of the surrounding atmosphere (a necessary condition for reaction).

To test this, a second series of experiments was performed, using a heating rate of 10° per minute. Thermal analyses carried out at several heating rates indicated the general shape of the curves to be independent of heating rate from 10° per minute to 40° per minute (Table 14) but showed a rate of 10° per minute to be desirable from the standpoint of ease of reading the curves, particularly with respect to detecting the onset of reaction. Data from the second series appears in Table 15.

Table 14

Thermal Analyses of Sodium Monohydrogen Orthophosphate in  
Dry Air at Several Heating Rates

<u>Heating rate</u> °C/min.	<u>Reaction first</u> <u>detected</u>	<u>Reaction became</u> <u>rapid</u>
38	274°	323°
32	279°	319°
19	277°	315°
11	276°	317°

Table 15

Thermal Analyses of Sodium Monohydrogen Orthophosphate at Controlled Humidities, Heating Rate 10°/min.

Partial pressure H <sub>2</sub> O, mm.	0	191	391	659	728
Reaction detected, °C	270°	277°	288°	295°	300°
Reaction rapid, °C	322°	316°	319°	320°	315°

Assuming that the temperature at which reaction was first detected was actually that at which reaction commenced (i.e., the temperature at which the dissociation pressure reached and exceeded the partial pressure of water in the atmosphere) and applying to the data for detection of the reaction the equation:

$$\ln \frac{p_1}{p_2} = - \frac{\Delta H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

led to a value for the heat of reaction of 37 kcal. per mole of sodium pyrophosphate formed. The heat of reaction calculated from heat of formation and heat capacity data in the literature was 30 kcal. per mole of sodium pyrophosphate formed at 300°C. This indicated the assumption made earlier was reasonable, namely that the increase in the temperature at which evidence of reaction first appeared that accompanied an increase in humidity could be attributed to the necessity for an increased dissociation pressure before reaction would commence. Actually, in studying reactions that may be slow or have induction periods, the technique of differential thermal analysis does not serve well to fix the temperature at which reaction is initiated. In such a dynamic study, with the temperature increasing steadily, the temperature may rise considerably between the time reaction starts and the time the reaction is proceeding rapidly enough to visibly affect the heating curves. It is quite likely that reaction set in here at temperatures distinctly below those listed.

It was evident that more had to be learned about "simple" hydrogen phosphate thermal decompositions, such as the conversion of sodium monohydrogen orthophosphate to sodium pyrophosphate, before a serious attempt could be made to understand the thermal decomposition processes that yield several products and to explain the role of water vapor in influencing the reaction path. Accordingly, the sodium monohydrogen orthophosphate thermal decomposition was studied further with a view to elucidating the mechanism of the reaction and explaining the fact that as a sample was gradually heated the reaction set in at some temperature below 300°, proceeded at a moderate rate, and then abruptly increased in rate when the temperature reached about 315°.

The simplest approach to an explanation of this phenomenon was to say that it merely reflected the temperature dependence of the

reaction rate and that as long as a sample contained unconverted sodium monohydrogen orthophosphate a thermal analysis of the sample would show the same general behavior. Table 16 presents data from thermal analyses of samples with and without previous thermal history. The area contained between the differential thermal analysis curve and the path the curve would have followed had no reaction occurred is a measure of the amount of heat absorbed (in this case) during reaction and hence a measure of the amount of reaction that occurred. From the areas pertaining to reaction below and above the abrupt rate increase the respective percentages of reaction were calculated. For those cases in which the sample was partially decomposed before thermal analysis, the percentages apply to that portion of the reaction occurring during thermal analysis only, i.e., to the reaction of the remaining undecomposed reactant.

