A STUDY OF PHOSPHITES

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The work described in this thesis is the original work of the author and has not been presented for any degree at this or any other University.

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Thanks are also due to Dr. Nancollas, Dr. Eglinton and Dr. Porte, and the staffs of their laboratories for polarographic, infra-red and nuclear magnetic resonance data, and the interpretation of the data.

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INDEX

(III), cont.,

(III), cont.,

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SUMMARY OF FINDINGS

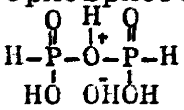
1) The pyrophosphite anion is greatly modified as compared to the pyrophosphate anion as regards its tendency to form metal complexes in solution; pyrophosphite is a relatively weak ligand, (p. 57-81).

2) The P-O-P bond in the pyrophosphite unit will not tolerate further attachment of P-O-P bonds as in the condensed phosphates, (c.f.p. 100-119).

3) The P-H bond in the phosphite ion undergoes two types of reaction leading to formation of higher oxy-acids of phosphorus, namely breakdown to gaseous phosphine, this occurs where there are P-OH groups attached to the phosphorus, or to gaseous hydrogen, where there are no P-OH groups present, in this latter case the formation of P-P bonds is favoured in the reaction product, (c.f. 112-119).

4) The kinetics of the oxidative breakdown of phosphorous acid have been elucidated in terms of a radical chain reaction, (c.f.p 107-112).

5) During the study of pyrolysis of metal phosphites numerous compounds have been prepared, simple and more complex salts of phosphorous acid which have not been described before. The properties of several salts which have been described in the literature have been more thoroughly investigated than heretofore.

6) Two types of hydrates of pyrophosphorous acid seem to be obtained best described as  $\mathrm{H{-}\underset{HO}{\overset{O}{\overset{\|}{P}}}{-}\overset{H}{\overset{|+}{O}}{-}\underset{\bar{O}H\;OH}{\overset{O}{\overset{\|}{P}}}{-}H}$ (c.f.p.87). and types based on the $P{-}O^-$ H_3O^+ structure, (c.f.p 85).

7) For the series of alkali metal hydrogen phosphites and the corresponding alkaline earth salts the ease of $\overset{3}{P}{-}O{-}\overset{3}{P}$ bond formation on heating is related in a simple way to the sizes of the cations, (c.f.p.91-99). Oxidative breakdown of the P-H bonds in these compounds and others are related to the same function of cations size, cross relationships between the ease of reaction and infra-red spectral data are also found particularly with the cases of P-H reactions, (c.f.96).

8) Sublimation of phosphorous acid has been investigated. The maximum amount of sublimation occurs when the pressure over the acid is such as to allow sublimation but retard the formation of pyrophosphorous acid, (c.f. p.100-106).

9) An unknown spot has been obtained on the acid chromatograms of products from the pyrolysis of phosphorous acid. It appears in advance of pyrophosphate in acid elutions, and probably corresponds to an unknown phosphorous oxy- anion, (c.f.p 183-191).

10) Pyrolysis of Rb_2HPO_3 leads to a product containing most of the original oxidation-reduction equivalent of the original product but no P-H bonds are detectable by infra-red spectroscopy (c.f.p.196-197).

INTRODUCTION

The following pages are devoted to the study of phosphites and related compounds. The work described was carried out in the Inorganic Department of Glasgow University under the supervision of Dr. D.S. Payne, as part of the requirements for the degree of Doctor of Philosophy of Glasgow University. Investigations were carried out from September 1959 to March 1962; preliminary work was done as part of the requirement for the degree of Bachelor of Science with Honours in Chemistry during January to March in 1959.

The work is presented in three main sections, the historical section, the complexing ability of pyrophosphite for a number of metal ions and the results and tabulation of thermogravimetric experiments on a variety of phosphites and related compounds. This last section comprises the bulk of the work presented. It is given in two sub-sections, the first being a general account of the experiments and the second being a more detailed experimental section.

This work is a continuation of the work of Dr.D.S.Payne on the lower oxy-acids of phosphorus, and much of the experimental data given here was obtained by repeating and extending the work of previous investigators of this school. In places the findings of these earlier workers have been radically reinterpreted, as regards the possible rationalisations of the observed facts.

Contemporary with this study the whole subject of the lower oxy-acids of phosphorus underwent a revival. The consequences of this are that some of the findings obtained by us have been duplicated by other groups of investigators; no serious differences are found between the results of other workers (notably Ebel and Hossenlopp on the question of the non-existence of polyphosphite units) and ourselves. Thus independent confirmation of our findings is available.

GENERAL INTRODUCTION.

GENERAL

The lower oxy-acids of Phosphorus

The study of this group of compounds comprises a separate discipline within phosphorus chemistry. The lower oxy-acids are those compounds of phosphorus with oxygen and hydrogen, the phosphorus being tetrahedrally co-ordinated by oxygen, hydrogen and phosphorus atoms. There are covalent P-O, P-H and P-P bonds present, the oxidation number of the phosphorus being less than five. All the known lower oxy-acids have the common structural feature HO-P=O, this hydroxyl group being dissociated in solution. The oxy-anion is the real structural unit. Other groups attached to the phosphorus are more weakly dissociated in solution.

The electronegativity of phosphorus is similar to that of hydrogen, the P-H bonds having relatively non-polar character when compared with N-H bonds and O-H bonds. Their properties are similar to C-H bonds. They tend to take part in reactions by homolytic bond breaking, and formation of radicals rather than by the formation of ions. The presence of P-H or P-P bonds in a phosphorus oxy-anion defines it as a lower oxy-anion. A major difference from the fully oxidised series, the phosphates, are the reactions which P-H and P-P bonds take part in. Products of pyrolysis of compounds with

P-H and P-P bonds present are, for example more complex than the pyrolysis products of corresponding phosphates.

The thermodynamic relationship between lower oxy-acids i.e. the relationship between different oxidation states of the phosphorus as regards available energy and the reactions of the lower oxy-acids, is as applicable to this branch of chemistry as it is to organic chemistry. This is due to the fact that there is a large activation energy barrier between different oxidation states.

Although these oxy-acids have been known for over a century and a half the constitution of even the simplest members have only been conclusively demonstrated in the last thirty years or so. Recently through the work of Bruno Blaser, who has greatly extended the number of known species, renewed interest is being shown in the properties of these compounds. It is considered that at present this subject is only just beginning as a separate field and in the coming years it will be greatly extended; there would seem to be no restriction on the numbers of different oxy-anions which can be foreseen.

Nomenclature.

In 1959 B. Blaser devised a system of nomenclature suitable for the written word based on the oxidation number concept, (I). Since the location of the numerals either below or above the symbol have different and quite specific meaning it is difficult to use in speech, but is a very convenient, clear and unambiguous form of representation for the written word.

The classical nomenclature was devised in its present form by Dulong in 1816, (2). Pelletier, prior to this had used the "ous", "ic" suffixes.

Dulong distinguished the four acids,

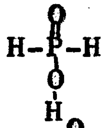
Phosphoric	Hypophosphoric)	Acids
Phosphorous	Hypophosphorous)	

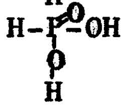
The nomenclature was later extended by the use of prefixes ortho, pyro and meta denoting different states of dehydration of the ortho or fully hydrated form. Thomas Graham, in 1833 was the first to use the meta prefix.

With increasing knowledge of molecular structure in modern times the nomenclature was adapted. Species previously classed under the general term "meta" were now distinguished into poly or chain anions and meta or ring anions. Further classification in terms of the number of phosphorus atoms present can be made, e.g. tripoly, trimeta and tetra meta etc. The prefix "ultra" is used to denote species dehydrated beyond the meta state, containing branched P-O-P chains.

The terms "isohypophosphoric acid" and "diphosphorous acid" based on an extension of the classical system of nomenclature were given to the earliest of the new group of lower oxy-acids. These are now referred to as $\overset{3}{P}-O-\overset{5}{P}$ and $\overset{4}{P}-\overset{2}{P}$ by Blaser.

Since the oxidation number of tetrahedrally bonded phosphorus uniquely defines the number of P-H bonds present, a skeleton structure only is required with the appropriate oxidation number indicated;

thus $\overset{I}{P}$ is 
$H-\overset{O}{\underset{OH}{P}}-H$

$\overset{3}{P}$ " 
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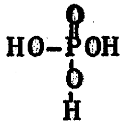
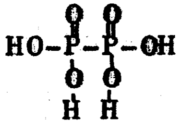
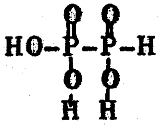
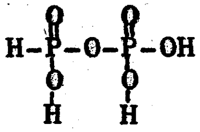
$\overset{5}{P}$ " 
$HO-\overset{O}{\underset{OH}{P}}OH$

$\overset{4}{P}-\overset{4}{P}$ " 
$HO-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-OH$

$\overset{4}{P}-\overset{2}{P}$ " 
$HO-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-H$

$\overset{3}{P}-O-\overset{5}{P}$ 
$H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-OH$

A number of suffixes fell out of use and have not been employed for about the last half century; thus "bi" and "sub" were originally used for acid phosphates "biphosphate of soda" was $Na_2H_2P_2O_7$. The term "sur phosphite" was used for acid phosphites which can be formulated as $M(I)H(HPO_3)_x(H_3PO_3)_y$.

(I) HISTORICAL INTRODUCTION

Progress in the field of the lower oxy-acids may be historically reviewed in two sections. The first deals with the early work. The outlook in chemistry generally was greatly altered by the advent of modern theories and techniques and the development of modern chemistry in this branch is taken from 1920. The period after Lavoisier up to 1920 may be considered as a "classical" period; during this time chemists developed the preparative methods still largely employed and discovered most "simple compounds" now known.

(I) a The early period

Soon after the discovery of phosphorus by Brandt, about 1674, (3), investigators began to study the easily obtained oxidation products. When phosphorus is oxidised in moist air mixtures of lower oxy-acids may be obtained. The Hon. Robert Boyle was the first to publish an account of the preparation of phosphorus. He carried out several experiments on the oxidation of phosphorus being particularly interested in the glow phenomena which can be observed under certain conditions. (At this time the name"phosphorus" was applied to a variety of substances which could be made to glow). Boyle observed the weight increase on oxidation of phosphorus, observed to be "at least three times" the initial weight. He obtained mixtures of lower oxy-acids by oxidation of his white phosphorus which on heating gave phosphine, and studied coloured products produced in oxidation experiments, (4).

Progress after this was slow until Lavoisier correctly interpreted the experiment on the oxidation of phosphorus. It became clear that the weight increase was due to combination with the oxygen of the atmosphere. This experiment was important in the overthrow of the Phlogiston Theory.

Pelletier, a contemporary of Lavoisier, devoted much attention to phosphorus chemistry. He was the first clearly to recognise two classes of phosphorus oxy-acids, which he demonstrated could be obtained from white phosphorus by different methods of oxidation. Using the oxidation method employed by Scheele, and also by Lavoisier, with nitric acid, phosphoric acid was obtained. The product from a process due to Sage, who oxidised white phosphorus with moist air, was found to be different, and named by Pelletier "phosphorous acid". In fact it contained a high proportion of hypophosphoric acid also, (5).

Another acid was prepared by Davy by the hydrolysis of phosphorus trichloride, (6). This was clearly distinguished from the then known acids by Dulong in 1816 and also distinguished from hypophosphorous acid which he was able to isolate from the hydrolysis products of barium phosphide, (2). He analysed a number of salts of hypophosphorous acid, and was able, by comparing his own results for the analyses of phosphorus oxy-acids and their salts, and studying the results of other workers, clearly to distinguish between phosphate, phosphite, hypophosphite and hypophosphate, (2). Although he established the nomenclature at present used, and probably appreciated the special position of the phosphorus hydrogen bond in phosphorous and hypophosphorous acid, chemical theory was not well enough developed at this time to allow true molecular understanding of the phenomena observed. The relationship between these different oxy-acids and salts as well as condensed phosphates began to be understood slowly. A large body of analytical data became available largely owing to the work of Berselius (7), Thompson (8), Gay Lussac and Rose. The work of Rose is important to our studies. He studied the products of pyrolysis of hypophosphites and phosphites. In general hydrogen was obtained on pyrolysis of normal phosphites while phosphine was observed with acid phosphites. A variety of coloured residues were obtained, (9). Rose helped to clarify the inter-relationship of different oxidation state phosphorus oxy-acids. Thus it was found that normal phosphites on oxidation by heating in air could give normal phosphates (i.e. neutral), while hypophosphites gave acid phosphates.

The similarity between the arsenates and the phosphates was demonstrated by the phenomenon of isomorphism. Thus Mitscherlich found that the salts $Na_2HPO_4 12H_2O$ and

$Na_2HAsO_4I2H_2O$; $NaH_2PO_4H_2O$ and $NaH_2AsO_4H_2O$ were isomorphic. This was an early example of the use of crystallography in the understanding of the molecular structure; some concrete reality was given to the atoms of Dalton by this type of phenomenon, (10).

In the early years of the nineteenth century a school of phosphorus chemistry grew up in Glasgow. Clark prepared pyrophosphates; he was the first to demonstrate the thermal P-O-P bond forming reaction. Graham also carried out investigations of a preparative and analytical nature. The interrelationship of the different oxy-acids of phosphorus had presented a theoretical problem since their discovery. Graham clarified the field of the phosphoric acids and salts; although he did not recognise the polymeric nature of many of the compounds which he prepared the existence of certain classes of phosphates and their stoicheometry became established. He was the first to prepare metaphosphates, (11).

Graham classified the phosphates in the following way,

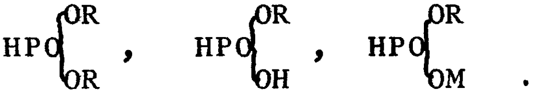
1st. class;	phosphoric acid subphosphate (of soda) biphosphate (of soda) phosphate (of soda)
2nd. class;	pyrophosphoric acid bipyrophosphate (of soda) pyrophosphate (of soda)
3rd. class;	metaphosphoric acid metaphosphate (of soda)

Perhaps the most important aspect of the work of Graham in this field was the recognition of the fact that condensed phosphates are related to each other and to ortho phosphates by loss of successive amounts of water from the ortho phosphate species.

It had been supposed by Berzelius that the different acids and salts of oxy-acids of phosphorus were derived from different phosphorus oxides. The then current theory of dualism in chemical compounds was modified by Graham's work. This early "electrovalency" conception of chemical interaction was due to the concepts of Berzelius. All compounds were thought of as being derived from two entities an electro + ve part and the electro - ve part. The latter was identified with the acid and the former with the base in salt formation; thus a salt was considered to be formed from an acid and a base where the acid was negatively charged and the base positively charged. The acid in turn was considered to be made up of a positive radical while the base was composed of a different type of positive radical, each combined with negative oxygen.

The lower oxy-acids of phosphorus had not fitted into the dualistic scheme; it is possible for this reason that there was a great deal of work carried out during the early nineteenth century, on these compounds. When interest in organic chemistry became dominant about the middle of the last century new theoretical approaches to chemical interaction were required. Thus with the advent of the substitution theory of Dumas and his contemporaries, which was the forerunner of the modern concept of covalency, progress was made in the understanding of the constitution of compounds with P-H bonds present.

A. Wurtz carried out a series of researches on the analyses and properties of hypophosphites and phosphites paying particular attention to the analysis for hydrogen not previously done, (12). He demonstrated the oxidation sequence Hypophosphite → phosphite → phosphate. This was correctly understood in terms of successive replacements of one half equivalent of oxygen by one equivalent of hydrogen. Wurtz prepared several normal, hydrogen and acid phosphites; mono and di esters of phosphorous acid and salts of the mono esters, e.g. he writes (1846),



$$HPO\left\{\begin{matrix}OR\\OR\end{matrix}\right. , \quad HPO\left\{\begin{matrix}OR\\OH\end{matrix}\right. , \quad HPO\left\{\begin{matrix}OR\\OM\end{matrix}\right. .$$

He also suggested that the PH_2 "radical" was present in hypophosphorous acid and suggested that oxidation of "PH_2", now known to be P_2H_4 should yield some hypophosphite. A table was drawn up of the then known oxy-acids of phosphorus excluding hypophosphoric acid ((12)b, p. 230), clearly demonstrating the interrelationship of the lower oxy-acids and phosphoric acids in almost modern terms, apart from the ignorance of molecular size; it is interesting to note that the then unknown pyrophosphorous acid was included. This was to be prepared some fifty years later, by Auger.

Salzer was the first to undertake a really systematic investigation on the hypophosphates. The acid and its salts were obtained in a pure form by treatment of the crude oxidation product of phosphorus obtained by Pelletier. Numerous salts were studied from the analytical and pyrolysis product point of view. Salzer seems to have favoured the correct P-P structure on chemical grounds, (13). However the subject of the constitution of the hypophosphate unit was not left to lie, numerous investigators pursued the question after Salzer. Amongst the classical workers were Philipp, Sanger, Joly, Drawe, Palme, Bansa and Rosenheim, (14-20).

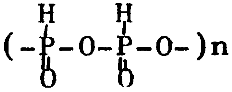
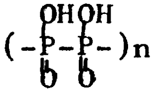
Amat, a disciple of Joly, investigated pyrophosphites towards the end of the nineteenth century. Although the pyrophosphite unit had been obtained earlier in the rearrangement products of hypophosphoric acid, (Joly considered that this was the case) Amat was the first to obtain pyrophosphites and study them in a systematic way. A series of hydrogen phosphites were prepared and the pyrophosphite obtained by heating in vacuum. Difficulties were encountered in the preparation of some alkaline earth pyrophosphites and the ammonium salt. He studied the hydrolysis of pyrophosphite noting the catalytic effect of acid, (21-24).

Amat had attempted to obtain the pyrophosphorous acid by action of sulphuric acid on the barium salt of pyrophosphorous acid, but had not succeeded owing to the ready hydrolysis of the P-O-P bond in this anion. Soon after this Auger obtained pure pyrophosphorous acid by the reaction of phosphorus trichloride and phosphorous acid under controlled conditions, $PCl_3 + 5H_3PO_3 \rightarrow 3\,H_4P_2O_5 + 3HCl$, (25). Previous work by Geuter (25a) on the reaction of all the known oxy-acids and halides and oxy-halides of phosphorus had failed to identify pyrophosphorous acid in the reaction product of phosphorus trichloride and phosphorous acid, however this older work probably led to the successful preparation of the pyrophosphorous acid by Auger.

Rammelsberg in 1867 and after had made important contributions to the study of phosphites and hypophosphites. He prepared a large number of salts and investigated their pyrolysis reactions. Much of the earlier work of Rose and Wurtz was repeated and reinterpreted in more modern terms. In general it was found that hydrogen, phosphine and water are evolved on heating above a certain temperature and polyphosphates are left in the residue.

It was noted that the products from the transition metal salts were usually more complex, the formation of hydrides and phosphides, as well as "red phosphorus", was noted, (26). Indeed the whole question of pyrolysis products could only be dealt with in the most general terms, the nature of polymeric material still not being recognised. Classical chemistry only succeeded in classifying small units like phosphate, phosphite, hypophosphite and hypophosphate. Metaphosphates and "meta phosphites" were thought of in similar terms.

Towards the end of the nineteenth century interchange of ideas between physics and chemistry occurred. Physical aspects of chemistry began to be studied. Kinetic experiments were carried out. The variation in reaction rate with temperature and the study of thermochemistry generally, led to the formulation of classical chemistry thermodynamics. The ionic theory, initially based on the concept of dissociation in solution was due to Arrhenius. He carried out the first measurements on the ionisation of P-OH groups, (27).

Oxidation of phosphine produces mixtures of phosphorus oxy-acids. Early kinetic measurements in this field established the pressure limits of the fast reaction. Continuing the work of Van't Hoff, Van de Stadt obtained a feathery product which was considered (on the basis of pressure measurements) to be HPO_2, metaphosphorous acid. Red products were usually obtained in these experiments and the initially produced colourless material seemed to decompose giving these. We have repeated this early work and confirmed these observations. Although the subject will not be discussed at length in this thesis the related observation on the formation of red material from the dehydration of phosphorous acid will be dealt with. Rearrangement of  $(-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-)n$ to form  $(-\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{OH}{|}}{P}}-)n$ appears to be a reasonable rationalisation of many of the facts, migration of the oxygen atoms from the P-O-P chain to the side groups is envisaged.

Mention of the early kinetic work on the hydrolysis of P-O-P bonds is appropriate here. Amat studied pyrophosphite hydrolysis in 1891 (21), and Abott was the first to investigate pyrophosphate hydrolysis, (1907), (29).

Oxidation of lower oxy-acids has continued to arouse interest ever since the work of Steele, (30), (1907), and the investigations of Sieverts who studied interesting reactions of the hypophosphite unit giving hydrogen in solutions containing various catalysts, (31).

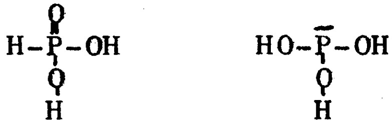
Also contemporaneous with this kinetic interest in chemistry was the development of improved methods of analysis; there is perhaps a link up between the two fields in that rapid analytic methods were required for kinetic work. Volumetric methods of analysis were applied to the oxidation of the P-H bond, the use of iodine and permanganate solutions for this purpose was first investigated at the beginning of the present century. Thus Rupp and Fink developed the iodometric technique in 1902, (32), (c.f. $KMnO_4$ oxidation (33) and the older Hg (II) method, (34)).

Werner applied his co-ordination theory to phosphorus oxy-acid chemistry, (35). He recognised the position of the hydrogen bonded directly to the phosphorus in the hypophosphites and the phosphites, and is generally considered to have been the originator of the correct formulation of these compounds.

(I) b The Modern Period

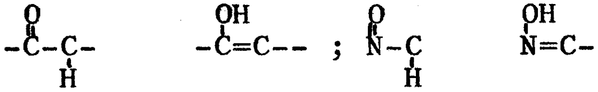
As indicated previously the modern period may be distinguished by the advent of the electronic theory of valency, (c 1920) by Kossel, Lewis, Langmuir and Sidgwick, (36).

From time to time the question of the basicity of phosphorous acid has attracted attention. There are several references in the literature to the preparation of salts of tribasic phosphorous acid viz. $M(I)_3PO_3$, c.f. (37); some of these references being of quite recent date. The electronic theory and the structural chemistry which derived from it allowed fresh speculation on this point. Two forms of phosphorous acid.



$$H-\overset{O}{\underset{\underset{H}{O}}{P}}-OH \qquad HO-\underset{\underset{H}{O}}{\bar{P}}-OH$$

seemed possible. Tautomerism, such as had been found in the systems

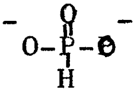


$$-\overset{O}{C}-\underset{H}{C}- \qquad -\overset{OH}{C}=C-- \ ; \ \overset{O}{N}-\underset{H}{C} \qquad \overset{OH}{N}=C-$$

appeared to be possible between the two forms of phosphorous acid shown. The analogy is not now considered to be exact since the hybridisation of the orbitals of phosphorus changes between the forms shown above, (41), p.347.

The slow rate of oxidation of phosphorous and hypophosphorous acids and anions has presented a problem. Numerous kinetic studies on the oxidation of P-H bonds have been undertaken, particularly in the years from 1920-1940. There was a tendency to regard different oxidation states of elements in oxy-anions as being in reversible equilibrium with each other; many oxidation reduction reactions could be rationalised solely on the basis of the difference in energy between the oxidised and reduced forms, reactions of the oxy-anions of sulphur, nitrogen, manganese and chromium being a case in point. The "problem" of the stability of phosphite only arises however if kinetic effects are ignored.

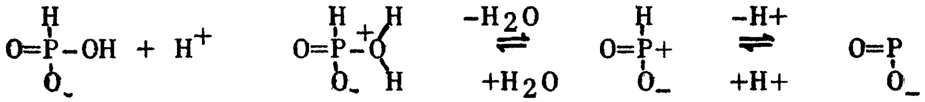
Mitchell, (38) and later Griffith and McKeown extended the results of the earlier workers. The oxidation of the hypophosphite anion was particularly well investigated,(39). The results were interpreted as indicating the presence of a tri-coordinate form of phosphorous and hypophosphorous acid. Agreement was found between the results of the kinetic experiments and deuterium and later, tritium exchange experiments. Good summaries of the work are available in textbooks on phosphorus chemistry, (40), and (41). The most recent work is that of tritium exchange on the hypophosphite unit, (42).

Only with the most sensitive methods can evidence for isotope exchange be obtained. The earliest work in this field suggested that no exchange was occurring but the reaction is now known to proceed with measurable velocity in all ionic and acidic forms of the hypophosphite and phosphite units except with the  $^{-}\mathrm{O}-\underset{\mathrm{H}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}}-\mathrm{O}^{-}$ anion. Exchange of the acidic hydrogens of the P-OH groups has been the subject of a number of investigations; it takes place relatively rapidly. Labelled oxygen exchange has also been studied; it proceeds at a slow rate. No proof for the exchange of ^{32}P between labelled and unlabelled anions has been found, (43)-(49).

In the field of the dialkyl phosphonates, recently reviewed, there is a similar position as regards the existence of tautomeric forms to that presently prevailing in the lower oxy-acid field. With the dialkyl phosphonates there is kinetic evidence for the existence of a tri-coordinate form. (50).

It is of some interest at this point to discuss the exchange of hydrogen bonded to phosphorus which has been observed as discussed above. The rate of P-OH oxygen exchange and that of P-H hydrogen exchange display some common features; both reactions are relatively slow when compared with the rate of exchange of the P-OH hydrogens; both reactions also display a variation in rate between the different species which have been studied, in particular between the exchange when salts are studied and when the acid is used. Exchange is found to occur relatively rapidly for the acid form and progressively slower as the number of phosphorus hydroxy groups becomes less; thus the HPO_3^{2-} anion has not been shown to exchange the

P-H hydrogen with water. Van Wazer has rationalised this state of affairs by suggesting that hydrogen bonding between the P-OH and water leads to a more rapid exchange when the exchange of the oxygen atoms from this group is considered. It seems that there need not be tautomerism occurring in this system to explain the exchange of P-H bonded hydrogens with water. Perhaps rationalisation of the difference in exchange rates with different anions suggests that the presence of a P-OH is necessary for the exchange of P-H hydrogens. Thus the following scheme:-



$$O{=}\underset{O^-}{\overset{H}{P}}{-}OH + H^+ \qquad O{=}\underset{O^-}{\overset{H}{P}}{-}\overset{+}{O}H_2 \quad \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} \quad O{=}\underset{O^-}{\overset{H}{P}}{+} \quad \underset{+H+}{\overset{-H+}{\rightleftharpoons}} \quad O{=}\underset{O^-}{P}$$

can be written for the $H_2PO_3^-$ ion. It must be admitted that hypophosphites are considered the equilibria involved may be quite different.

It is interesting to note that Mitchell studied the oxidation of phosphorous acid samples, obtained from the hydrolysis of phosphorus trichloride, and found that the rate of oxidation of freshly hydrolysed samples of the trichloride was different from that of solutions of phosphorous acid. This led to the postulate that there was some $P(OH)_3$ present in solutions of freshly hydrolysed phosphorus trichloride; it was to be expected that replacement of the halogen by OH groups would lead to $P(OH)_3$ which would rearrange to the normal P-H form of phosphorous acid. Since the rate of oxidation of solutions postulated as containing this tri-coordinate phosphorus species was greater than that of ordinary phosphorous acid, these results seemed to confirm that the oxidation of phosphorous acid in general proceeded through the intermediate equilibrium involving this "active form", i.e. tautomerism occurred, (51). Kolitowska came to similar conclusions calling the active form of H_3PO_3 α phosphorous acid, (52). However the solutions discussed above are now known to contain other oxy-acids of phosphorus, the existence of which was previously unsuspected. Blaser, in some of his earlier work demonstrated the presence of species like $\overset{3}{P}-O-\overset{5}{P}$ and $\overset{4}{P}-\overset{2}{P}$ in these hydrolysis products of phosphorus trihalides, and this appears to be an adequate explanation of the results of Mitchell.

The advent of direct physical methods of structure analysis is very important in that direct verification of chemically postulated structures leaves no doubt as to the constitution of the lower oxy-anions. With increasing accuracy of physical methods it became possible to investigate complicated structures in the field of the lower oxy-acids; the great increase in the number of known species in this field in the last few years demonstrates the effect of new techniques on the subject, the verification of the structure of Blaser's $(-\overset{3}{P}-)_6$ ring acid by the use of X-ray structural analysis methods is a striking example of the importance of physical methods, (53). Confirmation of the structure of other species prepared by the Blaser school by N.M.R., (Van Wazer), (54) and by Raman spectra (Baudler), (55) further shows the fundamental importance of the newer techniques.

The first results in this field using physical techniques were not unambiguous however; although early X-ray work suggested the correct structure for phosphites and hypophosphites (56), the first spectral investigations suggested that the tri-coordinate forms were present, (57).