Table 16

Effect of Previous Thermal Treatment on Thermal Decomposition  
of Sodium Monohydrogen Orthophosphate

Previous treatment		% Reaction occurring	
<u>Time</u>	<u>Temp.</u>	<u>Below</u>	<u>Above abrupt increase</u>
None	-	40%	60%
4 min.	304°C	0	100
22 min.	307°	0	100
33 min.	307°	0	100

The data made it clear that once the sodium monohydrogen orthophosphate was partially decomposed further decomposition below the temperature of the abrupt change did not occur, at least not at a rate sufficient to be detected by our differential thermal analyses. This suggested that reaction first occurred on or near the surface of particles and that as reaction proceeded in each particle a product layer built up which acted as a barrier to further reaction, probably by interfering with the diffusion of water vapor (a reaction product) from the reaction zone to the surface of the particle. The effectiveness of this diffusion barrier must, according to this viewpoint, have diminished at the abrupt break, perhaps as the result of a recrystallization.

Qualitative evidence that the amount of reaction that occurred below the abrupt break was related to the amount of surface available or, since the material was a powder, to the particle size is presented in Table 17. The percentages of reaction that occurred below and above the abrupt break were determined in the same way as for the preceding Table.

An attempt was made to determine whether the reaction was diffusion-controlled at temperatures below the abrupt break. Sodium monohydrogen orthophosphate particles of between 45 and 50 mesh were heated in a single layer in an aluminum foil dish. The dish was placed in a muffle furnace on a one-half inch thick aluminum block

Table 17

Effect of Particle Size on Thermal Decomposition of Sodium Monohydrogen Orthophosphate

<u>Sample</u>	<u>% of reaction occurring</u>	
	<u>Below</u>	<u>Above abrupt rate increase</u>
Unground	8%	92%
Moderately ground in porcelain mortar	40	60
Finely ground in agate mortar	61	39

(furnace and block already at the temperature to be used) to start each heating period. Preheated dry air passed through the furnace continuously. On removal from the furnace the aluminum dish containing the sample was cooled rapidly by placing it on another heavy aluminum block in a desiccator. The dish was weighed in a desiccated balance case and returned to the furnace. Knowledge of the sample weight and of the losses experienced in each heating period permitted calculation of  $\alpha$ , the extent of reaction, as a function of time at the temperature used. The data had the general character of that expected from diffusion-controlled reactions, i.e., the reaction rate was maximum initially and fell off steadily as the reaction progressed. The data, however, were not susceptible of convincing treatment by any of the standard mathematical expressions used to describe the progress of thermal decompositions of solids, either by diffusion-controlled reaction or by non-diffusion controlled reaction.

Microscopic observation was made of the appearance of sodium monohydrogen orthophosphate before and after the material had been heated for various periods at temperatures below and above the abrupt break. The observations appear in Tables 18 and 19. The observations were consistent with the suggestion that at the critical point a recrystallization (or crystallization) became possible which lessened a diffusion barrier to reaction.

The work described does not furnish a basis for a detailed explanation of the behavior of sodium monohydrogen orthophosphate on heating in dry or humid atmospheres. It is, however, a basis for designing experiments to elucidate the reaction mechanism. We plan further investigations at a later date.

#### 4. The thermal decomposition of sodium dihydrogen orthophosphate.

To evaluate the effect of a humid atmosphere on the thermal decomposition of sodium dihydrogen orthophosphate thermal analyses were run on samples of that compound in dry and humid atmospheres. The results appear in Table 20. The reaction becoming rapid at slightly above 190° is:

Table 18

Microscopic Observation of 45-50 Mesh Crystals After Heating Below the Critical Temperature<sup>a/</sup>

<u>Cumulative time of heating</u>	<u>Extent of reaction</u> <sup>b/</sup>	<u>Observation</u>
0 min.	0.00	Translucent, irregularly shaped particles, some agglomeration of small particles adhering to large particles.
30	0.15	No change evident.
60	0.37	No change evident.
120	0.75	Crystals appeared slightly less translucent. Some of the adherent small particles had detached from the large particles.
195	0.96	Somewhat less translucent.
840	1.0	Slightly increased opacity, although crystals were still largely translucent. No well defined opaque areas.

<sup>a/</sup> The sample was heated at 316°C.

<sup>b/</sup> The extent of reaction was estimated from data for a kinetics run carried out at 316°C.

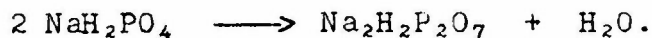
Table 19

Microscopic Observation of 45-50 Mesh Crystals After Heating Above the Critical Temperature<sup>a</sup>

<u>Cumulative time of heating</u>	<u>Extent of reaction</u> <sup>b</sup>	<u>Observation</u>
0 min.	0.00	Translucent irregularly shaped particles.
1.1	0.07	No change evident.
3.2	0.48	Some crystals appeared unaffected. Others had opaque spots, some were covered with opaque layer.
5.0	0.79	Most crystals covered with opaque layer, although some exhibited translucent regions between large opaque spots.
7.1	0.96	Very few translucent regions.
11.7	1.06	All crystals opaque in appearance.

<sup>a</sup> The sample was heated in an aluminum foil pan placed in a furnace at 339°C, the furnace floor being a heavy aluminum block. It is questionable, however, whether the samples actually attained a temperature of 339° because of the short heating periods and endothermic nature of the process.

<sup>b</sup> Determined by weighing sample after each heating period.



Although the pronounced effect observed with sodium monohydrogen orthophosphate is not evident here, the data do indicate a repression of the initiation of the reaction by humid atmospheres.

Table 20

Thermal Analyses of Sodium Dihydrogen Orthophosphate at Controlled Humidities, Heating Rate 12°/Min.

Partial pressure H <sub>2</sub> O, mm.	0	22	257	353	737
Reaction detected, °C	182°	186°	183°	185°	191°
Reaction rapid, °C	191°	194°	193°	190°	194°

5. The thermal decomposition of potassium dihydrogen orthophosphate.

Thermal analyses were run on potassium dihydrogen orthophosphate under several conditions of humidity. The data obtained in these experiments are listed in Table 21. A distinct effect on the temperature at which reaction was rapid enough to be detected is evident. This system differs from the previous ones in that the "rapid break" is accompanied by liquefaction and its strength may simply reflect that change in state and not an increase in reaction rate.

Table 21

Thermal Analyses of Potassium Dihydrogen Orthophosphate at Controlled Humidities

Partial pressure, H <sub>2</sub> O, mm.	0	670	670	733
Heating rate, °C/min.	21	21	15	35
Reaction detected, °C	197°	219°	220°	226°
"Reaction rapid" <sup>a/</sup> , °C	246°	251°	250°	251°

<sup>a/</sup> See text.

#### IV. Final Project Report

##### A. Introduction

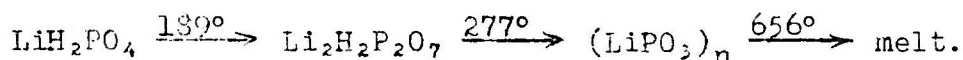
To provide a basis for a better understanding of phosphate aggregation reactions this project undertook to augment available data concerning the thermal aggregation (thermal decomposition) of sodium and potassium hydrogen phosphates with comparable data for other systems. In connection with these investigations information was obtained concerning the phase diagrams for several phosphate systems and the thermal stability of some of the condensed phosphates. A study of the effect of humidity on the thermal decomposition reactions was commenced.

The principal contributions and conclusions of the work carried out on this project are summarized in the sections immediately following. Temperatures listed in connection with chemical reactions are ones at which the reactions are known to occur at an appreciable rate. The reactions will generally proceed very slowly at temperatures distinctly below those listed.

Publications derived from work carried out under this contract are now in preparation. Manuscripts of these will be submitted when ready.

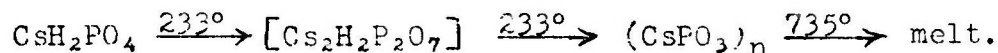
##### B. Thermal Decomposition of Dihydrogen Orthophosphates

1. The thermal decomposition sequence for lithium dihydrogen orthophosphate was found to be:



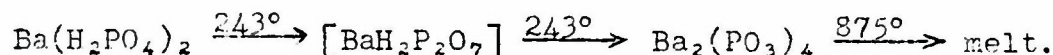
It was noted that considerable amounts (about 10% of the sample) of lithium metaphosphate are formed in a side reaction when the first step is carried out at temperatures in the range of 189°-230°.