Phosphine was the first substance to be studied by spectral methods, where there is a P-H bond present, (58); the assignment of the frequency range of the $P-^{H}$ vibration allowed further workers to correctly interpret the spectra of phosphites and hypophosphites. Thus Ananthakrishnan in 1936 showed that the P-H bond was present in phosphorous acid and disodium phosphite, and Simon and Feher in 1937 demonstrated the presence of the $P-^{H}$ bond in hypophosphites, (59) and (60). These latter workers also studied the Raman spectra of phosphorous and phosphoric acids giving an interesting review of earlier literature on the subject of the constitution of these oxy-acids.

Further workers in the field of Raman spectra of the lower oxy-acids demonstrated that the three P-O groups of the phosphite anion were spectroscopically equivalent. Later infra-red work however showed that the symmetries of phosphite units was lower than this; one of the phosphorus oxygen bonds was best represented as P=O, (61) and (62).

Baudler, previously mentioned, has carried out much important work in the field of phosphorus Raman spectra. Numerous different kinds of phosphorus compounds have been investigated; the symmetries of compounds with P-O-P; P=O, P-OH, $P-O^-$, P-R, P-OR and P-H bonds present have been studied. Impure P_2H_4 was found to show characteristics suggesting the presence of condensed P-^{H} units, named by Baudler "phosphanes", (63), c.f. (41) p. 215-9.

Outside of the field of Raman spectra Baudler also suggested that the $\overset{2}{P}-\overset{2}{P}$ oxy-acid was present in the hydrolysis products of P_2I_4, (64).

Pyrophosphorous acid prepared by the method of Auger was shown to have the P-O-P structure. An interesting point, from the solid state Raman spectrum, was the absence of the expected P-O-H hydroxyl frequency. Presumably the acid is present in the ionised form in the solid state, (63a).

When molecules are considered which contain more than two phosphorus atoms, the absolute interpretation of the spectra, in the Raman and infra red region, becomes too complicated. However the characteristics absorption of stretching vibrations, and other simple deformations of bonds, may be used to diagnose such bonds. P=O, P-OH, PO-H, P-H, $P-O^-$, P-O-P, for example may be assigned stretching and deformation frequencies. The regions of absorption of the units remain relatively unaltered from compound to compound. Changes occur in the bond absorptions, of a different order of magnitude from the changes found from one bond to the next. The position of the absorption is directly related to the bond strength, and the intensity to the polar nature of the bond. So comparison of a number of compounds containing the same bond, by means of their spectra enables subtle differences to be detected, e.g. P-H bond frequencies (stretching), were found by Baudler to vary from compound to compound. In this case the non-polar nature of the P-H bond precludes the usual type of polar differences, such as is found with P=O bonds, accounting for these observed differences. An increase in frequency of the P-H bond from the salt to the acid is found for phosphorous acid, pyrophosphorous acid, and hypophosphorous acid, (63). The P-H stretching shows no hydrogen-bonding effects, (65), and is double, (66). The cause of this doubling is really not known with certainty at the present time although it is possibly due to there being two environments of the P-H bond in such cases where the doubling is found to occur. Examination for Fermi resonance has been carried out; no explanation on this basis is possible, (66).

The spectral techniques provide a means of identifying types of units present although P-P bonding cannot be identified by infra-red spectra on account of the non-polar nature of the P-P bond; however it may be distinguished by Raman spectroscopy, at least in theory, (67).

Apart from the diagnostic value of spectral methods when dealing with unknown compounds, since each chemical compound gives an individual spectrum, a chemical "fingerprint"; spectra may be used as a criterion of purity. X-ray diffraction patterns as obtained with powder photographs are also similar in this respect.

Tabulations of infra-red spectra of phosphorus compounds have been carried out by Daasch and Smith, (68), the U.S. Navy, (69) and by Corbridge, (70). The first two are of organo-phosphorus compounds and the latter for inorganic compounds. At the time of writing the amount of published spectral data in this field is increasing enormously.

Perhaps preparative chemistry after c.1920, in the lower oxy-acid field has not been studied as much as in the years preceding this. In the last few years however the subject has been greatly extended by the work mainly of the Blaser school. In the period 1920-1950 some gaps in the classical preparative work have been removed however. Thus Kiehl and Moose succeeded in preparing ammonium pyrophosphite which Amat had failed to obtain and the previously uninvestigated thallous pyrophosphite was prepared, (71) and (72). Rosenheim prepared a number of phosphites and hypophosphites measuring solubilities, $Li_2HPO_3H_2O$ was found to have a negative temperature coefficient of solubility, (73). He also prepared some uranium salts and molybdenum heteropolyacids based on phosphite, as well as numerous complex phosphites and hypophosphites, (74). A review of the classical and early modern work is given by Mellor, (75). There is however no comprehensive list of salts of the lower oxy-acids available for compounds prepared after Mellor's treatise was published (1928).

In the modern period the following salts have been prepared:- Cs and Rb hypophosphites, (76); Tl (I) hypophosphite, (77), phosphite, (72); recent work on the alkali metal phosphites, (78), alkaline earth phosphites, (79) and Tl (I) phosphites, (80) as well as Cr (II) and Cr (III) phosphites,(81) and ammonium phosphites, (82), has been carried out by Ebert. Pb phosphite, (83); UO_2^{2+} phosphites, (84), complex phosphites of U(IV), (84); complex phosphites of Nd(III) and Pr(III), (85), have been studied. Studies on the lanthanide and uranium salts also covered the appropriate hypophosphites and often the hypophosphates also. Part of the object of the earlier studies particularly by Rosenheim et al. was to investigate the constitution of the lower oxy-anions. In general more hypophosphites have been prepared than phosphites. The following salts have been prepared in the modern period, Bi(III) and BiO^+ hypophosphites, (86), and hypophosphites of Ti(IV), Sn(II), Ge(IV), Tl(I), In(III), Ga(III) and Al^{3+}, (41) p. 357. More recent studies have indicated the preparation of the hypophosphites of Sc, Zr, Hf, Th, Ta and Ge, (87), (88).

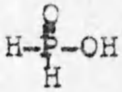
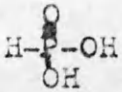
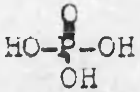
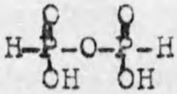
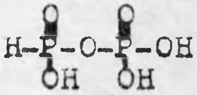
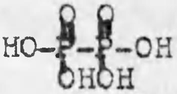
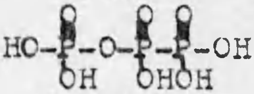
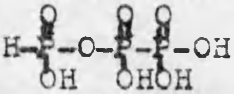
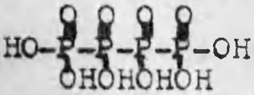
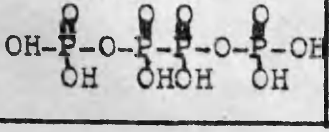
The preparative work of Kiehl and Moose had been briefly mentioned above; however these workers followed up their studies on the preparation of ammonium pyrophosphite by carrying out kinetic measurements on the hydrolysis of the $\overset{3}{P}-O-\overset{3}{P}$ bond and studying the oxidation of the pyrophosphite anion by iodine, (neutral pH). The rate of hydrolysis of the $\overset{3}{P}-O-\overset{3}{P}$ bond was markedly dependent on the pH, being at a minimum at neutral pH. There appears to be a number of discrepancies in their work however; nevertheless this work is important since it is the only investigation of the hydrolysis of the $\overset{3}{P}-O-\overset{3}{P}$ bond, apart from the original work of Amat, which appears in the literature, (89). This should be contrasted with the numerous investigations which have been undertaken to investigate the hydrolysis of the $\overset{5}{P}-O-\overset{5}{P}$ bond, c.f. (41) p. 452--459.

The lack of reaction of the $\overset{3}{P}-O-\overset{3}{P}$ bond with halogens is important also; recent investigations by Blaser have shown that in general where one or more phosphorus atom in the P-O-P unit have an oxidation number less than five, oxidation by halogen at neutral pH will not take place. This approach is used in the chemical approach to the elucidation of the constitution of unknown oxy-anions.

Of the salts of the lower oxy-acids which were relatively well known many properties have been investigated and sometimes correlations between pyrolysis reactions have been possible. An example of this is the study of Ba^{2+} phosphite and Ba^{2+} hydrogen phosphite by Simon and Schulze, (90).

Perhaps the X-ray structural work which has been done in this field merits special attention. $MgHPO_36H_2O$ has been studied, (94); H_3PO_3 (95); $Cs(PO_2)_6$, (53); $(NH_4)_2H_2P_2O_6$, hypophosphate, symmetry correlations only, (92), and Ti_2HPO_3, preliminary data only, (93). Perhaps the most interesting of these crystal structures is that of phosphorous acid. The short "P-O" bond is I.47A, this is to be compared to the value of I.57A found for the similar bond in phosphoric acid the crystal structure of this compound also being known. Replacement of the P-OH in this latter compound by P-H in phosphorous acid produces a shortening of the P-O bond lengths. This is likely to be due to an increased amount of π bonding character with the phosphorous acid. In phosphorous acid the hydrogen bonding arrangement is as would be expected, the P-H hydrogen does not take part, the P-O bond forms two hydrogen bonds while the remaining two oxygen atoms only form one. Numerous X-ray studies of phosphates and condensed phosphates as well as organo-phosphorus compounds have been published.

By 1940 the polymeric nature of the condensed phosphates was appreciated, (96), the biological importance of the condensed phosphates prompted a number of interchanges between biochemical organic chemistry and inorganic chemistry. Techniques used with carbonhydrates and other organic polymers

			Rf acid	Rf basic
 $\mathrm{H{-}\underset{H}{\overset{O}{P}}{-}OH}$	Hypophosphorous	$\overset{1}{\mathrm{P}}$	0.84	0.75
 $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}OH}$	Phosphorous	$\overset{3}{\mathrm{P}}$	0.86	0.49
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}OH}$	Phosphoric	$\overset{5}{\mathrm{P}}$	0.82	0.39
 $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}H}$	Pyrophosphorous	$\overset{3}{\mathrm{P}}\mathrm{-O-}\overset{3}{\mathrm{P}}$	0.86	0.66
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH}$	Pyrophosphoric	$\overset{5}{\mathrm{P}}\mathrm{-O-}\overset{5}{\mathrm{P}}$	0.61	0.29
 $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH}$	Isohypophosphoric	$\overset{3}{\mathrm{P}}\mathrm{-O-}\overset{5}{\mathrm{P}}$	decomp.	0.49
 $\mathrm{(HO{-}\underset{H}{\overset{O}{P}}{-}\underset{H}{\overset{O}{P}}{-}OH}$		$\overset{3}{\mathrm{P}}\mathrm{-}\overset{3}{\mathrm{P}}$	decomp.	decomp.
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{H}{\overset{O}{P}}{-}OH}$	Diphosphorous	$\overset{4}{\mathrm{P}}\mathrm{-}\overset{2}{\mathrm{P}}$	-	-
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$	Hypophosphoric	$\overset{4}{\mathrm{P}}\mathrm{-}\overset{4}{\mathrm{P}}$	0.48	0.21
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$		$\overset{5}{\mathrm{P}}\mathrm{-O-}\overset{4}{\mathrm{P}}\mathrm{-}\overset{4}{\mathrm{P}}$	0.3	-
 $\mathrm{H{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$		$\overset{3}{\mathrm{P}}\mathrm{-O-}\overset{4}{\mathrm{P}}\mathrm{-}\overset{4}{\mathrm{P}}$	decomp.	0.3
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$		$\overset{4}{\mathrm{P}}\mathrm{-}\overset{3}{\mathrm{P}}\mathrm{-}\overset{4}{\mathrm{P}}$	0.2	-
 $\mathrm{HO{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}OH}$		$\overset{4}{\mathrm{P}}\mathrm{-}\overset{3}{\mathrm{P}}\mathrm{-}\overset{3}{\mathrm{P}}\mathrm{-}\overset{4}{\mathrm{P}}$	0.2	-
 $\mathrm{OH{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}\underset{OH}{\overset{O}{P}}{-}O{-}\underset{OH}{\overset{O}{P}}{-}OH}$		$\overset{5}{\mathrm{P}}\mathrm{-O-}\overset{4}{\mathrm{P}}\mathrm{-}\overset{4}{\mathrm{P}}\mathrm{-O-}\overset{5}{\mathrm{P}}$	0.4	0.2

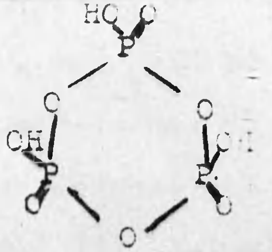
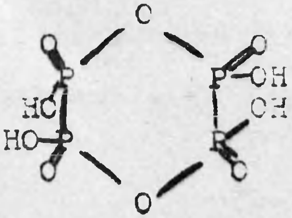
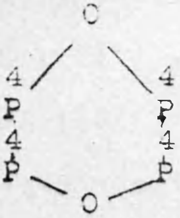
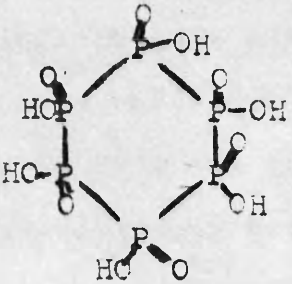
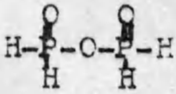
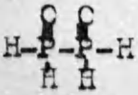
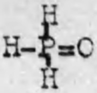
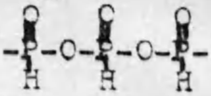
were applied successfully to the inorganic field. Thus for condensed phosphates, ultracentrifugation, dialysis and diffusion, end group titrations, viscosity, anistropy of flowing solutions and conductivity, light scattering and chromatography, both ion exchange and on filter paper, were applied. The chromatographic techniques are of especial importance. Hanes and Isherwood developed the method for phosphate esters, (97), Ebel and also Westman applied it to purely inorganic species of phosphorus oxy-anion; the work of Ebel and co-workers is particularly important, (98-100). Others who developed the techniques are Thilo and Karl-Kroupa, (101) and (102).

The products of pyrolysis of phosphites have been studied by this method, by Ebel, Japanese and Polish workers (103-105). However all these investigators only studied the phenomena in the most general terms, and without reference to the work of Blaser. The newly discovered lower oxy-acids are difficult to distinguish from the longer established species by chromatography alone.

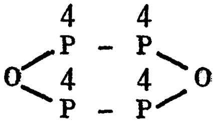
The work of Blaser may now be dealt with. This is found in two places in the literature, in the literature of both the 1930 period and that of the present day, the modern work of the 1950s being to a large extent a continuation of the older work. The earlier work deals with the polymeric lower oxides of phosphorus (106), the constitution of hypophosphate, and its oxidation and hydrolysis (107), (ambiguous results were obtained as to the constitution of the hypophosphate unit), and the oxidation of P-H bonds by HNO_3 etc., (108). The hydrolysis of phosphorus trichloride was studied, (109). Mention should also be made here of other workers in this period. Thus, Kolitowska, (110-111); Nylen, (112); Ipatiev, (113); Hantzsch, (114); Schwarzenbach, (115); Osipov, (116); Jung, (117); Raistrick, (118), carried out work in the lower oxy-acid field.

Blaser's modern work deals with the general field of the lower oxy-acids, outlined on page 1. Opposite pages 31 and 32 are tables of the oxy-acids known at the time of writing; the chromatographic Rf values, collected from the literature have been added. All the species which have no classical names are due to the work of the Blaser school, except the $\overset{2}{P}-\overset{2}{P}$ acid which, as has been mentioned was considered to be obtained by Baudler when hydrolysis of P_2I_4 proceeds. Other workers played a part in the discovery of the $\overset{3}{P}-O-\overset{3}{P}$ and $\overset{4}{P}-\overset{2}{P}$ acids, however the chemistry of these units has largely been developed by Blaser, (119-128); a note is given of the subjects studied in the list of references.

The methods by which these compounds were obtained are interesting. The simple two phosphorus units are found in the

			Rf acid	Rf
	Trimetaphosphoric	$-(\overset{5}{P}-O)_3$ ring	0.29	0.5
				
		$-(\overset{3}{P}-)_6$ ring	(0.00)	(0.0
	HYPOTHETICAL STRUCTURES (unstable)			
 $H-\underset{H}{\overset{O}{P}}-O-\underset{H}{\overset{O}{P}}-H$		$\overset{1}{P}-O-\overset{1}{P}$		
 $H-\underset{H}{\overset{O}{P}}-\underset{H}{\overset{O}{P}}-H$		$\overset{0}{P}-\overset{0}{P}$		
 $H-\underset{H}{\overset{H}{P}}=O$		$-(\overset{3}{P}-O)_n$		
 $-\underset{H}{\overset{O}{P}}-O-\underset{H}{\overset{O}{P}}-O-\underset{H}{\overset{O}{P}}-$				

hydrolysis products of phosphorus halides, the $\overset{2}{P}-\overset{2}{P}$ species being the most recently found. The $(-\overset{3}{P}-)_6$ species is obtained in the oxidative breakdown of red phosphorus. The other P-P-P-P forms are derived from this by degradation, (by action of alkali and also on reaction with iodine in bicarbonate buffer). Bromometric degradation of the $(-\overset{3}{P}-)_6$ unit leads to the formation of P-O-P bonds, oxygen being "inserted between" phosphorus atoms in the P-P-P-P chains, leading to the P-O-P-P-P type of unit. After this, studies were made to synthesise P-O-P-P units by means of the reaction step P-OH + P-OH → P-O-P, chemical reagents being used here e.g. carboxylic acid anhydrides (c.f. Thilo (129)), the six membered ring species

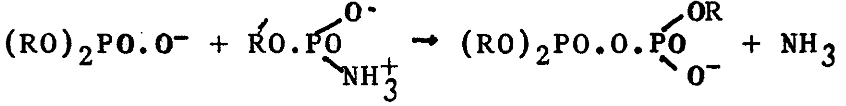


being so obtained. Degradation of this by breaking one P-O-P bond gives a chain species. The chemical synthetic route may be extended to the preparation of $\overset{3}{P}-O-\overset{4}{P}-\overset{n}{P}$ types of compounds. This constitutes the first use of synthetic route in this branch of chemistry. It is expected that in the future synthetic methods will be extended in their scope, inorganic phosphorus chemistry developing in a similar way to that found for organic chemistry after c. 1840.

The position of the synthetic steps which have been used in other, related branches of phosphorus chemistry can be fruitfully discussed in this context. Todd and co-workers at Cambridge, have succeeded in carrying out syntheses of C-O-P-O-P and C-O-P-O-P-O-P types of structures where these are present on sugar groupings in the nucleic acid field, (130). Several methods have been employed to affect a P-O-P bond, viz.

$$(RO)_2PO.O^- + (R'O)_2POCl \rightarrow (RO)_2PO.O.PO(OR')_2 + Cl^-$$

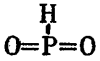
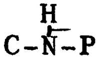
$$2\ (RO)_2PO.O^- + (R'O)_2PO.O.PO(OR')_2 \rightarrow (RO)_2PO.O.PO(OR')_2 + 2\ (RO)_2PO.O^-$$

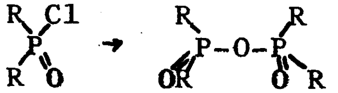


$$(RO)_2PO.O^- + R'O.PO\genfrac{}{}{0pt}{}{O^-}{NH_3^+} \rightarrow (RO)_2PO.O.PO\genfrac{}{}{0pt}{}{OR'}{O^-} + NH_3$$

It has been postulated that the intermediate formation of the metaphosphate monomer $RO.PO_2$ occurs in the latter case, the heterolysis of the P-N bond preceding the formation of the P-O-P bond. A similar postulate of the intermediate formation of the monomeric metaphosphate unit is used to explain oxidative phosphorylation reactions which quinol mono phosphate will undergo.

The use of carbodi-imides and keten imides as reagents for the formation of P-O-P bonds has been developed. Where two different phosphate esters are used, random mixtures of all the P-O-P types of compounds are formed. (131).

In nature phosphorylation is considered to proceed through quniol phosphate types and studies of "oxidative phosphorylation" as a synthetic route for P-O-P bonds have been made. Nucleoside phosphites are required for syntheses of these quinol phosphate esters. These are prepared from the reaction of phosphorous acid and the appropriate nucleoside with stoicheometric proportions of di-p-tolycarbodiimide, (133). The intermediate formation of the "meta phosphite" monomer  $O{=}\overset{H}{P}{=}O$ is considered to take place. Other biological intermediates which donate phosphate groups to other phosphate esters of the adenosine mono and di phosphate types, like quinol phosphates have a labile C-O-P bridge. There is some analogy here to labile types of P-O-P bonds, such as is found in the pyrophosphite anion. The C atom of this C-O-P bridge has =O or $=CH_2$ attached to it. Similarly  $C{-}\overset{H}{N}{-}P$ bonds are found naturally, the $HN{=}C{-}NH{-}P{=}O(OH)_2$ grouping being labile, (134).

Other reagents for the formation of P-O-P bonds are $(CN)_2$, (135), $SOCl_2$, (136), paraformaldehyde (this has been used to make labile P-O-P bonds in compounds of the type ), (137), and carboxylic acid anhydrides, (129).

Elimination of water between two P-OH bonds has been long known to lead to P-O-P bonds. Thilo, (138) and Van Wazer, (139) have extensively studied the chemistry of the polyphosphates. The former worker carried out a series of researches on the pyrolysis of various phosphates; it was found that the thermal reaction and its products depended on the size of the cation of the particular salt which was studied. Paper chromatography is an important tool in these studies. Transformations of polyphosphates into trimetaphosphate have also been studied by Thilo.

When a number of salts of phosphoric acid are compared as to the velocity of the P-O-P forming reaction, it is found that this depends on the cation, in a purely dimensional way. Studies on the dehydration of a series of alkali metal phosphates of the general formula MH_2PO_4 showed that the salts with the smaller cations dehydrated at lower temperatures on heating, it being suggested that polarisation of oxygen by smaller cations weakens the O-H bonds and O-P bonds, (140). A more recent study of P-O-P bond formation in the same series of salts, using a chemical reagent, acetic anhydride, to form the P-O-P bonds shows that no dependence on the cation occurs in this case, (141).

A linear relationship between the temperature at which $\overset{3}{P}$-O-$\overset{3}{P}$ bonds can be observed to be formed and the volume of the cation may be valid, c.f. (142).

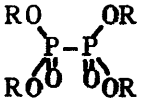
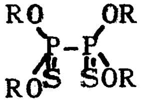
P-O-P bonds may also arise by the thermal or oxidative breakdown of P-H and P-P bonds, c.f. (121).

Synthetic methods for the formation of P-P bonds are less well known than are the ways of making P-O-P bonds. By analogy with the methods available for the formation of C-C bonds, the use of Grignard type reactions might be considered. A number of organo substituted P-P-P-P- rings and chains, with tri-coordinate phosphorus have been studied by Burg and co-workers, and others. Compounds previously thought of as containing P=P bonds have been shown to contain in fact P-P-P-P- etc. chains, (143), (144), p. 22-25. These compounds with catenated P-P bonds are generally obtained by polymerisation of the monomer unit. Such units as have been used are as CF_3PI_2, polymerising at room temperature; polymers with groups other than CF_3 may also be prepared, the phenyl-P polymers are known, of which the four membered P ring member has been long known, although not understood to be a P_4 compound. Attempts to prepare substituted phosphines having two hydrogen or halogen atoms attached to the phosphorus, frequently gives polymers, the polymer form appears to be thermodynamically favoured. Compounds with a P-H bond may be used to prepare units containing P-P bonds, (145). The $(PCF_3)_4$ and $(PCF_3)_5$ rings may be used to prepare other P-P compounds. Thus reaction occurs with these compounds and $(CH_3)_3P$ giving $(CH_3)_3PPCF_3$, a compound containing an interesting electronic structure, the phosphorus chain may be represented as a -P=P- unit, pictorally, it having a "bidentate" phosphorus atom, (151).

The synthetic properties of compounds with the P-Li bond have been used to obtain P-P-P-P etc. polymers and to prepare P substituted polymers. One such reaction is considered to proceed as follows:-

$$\phi PCl \rightarrow \phi PCl.\phi PCl \rightarrow (\phi P)_n \rightarrow Li\phi P.Li\phi P \rightarrow Li_2P\phi \xrightarrow[XRX]{} (-\underset{\phi}{P}-R-)_n$$

, the first stages proceeding under the influence of lithium, (146). The action of lithium on dichlorophenyl phosphine oxide gives the $(\phi P{=}O)_n$ polymer which appears to rearrange to the $(-\underset{\phi}{P}-O-)_n$ polymer.

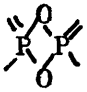
Other reactions which have been used to obtain P-P bonds are the following, $(RO)_2PCl + (RO)_3P \rightarrow$  ,(147a), and $(RO)_2\underset{S}{\overset{}{P}}-H \rightarrow$  (147b).

The controlled synthesis of P-H bonds might be considered. The P-H bond of phosphorous acid can not be thought of as being formed directly, rather, when hydrolysis of phosphorous trichloride proceeds the initially formed P-OH bond rearranges giving the O=P-H unit. In reactions where hypophosphorous acid is formed however, as in the hydrolysis of elemental phosphorus or certain phosphides the P-H bond can be considered as arising from the addition of water across the P-P bonds present. Phosphine is prepared by similar reactions. Phosphorous and hypophosphorous acids when heated rearrange to phosphine and phosphates mainly, under specific conditions this type of reaction can be made to go almost quantitatively.

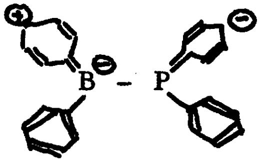
Phosphorus hydrogen bonds can also be produced by chemical reduction of P-X bonds, where X is a halogen, using reagents like $LiAlH_4$. Attempts to produce phosphine oxide by this method suggested that the compound PH_3O, analagous to the phosphine oxides which are known with organic groupings, PR_3O, decomposes as soon as it is formed, (148).

In the last few years the types of bonds which have been observed have grown in number. In particular, several types of "multiple bonds" have been found. This work has been done with organo phosphorus compounds but the question is posed as to whether such multiple bonding can occur in purely inorganic systems. There seems to be no reason why this should not be so, some authors have considered that there might be multiple bonding in phosphorus polymers like "red phosphorus" and "phospham", (149). The colour in many polymeric phosphorus oxides, hydrides and differently coloured forms of elemental phosphorus might suggest the presence of electronic energy levels suggesting π bonding. It has been found that in the $(CF_3P)_n$, n=4 and 5, compounds some interaction occurs with the "lone pair" electrons; they play some part in the bonding and X-ray data is available on this point, (150).

Recently a genuine case of a P-P bond has been found. Decomposition was found to occur however to the P-P forms at normal temperature, (151). Genuine P=C bonds have also been found, (152), and the compound $\phi_3P=C=P\phi_3$ prepared, (153). A $P\equiv C$ bond analogous to the $N\equiv C$ bond, has been found in HCP, this compound breaks down at normal temperature giving a polymer, (154).

To consider for a moment P-O-P bridges, although no  structure has ever been obtained, recent X-ray structure analysis of $(CH_3PS_2)_2$ shows that it contains the  double P-S-P bridge, this may reasonably be expected to be found for a P-O-P system in due course, (155), c.f.p.425-429 of (41). The relative stability would perhaps be expected to be lower with the double P-O-P bridge owing to the different size factors.

Studies in the field of multiple bonding in boron phosphorus organo derivatives has suggested that true π bond character is not found. The electronic structure of a compound containing a formally boron phosphorus double bond seems to be



, (156).

It is of interest at this point to consider the phosphorus oxy-ions as ligands. An experimental section will deal later with a comparison of the complexing action of pyrophosphite and pyrophosphate in solution. The most investigated ion in this respect is the hydrogen ion. Since the

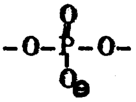
1930s PK values for the phosphorus oxy-acids have received continuous interest. Van Wazer, (41), p.360 quotes a tabulation made by Farr in 1950. The values given and that of the $\overset{5}{\mathrm{P}}\text{-O-O-}\overset{5}{\mathrm{P}}$ oxy-anion are listed, (those of the first dissociation).

$\overset{1}{\mathrm{P}}$	1.1	$\overset{4}{\mathrm{P}}\text{-}\overset{4}{\mathrm{P}}$	(2.0)
$\overset{3}{\mathrm{P}}$	1.3	$\overset{5}{\mathrm{P}}\text{-O-}\overset{5}{\mathrm{P}}$	1.0
$\overset{5}{\mathrm{P}}$	2.1	$\overset{5}{\mathrm{P}}\text{-O-O-}\overset{5}{\mathrm{P}}$	-0.3

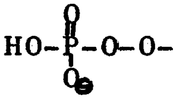
Investigations of the acid dissociation and complexing action of the peroxy-diphosphate ion have been carried out recently, (157). The series $\overset{4}{\mathrm{P}}\text{-}\overset{4}{\mathrm{P}}$, $\overset{5}{\mathrm{P}}\text{-O-}\overset{5}{\mathrm{P}}$ and $\overset{5}{\mathrm{P}}\text{-O-O-}\overset{5}{\mathrm{P}}$ was compared. It was found that there was a linear relationship between the third and fourth dissociation constants in this series and, arguing from the probable validity of this relationship with the first and second dissociation constants, these values were estimated. The appearance of a simple relationship in this series of acids shows the effect of oxygen bridges between the phosphorus atoms on the acid dissociation. The order of increasing acid strength is $\overset{5}{\mathrm{P}}\text{-O-O-}\overset{5}{\mathrm{P}} > \overset{5}{\mathrm{P}}\text{-O-}\overset{5}{\mathrm{P}} > \overset{4}{\mathrm{P}}\text{-}\overset{4}{\mathrm{P}}$.

One P-OH in $\overset{5}{\mathrm{P}}\text{-O-}\overset{5}{\mathrm{P}}\text{-O-}\overset{5}{\mathrm{P}}$ is completely dissociated in solution and polyphosphoric acid with long chains of $(\text{-}\overset{5}{\mathrm{P}}\text{-O-})_n$ present, titrates as a monobasic strong acid, (158), c.f.(41), p.438. Meta phosphoric acid behaves similarly, trimetaphosphoric acid for example giving a single inflexion at the end point in the pH titration.

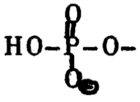
When a number of dissociation constants which have been corrected for activity are compared, one is really comparing the relative stabilities of the phosphorus oxy-anions, since to a good approximation the changes in entropy from the P-OH to the P-O$^-$, H_3O^+ ions is the same with the different oxy-acids. Thus the anionic forms:


$-O-\overset{O}{\underset{O^{\ominus}}{P}}-O-$,

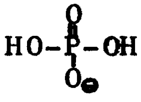
a


$HO-\overset{O}{\underset{O^{\ominus}}{P}}-O-O-$,

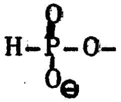
b


$HO-\overset{O}{\underset{O^{\ominus}}{P}}-O-$,

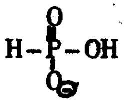
c


$HO-\overset{O}{\underset{O^{\ominus}}{P}}-OH$

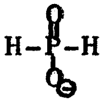
d


$H-\overset{O}{\underset{O^{\ominus}}{P}}-O-$,

e


$H-\overset{O}{\underset{O^{\ominus}}{P}}-OH$

f

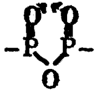

$H-\overset{O}{\underset{O^{\ominus}}{P}}-H$

g

form a series proceeding from left to right of decreasing relative "stability". This "stability" measures the tendency for the anionic form to be present in solution, in equilibrium with the non-ionised form. Proceeding from top to bottom also increases the stability of the anion. (The precise position of the pyrophosphorous acid on this scheme is not determined certainly; Van Wazer, (41), p.361 shows a titration curve, suggesting the apparent dissociation of pyrophosphorous acid as being between the values of phosphorous acid and hypophosphorous acid. This point will be dealt with later).

Two trends can be distinguished. Along the top row, a-d, stability decreases as the number of oxygen atoms taking part in bridges between phosphorus atoms decreases. Stability also increases as the number of P-H bonds increases. The first trend can be rationalised in terms of electronegativity, if only the bridge oxygens are considered. Since the electronegativity of phosphorus is about the same as that of hydrogen a $\mathrm{H{-}O{-}\underset{\underset{O}{\|}}{P}{-}}$ and $\mathrm{-\overset{\|}{\underset{|}{P}}{-}O{-}\overset{|}{\underset{\underset{O}{\|}}{P}}{-}}$ group might have been expected to have the same stability. The difference arises because of the different bonding possibilities of the phosphorus atoms, d orbitals are available. The observation is that where P-O-P bonds are present there is an increased probability of obtaining the $\mathrm{P{-}O^{-}}$ group and different kinds of P-O-P bonds can be compared in terms of electronegativity. Thus comparing ions a, b, c and d, a has two bridge oxygens, b also has two, but in a different position; c has one but d has none. The electronegative nature of oxygen relative to phosphorus tends to cause a movement of electrons from the -O-H bond → $-O^{-}$, H+. The differences between the acids with P-H bonds however cannot be explained in terms of electrons being withdrawn from the -O-H bond, as has been discussed for different P-O-P species, since the electronegativity of H and P are about the same. Nor can this be dealt with in terms of the number of oxygen atoms co-ordinated to a phosphorus atom, since the observed effect is in the opposite sense to what would be expected if differences were simply due to the attraction of electrons away from the -O-H bond. Perhaps the effect is due to a tendency for the tetrahedrally arranged oxy-anion to attract electrons into the molecular orbitals of the phosphorus, more so when the total number of electrons in the oxy-anion becomes less.

The sequestering action of many of these anions has been applied commercially. It was found early that transition metal pyrophosphates would dissolve in excess pyrophosphoric acid solution to produce soluble complexes. The colours of pyrophosphate complexes in solution were often markedly different from those of simple aqueous solutions of the cations, (159). Crystalline pyrophosphate complexes may be obtained from such solutions; salts containing the complex ions (M(II) $(H_2P_2O_7)_2$ $)^{2-}$ can be obtained in the crystalline state.

Although no X-ray structural data is available on the manner of co-ordination of the central ion in this type of complex, it has been considered that the bidentate  group is present, (160).

The complexing action of P=O bonds is now well known, organic derivatives like tributyl phosphate finding industrial application as complexing agents, e.g. in extraction of uranium. Numerous studies have lately been done, particularly using the infra-red spectral technique, on these complexes,(161).

Alkali metal and alkaline earth ions also interact with phosphate and condensed phosphate ions, although the interaction is of a different order of magnitude, (162).

The formation of complexes may accompany catalysis of reactions involving the phosphate group, e.g. hydrolytic breakdown of P-O-P bonds is subject to metal ion catalysis and the effect of metal ions in biological systems involving these and similar bonds may be similar, (163).

No systematic study has yet been undertaken of the complexing of metal ions by lower oxy-acids of phosphorus. It will be shown later that the complexing ability of the pyrophosphite anion is much weaker than that of the pyrophosphate unit. Weak interaction is observed in cases studied similar in magnitude to the interaction of metal ions with ortho phosphite. Some metal ions do show complexing action however, soluble complexes are found with Cr(III) and UO_2^{2+} in solution, with phosphite (Ebert described the species (Cr(III) $(HPO_3)_3$)H_3, recently, (81)).

This latter complex is formally analogous to the acid phosphites which may be prepared for the alkali metal and alkaline earth types of ions. With the chromium salts it seems likely that there is a centrally co-ordinated chromium atom present. All the alkali metal salts studied, (see later), exhibit anomalous spectra, having areas of continuous absorption, c.f. (164). The stability of these salts will be related to the hydrogen bonding arrangements of the phosphite anions and the phosphorous acid units in the crystal, there being no special effect of co-ordination of the central metal ion by ligands.

In the past few years important contributions have been made to the field of phosphorus chemistry by the Van Wazer school, amongst which the Reorganisation Theory is especially important. This theory is the result of experiments carried out on the size distribution of units in polyphosphate type systems. In fields of chemistry where thermodynamically metastable compounds are dealt with as in phosphorus and organic chemistries reorganisation equilibria will be displayed at a suitable temperature. The theory is probably valid for "covalent chemistry" in general, (41), p. 80-83, 218, 249, 400, 722-69. The distribution of units like those present in condensed phosphoric acids may be worked out from statistical considerations. Agreement has been obtained between the calculated and theoretical distribution of units. Application of this theory to the field of the lower oxy-acids is not as straightforward as it is for the systems like the polyphosphates.

Systematic studies for a large number of systems are being reported at present, (165-178).

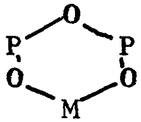
Studies on rearrangements of the lower oxy-acids have been reported from time to time in the literature. Hypophosphoric acid when allowed to stand exposed to the atmosphere absorbed moisture and underwent rearrangements. Joly, (16), suggested that the pyrophosphite unit was formed. Modern studies using paper chromatography showed that $\overset{3}{P}\text{-O-}\overset{5}{P}$ and $\overset{5}{P}\text{-O-}\overset{5}{P}$ were present in the rearrangement products, (180). In pyrolysis studies on disodium dihydrogen hypophosphate Kolitowska considered that the rearrangement of the dihydrogen hypophosphate anion produced, at 230°, pyrolysed material containing pyrophosphite and pyrophosphate. The equation $2H_2P_2O_6{}^{2-} \rightarrow H_2P_2O_5{}^{2-} + H_2P_2O_7{}^{2-}$ was suggested, (179). Rearrangements of hyphosphites have also been found to lead to material which shows the presence of the $\overset{3}{P}\text{-O-}\overset{3}{P}$ species on the chromatogram, (105). The pyrolytic breakdown of phosphorous acid has also been studied and found to proceed, under suitable conditions according to the equation, $4H_3PO_3 \rightarrow PH_3 + 3H_3PO_4$ (181), (182).

When attempts were made to condense phosphorous acid units beyond the pyrophosphorous acid stage a variety of coloured products were found by Ebel and Hossenlopp; no further condensed phosphorous acid unit than the pyro acid could be prepared. Thermal dehydration, (under vacuum), the Auger reaction (25), hydrolysis of P_4O_6, action of phosphorous acid on P_4O_6 and the dehydration of phosphorous acid with dicyclohexylcarbodi-imide were studied, (183), (184).

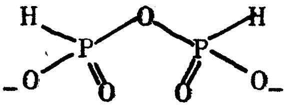
(II) THE COMPLEXING ACTION OF PYROPHOSPHITE

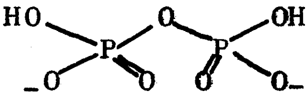
(II)

The Complexing of Pyrophosphite with Metal Ions compared with the Complexing Action of Pyrophosphate

As has already been discussed pyrophosphate is a good complexing agent. The P-O-P bond allows the six membered chelate ring  to be formed.

The pyrophosphite anion also has a P-O-P bond. Two of the pyrophosphate OHs are replaced by Hs,





These forms are present in solution at neutral pH.

It is likely that the structures of the ions in solution will be similar, the bent bridge P-O-P bond being present; spectral studies have been made of pyrophosphate in solution and of pyrophosphite in solution, (63) and (185).

It was therefore of interest to compare the complexing action of the two anions, and possibly stabilise the $\overset{3}{P}$-O-$\overset{3}{P}$ bond to hydrolysis. If a suitable metal ion could be found measurements of the dissociation of the pyrophosphite P-OH groups in acidic and basic media would have been possible.

Experiments were carried out using firstly a comparison between the solubilities of pyrophosphite and pyrophosphates in excess pyrophosphite or pyrophosphate solution, and secondly by polarographic experiments. The results of the polarographic experiments were compared with published data on polarographic investigation of the complexing of pyrophosphate and metal ions.

Experiments on the Solubility of Pyrophosphites and Pyrophosphates as a Function of the Pyro-Anion Concentration

Bassett and co-workers, (186), and Rodgers and Reynolds, (187), studied the formation of complex pyrophosphates by redissolution of an initially precipitated normal salt.

About 0.3g. of various metal salts in 10ml. water were treated by adding a 0.145M tetra sodium pyrophosphate solution from a burette. Some of the initially formed precipitates re-dissolved in excess pyrophosphate solution; a colour change was evident here.

Salt	
$Ni(NO_3)_2$	green ppt. dissolved to give a red solution
$Ag(NO_3)$	ppt. did not re-dissolve
$MgCl_2$	" " " "
$CaCl_2$	" " " "
$BaCl_2$	" " " "
$PbCl_2$	ppt. may re-dissolve slightly
$CoCl_2$	ppt. forms then re-dissolves.

Further experiments were carried out in a more quantitative manner. Solutions of transition metal ions were obtained and a known quantity of these ions was titrated with a pyrophosphate solution, the resulting colour changes and precipitates being noted. It is seen from the above experiment that the Mg, Ca, Ba and Ag salts and possibly the Pb salt do not redissolve in excess of the pyrophosphate reagent, while those of Co and Ni do; the following salts were now studies:

Salt Solution,	concentration M.10-4	Pyrophosphate concentration where re-dissolution occurs
$Cu(NO_3)_2$	2.14	12.8
$Ni(NO_3)_2$	1.48	1.45
$CrCl_3$	0.68	7.22
$CoCl_2$	1.07	1.08
$CdCl_2$	no re-dissolution observed.	

In all cases an insoluble precipitate is produced initially, this redissolves at the metal ion and pyrophosphate ion concentrations shown in the table. Under the experimental conditions employed Cu pyrophosphate re-dissolves at a 1:5.7, the Ni at 1:1, the Cr at 1:10.6 and the Co at 1:1 metal to pyrophosphate ion ratios. As the pyrophosphate solution is run into the metal salt solution a precipitate is obtained when the metal is present in excess of the ratios given. Cd does not re-dissolve, suggesting that, if solution is a measure of complex formation, this ion forms weaker complexes than the rest. The solutions have characteristic colours, different from the original solution of the cation.

The experiment was repeated using pyrophosphite solution of similar concentration. Sodium pyrophosphite, incidentally is much more soluble in water than the pyrophosphate.

Solutions of Cu, Ni, Cr, Co,Cd studied as in the pyrophosphate experiments, in no case showed precipitation or colour change. Slight darkening of the Cu(II) blue colour may have taken place, although no reduction to the metal or "red hydride" occurred. Solutions of the metal ions with, (a), no added phosphorus oxy-anion, (b) with pyrophosphite solution, (c) with pyrophosphate solution present were made up and the colours compared visually. Solutions (a) and (b) showed no visible difference, (c) however was markedly different. After standing for two days the Cr pyrophosphite solution showed a colour change. Oxidation of the P-H may have been taking place. With Fe(III) chloride solution, which was also studied, pyrophosphite produced an immediate discolouration of the brown Fe(III) giving the green colour of Fe(II).

These direct experiments suggest that in general the complexing action observed for pyrophosphate is not found with pyrophosphite.

Quantitative Investigation of the Complexing of Metal Ions by Pyrophosphite, using Polarographic Methods

a), Theoretical Introduction, c.f. (188).

When a varying potential is applied to a dropping mercury electrode, in a solution containing metal ions, the current which is carried by the metal ions in solution varies with the applied potential. A specific minimum potential is required for the discharge of a particular metal ion at the electrode and the current, (diffusion current) due to this ion is proportional to its concentration in solution. When the ion is complexed in solution the voltage at which discharge occurs varies. Equilibrium constants for the complexing process may be obtained by comparing the polarographic curves of solutions with varying concentrations of ligand and a constant concentration of metal ion.

Where the electrode process is reversible the equation

$$E=E_0 - \frac{0.059}{n} \log_{10} \frac{i}{i_d - i}$$

may be shown to be obeyed, (188), for the electrode reaction in the electrode process

E is the applied potential, volts
E_0 is the standard polarographic electrode potential, volts
n is the number of electrons involved
i is the current flowing
i_d is the diffusion current.

For the ion association process,

$$M^{n+} + pL^{z-} \rightleftharpoons ML_p^{(n-pz)+} \; ;$$

the equilibrium constant K is defined as

$$K = \frac{[ML^{(n-pz)+}]}{[M^{n+}]\,[L]^P}$$

the terms inside the square brackets denote activities,

and it may be shown that

$$E_{\frac{1}{2}} = \frac{0.059}{n} \log_{10} K - \frac{p}{n} 0.059 \log_{10} (L), \text{ c.f. (188)}$$

where $E_{\frac{1}{2}}$ is the value of E when i = id/2, the half wave potential. Terms inside round brackets are used here to denote concentration terms.

Determination of values of K and p thus involved determining $E_{\frac{1}{2}}$ values for different concentrations of ligand and from the linear plot of $E_{\frac{1}{2}}$ vs. $\log_{10}$ (L) the intercept on the $E_{\frac{1}{2}}$ axis is used to calculate the value of K while the slope of the line is used to obtain p.

When the electrode process is not reversible values of K and p cannot be obtained by this method. However an estimate of the complexing ability may be obtained by comparison of the shifts in half wave potential on adding ligand.

The experimental procedure involves first checking the process being used for reversibility by plotting E against $\log_{10} \frac{i}{i_d - i}$ and calculating n from the slope of the line obtained. For a reversible wave the slope will be linear and n will be a whole number. Sometimes the process may be made reversible by addition of wave "maxima depressants" such as gelatine solution.

If various complexes are being formed in solution over the ligand concentration range studied the $E_{\frac{1}{2}}$ vs. $\log_{10}$ (L) plot will not be linear. Different linear sections may be distinguished, however, corresponding to different values of p and K.

Apparatus employed

The apparatus was a standard commercial polarograph with automatic recording and voltage sweep devices, (the Tinsley recording polarograph). A voltage sweep of 3 or 0.3 volts could be employed. Using the highest sensitivity $E_{\frac{1}{2}}$ values of 0.ImV or even better could be obtained. No attempt was made to obtain diffusion coefficients from the current readings since the absolute accuracy of these is not as great as the voltage accuracy. The polarographic cell was immersed in a thermostat kept at 25±0.05°C using a Circotherm temperature control. The cell was deoxygenated before a run by bubbling nitrogen, which had been freed from traces of oxygen, through it. The apparatus had been in regular use prior to these experiments and the normal routine procedure was continued. Washing of the cell between runs was carried out with care using conductivity water and "Analar" acetone. The starting voltage was applied to the cell by means of an accumulator circuit, standardised in turn before each run against a standard cell, (Weston cell E.M.F. 1.01839V., 25°). The polarographic cell had a saturated KCl calomel electrode.

Reagents employed

The metal salts were of analytical grade. Sodium pyrophosphite was prepared from $NaH(HPO_3)_2.5H_2O$ by heating it at 220°C until the correct amount of water had been lost for the $Na_2H_2P_2O_5$ stoicheometry. Analysis showed that any oxidised species present were less than 1%.

b), Experimental Section.

Complexing of Cd^{2+} by Pyrophosphite

Expt. 1 A (Cd^{2+}) of 1.627. 10^{-3}M, (from $CdCl_2$) and KCl base electrolyte, 2.1 M was employed. The Cd^{2+} wave is reversible, and Cd^{2+} solutions are particularly suitable for polarographic studies for this reason.

$(H_2P_2O_5^{2-})$ M	$E_{\frac{1}{2}}$V	step height cm.10^{-2}
0	0.674(2)	571
0.0194	0.676(3)	563
0.0485	0.676	532
0.0969	0.679(5)	558
0.194	0.680(3)	578

The step heights are given for comparison only, they are proportional to the current.

Values of p=0.151 and log K=0.32 are obtained.

Expts. 2 and 3 A lower base electrolyte concentration of 0.349 M was used, the (Cd^{2+}) being as above.

Time after dissolution of P-O-P	$(H_2P_2O_5^{2-})$ M	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
1 day	0	0.625(6)	606
"	0.0097	0.629(4)	569
4 days	"	0.624(3)	578
"	0.0485	0.622(6)	539
"	0.097	0.626(4)	533

Little change is observed in the position of the wave when small amounts of phosphite are present in the pyrophosphite solution, such as is found with pyrophosphite solutions which have been allowed to stand several days.

When the experiment was repeated the following values were obtained.

$(H_2P_2O_5^{2-})$ M	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0.	0.624(9)	646
0.00829	0.625(8)	632
0.0249	0.628(6)	627
0.0414	0.627(1)	596
0.124	0.630	598

giving p=0.14, log K=0.32.

Expt. 4 It appeared that the small shifts observed in the above experiments were due to the swamping effect of the chloride ion, under the conditions employed this complexed the Cd^{2+} almost completely, no pyrophosphite complexes being allowed. This demonstrated the extremely weak complexing action of pyrophosphite for Cd^{2+}. A KNO_3 base electrolyte 0.336 M was employed in this experiment, the same $CdCl_2$ solution was employed, giving a constant (Cl^-) of $3.254.10^{-3}$M. Since the complexing action of the nitrate ion is weaker than that of the chloride ion it was expected that complexing action between the pyrophosphite and the Cd^{2+} would now be observable,

$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	0.610(5)	561
0.0084	0.614(0)	559
0.1263	0.626(0)	521

giving, p=0.288, log K=0.703.

Expt. 5 It appeared from the results of expt. 4 that even the small chloride ion concentration employed here inhibited the pyrophosphite complex formation. A chloride free system was now employed; the Cd^{2+} was obtained from $Cd(NO_3)_2 4H_2O$, (Cd^{2+}) in the cell was $1.658. 10^{-3}$ M and the base electrolyte was KNO_3, 0.336 M.

No.	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
1	0	0.581(5)	597
2	0.00639	0.584(5)	603
3	0.03195	0.590(9)	577
4	0.0959	0.601(2)	573

Solution 3 was left with nitrogen bubbling through it for $\frac{3}{4}$ hour, $E_{\frac{1}{2}}$ changed to 0.591(6), solution 4 was allowed to stand for 2 hours $E_{\frac{1}{2}}$ 0.600(8) was now found. This demonstrates the stability of the system. The values p=0.733 and log K=1.408 are obtained. The value of p obtained is considerably higher than in the previous experiments.

Expt. 6. Since the shifts in half wave potential which were obtained in the foregoing experiments are small it was necessary to employ larger concentrations of ligand to obtain large shifts in this value. However in order for the polarographic theory to be valid the ionic strength must remain constant in the different solutions of ligand, metal ion and base electrolyte. This is in general done by having an excess of an inert electrolyte present, so that the changes in the ligand concentration do not appreciably alter the ionic strength. In order to obtain large shifts in $E_{\frac{1}{2}}$ values it would be necessary to use a base electrolyte concentration of about IOM. This did not seem likely to give reliable results. $Na_2H_2P_2O_5$ however may be treated as a 2:1 strong electrolyte. It was possible to vary both the pyrophosphite and inert electrolyte concentrations and thus to keep the ionic strength constant over a series of solutions. The ionic strength is defined as $\frac{1}{2}\Sigma cz^2$, c being the ion concentration and z the ion change. The ionic strength of $Na_2H_2P_2O_5$ is thus $3(Na_2H_2P_2O_5)$, and that of KNO_3 is (KNO_3). Weighed quantities of $Na_2H_2P_2O_5$ were transferred to 20ml. standard flasks and the appropriate quantity of KNO_3 solution added to bring the ionic strength to 1.8.

$Na_2H_2P_2O_5$g.	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	18	0	0.5797	629
0.1451	16.8	0.0382	0.5866	643
0.4610	14.3	0.1215	0.599	618
1.1224	9.1	0.294	0.593(3)	568
1.6922	4.7	0.444	0.608(1)	536

When the $E_{\frac{1}{2}}$ values are plotted against the pyrophosphite concentrations a maximum occurs roughly at the point where half the ionic strength contribution is due to the pyrophosphite. The step height also shows a decrease at this point. The occurrence of this maximum may mean that $Na_2H_2P_2O_5$ cannot be treated as an inert electrolyte in this, or the electrode reaction may be different in a predominantly pyrophosphite solution. Alternatively the nitrate ion may play some part in the mechanism of complex formation. With Cu(II) solutions discussed later no anomalies are found with this type of experiment, so the observations may depend on the presence of Cd^{2+}. The values obtained from solutions where the ionic strength was due mainly to KNO_3 are analagous to the previous experiments, the values of p=0.84 and log K=1.41 are obtained.

Expt. 7. The complexing of Cd^{2+} and phosphite was studied. A 1M KNO_3 base electrolyte solution with $(Cd^{2+}) = 1.658.10^{-3}M$, obtained from $Cd(NO_3)_2$, was used. The possibility of precipitation was likely since phosphites are less soluble than pyrophosphites.

(HPO_3^{2-})	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0.01269	0.582(1)	556
0.03808	0.586(7)	452
0.02539	0.584(6)	553

and using $(Cd^{2+}) = 8.29,10^{-4}$

0	0.579(5)	662
0.06348	0.596	628
0.08887	0.585(8)	518

The change of the Cd^{2+} concentration produces a marked change in the $E_{\frac{1}{2}}$ and step height values. A trace of cloudiness was noted in the more concentrated solutions indicating the start of a precipitation process. The depression of the wave in the more concentrated cases occurs at the lowest concentration employed (phosphite) but when the $(Cd^{2}+) = 8.29.10^{-4}$ it becomes depressed at about $(HPO_3^{2-}) = c. 8.12.10^{-2}M$. The $E_{\frac{1}{2}}$ values obtained with the highest concentration of phosphite will be somewhat suspect since precipitation of both Cd^{2+} and phosphite will alter the concentration in solution. The values obtained for the p and log K factors calculated for the $(Cd^{2+}) = 1.658.10^{-3}$ are p=0.49 and log K=0.95. It is found that when the ratio of Cd^{2+} to phosphite is plotted against the $E_{\frac{1}{2}}$ values all points lie on the same curve. However plots for the two concentrations used give different curves. This means that the p and log K values obtained from such data depend on the metal ion concentration, even although a large excess of ligand is present. This perhaps serves to demonstrate the weak nature of the interaction between the two ions.

Discussion of the Results for the Cd^{2+} Ion

Interaction of only a weak nature occurs with pyrophosphite and phosphite ligands. Comparison with the data of Souchay and Fouchere, (189), is interesting. In polarographic experiments using 3.5 M KCl base electrolyte, a shift of 85mV for a variation in pyrophosphate concentration up to 0.2 M, gave p=2 and log K=4. This shows interaction between the pyrophosphate and Cd^{2+} to be several orders of magnitude greater than is observed for pyrophosphite complexing.

The results which have been obtained in the present work are tabulated:-

Expt.	p	log K	Base electrolyte	(Cd^{2+}), M 10^{-3}
1	0.15	0.32	KCl 2.1 M	1.63
2, 3	0.14	0.32	KCl 0.35M	"
4	0.29	0.70	KNO_3 0.36M	"
5	0.73	1.41	" (Cl^-), 3.25 10^{-3}M	"
6	0.84	1.41	KNO_3 varies	0.83
7	0.49	0.95	KNO_3 1.0 M	1.66

1-6 are with pyrophosphite and 7 is with phosphite.

These results demonstrate the effect of the chloride ion concentration on the pyrophosphite-Cd^{2+} interaction. As the chloride ion is decreased in amount the p and log K values also increase, suggesting that the log K value for the species $CdH_2P_2O_5$ may be around 1.4.

Although, as has been described, the values obtained for the interaction of phosphite and Cd^{2+} are markedly dependent on the ratio of ligand to metal ion in the solution this is not the case for the interaction with pyrophosphite. Perhaps an important factor in this is the lower solubility of cadmium phosphite relative to the pyrophosphite.

The type of interaction of the two ligands phosphite and pyrophosphite for the metal ion, although weak, is of the same order of magnitude. This is to be contrasted to the marked differences between phosphate and pyrophosphate where strong complexes are obtained for the pyro-anion with metal ions whereas phosphate complexes are much less stable.

Tabulations of stability constants are available for phosphate and pyrophosphate ligands, (190), p.57-63. Further discussion on this point will be made later.

Complexing of Cu(II)

The Cu(II) polarographic wave is suitable for this type of study, however maxima may occur in the wave requiring the addition of a suppressor. Initial experiments were carried out to determine the minimum quantity of gelatine required for this suppression. Pyrophosphite was also found to act as a maximum suppressor, so that when this anion was present no addition of gelatine was required.

Expt. 8. In this experiment, Cu(II) = $1.2710.10^{-3}$ M (from $Cu(NO_3)_2 3H_2O$) with a KNO_3 base electrolyte 0.336M, was employed.

$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	Nature of the curve
0	+0.010(5)	max.
$6.39.10^{-3}$	+0.012	"
$1.92.10^{-2}$	+0.007(5)	"
$3.20.10^{-2}$	+0.006(8)	no max.
$9.59.10^{-2}$	-0.005(5)	" "

It is found that the critical concentration of pyrophosphite for suppression is about $2.5.10^{-2}$ M. It appears that the same diffusion current is found over the concentration range studied. The wave was tested for reversibility by plotting $\log \frac{i}{i_d - i}$ vs. E. A good straight line was obtained and the value of n found, 2, agrees with the reversible electrode process Cu(II) + 2e $\rightleftharpoons$ Cu(0), as expected. The presence of maxima and the possible distortion of the curve is revealed in a plot of $E_{\frac{1}{2}}$ against the pyrophosphite concentration. The best approximation may be a linear one, which gives a logarithmic curve when $E_{\frac{1}{2}}$ is plotted against log $(H_2P_2O_5^{2-})$. From this a tangent for the value p=I, may be constructed, giving log K=1.54. Only weak complexing action was observed, similar to that found with Cd^{2+}.

Expt. 9. The method of varying the amount of base electrolyte used with Cd^{2+} was also employed here. The calculated ionic strength was adjusted to 1.8, as before, using various amounts of KNO_3 solution and solid $Na_2H_2P_2O_5$.