2. The thermal decomposition of cesium dihydrogen orthophosphate was found to be best expressed by:

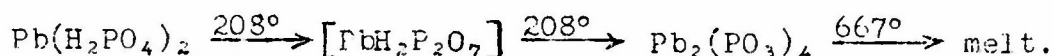


The brackets [ ] label the dihydrogen pyrophosphate as an unstable intermediate; an additional intermediate may have been involved. The cesium metaphosphate exhibited a reversible crystallographic transition at 480°.

3. The thermal decomposition of barium dihydrogen orthophosphate was found to be:



4. The thermal decomposition of lead dihydrogen orthophosphate was found to be best described by:



An additional unstable intermediate may have been involved.

5. Summary and conclusions. Combining the above with data from similar earlier studies of the thermal decomposition of sodium and potassium dihydrogen orthophosphates produces the following summary:

<u>Reactant</u>	<u>Rate appreciable at</u>	<u>Product</u>	<u>Ultimate Product</u> ✓
$\text{LiH}_2\text{PO}_4$	189°C	$\text{Li}_2\text{H}_2\text{P}_2\text{O}_7$	$(\text{LiPO}_3)_n$
$\text{NaH}_2\text{PO}_4$	200°	$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$	$(\text{NaPO}_3)_3$
$\text{KH}_2\text{PO}_4$	208°	$[\text{K}_2\text{H}_2\text{P}_2\text{O}_7]$	$(\text{KPO}_3)_n$
$\text{CsH}_2\text{PO}_4$	233°	$[\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7]$	$(\text{CsPO}_3)_n$
$\text{Pb}(\text{H}_2\text{PO}_4)_2$	208°	$[\text{PbH}_2\text{P}_2\text{O}_7]$	$\text{Pb}_2(\text{PO}_3)_4$
$\text{Ba}(\text{H}_2\text{PO}_4)_2$	243°	$[\text{BaH}_2\text{P}_2\text{O}_7]$	$\text{Ba}_2(\text{PO}_3)_4$

✓<sup>a</sup> Short of fusion.

The first observation is that the range of the temperatures listed is relatively small (compared, for example, to the thermal decomposition of carbonates:  $\text{PbCO}_3$  d. 315°,  $\text{BaCO}_3 > 1000^\circ$ ). Unfortunately, of the reactants listed the crystal structure of  $\text{KH}_2\text{PO}_4$  alone is known. The  $\text{H}_2\text{PO}_4^-$  anions of this compound are considered to be completely hydrogen bonded into a three-dimensional network such that all oxygen atoms and all hydrogen atoms are involved in hydrogen bonds. Although details of their structures are unknown, it may be presumed that comparable hydrogen bonding occurs in the other crystalline reactants. The thermal decompositions under consideration then may all be viewed as the conversion of one type of anionic condensation (hydrogen bonding) to another (oxygen bridging), the actual details of the reaction and the immediate surroundings of the reaction site probably being quite similar in the several reactants. Thus the small range of temperatures is not surprising.

Table 22

## Thermal Decomposition of Cesium Hydrogen Phosphates

Hours at 250°C	$\text{CsH}_2\text{PO}_4$			$\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ <sup>a</sup>	
	% of total P as: $\text{PO}_4^{-3}$	$\text{P}_2\text{O}_7^{-4}$	( $\text{PO}_3^-$ )	% of total P as: $\text{P}_2\text{O}_7^{-4}$	( $\text{PO}_3^-$ )
0	100	0	0	100	0
2	52	46	2	84	16
4	29	60	11	70	30
6	19	42	38	52	42
8	14	23	64	42	-
10	10	14	75	32	68
12	6	9	85	23	75
14	-	-	-	15	84
16	-	-	-		
18	1	1	98		

<sup>a</sup> Crystalline, see Section III B 2 e for preparation.

It is interesting that the ultimate crystalline metaphosphate product may be the trimetaphosphate, the tetrametaphosphate, or the long-chain polymetaphosphate. It seems likely that at temperatures sufficiently high to provide needed mobility the lattice energies of the possible products are important in determining which of the several possibilities will actually form. Thus, naively, the tetravalent tetrametaphosphate anion would appear likely to pack well with the divalent metal cations.

## C. Thermal Decomposition of Monohydrogen Orthophosphates

1. Cesium monohydrogen orthophosphate was found to convert to the pyrophosphate at an appreciable rate at 339°:



2. Combining the above with similar studies of sodium and potassium monohydrogen orthophosphate produces the following summary:

Reactant	Rate appreciable at	Product
$\text{Na}_2\text{HPO}_4$	240°	$\text{Na}_4\text{P}_2\text{O}_7$
$\text{K}_2\text{HPO}_4$	282°	$\text{K}_4\text{P}_2\text{O}_7$
$\text{Cs}_2\text{HPO}_4$	339°	$\text{Cs}_4\text{P}_2\text{O}_7$

From purely stoichiometric considerations the degree of hydrogen bonding in these crystalline reactants is of necessity less than in the dihydrogen orthophosphates, and the hydrogen bonding can be considered to make a smaller contribution to crystal properties. Here, with a smaller variety of cations a greater range of temperatures was recorded. It was noted, however, that the variation in reaction temperature with a change in cation is in the same direction as for the dihydrogen orthophosphates.

#### D. Pyrophosphate-Metaphosphate Phase Studies

1. Lead tetraphosphate, incongruent melting point  $700^{\circ}$ , was shown to form in the lead pyrophosphate-lead tetrametaphosphate phase system.

2. Indications were found of the presence of polyphosphates in the barium pyrophosphate-barium tetrametaphosphate and in the cesium pyrophosphate-cesium metaphosphate phase systems. In neither case could the polyphosphate be identified.

3. Other studies have shown only triphosphate to form in sodium pyrophosphate-sodium metaphosphate (15) and potassium pyrophosphate-potassium metaphosphate (16) systems. Once again lattice energies are probably most important in determining that the charge type 1:5 compounds  $\text{Na}_5\text{P}_3\text{O}_{10}$  and  $\text{K}_5\text{P}_3\text{O}_{10}$  form, but the 2:6 compound  $\text{Pb}_2\text{P}_4\text{O}_{13}$  forms.

#### E. Metaphosphate Glass Formation

Data pertinent to glass formation obtained in the course of this project for lithium, cesium, lead, and barium metaphosphates and data from earlier investigations by us on sodium, potassium, and silver metaphosphates are summarized in Table 23. The formation of glasses when lithium, sodium, silver, and lead metaphosphate melts are cooled at moderate rates is attributed to the greater viscosity of these melts at the temperatures at which crystallization should occur on cooling (i.e., at the freezing points of the crystalline metaphosphates). Considerable mobility in the melt is required to permit the organizational processes of crystallization to occur. From the data listed it appears that the viscosity of metaphosphate melts generally becomes great enough on cooling below about  $700^{\circ}$  to seriously interfere with the crystallization process. Of course, there is no reason to believe that the viscosities of all metaphosphate melts have the same temperature dependence. It is particularly likely that metaphosphate melts containing the smaller, more highly charged cations will generally be the more viscous at a given temperature due to the possibility of crosslinking of the metaphosphate anions by those cations. Actual viscosity data are not available.