$Na_2H_2P_2O_5$g.	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0.	18	0	+0.013(1)	466
0.2165	16.3	0.057	+0.007(5)	477
0.3542	15.2	0.0932	+0.005(6)	458
0.7158	12.4	0.1882	-0.001(2)	456
1.8231	3.6	0.479	-0.014(4)	414
2.2318	0.6	0.588	-0.019(0)	417

The shift obtained in $E_{\frac{1}{2}}$ is now comparatively large. No maxima were obtained at this ionic strength, in the Cu(II) wave. The plot of $E_{\frac{1}{2}}$ vs. the pyrophosphite concentration is a smooth curve, with no irregularities, such as were noted in a similar experiment using Cd^{2+}, expt. 6. The plot of $E_{\frac{1}{2}}$ vs. log $(H_2P_2O_5^{2-})$ becomes linear above the pyrophosphite concentration of 0.3M. Different log K and p values may be calculated for the upper and the lowest sections of the curve. It is suggested that there is a range of different complexes present at intermediate ranges of concentration. The upper section gives p=2.0 and log K=1.44, while the lowest section, p=0.5, log K 0.51. The value p=2 corresponds to the species $(Cu(II).(H_2P_2O_5)_2)^{2-}$ in solution.

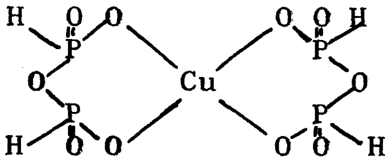
Expt. 10. The complexing of Cu(II) and phosphite was studied using 1.4M KNO_3 as base electrolyte, with Cu(II) $0.65.10^{-3}$M. Difficulties were encountered due to chemical reactions distorting the shape of the Cu(II) wave, a phenomenon not noted with pyrophosphite. The solutions were made up in a series of standard flasks before transferring to the polarographic cell by adding a Cu(II) nitrate solution, a KNO_3 and a phosphite solution (from $NaH(HPO_3).2.5H_2O$), in that order.

No.	$(H_2PO_3^-)$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
1	0	+0.0199	553
2	$1.27.10^{-2}$	+0.0065	486
3	$2.539.10^{-2}$	+0.0178	486
4	$3.81.10^{-2}$	+0.0063	438
5	$5.08.10^{-2}$	+0.0163	523
6	$1.016.10^{-1}$	+0.0158	511

Solutions No. 2 and 4 gave differently shaped polarographic waves from the remainder which were normal. No. 2 appeared to be stable (reproducible), while No, 4 was found to drift with time. Considering only Nos. 1, 3, 5, and 6 a smooth variation of $E_{\frac{1}{2}}$ with concentration is found. It seems best to explain the divergencies noted with Nos. 2 and 4 as arising from irreversible interaction of the phosphite anion and the Cu(II) ions in solution. This is not unexpected, but it is surprising perhaps that it does not occur in all cases. A log $\frac{i}{i_d-i}$ vs. E plot for wave No. 2 gave a value of n of 1.16 which suggests that a different electrode reaction is occurring in this case. It seems more likely that chemical reduction of the Cu(II) to Cu(I) occurs and the electrode reaction in this case is mainly Cu(I) + e $\rightleftharpoons$ Cu(I). Where no chemical reduction seems to have occurred the values p=0.114 and log K=0.26, are found.

Discussion of the Results for the Cu(II) Ion

It appears from the results given above that Cu(II) is somewhat more complexed by pyrophosphite than by phosphite. Interaction in both cases is still weak however. Numerous investigators have reported stability constants of the pyrophosphate Cu(II) complexes, (190). All the values are several orders of magnitude greater than the present results suggest for the pyrophosphite complexes. In the present case when compared with the results of the interaction with Cd^{2+}, Cu(II) is appreciably complexed by the pyrophosphite anion and the difference in the degree of interaction when compared with that between phosphite and Cu(II) is probably due to the fact that copper is a transition metal element. Relative stabilisation of interaction when there is a P-O-P bond present can be interpreted as a chelation effect; the structure of the complex found with pyrophosphite for example might be similar to that which has been suggested for the Cu(II) di-pyrophosphate complex, viz.



Complexing of Ni (II)

The Ni(II) polarographic wave is not reversible and the standard procedure cannot be used to obtain p and log K values. The shape of the wave also changes as the ligand concentration alters. A special method has been used to obtain stability constants from the results.

Expt. 11 A series of experiments was carried out using the variable base electrolyte method, varying the amounts of KNO_3 and $Na_2H_2P_2O_5$ present. The ionic strength was adjusted to the calculated value in each case, (1.8); the Ni(II) was $1.021.10^{-2}$M, (from $Ni(NO_3)_2 6H_2O$).

$Na_2H_2P_2O_5$g.	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	18	0	1.035	289
0.0184	17.9	0.00484	1.039-	321
0.1553	16.8	0.0408	1.0395	257
1.1743	10.8	0.308	1.0516	298
1.3187	6.6	0347	1.0525	292

This shift in $E_{\frac{1}{2}}$ although not as great as was found for Cu(II) suggests that some complex formation is occurring here.

Treatment of Results

When the $E_{\frac{1}{2}}$ values obtained by the standard procedure from the experimental graph are plotted against the ligand concentration a smooth curve is obtained. The upper section probably becomes linear. As the ligand concentration is increased, two effects can be distinguished. One is the shift of the wave to more negative voltages with increasing ligand concentration, while the other effect is a variation in the curvature of the wave. When log $\frac{i}{i_d - i}$ is plotted against E for these waves a linear section is obtained, around the centre of the curve. The value of n obtained from the slope of this line, varies over the above concentrations from 1.023 to 0.645 with increasing ligand concentration. Since the relationship between $E_{\frac{1}{2}}$ and the logarithm of the ligand concentration is derived by substituting the concentration terms of the definition of K in the term $\frac{i}{i_d - i}$, this being possible due to the direct proportionality between the current i and the concentration of metal ions in solution, then if an equation for the irreversible wave be set up of the same form as that of the reversible wave, providing that the i values are still related to the concentration of the metal ions in solution, it will be possible to obtain K values from irreversible waves. The difficulty is that two variables are present, both E and n values changing with changing ligand concentration. It is therefore necessary to correct $E_{\frac{1}{2}}$ values for changes in the n values.

On plotting $\frac{i}{i_d - i}$ against E for each wave the following values were found;

$(H_2P_2O_5^{2-})$	n
0	1.023
0.00484	1.042
0.0408	1.128
0.1473	1.145
0.308	0.978
0.347	0.642

It is seen that the value of n is about 1 in all cases except the last. There may be some correlation between the observed value of n and the amount of KNO_3 base electrolyte present, in the last case there is less contribution to the ionic strength from the KNO_3 present than from the $Na_2H_2P_2O_5$, in the other cases there is excess KNO_3. An analogous situation was found in expt. 6 when the discrepancies found in the variation of $E_{\frac{1}{2}}$ with increasing ligand concentration occurred when KNO_3 ceased to be present in excess. A mean value of n obtained from the first five values shown may be employed in the usual equations and a plot of $E_{\frac{1}{2}}$ vs. log(L) may be made in the usual way, giving p=0.45 and log K=0.52, corresponding to the species $(Ni(II)_2(H_2P_2O_5))^{2+}$ being formed in solution when the ligand concentration is less than 0.1M. At this point a break occurs in the $E_{\frac{1}{2}}$ vs. log(L) plot.

Complexing of Pb(II)

The complexing with pyrophosphite was studied. Difficulties were encountered due to the tendency for some of the lead to precipitate, presumably as the normal pyrophosphite. The (Pb(II)) used was $1.729.10^{-3}$M, from $Pb(NO_3)_2$

$Na_2H_2P_2O_5$g.	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	18	0	0.413(3)	578
2.6067	0	0.686	0.427(9)	341

From this data for p=I, log K=0.68. This shows that interaction again is of a weak nature. An estimate may be made of the solubility of $PbH_2P_2O_5$ from the step height data. If equilibrium has been reached this is, expressed as a concentration, $1.02.10^{-3}$M.

It should be mentioned that Pb(II) gives a reversible polarographic wave with a n value of about 2 corresponding to the electrode reaction $Pb(II) + 2e \rightleftharpoons Pb(0)$.

The Complexing of Co(II)

This experiment was carried out in the same way as the previous one. The Co(II) was $1.667.10^{-3}$M, from $Co(NO_3)_2 6H_2O$

$Na_2H_2P_2O_5$g.	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	18	0	1.368	648
			1.3663	578
1.8975	0	0.498	1.424	600

The first solution was studied at several different sensitivities, the second value quoted is probably more accurate. The presence of pyrophosphite appears to change the shape of the wave, producing a continuous current increase. It was therefore not certain to what extent the shift observed is a property of the complexing of the Co(II) by the pyrophosphite or is due to a change in the electrode reaction which the presence of pyrophosphite brings about. From a plot of log $\frac{i}{i_d - i}$ vs. E for the wave when no pyrophosphite was present a value of n=0.79 was obtained. Since $p = \frac{E_{\frac{1}{2}} \quad n}{\log_{10}(L) \cdot 0.059}$, for postulated values of p, values of $\frac{E_{\frac{1}{2}}}{\log_{10}(L)}$ may be obtained, enabling log K values to be worked out, employing the experimental value of $E_{\frac{1}{2}}$. The experimental data fits the theoretical relationship for small values of p. Thus for p=I, log K=1.08; p=2, log K=1.42. This provides an estimate of the type of interaction occurring and this is seen to be of a weak nature.

The Complexing of Ba^{2+}

Expt. 14. The same approach was used as in the previous experiment. The (Ba^{2+}) was $1.64.10^{-3}$M, from $Ba(NO_3)_2$

$Na_2H_2P_2O_5$g.	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	18	0	below 1.56	continues
1.1315	0	0.297	"	"

The waves are best compared by superposing traces made from the experimental plots. When this is done it was found that the presence of pyrophosphite shifted the wave in the opposite sense to what is expected for complex formation. Thus no complexing is revealed between pyrophosphite and Ba^{2+}. The positive shift in potential was 18mV. Perhaps this is due to the method employed. Where there is no KNO_3 in the solution the ionic strength may actually be less than 1.8, the $Na_2H_2P_2O_5$ not behaving as a strong electrolyte in these circumstances.

The Complexing of Cr(III)

The same approach was used again. The (Cr (III)) was $9.508.10^{-4}$M, from $Cr(NO_3)_3.6H_2O$

$Na_2H_2P_2O_5$	ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
0	18	0	0.893	128
1.040	0	0.274	0.995	100
			0.971	92

The Cr(III) + e   Cr(II) wave was used. It was found to be reversible when no pyrophosphite was present, having a value of n obtained from the log $\frac{i}{i_d - i}$ plot of 1.065. Where pyrophosphite was present the wave was flattened, however a relatively large shift in the position of the wave on the voltage scale also was obvious, indicating complexing between the Cr(III) and the pyrophosphite. The $E_{\frac{1}{2}}$ value of 0.971 V was obtained at a higher sensitivity than the other shown for this solution. $E_{\frac{1}{2}}$ was obtained from the shift in $E_{\frac{1}{2}}$ at a selected current reading. An indication of the type of interaction involved here is obtained from the following figures. For p=I, log K=1.92; p=I.5 log K=2.15; p=2, log K= 3.04. This suggests that the complexing is stronger than for the cations previously discussed. This is expected for a (formally) M^{3+} transition metal ion, compared with M^{2+} ions.

The Complexing of Tl(I)

The same routine was employed. The Ti(I) + e $\rightleftharpoons$ Tl(0) polarographic wave is suitable for this type of study since it is reversible. A value of n of 1.07 was found. A difficulty arises due to the formation of maxima when pyrophosphite is not present, there being some similarity to the phenomena encountered with the Cu(II) wave previously discussed. Addition of gelatine suppresses the maximum. The (Tl(I)) was $1.313.10^{-3}$M, from $TlNO_3$.

$Na_2H_2P_2O_5$g.	Ml. 2M KNO_3	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	Step height cm.10^{-2}
0	18	0	0.483	369
1.6119	0	0.423	0.479	269

This shows a shift of $E_{\frac{1}{2}}$ in the opposite sense to that expected for complex formation, similar to what has already been noted for Ba^{2+}, expt. 14. The rationalisation of the direction of the shift will be the same as for Ba^{2+}. No complex formation is indicated.

The Complexing of UO_2^{2+}

Studies were carried out to investigate the interaction between the uranyl ion and pyrophosphite using the constant base electrolyte method. Both nitrate and perchlorate media were employed. Reversible waves can be obtained in the polarographic reduction of uranyl solutions, the ion is this suitable for this type of investigation. It is also well known that uranyl will complex with a variety of oxy anions which do not normally form complexes with other central metal units. It was therefore expected that positive complex formation would be observed in this case; as was in fact found. The studies are somewhat complicated by the tendency for insoluble phases to be formed at relatively high ion concentrations. There is also the possibility in the present case of chemical interation occurring leading to reduction of the uranyl species.

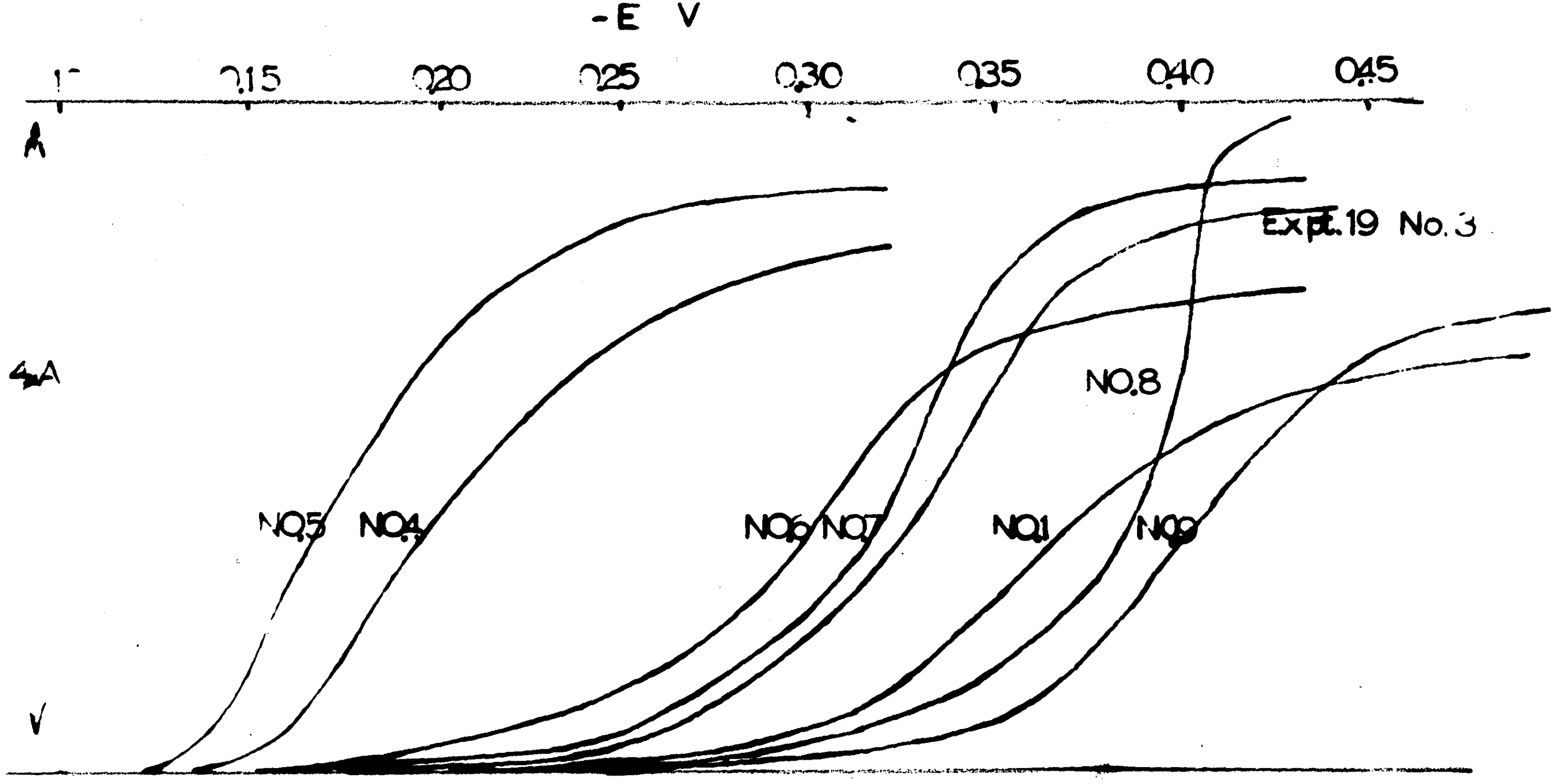
Expt. 17. $NaClO_4$ base electrolyte, 2.3M and (UO_2^{2+}) = $1.128.10^{-3}M$, from $UO_2(NO_3)_2.6H_2O$, was used. Different weights of $Na_2H_2P_2O_5$ were taken and dissolved immediately prior to use.

No.	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V
1	0	0.167(5)
2	0.1376	0.505 0.555
3	0.2065	0.809 0.906
4	0.0462	(0.298(7))

The results are complicated by changes in the waves, other than purely due to complex formation. Chemical interaction probably occurs between the pyrophosphite and the uranyl ions. Similar phenomena were encountered with Cu(II) and phosphite, expt. 10. As in the Cu(II) experiments a regular chemical behaviour with respect to concentration and other factors cannot be distinguished. Rather, it seems as though reaction, probably reduction of the uranyl by the pyrophosphite, occurs in a random fashion. Perhaps some subtle reaction initiation occurs. The reaction is not observed in all cases. When no pyrophosphite is present, No.I, a single wave is found; No. 4 shows two distinct waves in the same voltage region, one of them being shifted by twice the voltage shift of the other. No. 2 shows two "fused" waves, different in appearance from the previous ones. No. 3 shows two waves, more distinctly than with No. 2.

The colour changes which can be observed when solutions containing uranyl and pyrophosphite ions are allowed to stand demonstrated the oxidation reduction reactions which are occurring. There is also a tendency for precipitation to occur after standing for several hours. In one case the solution was kept in the polarographic cell overnight. On running a polarograph on this, no current rise was observed before 1.05 V, indicating that all the uranyl ions had precipitated (and any other uranium ions which might have been formed also).

SOME POLAROGRAPHIC WAVES **mainly** from **expt.18** UO_2^{2+} NO_3^- medium 1.98 M



Strong complexing is however indicated by these results, several orders of magnitude greater than observed for the other cations studied.

Expt. 18. The complexing of pyrophosphite by UO_2^{2+} in 1.08M KNO_3 base electrolyte using the same uranyl concentration as before was investigated. In the previous case several oxidation-reduction possibilities existed, one involving a possible oxidation of pyrophosphite by perchlorate. Any such oxidation would have produced species in solution which would have been expected to complex strongly with the uranyl. It was therefore of interest to see if large shifts were also observed where no perchlorate was present.

The results are presented in the table below. The polarographic curves obtained experimentally are also presented.

No.	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
1	$9.36.10^{-2}$	0.345(4)	676
2	$2.91.10^{-2}$	0.42	?
3	"	1.052	rises
4	0	0.195	592
5	0	0.171	662
6	$7.88.10^{-3}$	0.299	523
7	$2.49.10^{-2}$	0.327	679
8	$6.50.10^{-2}$	0.395	722
9	$2.15.10^{-2}$	0.401	552
10	$1.16.10^{-1}$	1.0672	539

Nos. 1-4 were carried out in the same way, with the same instrument sensitivity, full scale deflection 2 A; Nos. 5-10 were carried out in a series, using a different sensitivity, full scale deflection, 4 A. Nos. 1-4 were studies on solutions which had been made up and left to stand overnight before taking the polarographs. The irregular results indicate that chemical reaction has occurred. It is somewhat surprising to note that the position of the wave changes even when there is no pyrophosphite present, presumably the "solution state" of the uranyl ion changes on standing, hydrolysis or ion association of the uranyl ions may occur. The waves obtained are close to a reversible shape. Thus for No. 6 a value of n=1.17 was found, corresponding to an apparent one electron reaction.

Some differences are also apparent in the waves from Nos. 5-10. The symmetries of waves, 5, 6, and 9 are the same, the others having somewhat distorted waves. This may be due to chemical reaction, as discussed for the previous experiment.

It is apparent however that large shifts are also found in nitrate medium. Using waves 5, 6, and 9 the values p=3.94 and log K=10.49 can be obtained.

<u>Expt. 19.</u> Another study was undertaken in perchlorate medium, $(NaClO_4) = 2.3M$ and $(UO_2^{2+}) = 1.128.10^{-3}M$. Again weighed amounts of $Na_2H_2P_2O_5$ were used.

No.	$(H_2P_2O_5^{2-})$	$E_{\frac{1}{2}}$ V	step height cm.10^{-2}
1	0	0.1815	640
2	$4.32.10^{-3}$	0.2405	161
3	$1.80.10^{-2}$	0.3306	632
4	$3.76.10^{-2}$	0.3198	612
5	"	0.3338	563
6	$7.62.10^{-2}$	0.3551	645
7	$1.38.10^{-1}$	0.3601	713

Precipitation appears to occur in certain cases only. Opalescence was noted particularly in No. 2, which shows a low step height, confirming the removal of UO_2^{2+} from solution. No. 5 is a re-run of No. 4 after some opalescence appeared in the solution. This demonstrates the changes which this phenomenon produces in the wave.

On plotting $E_{\frac{1}{2}}$ against the concentration of ligand two regions are distinguishable in the curve. In the lower region of ligand concentration up to about 2.10^{-2}M, large $E_{\frac{1}{2}}$ shifts indicate strong complex formation. Above this limit the $E_{\frac{1}{2}}$ values increase more slowly with increasing ligand concentration. The waves at the lower ligand concentration appear reversible, giving, from the customary plot, a value of n close to 1. However some distortion occurs in the higher concentration range. Some reaction other than complex formation may be taking place here. From the lower concentration range the values p=2.0 and log K=6.69 may be obtained. This corresponds to the species $(UO_2^{2+}(H_2P_2O_5)_2)^{2-}$, present in solution.

c), Discussion of Results.

General Discussion of the Results of the Polarographic Experiments

The results are summarised in tabular form:-

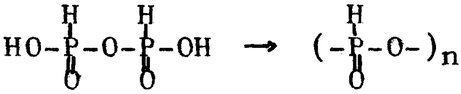
Expt. No.	M^{n+}	L	Ionic medium	Complex unit* suggested	log K
5	Cd^{2+}	$\overset{3}{P}-O-\overset{3}{P}$	KNO_3 0.36M	$Cd(H_2P_2O_5)$	c.1.4
6	"	"	" varying	"	"
7	"	$\overset{3}{P}$	" I M	$Cd_2(HPO_3)^{2+}$	0.95
9	Cu(II)	$\overset{3}{P}-O-\overset{3}{P}$	" varying	$Cu(H_2P_2O_5)_2^{2-}$	1.4
11	Ni(II)	"	" "	$Ni_2(H_2P_2O_5)^{2+}$	0.52
12	Pb(II)	"	" "	$PbH_2P_2O_5$ *	0.7
13	Co(II)	"	" "	$CoH_2P_2O_5$ *	1.1
14	Ba^{2+}	"	" "	no complexing observed	
15	Cr(III)	"	" "	$Cr(H_2P_2O_5)_{1.5}$ *	2.2
16	Tl(I)	"	" "	no complexing observed	
18	UO_2^{2+}	"	" I.9M	$UO_2(H_2P_2O_5)_4^{6-}$	10.5
19	"	"	$NaClO_4$ 2.3M	$UO_2(H_2P_2O_5)_2^{2-}$	6.7

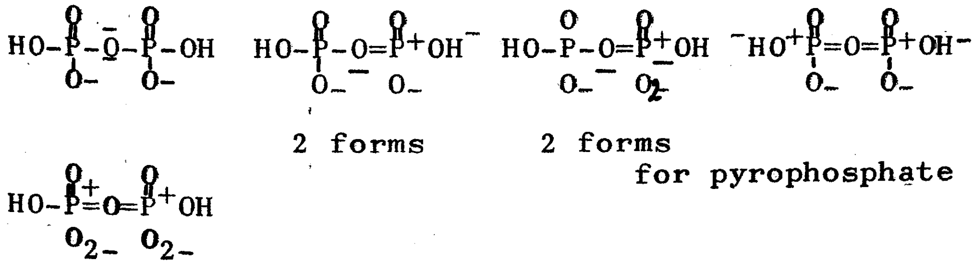
With the cases marked thus * the log K values were obtained by assuming the stoicheometry for the complex formed. These values are thus only indications of the type of ionic interaction occurring, but they may be profitably compared with the other values.

When the interaction between the pyrophoshite anion and various metal cations are compared, it becomes obvious that the formally 2+ cations Cd, Ni, Co, and probably Pb too, behave similarly although Ba^{2+} shows no complex formation. Comparison with the published values for the complexing of various cations by pyrophosphate shows that different tendencies can be seen in this latter system, (190). Complexing occurs with increasing stability of complexes in the series Tl(I), Ba^{2+}, Pb(II), Cd^{2+}, Cu(II)

β_2, 1.9 4.5 5.3 4.2 12

the β_2 values quoted in (190) are equivalent to the log K values used in the preceding pages. Interaction between pyrophosphate and cations is of a higher order of magnitude than interaction between pyrophosphite and cations. There is however probably a particular increase in stabilisation of transition metal complexes with the pyrophosphate anion. It seems that a special factor is at play in the pyrophosphate series stabilising pyrophosphate-metal ion bonding in solution, which is absent in the pyrophosphite series. The effect of the charge on the anions which enter into complex formation will be important; the pyrophosphate case can be written as a formally 4- anion while the pyrophosphite is 2-. However aqueous solutions of the two anions at pH around 7 exist predominantly in the 2- form. Often it is not known with certainty which anions in solution are actually complexing with the metal ion.

Differences between the complexing ability of pyrophosphate and pyrophosphite can be discussed in terms of the effect which "replacement" of two pyrophosphate OH groups by H in pyrophosphite has on this complexing ability. It seems likely that the effect is due to differences in the P-O-P bonds. It is found that, for example, the P-O-P bond in the pyrophosphite anion is subject to acid catalysed hydrolysis in the same way as is found for the pyrophosphate anion, but hydrolysis occurs several orders of magnitude more rapidly for pyrophosphite than for pyrophosphate under similar conditions. Also it is found that catenation of $\overset{3}{P}-O-\overset{3}{P}$ bonds is not obtained beyond the pyro-stage; dehydration like  $HO-\underset{O}{\underset{\|}{\overset{\overset{H}{|}}{P}}}-O-\underset{O}{\underset{\|}{\overset{\overset{H}{|}}{P}}}-OH \rightarrow (-\underset{O}{\underset{\|}{\overset{\overset{H}{|}}{P}}}-O-)_n$ is not found to be possible whereas such condensed P-O-P bonds are easily formed from the pyrophosphate unit. These points are discussed more fully later. Some insight into the problem is obtained when valence bond structures are written for possible electronic distributions in the two anions, thus



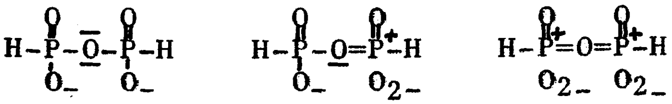
$$HO-\underset{O^-}{\overset{O}{P}}-\bar{\underline{O}}-\underset{O^-}{\overset{O}{P}}-OH \quad HO-\underset{O^-}{\overset{O}{P}}-O=\underset{O^-}{\overset{O}{P^+}}OH^- \quad HO-\underset{O^-}{\overset{O}{P}}-O=\underset{O^{2-}}{\overset{O}{P^+}}OH \quad {}^-HO^+\underset{O^-}{\overset{O}{P}}=O=\underset{O^-}{\overset{O}{P^+}}OH^-$$

2 forms 2 forms

for pyrophosphate

$$HO-\underset{O^{2-}}{\overset{O^+}{P}}=O=\underset{O^{2-}}{\overset{O}{P^+}}OH$$

and,

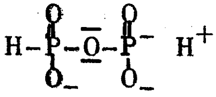
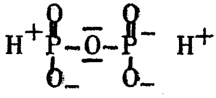
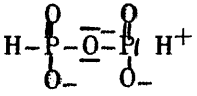


$$H-\underset{O^-}{\overset{O}{P}}-\bar{\underline{O}}-\underset{O^-}{\overset{O}{P}}-H \quad H-\underset{O^-}{\overset{O}{P}}-\underline{O}=\underset{O^{2-}}{\overset{O}{P^+}}-H \quad H-\underset{O^{2-}}{\overset{O}{P^+}}=O=\underset{O^{2-}}{\overset{O}{P^+}}-H$$

2 forms

for pyrophosphite

It is seen that seven forms may be written for the pyrophosphate anion and four for the pyrophosphite anion, considering the ions in neutral solution, (the same number of these structures may be written for the other ionised forms of the pyrophosphate anion), with different electron distributions along the P-O-P bonds. The P-H bond being between two atoms of like electonegativity need not be considered to "ionise" in such valence bond structures. The tendency for the $-P^+ H^-$ to form will be much less than for the distribution $-P^+ O^{2-}$ arising from a $P-O^-$ bond. However hypothetical ionisation like $-P-H \quad -P^- H^+$ is more probable. Additional structures for the pyrophosphite anion can be considered, having lesser "weight" than the above forms viz.,

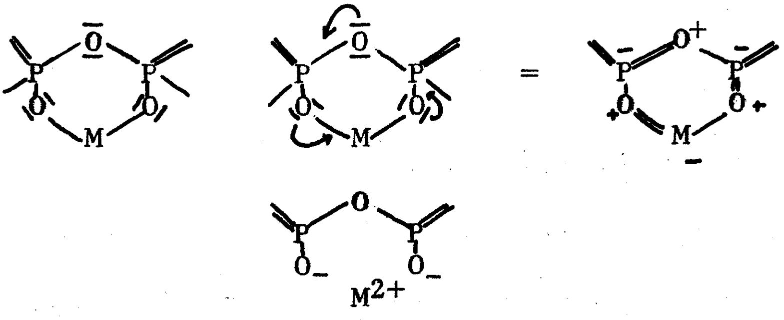




2 forms 2 forms

These latter forms can be considered to lead to a destabilisation of the P-O-P; the forms written initially increase the electron density between phosphorus and oxygen in the P-O-P bridge.