Table 23  
Metaphosphate Glass Formation

<u>Metaphosphate</u>	<u>M.p.</u>	<u>Behavior on cooling melt</u>	
		<u>Quenching</u>	<u>Slow cooling</u>
$\{\text{AgPO}_3\}_3$	495°C	Glass	Glass
$\{\text{NaPO}_3\}_3$	625°	Glass	Glass
$\{\text{LiPO}_3\}_n$	656°	Glass	Crystal
$\text{Pb}_2(\text{PO}_3)_4$	667°	Glass	Glass
$\{\text{CsPO}_3\}_n$	735°	Crystal	Crystal
$\{\text{KPO}_3\}_n$	805°	Cloudy glass	Crystal
$\text{Ba}_2(\text{PO}_3)_4$	875°	-	Crystal

#### F. Effect of Humidity on the Thermal Decomposition of Hydrogen Phosphates

Changing the humidity of the atmosphere in which a hydrogen phosphate thermal decomposition is carried out has been found to: 1) repress the initiation of the decomposition and 2) change the product of the decomposition. This project was particularly interested in studying the second effect but found it necessary first to study effect 1) and to study the details of the thermal decomposition mechanism. Work on this subject was delayed by the call to service of the man first assigned to it and when the project terminated was not advanced sufficiently to permit drawing firm conclusions. The speculations of the terminal report will not be repeated here.

#### G. Miscellany

Miscellaneous information incidental to the investigations of the several subjects appears in the technical reports accompanying this summary. In particular, there are data on the thermal stability of many of the condensed phosphates encountered in the course of the work. Also, some preliminary conclusions are drawn on the mechanism of the hydrogen phosphate thermal decompositions.

## V. X-ray Diffraction Patterns

Interplanar spacings (d) are expressed in Angstrom units.

Line strengths are estimated in terms of very, very weak (VW); very weak (W); weak (V); medium (M); strong (S); very strong (VS); and very, very strong (VVS).

A.  $\text{Ba}(\text{H}_2\text{PO}_4)_2$ 

<u>d</u>	<u>Strength</u>
6.15	VS
5.03	W
4.26	W
3.92	M
3.83	M
3.73	M
3.50	VW
3.35	VW
3.25	VW
3.11	VS
3.01	W
2.88	W
2.76	M
2.66	M
2.51	W
2.21	S
2.14	W
2.12	W
2.06	W
2.03	W
1.98	W
1.91	W
1.87	W

B.  $\text{Ba}_2\text{P}_2\text{O}_7$ 

<u>d</u>	<u>Strength</u>
3.93	VS
3.58	M
3.37	W
3.07	W
2.81	S
2.71	S
2.32	M
2.24	W
2.15	M
2.11	W
2.03	W
1.81	W
1.76	W
1.72	W
1.62	W
1.58	W
1.54	W
1.48	W
1.46	W
1.41	W
1.35	W

C.  $\text{Ba}_2(\text{PO}_3)_4$  from  $\text{Ba}(\text{H}_2\text{PO}_4)_2$  thermal decomposition

<u>d</u>	<u>Strength</u>
5.16	W
4.24	M
3.76	VW
3.39	VS
3.18	M
3.00	VS
2.70	VW
2.56	VW
2.52	W
2.36	VW
2.25	VS
2.15	W
2.07	W
2.01	W
1.86	W
1.70	W
1.64	W
1.60	W
1.55	W
1.52	W

D.  $\text{Ba}_2(\text{PO}_3)_4$   
from Warshauer  
method

<u>d</u>	<u>Strength</u>
5.20	W
4.25	H
3.76	VW
3.40	VS
3.18	M
2.99	VS
2.72	VW
2.58	VW
2.53	W
2.46	VW
2.25	VS
2.16	W
2.07	W
2.01	W
1.88	W
1.71	W
1.65	W
1.62	W
1.56	W
1.52	W

E. Soluble product  
of  $\text{Ba}(\text{PO}_3)_2$ -  
 $\text{Na}_2\text{SO}_4$  metathesis

<u>d</u>	<u>Strength</u>
4.82	W
4.60	W
3.85	S
3.77	M
3.51	W
3.20	M
3.03	M
2.92	M
2.80	VS
2.71	M
2.65	S
2.37	VW
2.31	VW
1.96	W
1.87	M
1.73	W
1.63	VW

F.  $\text{CsH}_2\text{PO}_4$

<u>d</u>	<u>Strength</u>
4.86	W
4.14	VW
3.68	VS
3.42	M
3.18	M
3.00	M
2.89	VW
2.60	M
2.58	W
2.42	M
2.32	S
2.17	W
2.04	W
1.94	M
1.88	W
1.81	VW
1.74	VW
1.68	VVW
1.61	W
1.57	VW
1.53	W
1.51	W
1.47	W
1.45	W
1.40	VW
1.35	VW
1.31	VW
1.27	VW
1.23	VW

G.  $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ 

<u>d</u>	<u>Strength</u>
5.67	W
4.46	W
4.06	M
3.93	W
3.47	VS
3.20	VS
2.95	S
2.79	W
2.61	M
2.49	VW
2.37	VW
2.29	VW
2.22	VW
2.13	VW
2.07	VW
2.03	W
1.97	W
1.85	W
1.81	VW
1.74	W
1.73	W
1.69	W
1.62	VW
1.55	VW
1.52	VW
1.49	W
1.45	W
1.40	W
1.36	W
1.31	W
1.28	VW
1.24	W

H.  $(\text{CsPO}_3)_n$ 

<u>d</u>	<u>Strength</u>
3.80	W
3.55	W
3.39	S
3.27	W
3.11	W
2.66	VW
2.55	M
2.44	VW
2.21	W
2.13	W
2.06	W
1.93	W
1.88	W
1.77	W
1.69	W
1.64	VW
1.54	VW
1.50	VW
1.42	VW
1.30	W
1.25	W
1.22	W

I.  $\text{Li}_3\text{PO}_4$ 

<u>d</u>	<u>Strength</u>
3.29	W
2.93	W
2.72	VVS
2.57	VS
2.32	S
2.03	VVS
1.95	S
1.83	VW
1.73	W
1.59	VW
1.57	W
1.52	M
1.43	W
1.37	W
1.33	S
1.27	S
1.24	VW
1.19	VW
1.16	M
1.14	W

J.  $\text{Li}_2\text{H}_2\text{P}_2\text{O}_7$ 

<u>d</u>	<u>Strength</u>
7.95	VW
5.96	W
5.53	W
4.87	M
4.50	S
4.18	VS
3.70	VS
3.44	VVS
3.22	M
3.03	M
2.71	M
2.54	S
2.38	W
2.32	VW
2.23	W
2.09	W
1.96	W
1.85	W
1.76	W
1.65	W
1.62	W
1.56	W
1.48	W
1.46	VW
1.38	W

K.  $(\text{LiPO}_3)_n$ 

<u>d</u>	<u>Strength</u>
5.47	M
4.66	VS
3.85	W
3.52	S
3.20	VVS
3.11	VW
2.93	VW
2.79	W
2.67	W
2.45	VW
2.33	W
2.25	M
2.17	M
2.07	W
2.01	W
1.92	W
1.87	W
1.80	VW
1.79	VW
1.70	VW
1.65	VVW
1.56	VVW
1.45	W
1.42	W
1.38	W
1.35	W
1.30	W
1.28	W
1.25	W
1.19	W

L.  $\text{Pb}(\text{H}_2\text{PO}_4)_2$ 

<u>d</u>	<u>Strength</u>
8.80	S
7.50	S
4.92	VW
4.38	VW
3.93	M
3.74	M
3.58	W
3.25	S
3.07	W
2.92	S
2.72	W
2.66	W
2.60	W
2.49	W
2.40	W
2.26	W
2.16	W
1.97	M
1.94	W
1.83	M
1.81	W

M.  $\text{PbH}_2\text{P}_2\text{O}_7$   
(presumed)d    Strength

6.95	W
5.40	M
4.87	M
4.00	M
3.67	S
3.50	W
3.32	W
3.20	W
3.16	S
2.91	M
2.77	S
2.42	W
2.37	W
2.28	W
2.24	W
2.20	M
2.14	W
2.07	VW
2.02	W
1.94	S
1.86	W
1.82	M
1.76	W
1.70	W