Such difference in the P-O-P bond as is suggested by this simple approach can be used to compare the properties of these types of P-O-P bonds. Thus the case of hydrolysis of the $\overset{3}{P}-O-\overset{3}{P}$ bond compared with the $\overset{5}{P}-O-\overset{5}{P}$ bond seems (see later) to be explicable in terms of a greater localisation of the bridge oxygen electrons with $\overset{3}{P}-O-\overset{3}{P}$ increasing the possibility of interaction with H^+. Again the non-existence of polyphosphites (at least the great difference between the energetics of formation or decomposition of $(\overset{3}{P}-O-\overset{3}{P})_n$ chains and polyphosphate chains is clear), indicates either that the activation energy of formation of these units is very high or that they very easily rearrange, which seems more likely, and which in turn can be correlated with the presence of a reactive P-O-P bond. The differences in complexing ability, too, between the $\overset{3}{P}-O-\overset{3}{P}$ and $\overset{5}{P}-O-\overset{5}{P}$ units will be a function of electron distributions in the two species.

If it is accepted that increasing the electron density along the P-O-P bond may increase the degree of interaction between $\overset{5}{P}-O-\overset{5}{P}$ bonds with transition metals then a likely postulate of the nature of the stabilisation can be see, again in valence bond terms, assuming the formation of a chelate ring;



(III) THERMOGRAVIMETRIC AND DERIVED EXPERIMENTS

(III)

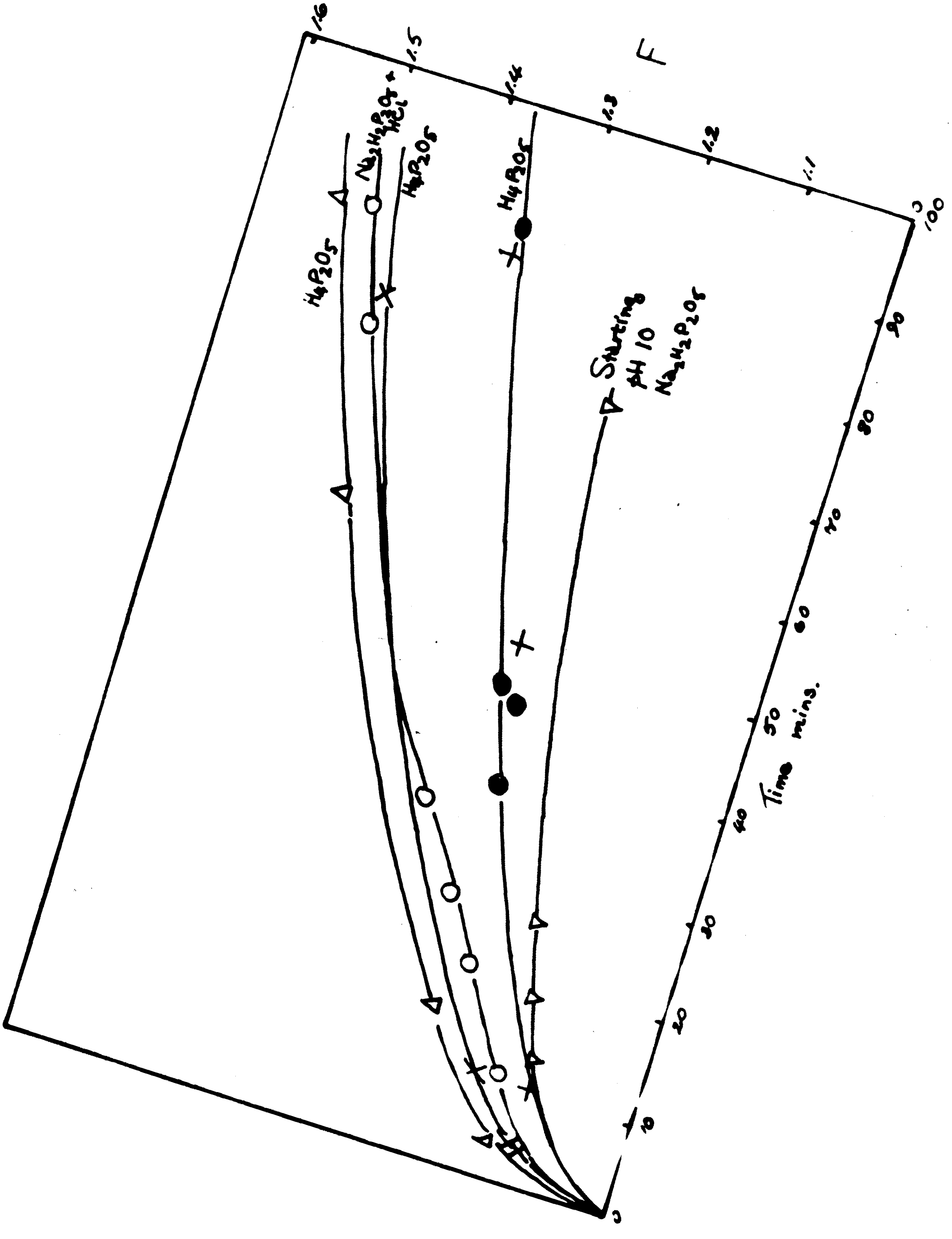
a) Some Experiments on Pyrophosphorous Acid and Pyrophosphites

(i) The Hydrolysis of the Pyrophosphite Anion

As has been indicated this has been studied by Amat, (21) and Kiehl and Moose, (89). Blaser has recently presented some data on the rate of hydrolysis of the anion and on the rate of hydrolysis of other P-O-P bonds in lower oxy-acids. He quotes for example the half life of the $\overset{3}{\text{P}}\text{-O-}\overset{3}{\text{P}}$ bond with a variety of reagents; in 0.2N HCl it is about 1 minute. The variation of the rate of the reaction with pH, being a minimum near pH7, is in general confirmed by this work. The work of Kiehl and Moose is similar although they give more data than Blaser. Thus they measured the rate of hydrolysis of ammonium pyrophosphite in 0.1 $^{\text{M}}$ NaOH, 0.01 M NaOH, distilled water, 0.1 M acetic acid, 0.1 M KHSO_4 and 0.1M HCl, using the iodometric method of analysis for phosphite in the presence of pyrophosphite (pyrophosphite reacts much more slowly with iodine than phosphite at pH c.7.). During the hydrolysis as studied by them the pH changes; this was measured and it was shown that the rate of hydrolysis is fast in acid and alkaline media, displaying a minimum in the rate of neutral pH. They considered that the reaction was of "unimolecular type" and seem to have also considered that the reverse reaction was possible in the neutral pH region. Amat studied the hydrolysis of sodium pyrophosphite using acid-base titrations to follow the course of the reaction. He considered that a simple first order process was occurring although some of the figures he gives do not fit the first order reaction curve very well.

As the subject stands it is poorly documented. Experiments have been carried out in the present work on the hydrolysis of the pyrophosphite anion as a sequel to thermobalance experiments. It was hoped to be able to measure the rate of hydrolysis of solutions obtained by exchanging cations in pyrolysis products by H^+, using an ion exchange resin, and obtain data diagnostic of $\overset{3}{P}-O-\overset{3}{P}$ bonds. It was also hoped to study the titration curves of pyrophosphorous acid solutions and from accurate pH measurements work out the dissociation constants. The results obtained are of a derived nature but it is worthwhile to discuss them as a separate topic since apart from the lack of temperature control (room temperature was used, this was virtually constant over the time of the experiments), the experiments were carried out as accurately as possible. A variety of different types of investigation have been conducted on the hydrolysis of the pyrophosphite unit apart from solution rate measurements. They are all usefully discussed in this section. All the data presented here are more fully dealt with in the experimental section.

FIG. 2a



F
1.6
1.5
1.4
1.3
1.2
1.1
0
Time mins.
0
10
20
30
40
50
60
70
80
90
100
H4P2O5
Na2H2P2O7 + HCl
H4P2O5
H4P2O5
Starting pH 10 Na2H2P2O5

FIG. 2b.

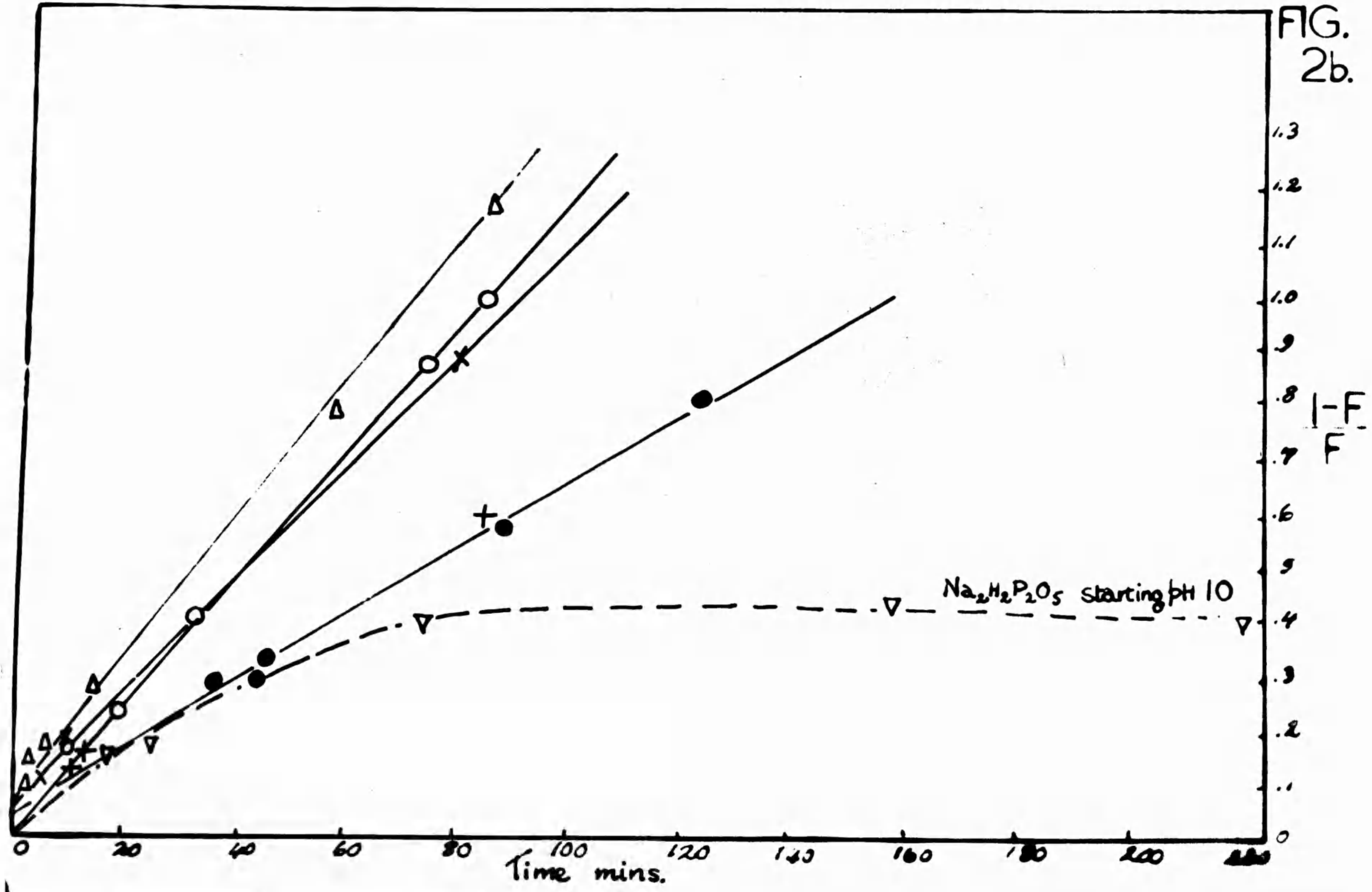
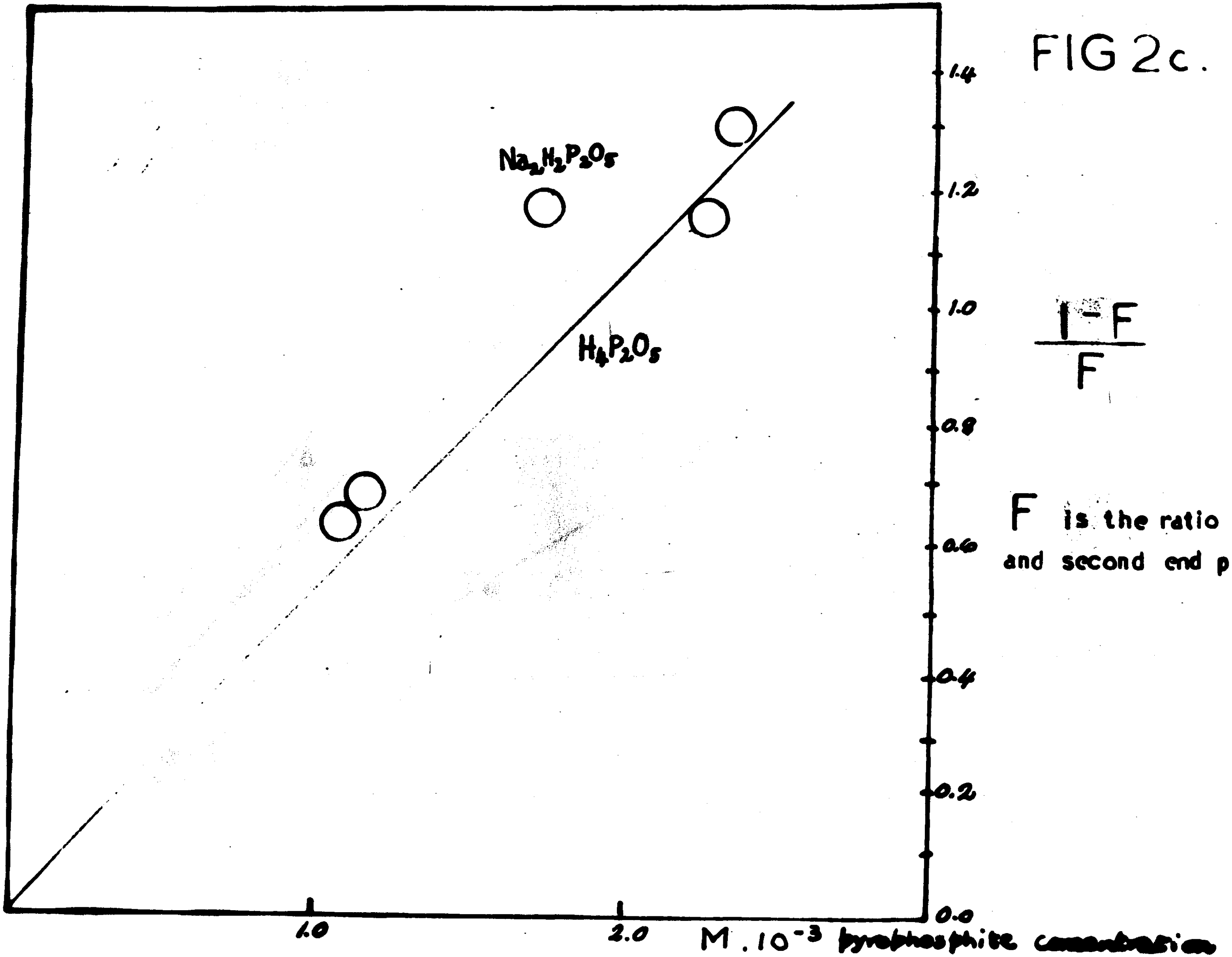

$\frac{1-F}{F}$
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
$Na_2H_2P_2O_5$ starting pH 10
0
20
40
60
80
100
120
140
160
180
200
Time mins.

FIG 2c.



F is the ratio of 1st and second end points

The hydrolysis of the pyrophosphite unit displays a number of surprising features. Thus the rate of hydrolysis varies with the concentration of the pyrophosphite unit, at least when the pyrophosphorous acid is considered. Hydrolysis is very slow in solutions with the molar ratio of water to pyrophosphorous acid up to 5.1. When pyrophosphorous acid is added to water, however in an attempt to obtain a solution of the acid, hydrolysis virtually occurs as solution takes place. When dilute solutions of the acid are studied such as can easily be prepared by use of an ion exchange column, it is found that hydrolysis is relatively slow. Kinetic measurements can be made in this case. The reaction is found to follow a second order rate curve. For the low concentrations studied about 10^{-2} to 10^{-3} M, the rate of hydrolysis at c.19^{o}C increases with the concentration; the pH shows a parallel increase in this region. Possibly the hydrogen ion concentration will be the controlling factor. During a hydrolysis run the pH of the solution remains virtually unchanged, the strongly dissociated hydroxyl groups of the ortho and pyrophosphorous acids are similar; at the concentrations studied the dissociation is nearly complete. An example of the rate of hydrolysis is, hydrolysis of a $1.14.10^{-3}$M solution was 30% complete in 33.5 minutes, the rate constant was $1.16.10^{I}$ moles^{-I}. litres. min,$^{-I}$. When HCl was added to a $Na_2H_2P_2O_5$solution and the pH adjusted to the value obtained using the same concentration of pyrophosphorous acid, it was found that the reaction proceeded sensibly faster than that of the free acid.

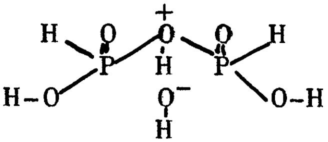
Rate curves, the second order rate plot and a plot of this rate constant against the concentration of pyrophosphite in solution are shown, Figs. 2a, b and c.

Studies on the uptake of water by pyrophosphorous acid (obtained by the vacuum dehydration of the ortho acid) were conducted using a thermobalance. A nitrogen stream with a partial pressure of water vapour of 6mm Hg was used. Water uptake approached the 5:1 ratio of water to $\overset{3}{P}-O-\overset{3}{P}$, and no hydrolysis of the P-O-P bond accompanied this. The following steps were observed in the hydration curve:- (20°C)

$$\begin{tikzcd}
H_4P_2O_5 \arrow[r] & H_4P_2O_5 0.2H_2O \arrow[r] & H_4P_2O_5H_2O \arrow[r] & H_4P_2O_5 2H_2O \arrow[d] \\
 & H_4P_2O_5 4.5H_2O & H_4P_2O_5 4H_2O \arrow[l] & (H_4P_2O_5 3H_2O) \arrow[l]
\end{tikzcd}$$

On raising the temperature this hydration water is lost again, details are given later.

It is of interest at this point to mention the growth of crystals from pyrophosphorous acid obtained by the Auger reaction (25). When the viscous reaction product was left to stand in a vacuum desiccator over a period of two years it was found that crystals were formed. Potassium hydroxide and phosphorus pentoxide were also present in the desiccator, as Auger describes. The crystals obtained were analysed by the ceriometric, pH titration, chromatographic and thermogravimetric techniques comparing the results with the behaviour of phosphorous acid and pyrophosphorous acid. All these techniques suggested that the material was simply ortho phosphorous acid. Some of the viscous reaction product of the Auger reaction was exposed to the atmosphere for one day and the formation of crystals noted. It seemed then that the initially formed pyrophosphorous acid takes up moisture from its surroundings and crystals of phosphorous acid are formed. However this is out of line with the thermobalance experiments described above where the hydration levels are found without the breaking of the P-O-P bond. It should be noted that this is conclusively proved by the fact that on increasing the temperature with these hydrates ready loss of water takes place about 100°, a situation totally different from the thermobalance plot of phosphorous acid where little weight loss occurs on heating at atmospheric pressure, except at higher temperatures, then this is due to the oxidative breakdown of the P-H bonds. The infra-red spectrum of the crystalline product being discussed showed that it was totally different from ortho-phosphorous acid; the presence of a P-O-P bond was indicated. No water absorption frequency was present, although there was rather unusual absorption in the O-H stretching region. The crystals do not lose water on heating, yet the species present on dissolution of these crystals is undoubtedly phosphorous acid. It is tentatively suggested that these crystals contain a hydrated P-O-P bond, the thermobalance hydration experiment described giving rise to hydrated P-O bonds, $P-O^{-}\ H_3O$. The hydrated P-O-P bond can be written thus,



Data are presented in the experimental section.p. 134-136

The infra-red spectrum is given opposite page 136

The available data on the hydrolysis of the $\overset{3}{P}-O-\overset{3}{P}$ bond will now be discussed. It is evident that it shows the same pH dependence as the hydrolysis of the $\overset{5}{P}-O-\overset{5}{P}$ bond, displaying a minimum rate at neutral pH. However with the pyrophosphite case the rate is several orders of magnitude faster than for $\overset{5}{P}-O-\overset{5}{P}$ bond hydrolysis under comparable conditions. With pyrophosphate and other $\overset{5}{P}-O-\overset{5}{P}$ bonds the reaction is first order in contrast to the second order kinetics found for the $\overset{3}{P}-O-\overset{3}{P}$ bond hydrolysis. The rate also appears to be greater than that of the $\overset{3}{P}-O-\overset{5}{P}$ species; thus with the increasing oxidation number on the phosphorus atoms the "hydrolysis stability" of the P-O-P bond increases. In this context other types of systems might be discussed. Acetyl phosphate appears to hydrolyse at a much faster rate than pyrophosphate; the stability is however higher than pyrophosphite although of a similar magnitude. When the hydrolysis of the P-O-P bonds in the $(CF_3PO_2)_n$ polymers are considered, it is found that very rapid hydrolysis to the $H_2(CF_3PO_2\text{-O-}PO_2CF_3)$ acid takes place. It is customary to rationalise differences in the rates of hydrolysis of P-O-P bonds and P-O-C bonds in terms of bonding in the side oxygens of the P-O-P chain; differences in bond lengths obtained from X-ray structural studies demonstrate differences in the bonding between the phosphorus atoms and these oxygen atoms. Hydrolysis is considered to proceed by way of attack of a proton on the side oxygen atom. Such correlations as that hydrolysis of polyphosphates proceeds by way of hydrolysis of terminal P-O-P bonds only are used as supporting evidence for this type of hydrolysis mechanism, c.f.(41) p.437 and 695, (191). The hydrolysis mechanism in the alkaline region is perhaps somewhat different. There is some doubt as to whether the OH^- ion displays any catalytic effect on the reaction with polyphosphates, it appears to do so with metaphosphates. The normally obtained acceleration with polyphosphates is considered to be due to catalysis of the reaction by the cation present.

The alternative explanation of the phenomena observed appears to be attack on the P-O-P bond directly by the solvent. As outlined previously, p.79-81 , it is possible to compare the properties of the $\overset{3}{P}\text{-O-}\overset{3}{P}$ species as regards its low complexing activity, its ready hydrolysis and its inability to take part in extended $\overset{3}{P}-O-\overset{3}{P}-O-\overset{3}{P}$ etc. chains, as a function of the P-O-P bond itself rather than as a function of the P-O side groups.

The fact that hydrates of pyrophosphorous acid can be obtained where no P-O-P bond scission occurs, in a situation where the expected reaction velocity for the hydrolysis reaction should be at a maximum, suggests strongly that in the case of pyrophosphite at least, hydrolysis proceeds by way of interactions with the electrons in the P-O-P bond oxygens. It can be seen that the $P-O^-\ H_3O^+$ grouping which will be present in the hydrates of this strongly acidic compound does not lead to hydrolysis, whereas when a certain ratio of water to acid molecules is surpassed hydrolysis proceeds immediately. Such a circumstance can be seen to have the implication that P-O-P attack now becomes possible.

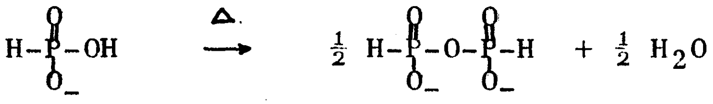
In biological systems, ease of hydrolysis of P-O-C bonds is accompanied by the presence of an unsaturated grouping on the carbon atom. This can be understood to lead to electronic "enrichment" of the P-O-P bond, c.f. p.34. Their ease of hydrolysis can be correlated with electron localisation in the P-O-M bond in a similar way to that proposed for the $\overset{3}{P}-O-\overset{3}{P}$ bond.

Kiehl and Moose, (89) considered the formation of $\overset{3}{P}-O-\overset{3}{P}$ bonds in solution as being conceivable. There appears to be no evidence for this however. Concentrated solutions of phosphites have been found to show no tendency for formation of P-O-P bonds when allowed to stand for long periods, nor when phosphorous acid is allowed to become liquid by the uptake of moisture and left to stand, do paper chromatograms of the product reveal the presence of anything other than ortho phosphite. The formation of P-O-P bonds will not be energetically favoured in the case of the phosphite and hydrogen phosphite anions. The activation energy for the $\overset{3}{P}-O-\overset{3}{P}$ bond forming and breaking reactions will be too high to allow equilibrium to be attained at room temperature.

Studies on the $\overset{3}{P}-O-\overset{3}{P}$ bond forming reaction show that this may proceed at a similar temperature to the loss of hydrate water as with $NaH(HPO_3)2.5H_2O$, see p.140-142 ; however in general two processes, loss of hydrate water and then loss of OH group water, can be distinguished by thermobalance plots. In cases like this Na salt, solid phase hydrates containing P-O-P bonds exist in the product at appropriate temperatures. This state of affairs is similar to the hydration of pyrophosphorous acid discussed earlier. In the polyphosphate field several examples of this type of phenomenon have also been found, pyrolysis reactions giving initially hydrated condensed phosphates. This demonstrates the irreversible nature of the P-O-P bond forming reaction, and the kinetic barrier to bond hydrolysis.

(ii) The Formation of $\overset{3}{P}$-O-$\overset{3}{P}$ Bonds

Pyrophosphites were first obtained by Amat, (21), using the thermal P-O-P bond forming reaction of hydrogen phosphites,



$$H-\overset{O}{\underset{O^-}{P}}-OH \xrightarrow{\Delta} \tfrac{1}{2}\,H-\overset{O}{\underset{O^-}{P}}-O-\overset{O}{\underset{O^-}{P}}-H + \tfrac{1}{2}\,H_2O$$

This reaction is also well known in the phosphate series. The ease of elimination of water is related to the cation present, (14). This is valid for studies conducted with single salt phases, no dependence on the cation is found when different salts are treated with a chemical dehydrating agent however, (141).

A good example of the dependence of the reaction temperature and the nature of the products, in the phosphite series is to be found in the differences between pyrolysis reactions of NaH(HPO$_3$) and KH(HPO$_3$), c.f. (142). NaH(HPO$_3$) undergoes $\overset{3}{P}$-O-$\overset{3}{P}$ bond formation, the reaction being detectable at 140° and rapid at 160°. At 330° in air oxidative breakdown occurs, all P-H bonds in the still solid product are then oxidised, with a simultaneous oxygen up-take, water loss, and possibly some hydrogen and phosphine loss. Condensed phosphate types of products are produced. KH(HPO$_3$), on the other hand undergoes an oxidative breakdown reaction involving the P-H bonds at a similar temperature to the $\overset{3}{P}$-O-$\overset{3}{P}$ bond forming reaction. The oxidation process becomes rapid at 200°, while the formation of $\overset{3}{P}-O-\overset{3}{P}$ bonds is detectable at 150° although it does not proceed to completion at this temperature. At 200° $KH(HPO_3)$ is a liquid. It is probable that rearrangement reactions are favoured by the molten state. $NaH(HPO_3)$, as normally obtained has 2.5 hydrate water molecules; on heating this phase, the solid first melts, then, as the pyrophosphite is formed solidification occurs. When the infra-red spectra of $NaH(HPO_3)$ and $KH(HPO_3)$ are compared differences are found in the P-H and P-O absorption regions. With the sodium salt the main peak in the P-H absorption region is at 2404cm^{-1}. The bond strength of the P-H in the sodium salt is actually greater then than in the potassium salt. Differences can be seen to arise due to the variations in the polarising of the anion by the cation. Perhaps the most important physical difference between these two salts is the occurrence of liquid phases at different points. This may control the reaction path on heating. This difference in the melting points could also arise from differences in the interaction between the cation and the hydrogen phosphite anion.

Thermobalance experiments were carried out to study effects on the $\overset{3}{P}-O-\overset{3}{P}$ bond forming reactions of the alkali metal, the alkaline earth, the ammonium and thallous ions. Hydrogen phosphites of the general formula $M^{+}H(HPO3)$ or $M^{2+}H_2(HPO_3)_2$, were prepared. Several other different types of acid phosphites may be obtained for most ions, of general formula $M^{+}_{x}H_{x+\underset{3}{2}y}(H\underset{3}{P}O_3)_{x+y}$ or $M^{2+}_{x}H_{2y}(HPO_3)_{x+y}$. Pyrolysis also leads to P-O-P bond being formed in these cases, and several salts of this type have been studied.

The results of the thermobalance experiments will now be discussed. In general three reactions are met with in these studies, loss of hydrate water, formation of $\overset{3}{P}$-O-$\overset{3}{P}$ bonds and the oxidation of the P-H bond. Some discussion of the techniques employed and the accuracy of the methods is appropriate here. Although the problem of obtaining an accurate temperature of the sample in the crucible by measuring the furnace temperature is well known, (192), it is considered that from a comparative point of view reaction temperatures can be obtained with an acuuracy of about 5° by using the standard Stanton thermobalance. Although, as has been mentioned, Rammelsberg, Wurtz and Rose studied the pyrolysis of numerous phosphites, the real nature of the pyrolysis products is still not understood. It must be admitted that whilst our work suggests that this field presents many new problems and types of product the full study of many reactions was not possible in a study such as this. The data presented, does however broadly outline the types of phenomena which occur.

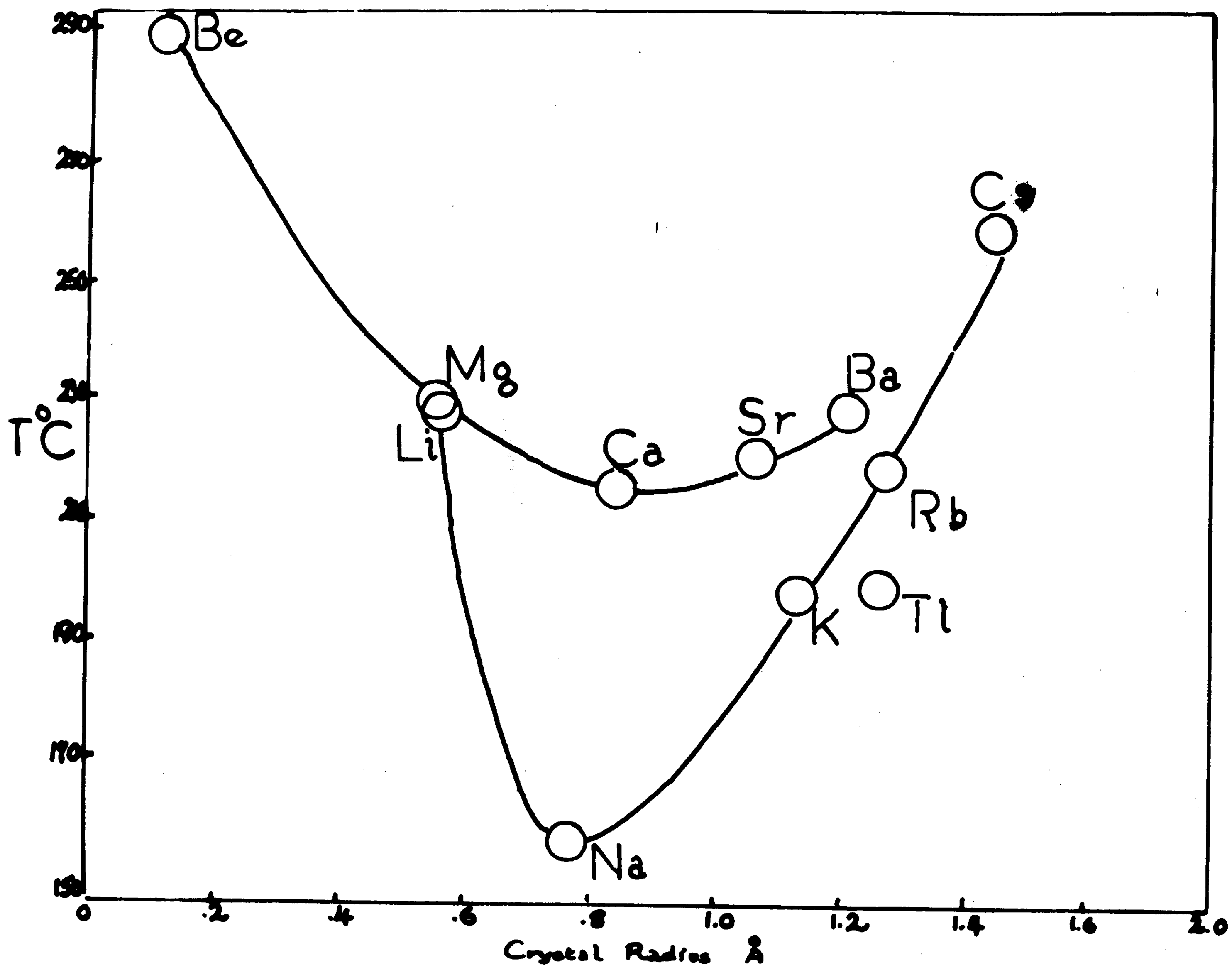

290
270
250
230
210
190
170
150
T°C
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
2.0
Crystal Radius Å
Be
Mg
Li
Ca
Sr
Ba
Cs
Rb
K
Tl
Na

FIG. 3.

Discussion of the P-O-P bond forming reaction temperatures

For the series of salts $M^{+}H_2PO_3$, $M^{2+}(H_2PO_3)_2$, where M^{+} is Li, Na, K, Rb, Cs, Tl, and NH_4; M^{2+} is Be, Mg, Ca, Sr and Ba, a simple variation of the temperature at which the P-O-P forming reaction proceeds with appreciable velocity (this term is somewhat arbitrary but all the thermobalance curves can be treated in the same way) with the size of the cation is found, Fig. 3. Smooth curves can be drawn through the alkali metal and alkaline earth series of points. In both these series the minimum temperature at which the reaction occurs is found for the cations with radii around 1Å, Ca^{2+} and Na^{+}. It is interesting to note that the Li^{+} salt behaves similarly to the Mg^{2+} salt, the cations have similar sizes. The special position of the Be^{2+} is evident from the highly polarising nature of this small cation. Apart from the special effects of the very small cations on the reaction the general tendency is seen to be an increase in the temperature of the reaction with increasing size of the cation, this state of affairs is quite general when series of different salts are studied in this way, e.g. with the decomposition of various carbonates. In the present series to draw an analogy with the pyrolysis of hydrogen phosphates the increasing temperature of reaction from Ca-Ba and Na-Cs may be considered as being due to the decreasing polarising

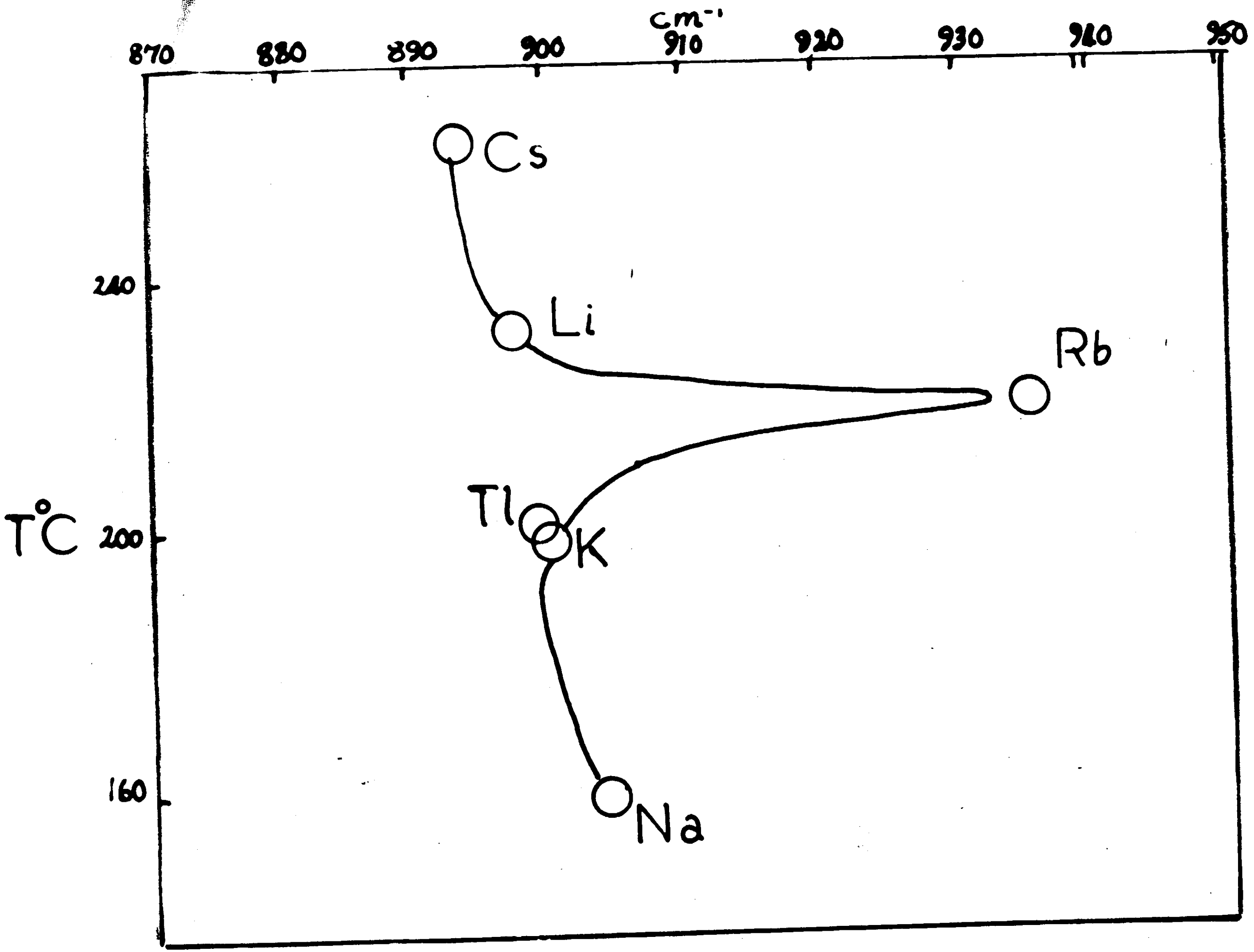

cm⁻¹
870
880
890
900
910
920
930
940
950
T°C
240
200
160
Cs
Li
Rb
Tl
K
Na

FIG
4a

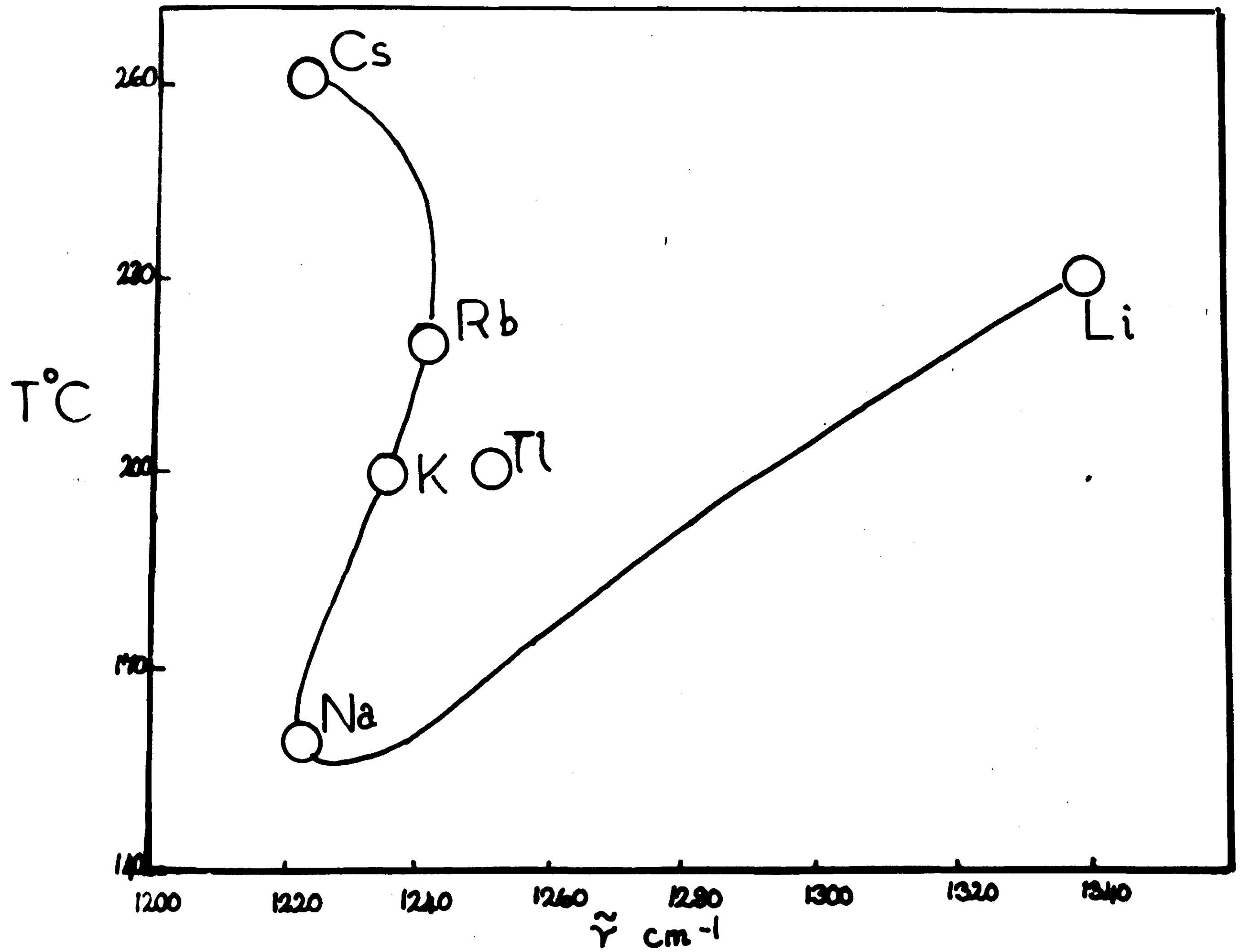
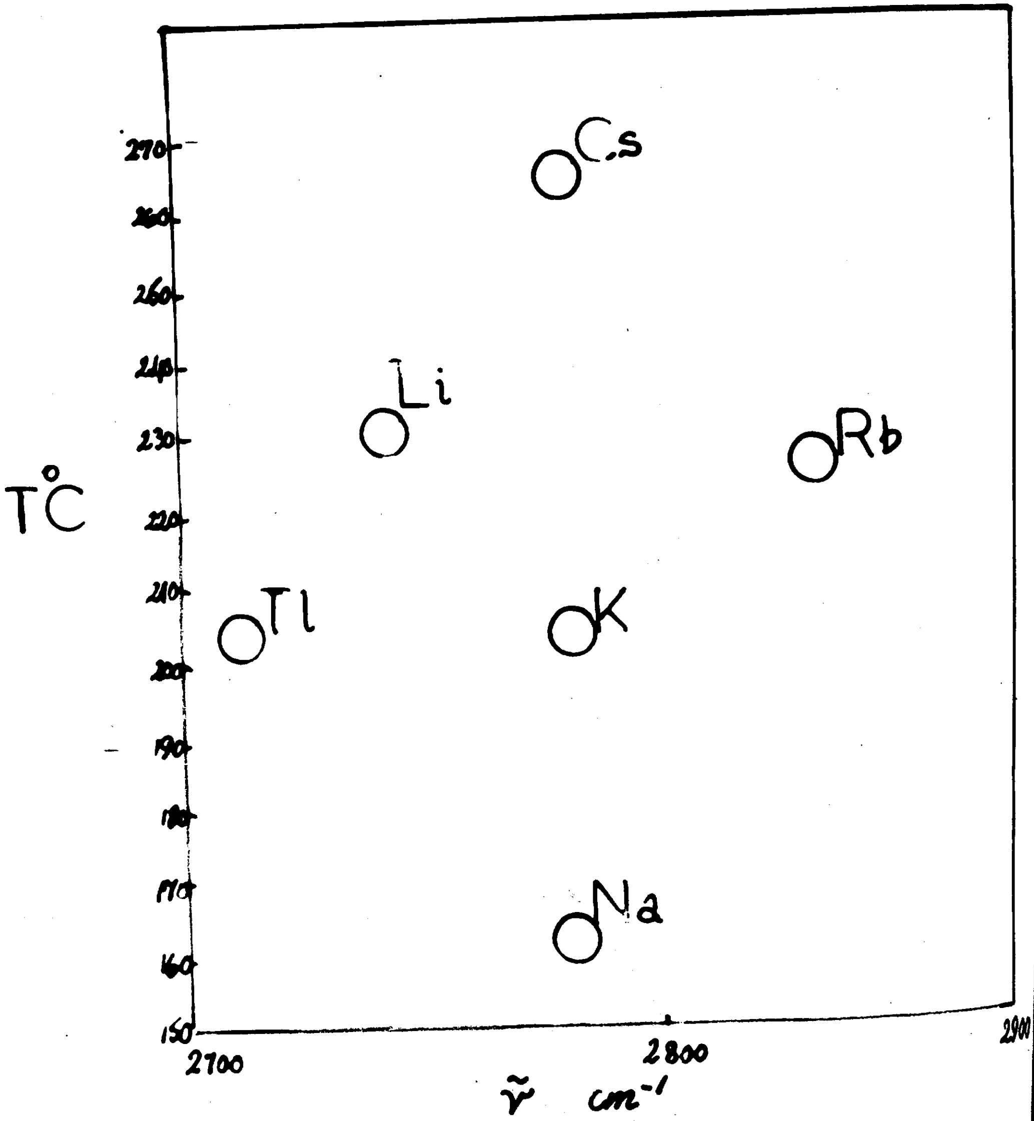

Cs
Rb
K
Tl
Na
Li
T°C
260
230
200
170
140
1200
1220
1240
1260
1280
1300
1320
1340
$\tilde{\nu}$ cm^{-1}

FIG. 4b.



270
250
260
240
230
220
210
200
190
180
170
160
150
T°C
Cs
Li
Rb
Tl
K
Na
2700
2800
2900
ν̃ cm⁻¹

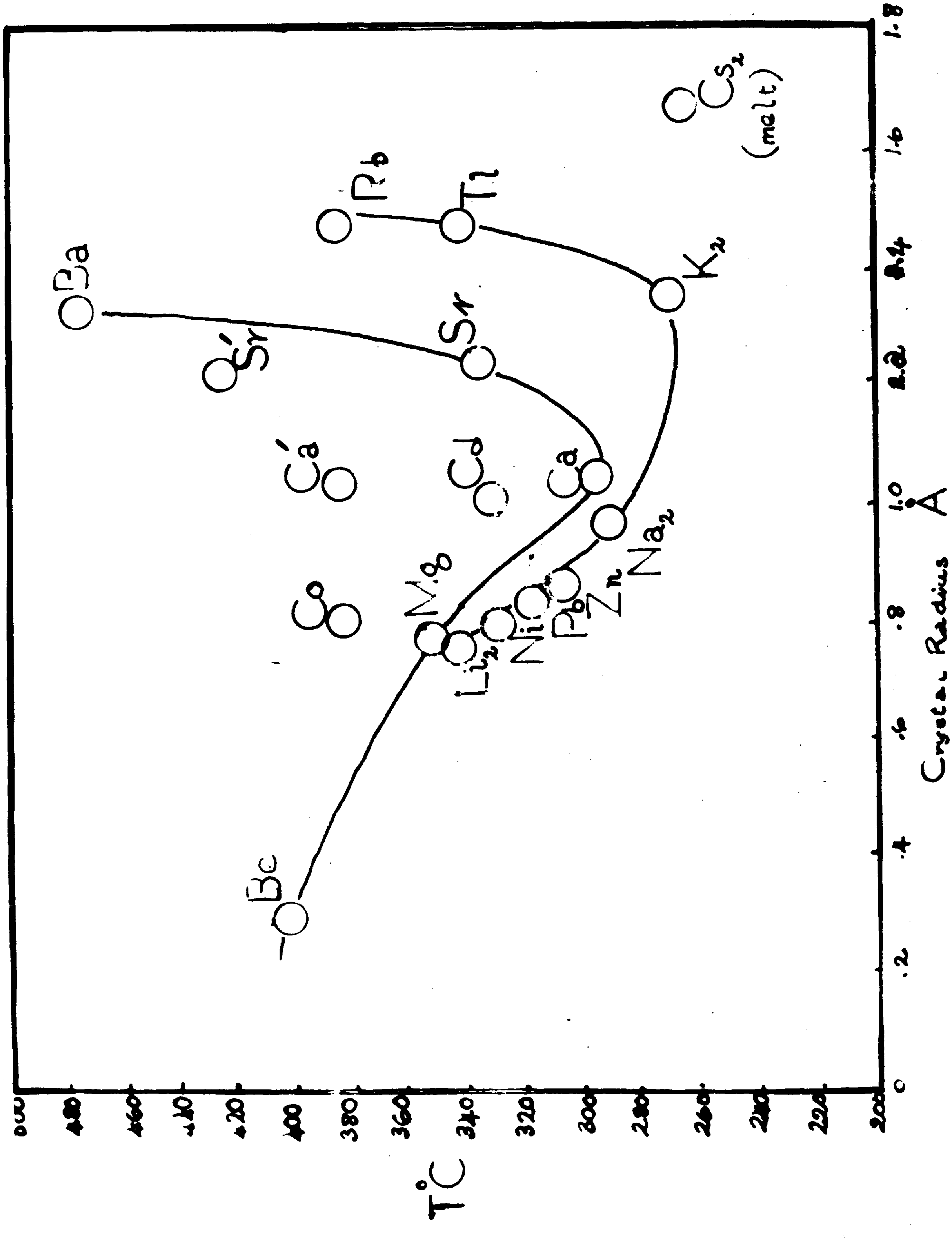
action in this sequence, although it must be admitted that rationalisations involving polarising actions of the cations should include the experimental observations for the cases where this becomes important, i.e. with Li+ and Be^{2+}. Specific interaction between the P-OH groups and the cation may be occurring here, preventing the approach of P-OH groups which will be necessary for the formation of P-O-P bonds.

At first sight when the characteristics of a solid phase reaction like this are presented in this way, it is surprising that smooth variation is apparent between different compounds; the variation of crystal structure here is an unknown factor. However the position of the cations relative to the phosphite unit cannot vary very much, the electrostatic attraction between opposite charges will lead to a proximity of the two units. Perhaps the differences between the smaller cations and the rest reflects a rather different crystal structure of the compounds in question. When infrared spectra of the salts are examined, correlations become possible between the ease of water elimination from P-OH groups and the frequency of the P-OH and PO-H vibrations. There is the problem here however that the position of the former vibration is not entirely unambiguous. The data are presented in graphical form, Fig, 4a and b, and c. There appears to be some tendency for the ease of reaction to be related to the ascribed P-OH frequency rather than the PO-H frequency, which may indicate that explanations of the differences in reactions based on varying polarisation of O-H bonds are in error.

Comparison of the variations in P-O-P bond forming temperatures noted with data on the oxidation of P-H bonds

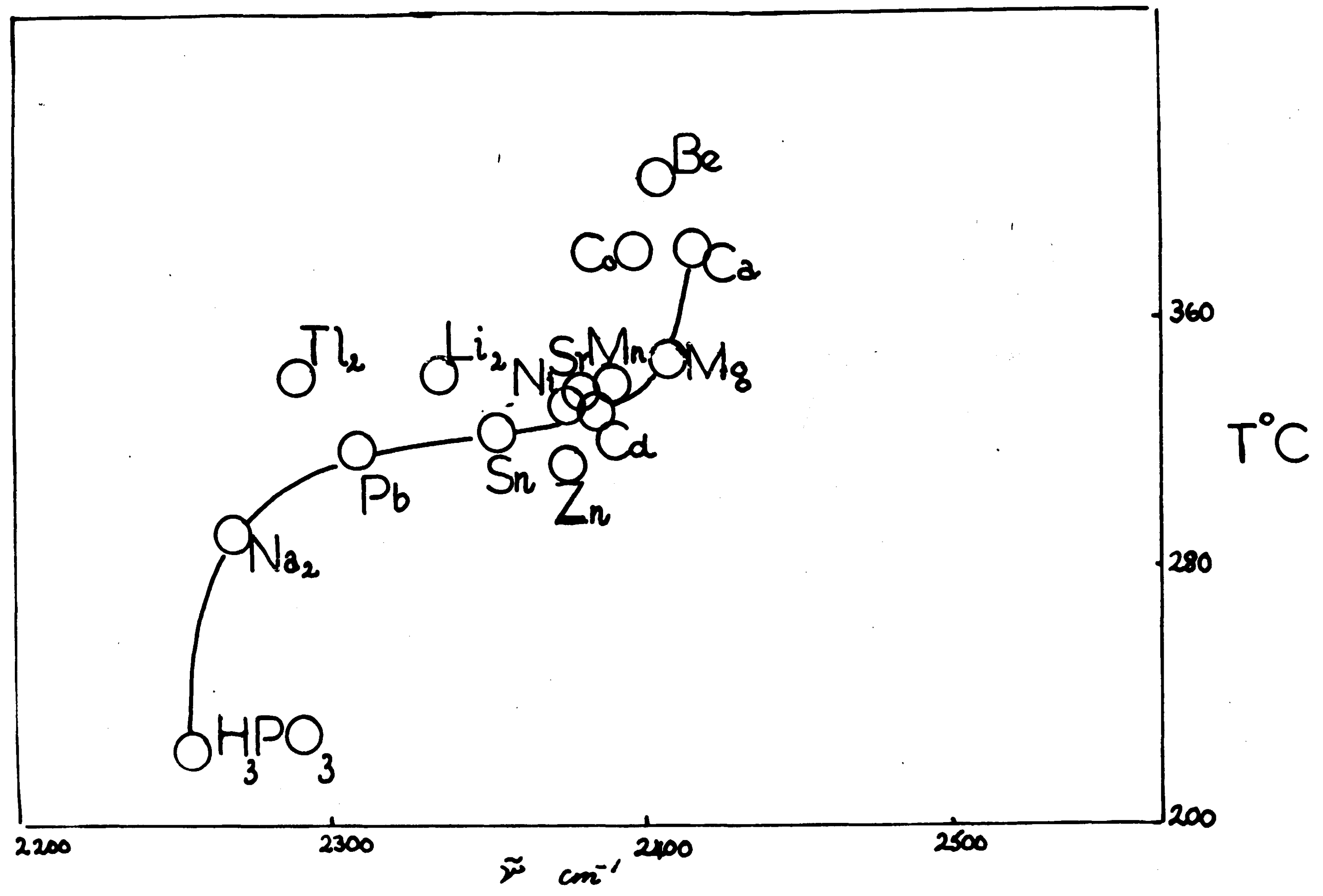
This has been studied for a series of normal phosphites using a wider range of cations than was employed with the P^{3}-O-P^{3} bond forming reactions just dealt with. Experimentally the temperature at which weight increase occurs is obtained from the thermobalance experiment (oxidation by atmospheric oxygen takes place at this point). As is discussed later, normal phosphites show no complicating factors to this type of study; the oxidation generally occurs at a rather sharply defined temperature. The same type of variation with the cation is noted as was found for the P-O-P bond forming reaction; when the temperature of the reaction is plotted against the ionic radius of the cation, minima are found in the curves for the alkali metal ions and the alkaline earth ions at Na^{+} and Ca^{2+}, as was found for the P-O-P bond forming reactions. However the ions Co(II), Mn(II), Cd^{2+}, Pb^{2+} Sn(II), Ni(II) and Zn^{2+} do not show any obvious variation in behaviour with ionic size on this plot, Fig. 5. A plot of the infra-red P-H absorption frequency against the temperature of breakdown of the P-H bond for these cases does however show reasonably smooth variation; those P-H bonds with higher

Fig. 5



T°C
500
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
Å
Crystal Radius
Be
Mg
Li2
Ni
Pb
Zn
Na2
Co
Ca'
Cd
Ca
Sr'
Sr
Ba
K2
Rb
Tl
Cs2
(melt)

FIG. 6.