N.  $\text{Pb}_2\text{P}_2\text{O}_7$ d    Strength

4.43	W
4.03	VW
3.70	VW
3.42	M
3.32	M
3.14	S
3.07	M
2.92	VW
2.68	VW
2.45	W
2.34	VW
2.30	VW
2.20	M
2.12	W
2.03	W
1.93	W
1.90	W
1.81	VW
1.75	W
1.68	W

O.  $\text{Pb}_3\text{P}_4\text{O}_{13}$ d    Strength

7.50	VW
6.25	VW
5.75	VW
4.96	W
4.60	M
3.80	VW
3.68	M
3.50	S
3.30	W
3.20	VS
3.03	M
2.97	M
2.72	M
2.49	W
2.34	W
2.27	W
2.17	W
2.13	M
2.03	W
1.98	W
1.93	W
1.86	W
1.83	W
1.78	W
1.73	W
1.67	W
1.54	W
1.48	W

P.  $\text{Pb}_2(\text{PO}_3)_4$  from  
 $\text{Pb}(\text{H}_2\text{PO}_4)_2$  thermal  
 decomposition

d    Strength

7.20	M
5.83	S
4.34	M
3.89	VS
3.25	W
3.14	W
2.95	W
2.66	M
2.56	VW
2.44	M
2.39	W
2.16	W
2.09	W
2.02	VS
1.89	VW
1.83	VW
1.77	W
1.67	VW
1.63	W
1.58	W
1.53	VW
1.48	VW
1.46	W

Q.  $\text{Pb}_2(\text{PO}_3)_4$  from  
 Warschauer  
 method

d    Strength

7.20	M
5.83	S
4.36	M
3.90	VS
3.25	W
3.14	W
2.97	W
2.67	M
2.56	VW
2.44	M
2.40	W
2.17	W
2.09	W
2.02	VS
1.89	VW
1.85	VW
1.77	W
1.67	VW
1.63	W
1.58	W
1.53	VW
1.48	VW
1.45	W

R. Soluble  
 product of  
 $\text{Pb}(\text{PO}_3)_2$ -  
 $\text{Na}_2\text{S}$   
 metathesis

d    Strength

5.68	S
4.86	M
4.36	W
3.80	M
3.50	M
3.35	S
3.07	M
2.99	W
2.91	VS
2.72	M
2.30	W

## VI. Bibliography

1. L. T. Jones, Anal. Chem. 14, 536 (1942).
2. R. N. Bell, Anal. Chem. 19, 97 (1947).
3. I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Chemistry," Macmillan, New York, 1948, pp. 329, 699.
4. J. R. Van Wazer, J. Am. Chem. Soc. 72, 647 (1950).
5. A. Travers and Mlle. Perron, Ann. chim. 1, 146 (1934).
6. R. N. Bell, "Inorganic Syntheses," Vol. 3, McGraw-Hill, New York, 1950, p. 99.
7. H. Lux, Z. Elektrochem. 45, 303 (1939).
8. H. Flood, et al., Acta Chem. Scand. 1, 592, 781, 790 (1947);  
ibid 4, 364, 559 (1950).
9. F. Warschauer, Z. anorg. Chem. 36, 137 (1903).
10. R. N. Bell, L. F. Audrieth, and O. F. Hill, Ind. and Eng. Chem. 44, 568 (1952).
11. K. R. Andress, W. Gehring, and K. Fischer, Z. anorg. Chem. 261, 333 (1950).
12. K. R. Andress and K. Fischer, Z. anorg. u. allgem. Chem. 273, 193 (1953).
13. A. Bouille, Compt. rend. 206, 915 (1938).
14. A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc. A172, 399 (1942).
15. E. P. Partridge, V. Hicks, and G. W. Smith, J. Am. Chem. Soc. 63, 454 (1941).
16. R. K. Osterheld, Ph.D. Thesis, University of Illinois, 1950.