Be
Co
Ca
Tl2
Li2
Sr
Mn
Ni
Mg
Cd
Sn
Zn
Pb
Na2
H3PO3
360
280
200
T°C
2200
2300
2400
2500
ν̃ cm⁻¹

bond energies oxidise at higher temperatures, Fig. 6. The P-H absorptions of some other species have been inserted for comparison.

Comparison of the variation in reaction temperature with cation size with data for the thermal removal of hydration water

Of the phosphites which have been studied by the thermogravimetric technique many salts contained water of hydration. Intermediate dehydration steps on the thermobalance plots were often found. A well known classical example of this is the dehydration curve of $CuSO_45H_2O$, where loss of 4 H_2O proceeds prior to the loss of the last water molecule; this has a structural cause, four of the water molecules are co-ordinated by the Cu(II) while the remaining one is associated with the anion. A similar state of affairs will probably be found in the cases where such marked differences of rate of dehydration for the different numbers of water molecules in the crystalline hydrate in the phosphite field occur. Thus the following sequences may be distinguished;

$$FeHPO_3IOH_2O \xrightarrow{\text{above } 50^\circ} FeHPO_3H_2O \xrightarrow{\text{above } 100^\circ} FeHPO_3$$

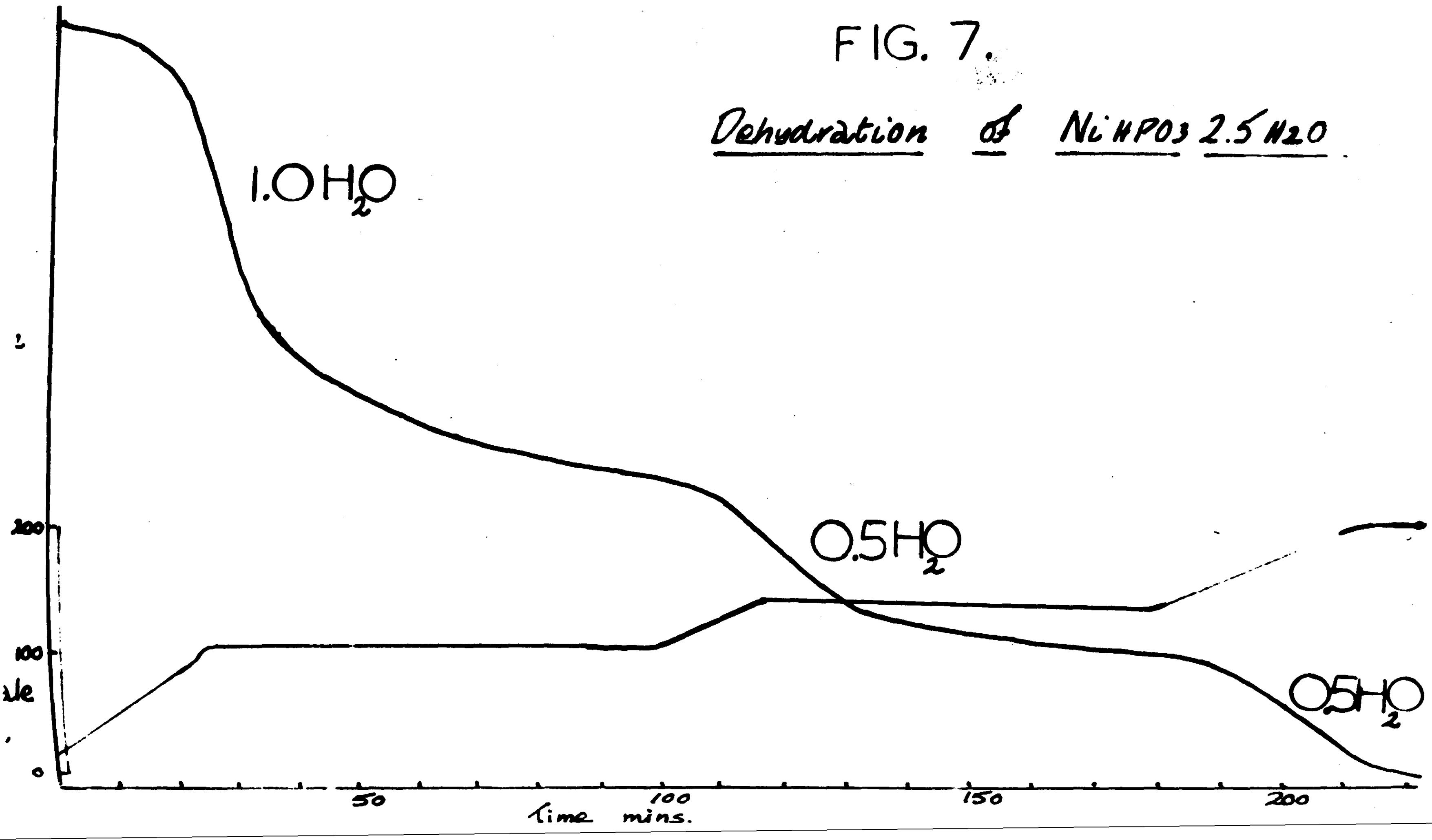
$$CoHPO_3I.5H_2O \xrightarrow{\text{to } 130^\circ} CoHPO_30.75H_2O \xrightarrow{250^\circ} CoHPO_3$$

$$\begin{tikzcd}
NiHPO_32.5H_2O \arrow[r, "45^\circ"] & NiHPO_3I.5H_2O \arrow[r, "125^\circ"] & NiHPO_3H_2O \arrow[d] \\
 & NiHPO_3 & NiHPO_30.5H_2O \arrow[l, "240^\circ"']
\end{tikzcd}$$

, Fig. 7.

FIG. 7.

Dehydration of NiHPO3 2.5H2O



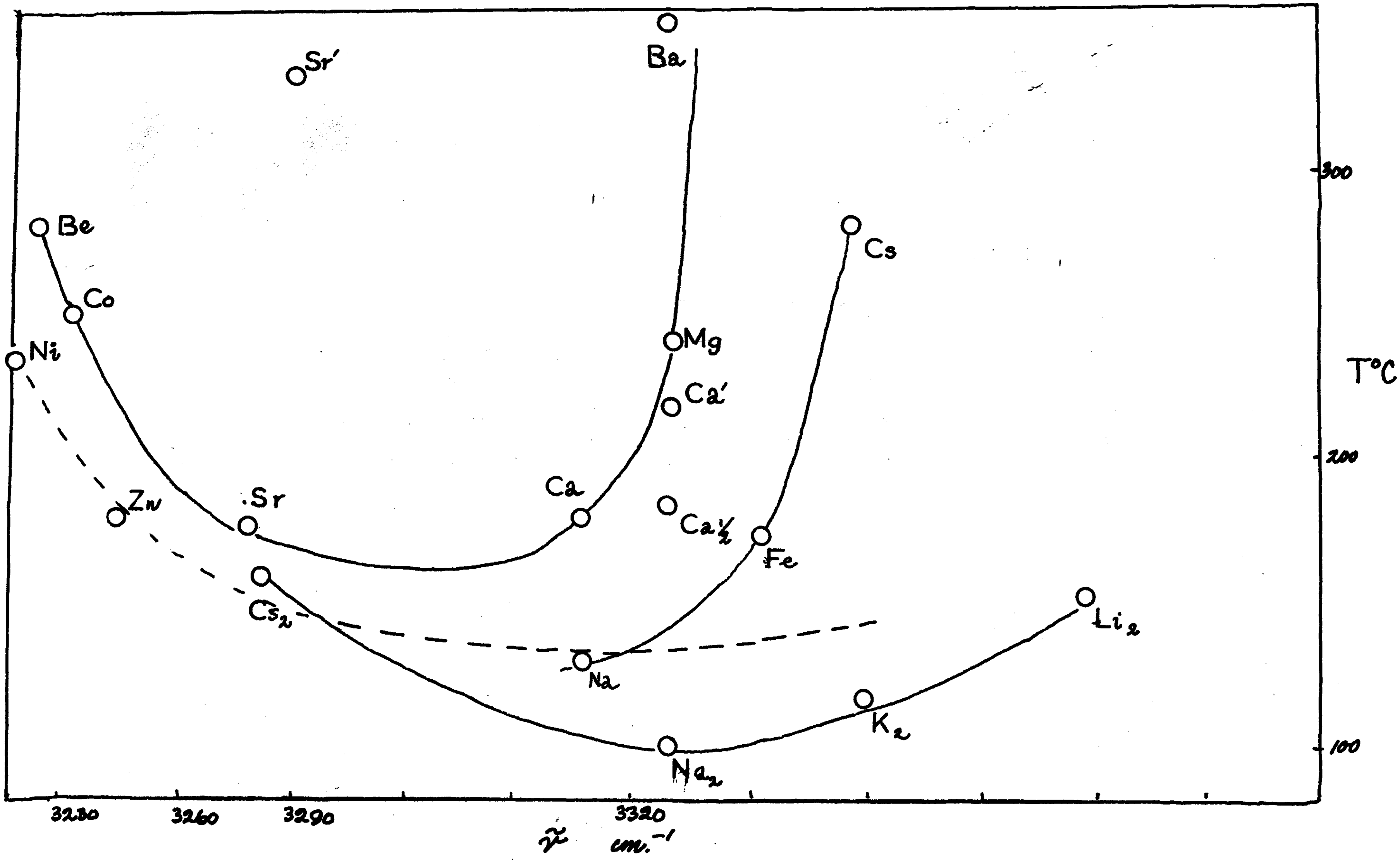
$ZnHPO_32H_2O \rightarrow (ZnHPO_3I.5H_2O) \rightarrow ZnHPO_30.5H_2O \xrightarrow{186^{o}} ZnHPO_3$
Changes in colour occur during the dehydration of the Fe(II), Co(II) and NI(II) salts.

Below are lists of the alkali metal andalkaline earth phosphites obtained in this investigation on hydrates.

$Li_2HPO_32H_2O$	$Li_2HPO_3H_2O$	$LiH(HPO_3)$	
$Na_2HPO_35H_2O$	$Na2HPO_3P.25H_2O$	$NaH(HPO_3)2.5H_2O$	$NaH(HPO_3)$ $I.5H_2O$
$K_2HPO_30.66H_2O$ (60°)		$KH(HPO_3)$	
Rb_2HPO_3		$RbH(HPO_3)$	
$Cs_2HPO_32.4H_2O$	$Cs_2HPO_32H_2O$	$CsH(HPO_3)H_2O$	
$BeHPO_3H_2O$		$BeH_2(HPO_3)_2I.5H_2O$	
$MgHPO_35H_2O$	$MgHPO_3H_2O$	$MgH_2(HPO_3)_25H_2O$	
$CaHPO_3H_2O$		$CaH_2(HPO_3)6H_2O$	
$SrHPO_3H_2O$		$SrH_2(HPO_3)_2$	
$BaHPO_3$		$BaH_2(HPO_3)_2I.5H_2O$	

Where two hydrates are shown these may be easily distinguished on the thermobalance curve. In addition to these markedly different degrees of hydration presumably due to different types of interaction between the water molecules and the ions present, further hydration levels may often be distinguished by the appearance of irregularities in the weight vs, time on the thermobalance plot. Detail of this and other relevant information is presented in the experimental section for all the salts which are discussed here.

FIG. 8.


Sr′
Ba
Be
Co
Ni
Mg
Ca′
Zn
.Sr
Ca
Ca½
Fe
Cs
Cs₂
Na
Li₂
K₂
Na₂
T°C
300
200
100
3230
3260
3290
3320
ν̃ cm.⁻¹

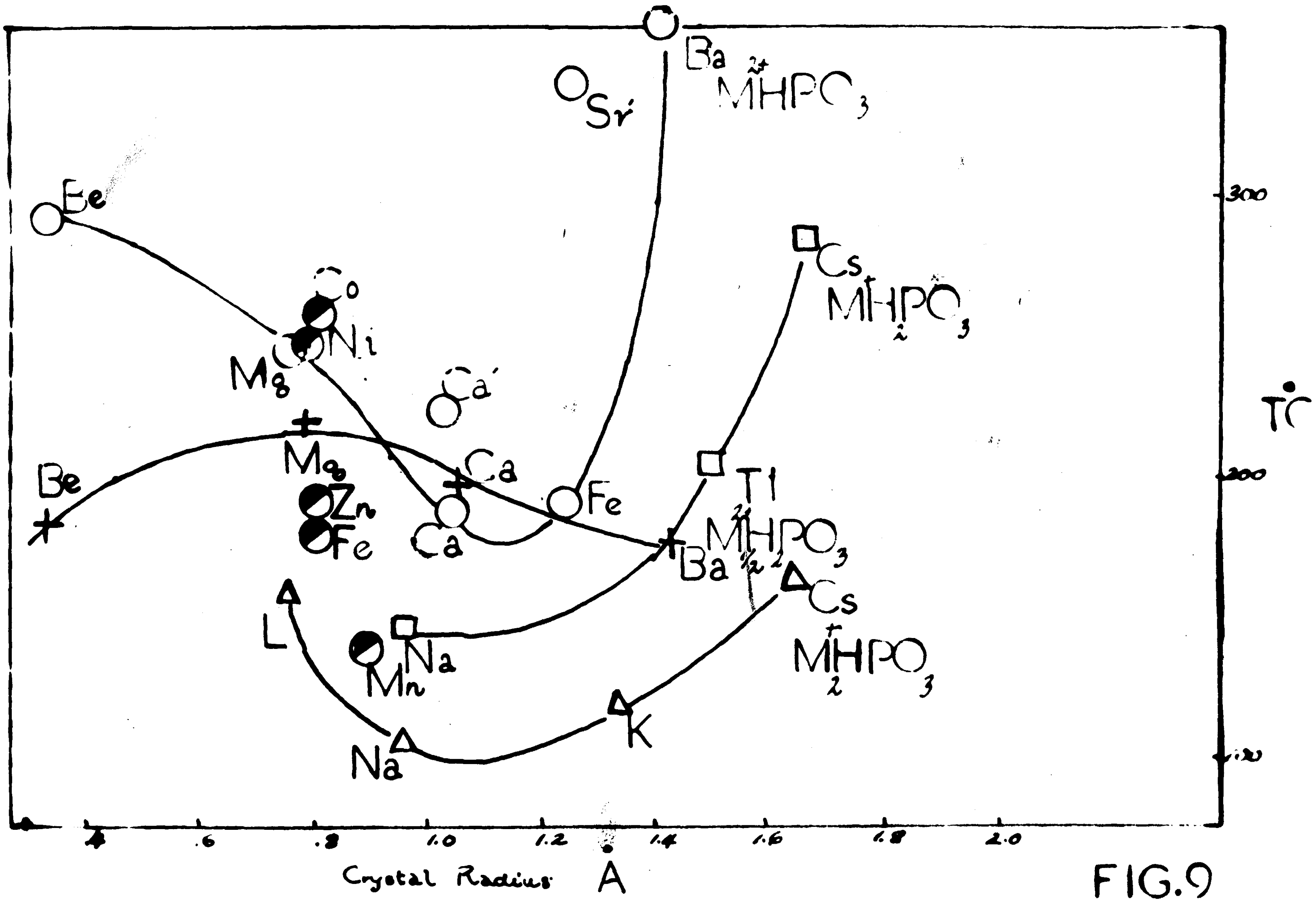

Ba
$M^{2+}HPO_3$
Sr
Be
Co
Ni
Mg
Ca
Be
Mg
Ca
Fe
Zn
Fe
Ca
Cs
$M^{+}H_2PO_3$
Tl
$M^{2+}H_{1/2}PO_3$
Ba
Cs
$M^{+}H_2PO_3$
L
Na
Mn
Na
K
300
200
100
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
Crystal Radius A
T°C

FIG.9

Comparison between the data which has been obtained and the ionic radii and infra-red spectral data can be made here in a similar way to the previous study of the correlations possible for the $\overset{3}{P}-O-\overset{3}{P}$ bond forming reactions. Similar trends are noted. The O-H stretching vibration in the infra-red is plotted against the temperature of the final dehydration stage of the hydrate in question, Fig. 8.

As the hydrate O-H frequency falls to lower wave number the hydrate water is more firmly bound, Co(II), Ni(II), and Be^{2+}, for example showing a greater interaction with the water than Na^+ does. This is due to the strong complexing activity of these ions, the first two because of covalent overlap of suitable orbitals and the Be^{2+} on account of its highly polarising character, Fig. 9. shows the temperature of dehydration plotted against the appropriate ionic radius. A similar type of variation in reaction temperature with the cation size is suggested by these results, to that found between the formation of $\overset{3}{P}-O-\overset{3}{P}$ bond reactions, although the relationship is not as simple here. Minima occur in the curves around cations with radii about I Å.

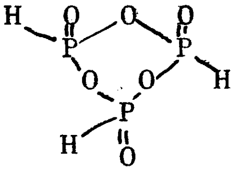
(III)

b) Some Experiments on Phosphorous Acid and Phosphites

(i) Vacuum Pyrolysis of Phosphorous Acid

Previous workers had reported the formation of condensed phosphorous acid units. "Meta phosphorous acid" was described as a product of the combustion of phosphine, (28), and studies on the kinetics of weight loss of H_3PO_3 heated in vacuum at 120° appeared to suggest the formation of several "poly or meta phosphorous acid" units, (193).

Experiments had been conducted to study the latter process. The main evidence for the formation of condensed phosphorous acid units had been the presence of breaks on the weight vs. time curve of the phosphorous acid heated under vacuum at 120°. Actual weight losses observed had approached the value required for the HPO_2 stoicheometry, breaks being observed at $\frac{1}{2}$ and $\frac{3}{4}$ H_2O/H_3PO_3 on the weight vs. time curve. It had also been observed that as the weight loss approached $\frac{3}{4}$ H_2O/H_3PO_3 some sublimation occurred. It seemed possible that volatile units like

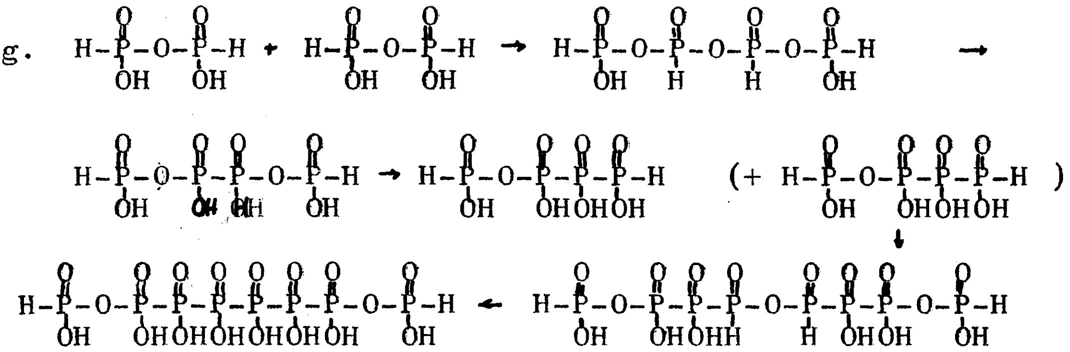


which contain no P-OH groups and hence would not be hydrogen bonded as the oxy-acids are, should sublime, (193).

In the present work samples of phosphorous acid, in platinum crucibles were heated in vacuum ($p = 10^{-4}$mm.Hg). As the temperature of the phosphorous acid was slowly increased in an isolated area of the vacuum system a sudden increase in pressure was found at the melting point of the acid. Equilibria, involving formation of water molecules form the condensation of ortho phosphorous acid units, occur much more easily in the liquid state than in the crystalline state. However, in this case true equilibria do not appear to be active, since on allowing the system to cool down to room temperature again, then reheating, much larger pressure increases occurred, indicating that P-O-P bonds, once formed, in this case rehydrate without P-O-P bond hydrolysis.

When the temperature is maintained at 120° for several hours the weight loss approaches the $\frac{1}{2}H_2O/H_3PO_3$, level. Beyond this level, contrary to the results of (193), no further condensed phosphorous acid are obtained. Heating pyrophosphorous acid (formed at this stage) at 120° induces an oxidative rearrangement. Slow evolution of phosphine and the build up of a red product was observed. This reaction is a slow one distinct from the oxidative breakdown of phosphorous or pyrophosphorous acids at higher temperatures, for which the equation $4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$ is usually given. This reaction is discussed later. It seems likely that in the present case the oxidative reaction may proceed through the intermediate formation of further condensed phosphorous acid units than the pyro acid,

e.g.



$$\mathrm{H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-H + H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-H \rightarrow H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{OH}{P}}-H \rightarrow}$$

$$\mathrm{H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{OH}{P}}-H \rightarrow H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-H \quad (+\ H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-H\ )\downarrow}$$

$$\mathrm{H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-H \leftarrow H-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-\overset{O}{\underset{OH}{P}}-\overset{O}{\underset{OH}{P}}-O-\overset{O}{\underset{OH}{P}}-H}$$

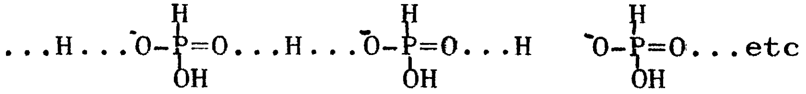
etc.

Coloured products may be produced by the formation of P-P bonds by the rearrangement of P-O-P bonds. Other rearrangements, possible involving radicals can be thought of as giving rise to gaseous phosphine. The red product is water in-soluble and may be isolated from the soluble reaction products, however treatment with water may cause decomposition of the red solid initially produced. It appears to be produced in different forms by such reactions and has a percentage of phosphorus always higher than phosphorous acid and may vary up to 95%. From spectral comparison of this type of product with red phosphorus the presence of P-H and P-O and P-O-P bonds in a general P-P-P-P-P-P type of structure seems likely. In the breakdown of pyrophosphorous acid the formation of variable amounts of gaseous hydrogen is also possible.

Although the bulk of the phosphorous acid decomposition products cannot be rationalised in terms of formation of colligative $\overset{3}{P}-O-\overset{3}{P}$ bonds, it remained possible that the sublimate observed could have been due to these types of compounds. Experiments were conducted with a view to obtaining sufficient quantities of this sublimate for analysis and other studies. It was found that the sublimation process was pressure dependent. Around 10^{-4} mm.Hg virtually no sublimation occurred, whereas when the pressure in the system was several mm. Hg considerable sublimation occurred on heating at 120^{o} for 1-2 days (the term "considerable" is relative only, the amount of sublimation under these conditions was about 3%). In the cases where sublimation occurred the dehydration of phosphorous acid had not proceeded beyond the pyrophosphorous acid stage, at least from the overall reaction point of view. Analysis of the sublimate showed that it was phosphorous acid. Where the experiment was conducted beyond the phosphine evolution stage in the hope of obtaining more sublimate, the products were less pure. In addition, in some cases where very little crystalline sublimate was obtained, traces of a liquid were observed. The results of acid-base and cerium (IV) oxidation analyses agreed with the phosphorous acid formulation. Initially the infra-red spectrum was thought to be somewhat different from a spectrum of phosphorous acid. However, this was found to be due to a descrepancy in the infra-red technique used. When a series of different amounts of phosphorous acid are mulled with the same amount of Nujol the spectra depend on the "concentration" of the acid in the Nujol. The nature of the variation suggests that some form of solution of phosphorous acid in Nujol occurs. Intermolecular hydrogen bonding between H_3PO_3 units which is dependent on concentration factors changes the relative intensities and moves the absorption frequency of several absorptions in the P-O region. When the spectra of the sublimate are interpreted, taking into account the concentration factors mentioned, no discrepancy is observed in the P-O region between these and the spectra of phosphorous acid.

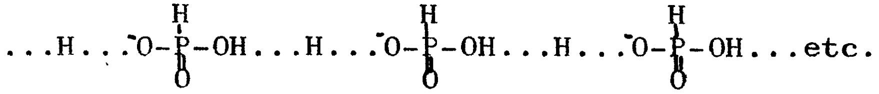
When observations were made to find when sublimation actually occurred in the process, it appeared that the rate ofsublimation decreased as the phosphorous acid content of the melt decreased. This also explains the dependence of the amount of sublimate obtained in a given experiment on the pressure in the system. At lower pressures the formation of pyrophosphorous acid and other reaction products is faster than at the higher pressures studied. The length of time for which sublimation of the phosphorous acid can occur is therefore greater.

Sublimation has not been observed for the other phosphorous oxy-acids. Perhaps with phosphorous acid special features are operating, e.g. the non-polar nature of the P-H bond allows the hydrogen bonding interaction to occur in a "linear" manner, viz.



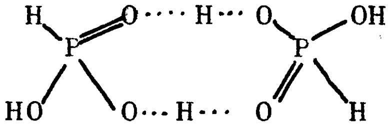
$$\ldots H\ldots{}^{-}O-\overset{H}{\underset{OH}{P}}=O\ldots H\ldots{}^{-}O-\overset{H}{\underset{OH}{P}}=O\ldots H\quad{}^{-}O-\overset{H}{\underset{OH}{P}}=O\ldots etc$$

or



$$\ldots H\ldots{}^{-}O-\overset{H}{\underset{O}{P}}-OH\ldots H\ldots{}^{-}O-\overset{H}{\underset{O}{P}}-OH\ldots H\ldots{}^{-}O-\overset{H}{\underset{O}{P}}-OH\ldots etc.$$

A distinction has been drawn between the strongly and weakly acidic P-OHs. In the crystal structure of phosphorous acid (95) each P=O forms two hydrogen bonds while each P-OH forms one such bond, no distinction between the two types of P-OH can be made. However the situation in the vapour phase might be quite different. It is expected that differences in hydrogen bonding may lead to small units in the vapour phase, c.f.

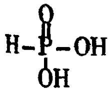
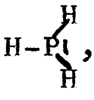


Pyrophosphorous acid, of similar molecular size has no "weakly ionised P-OHs". It does not sublime.

The volatile products of the vacuum pyrolysis of H_3PO_3 were examined in a vacuum system. The phosphine was shown to be pure by infra-red spectra and vapour density measurements. It might be added here that the pyrolysis of phosphorous acid is a convenient source of phosphine particularly for vacuum system work. Water produced in the experiments was condensed into a weighed finger. Substantial agreement was found between the weight loss; ceriometric oxidation and phosphine pressure measurements supporting the hypothesis that phosphine evolution and the resultant increase in oxidation equivalent of the residue takes place after the formation of pyrophosphorous acid at 120°. The results are presented in detail in the experimental section.

(ii) Pyrolysis of Phosphorous Acid at Atmospheric Pressure

Studies were conducted using a thermobalance with both nitrogen and air atmospheres. Some of the runs were conducted with controlled humidity conditions. Formation of pyrophosphorous acid in general cannot be obtained at atmospheric pressure other than in amounts of a few percent admixed with phosphorous acid. Two types of oxidation reduction rearrangements can be distinguished, a slow one and a fast one. The fast process occurs at a temperature which tends to be specific for the particular conditions employed, e.g. at 225° using a linear temperature increment in air. The slow process occurs below this temperature. It can be observed at temperatures above 140° when the phosphorous acid melt is held at constant temperature. The slow reaction would appear to occur by a reorganisation mechanism whereby gaseous phosphine is produced which escapes from the melt thereby reducing the P-H bond content of the overall composition. The fast reaction has the features of an explosive chain reaction. The rate of phosphine evolution increases rapidly. All P-H bonds tend to be removed from the product as phosphine. Some evolution of gaseous hydrogen also occurs however.

There is an analogy between this oxidative breakdown of P-H bonds and the phenomena encountered in the oxidation of gaseous phosphine, which is known to proceed by a radical reaction and its explosive nature at certain pressures of reacting gases displays the features of an explosive chain reaction. With the phosphorous acid case that a fast and a slow reaction occur in this way indicates perhaps that the presence of reaction intermediates capable of initiating an explosive reaction occurs below the fast reaction temperature, and that the explosive nature of the fast reaction is controlled by the nature of these intermediates. When this explosive breakdown for a number of phosphites containing the P-OH group is compared it is found that the P-H absorption frequency is often directly related to the temperature at which the reaction occurs, as has already been discussed. This suggests that, since the P-H bond energy is related directly to the P-H stretching frequency, breaking of the P-H bond to form radicals is important in the process. There is no direct proof that radicals are present in the phosphorous acid melt, however it is a likely postulate. The rapid rearrangement of  $\mathrm{H{-}\overset{O}{\underset{OH}{P}}{-}OH}$ to  $\mathrm{H{-}\overset{H}{\underset{H}{P}}}$, whereby three P-H bonds are formed on the same phosphorus atom is difficult to rationalise in any other way. The scheme

$$\begin{aligned} H_3PO_3 &\rightarrow HO\cdot + H_2PO_2\cdot \\ &\rightarrow H\cdot + H_2PO_3\cdot \\ &\rightarrow HO_2\cdot + H_2PO\cdot \\ H_2PO_2 &\rightarrow H\cdot + HPO_2\cdot \\ & OH\cdot + HPO\cdot \end{aligned}$$

$$H\cdot \quad + \quad H_3PO_3 \rightarrow OH\cdot \quad + \quad H_3PO_2 \rightarrow H\cdot \quad + \quad H2PO_2 \quad \text{etc.}$$

$$H\cdot \quad + \quad H_3PO_2 \rightarrow OH\cdot \quad + \quad H_3PO$$

$$H_3PO \rightarrow O\cdot \quad + \quad H_3P$$

$$H\cdot \quad + \quad OH\cdot \rightarrow H_2O$$

$$H_2PO_3\cdot + OH\cdot \rightarrow H_3PO_4$$

$$H_2PO_2\cdot + H_2PO_2\cdot \rightarrow H_4P_2O_4$$

$$H_2PO_3\cdot + H_2PO_3\cdot \rightarrow H_4P_2O_6$$

$$H_2PO_4\cdot + H_2PO_3 \rightarrow H_2P_2O_7$$

etc., which accounts for all the observations which have been made on the fast reaction, may be written. Experimentally the evolution of about $\frac{1}{2}$ H_2O / H_3PO_3, less than $\frac{1}{4}$ PH_3/ H_3PO_3 and some hydrogen is found during the fast reaction. The products present during the fast reaction are difficult to assess experimentally. Paper chromatography shows that there is a variety of condensed phosphate units present after the evolution of phosphine has come to an end, chiefly pyrophosphate and tri-polyphosphate. Ortho phosphate and ortho phosphite (possibly from $\overset{3}{P}-O-\overset{5}{P}$) as well as an unknown oxy-anion are present to a lesser extent. If the explosion step is cut short a reddish liquid is obtained, which on dissolution in water evolves phosphine. Samples removed after the explosion step showed no colour, nor is the evolution of phosphine now noted. Perhaps units like $(P-\overset{H}{\underset{H}{P}}{}^{\pm})_n$ as well as dissolved phosphine are present in the melt, formation of red products would indicate the presence of colligative P-P bonds. Studies of the ceriometric oxidation of the reaction products confirms the rapid drop in the amounts of oxidisable units present during the fast reaction. Some oxidisable material remains however largely correlatable as due to the presence of the unknown oxy-anion mentioned above. The presence of P-P bonds is indicated since P-H bonds have less pyrolysis stability.

No hypophosphite has been found in the pyrolysis products, the presence of the two P-H bonds make it less stable than phosphite to oxidative breakdown under these conditions. It is conceivable however that it may be a reaction intermediate in the radical scheme outlined above. It seems likely that phosphine will be built up through the medium of an unstable intermediate having two P-H bonds per phosphorus atom. This need not, of course be hypophosphite, other types of unit indicated above may be responsible. A series of pH titrations carried out on the products studied by chromatography confirms this as far as possible. The equivalent weight at the inflexion due to strongly ionised phosphorus (there being one for each phosphorus atom present in the product) agrees with the overall stoicheometry $H_4P_2O_7$ after the evolution of phosphine stage; the equation for the overall reaction can be written,

$$8H_3PO_3 \longrightarrow 3H_4P_2O_7 + 3H_2O + 2PH_3,$$

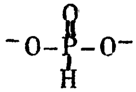
In addition about 10% of the P-H bonds originally present give rise to hydrogen.

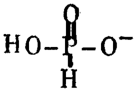
When the reaction under nitrogen is compared with that in air it is found that the fast reaction starts more gradually. This is due to the burning of phosphine in the furnace increasing the temperature. No temperature increase is observed under nitrogen. This shows that the acceleration of the reaction is not due to thermal effects. Sometimes two sections can be observed in the explosion step, the first approximating to the weight loss required for the formation of $\overset{3}{P}-O-\overset{3}{P}$ in the melt, but it is obvious that the oxidative breakdown reaction occurs as this progresses. When the nitrogen stream is specially dried by passing through silica gel and phosphorus pentoxide columns before passing through the furnace the weight loss curve proceeds slightly differently. This suggests that 7% pyrophosphorous acid forms in the melt before the oxidative breakdown. Again under this dry nitrogen the rate of the fast reaction does not increase quite as much as under moist nitrogen. Water vapour may play an integral part in the chain reaction occurring in the melt.

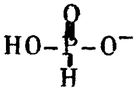
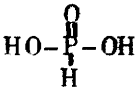
Apart from the studies undertaken to investigate the oxidative breakdown reaction the uptake of water by phosphorous acid may be studied. Phosphorous acid is hygroscopic at room temperature, up to 118° weight increase occurs in air. Under atmospheric conditions uptake of water occurs to about the $H_3PO_3I.5H_2O$ stoicheometry. The composition was found to vary from day to day and comparison of the weights of phosphorous acid hydrates from day to day may be used to obtain comparative humidity measurements.

(iii) Some Salts of Phosphorous Acid, (Phosphites)

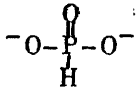
Three main types of phosphites may be distinguished,

normal phosphites, the  $^{-}O-\overset{O}{\underset{H}{P}}-O^{-}$ anion being present

hydrogen phosphites, the  $HO-\overset{O}{\underset{H}{P}}-O^{-}$ anion being present

acid phosphites, the  $HO-\overset{O}{\underset{H}{P}}-O^{-}$  $HO-\overset{O}{\underset{H}{P}}-OH$

species being present, in simple ratios.

Properties of the three classes are different, sometimes markedly different. The difference between the infrared absorptions of these units shown above may be used to distinguish which units are present. In general a major distinction exists between the properties of compounds where P-OH groups are present and those with only P-O^{-} present. Loss of water from hydroxyl groups leads to the formation of $\overset{3}{P}-O-\overset{3}{P}$ bonds. In addition the fast oxidation reduction reaction discussed for H_3PO_3 in general is also found to occur only when P-OH groups are present, although this reaction may be preceded by the $\overset{3}{P}-O-\overset{3}{P}$ bond forming reaction, if all P-OH bonds are transformed into $\overset{3}{P}-O-\overset{3}{P}$ bonds no oxidative breakdown involving the loss of phosphine will be found to occur. The controlling factor of the presence of P-OH groups for this to occur may be related to the possibility of the formation of radicals; OH radicals can be formed by the breaking of the P-OH bond. Another type of reaction is found with the  $^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O^{-}$ anion. Oxidative breakdown now involves the formation of hydrogen, phosphine being only a minor product. The thermal reactions of acid phosphites can be interpreted in terms of the different units, phosphorous acid and hydrogen phosphite anion, present. In the molten state these salts behave as intimate mixtures of the appropriate hydrogen phosphite and phosphorous acid. It appears that they owe their separate existence in the crystalline state to special hydrogen bonding phenomena, their infra-red spectra displaying the special feature of almost total absorption over the infra-red region.

The effect of the cation on the general properties of phosphites has already been outlined. A distinction can be drawn between the alkali metal, the alkaline earth and the transition metal salts. The special effect of the polarisation of the anion by cations like Li^+ and Be^{2+} is important.

Basic phosphites can be obtained from a variety of metal ions; on heating water loss from OH groups can be considered to build up M-O-M bonds in the product. Such basic phosphites are sometimes produced by the hydrolysis of hydrogen phosphites in solution, this seems to be the case for the salt $SrH_2(HPO_3)_2$.

Phosphites are frequently obtained from solution in a hydrated state. For a particular cation regularities are observed between the number of water molecules associated with the salt and the ratio of hydrogen to oxygen atoms present, excluding the hydrogens of the P-H bonds. Such crystalline hydrates present interesting dehydration curves on the thermobalance. Discussion has already been made of the well defined hydration states met with for a number of salts, p.97-99 . The kinetics of water loss from the solid state shows that there are three main types of reaction observed, viz, linear, logarithmic and hyperbolic. Hyperbolic curves, are found where large numbers of water molecules are associated with the phosphite. In these cases the hydrate water is loosely bound. This is analogous to zeolitic dehydration. Perhaps the most common situation, however, is the logarithmic dehydration. During a dehydration stage a uniform reaction is followed. In these cases it appears that interaction between the hydrate water and the ionic units present controls the rate of the reaction. During a single rate step this interaction will not change. Sometimes as in the curve of $NaH(HPO_3)2.5H_2O$ a logarithmic process changes to a linear one. The change in the kinetics of water loss will be related to the change of structure which occurs at this point. In the case mentioned the linear stage occurs towards the end of the dehydration stage and re-orientation of the phosphite units may occur c.f.

The alternative explanation of the phenomenon is that P-O-P bonds are formed alongside the dehydration of structure water. Both factors may be of importance. Sometimes dehydration may proceed at several well defined linear rates there being no stoicheometric correlation possible between the change of rate and the amount of dehydration which has occurred. In these cases, e.g. with $SrH_2(HPO_3)_2$, the phenomenon may be related to different hydrogen bonding arrangements being possible during the dehydration step. Arguments from such breaks in linear dehydration curves are open to question; the previous work on the dehydration of phosphorous acid is a case in point, (193).

When salts of phosphorous acid are obtained from solutions other than aqueous, similar solvent participation in the crystal structure is encountered. This is found for example with the salts obtainable from acetone, dimethyl formamide and methanol solutions. Experimental details will only be given for salts obtained from aqueous solutions in the present account.

The methods which have been used to prepare phosphites are straightforward. The appropriate metal hydroxide or carbonate is mixed with the required quantity of phosphorous acid solution and crystallisation allowed to proceed slowly. In some cases insoluble normal or basic salts precipitate from solution of different overall stoicheometry. In general the phosphite anion is stable under normal conditions to oxidation by atmospheric oxygen and no special precautions need to be taken to exclude air. A nitrogen atmosphere is required when dealing with easily oxidised metal ions like Fe(II).

Crystallisation of acid phosphites from solution is in general difficult. Often a viscous solution may not form crystals easily, unless seeded.

Although the experiments which are reported here have often been investigated in classical times, e.g. by Rammelsberg, (26), re-interpretation of these experiments in modern terms is often necessary. A recent investigation, the pyrolysis of $NaH(HPO_3)$ by Ebel using chromatography to investigate the products, and the other similar work, demonstrates the growing interest in the products obtained by the pyrolysis of phosphites. It seemed that by use of modern techniques of controlled pyrolysis and by using modern methods of analysis the nature of these pyrolysed phosphites should become clearer. Progress has been made in the solution of the problem. Thermobalance experiments were carried out on all products obtained. Analysis of the products by means of infra-red spectroscopy, paper chromatography, pH titrations and ceriometric analysis was carried out. The bonds present in the product may be obtained from the infra-red spectra, however the presence of P-P bonds cannot be ascertained by this method. The absence of P-H absorption in the infra-red accompanied by the presence of oxidisable material in ceriometric oxidation has been used to diagnose the presence of P-P bonds.

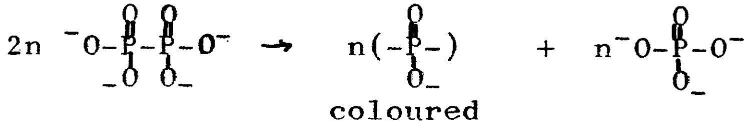
Since the ceriometric analytical method is important to the interpretation of the nature of the pyrolysis products a special study was undertaken of the oxidation of phosphite by cerium (IV) and the possibility of the oxidation of water by the cerium (IV) during the experiments. The effect of various types of cations on the ceriometric oxidation was also investigated. These results which enabled an accurate estimate of the amount of oxidisable phosphorus present in a sample to be made, will not be dealt with further here,(194).

The techniques of pH titration and paper chromatography can only be used if the products are soluble, or can be hydrolysed. Treating the pyrolysis product with different reagents sometimes allows the detection of different polymer fragments in solution, although the "structural" interpretation to be put on such data are perhaps doubtful.

In general the pyrolysis of phosphites leads to the formation of condensed phosphates in which there is to be found some P-P bonds but no P-H bonds. Above a certain temperature which depends on the nature of the anion being studied as well as on the cation, P-H bonds become energetically unfavourable, and reactions occur leading to the disappearance of these bonds. As discussed above phosphine is formed where P-OH bonds are also present.

When ammonium and substituted ammonium salts are considered, additional possibilities exist. Ammonia is evolved with the formation of P-OH bonds; in addition there is some evidence that rearrangements leading to structures like $\text{P-}\underset{\text{H}}{\text{N}}\text{-P}$ and P-NH_2 occur. The amount of P-P bonding in this system is negligible.

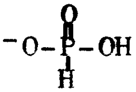
Products are frequently coloured and there seems to be a correlation between the ceriometric equivalent and the "amount of colour". Polyphosphates are known to be colourless and the presence of P-P bonds is indicated in these coloured products. This correlation was confirmed when it was found that the hypophosphate anion also gave rise to coloured products on heating, with little accompanying weight change, the scheme



$$2n\ {}^{-}\text{O-}\underset{{}^{-}\text{O}}{\overset{\text{O}}{\text{P}}}\text{-}\underset{\text{O}^{-}}{\overset{\text{O}}{\text{P}}}\text{-O}^{-} \rightarrow \underset{\text{coloured}}{n(\text{-}\underset{\text{O}^{-}}{\overset{\text{O}}{\text{P}}}\text{-})} + n\,{}^{-}\text{O-}\underset{\text{O}^{-}}{\overset{\text{O}}{\text{P}}}\text{-O}^{-}$$

may be written. The coloured product gave a yellow, (possibly colloidal) solution, **which** when studied by paper chromatography, gave a yellow zero spot, confirming the polymeric nature of the species. The tetra sodium salt was studied. This work will not be further dealt with here.

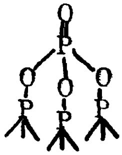
Variations of the oxidation temperatures etc. with the cation size have already been discussed, a comparison being drawn with $\overset{3}{\mathrm{P}}\text{-O-}\overset{3}{\mathrm{P}}$ formation, c.f.p. 96 et seq.

Studies have been undertaken of several acid salts particularly those of the alkali metals. The salts all behave similarly in the thermobalance experiments. On increasing the temperature loss of water is first found with the formation of $\overset{3}{\mathrm{P}}\text{-O-}\overset{3}{\mathrm{P}}$ bonds between the  $^{-}\text{O-}\underset{\mathrm{H}}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}\text{-OH}$ present, no condensation of the phosphorous acid units present takes place e.g. $NaH_3(HPO_3)_2$ and $KH_3(HPO_3)_2$ behave similarly. Minor differences are observed between the temperature of $\overset{3}{\mathrm{P}}\text{-O-}\overset{3}{\mathrm{P}}$ bond formation between these salts and the appropriate hydrogen phosphites, $\overset{3}{\mathrm{P}}\text{-O-}\overset{3}{\mathrm{P}}$ bond forming reactions for $NaH_3(HPO_3)$ and $NaH(HPO_3)$ take place at different temperatures, the former case at 40° more than for the latter.

c)

General Discussion

Of the compounds which can be formed between the elements, phosphorus, oxygen and hydrogen, two main types can be distinguished, viz. those with a tetra-co-ordinate phosphorus and those with tri-co-ordinate phosphorus. In the first class sp^3 hybridisation of the orbitals of phosphorus can be considered to give rise to a tetrahedrally co-ordinated phosphorus, bonding arising from the donation of oxygen 2p electrons into the vacant 3d energy levels of the phosphorus. With the tri-co-ordinate forms the 2s electrons of the phosphorus can be considered not to take part in bond formation; the oxidation state of the phosphorus is lower than with the compounds with tetra-co-ordinate forms. The types of unit which can be envisaged are considered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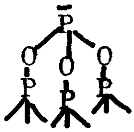
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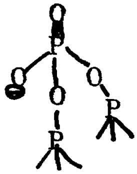
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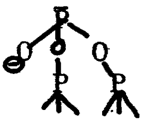
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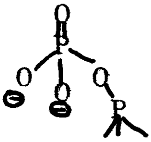
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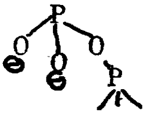
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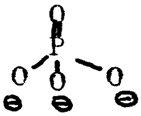
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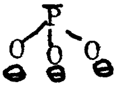
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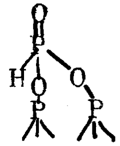
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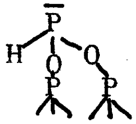
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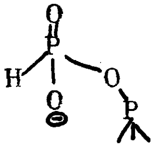
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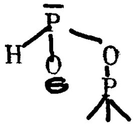
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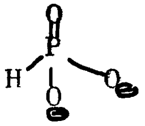
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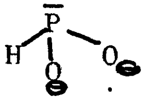
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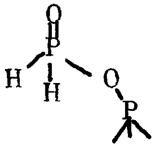
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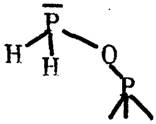
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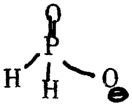
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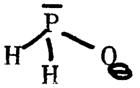
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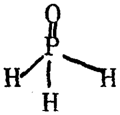
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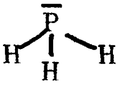
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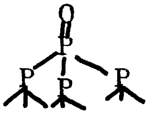
All P-H and P-O-P bonds can in theory be replaced by P-P bonds, for example three forms can be derived from structure 'a' by replacing the P-O-P bonds by P-P bonds up to the structure



The total number of forms which are theoretically possible for these two co-ordination numbers are written

a	a1	a2	a3	a*	a*1	a*2	a* 3
b	b1	b2		b*	b*1	b*2	
c	c1			c*	c*1		
d				d*			
e	e1	e2		e*	e*1	e*2	
f	f1			f*	f*1	(for an explanation	
g				g*		of terms, see below)	

h	h1	h^*	h^*1
i		i^*	
j		j^*	

The numbers after the form shown in this table refer to the number of P-O-P bonds which we are replacing by P-P bonds; when the replacement of P-H bonds by P-P bonds is considered we merely duplicate structures obtained by the replacement of P-O-P bonds. These forty forms are the basic units which can be formed, in theory, from phosphorus, oxygen and hydrogen. The number of chemical compounds which can be formed from these units, however, will be much larger, indeed it is infinite, since each phosphorus atom shown in the above structures can be "replaced" by any of the other structures having a P-P or a P-O-P bond. Of these forty basic structures about fourteen are known at present. About twice as many of the tetra-coordinate structures than the tri-co-ordinate structures are known.

In addition to these structures another series of tetra-co-ordinate structures can be derived from the tri-co-Ordinate structures by adding H^+ forming the phosphonium type of unit and additional forms are thus obtained. Also the addition of hypothetical units like $-P-O^+$ and $-P^+$ to the tri-co-ordinate forms can be considered to build up numerous basic structures, greatly extending the number theoretically possible. The interaction of two of the tri-co-ordinate forms by overlap of the orbitals of the lone pair electrons would lead to phosphorus - phosphorus π bonding, again increasing the number of possible forms.

It does not seem possible from a theoretical point of view to determine the relative possibilities of the various forms envisaged. Thermodynamically speaking, those forms with higher oxidation number on the phosphorus atom are more stable, however the kinetics factors remain unknown. From the present work it appears to be likely that where P-H bonds are present in the tetra-co-ordinate forms, if rearrangement can occur giving a non P-H bonded form, this will occur. The attempts to obtain polyphosphites by dehydration of ortho phosphorous acid were not successful since migration of the P-H and P-O-P bonds will lead to the formation of the $(-\overset{O}{\underset{O}{P}}-)_n$ unit. There may be a tendency for the formation of the $P-O^-$ ionised form where this is possible. When all the known oxy hydrogen phosphorus compounds are considered, c.f. the tables given opposite pages 31 and 32, it is seen that only those containing this $P-O^-$ bond have been characterised. Phosphorus oxides and phosphorus hydrides, are of course known where there is no ionised group on the phosphorus. The generalisation is valid for compounds containing all three elements. Although it must be admitted however that this is the case for compounds stable at room temperature the situation may be considerably different at lower temperatures. Attempts to prepare the form 'j' suggested that it was indeed formed at liquid air temperatures but rapidly rearranged, (148).

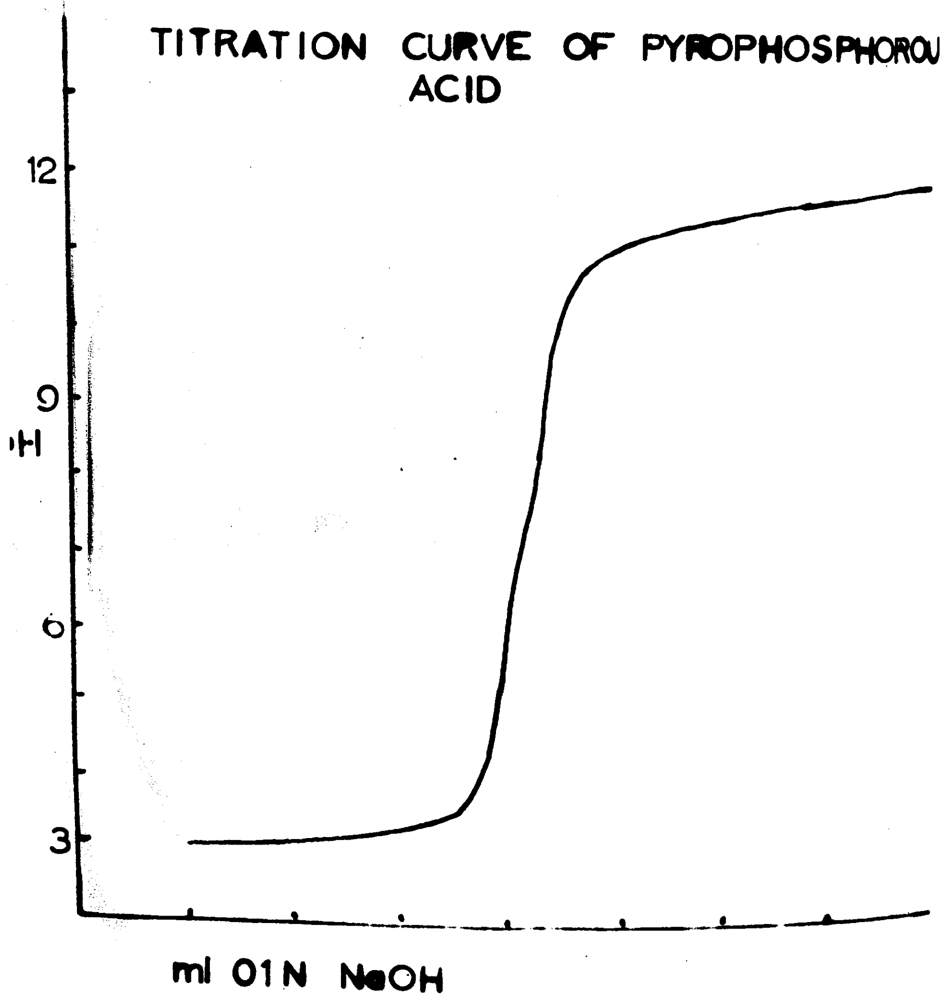
The question of the formation of tri-coordinate phosphorus species by rearrangement of the H-P=O structure has been greatly discussed in the literature, the question of "tautomerism" of the phosphite unit being considered. In the thermobalance experiments which have been carried out in the present study, whilst it must be admitted that the bulk of the results can be fully rationalised simply by the breakdown of P-H bonds at a certain temperature leading to the formation of P-O-P and P-P bonds, where the phosphorus is tetra-co-ordinated, the formation of tri-coordinate phosphorus is also possible. This appears to occur in the pyrloysis of Rb_2HPO_3, the product may correspond to the form 'c^x' in the above tabulation. As has been suggested by Simon, (185), the same type of reaction may occur in the case of $BaHPO_3$.

The experimental techniques which are at present available involving the solution of a sample, for example for paper chromatography, do not allow the isolation of material which is easily hydrolysed. It is expected that with the advent of new methods, overcoming this difficulty, the numbers of fundamental units which are known will increase.

(III) EXPERIMENTAL SECTION

FIG. 10

TITRATION CURVE OF PYROPHOSPHOROUS ACID



(III) Experimental Section

a)

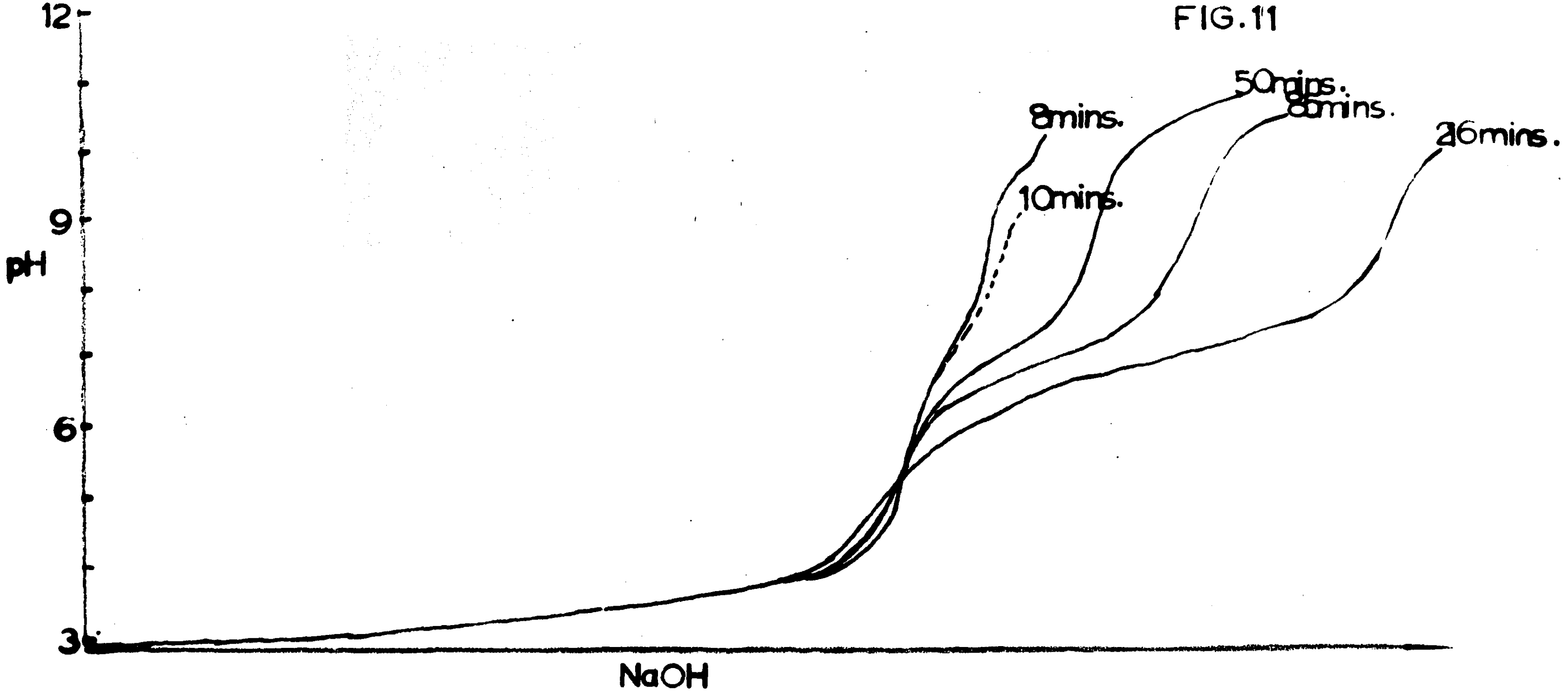
(i) The Hydrolysis of the Pyrophosphite Anion

Using an ion exchange column, working on the hydrogen cycle, employing Amberlite IR 120 resin, solutions of sodium pyrophosphite were exchanged. By titration of the acid solution using a pH meter (Cambridge) the titration curve for pyrophosphorous acid was obtained. When the acid solutions are allowed to stand hydrolysis occurs to phosphorous acid, and the amount of hydrolysis which has occurred may be obtained directly from the titration curve, by measuring the amount of weakly dissociated P-OH present. The ratio of the strongly to weakly dissociated P-OH groups may be determined after hydrolysis for various lengths of time.

Regeneration of the resin between experiments was carried out by slowly running 2N HCl through the column for about one hour and then washing it with water until free of Cl^-.

Expt. 1 34.22 mg. $Na_2H_2P_2O_5$ was dissolved in 150 ml. H_2O and passed rapidly through a 4 cm. column. 89% exchange occurred. The acid was titrated rapidly using the pH meter. The pH titration of the $H_4P_2O_5$ is shown, Fig.10. On attempting to obtain complete exchange of the sodium salt by passing through a longer column the effect of hydrolysis became more noticeable in the titration curve.

FIG.11



In the following experiments the following method of exchange was adhered to. The freshly prepared solution of $Na_2H_2P_2O_5$ was added to the top of a column containing 12 ml. resin, in 5 or 10 ml. amounts. This was run through at a drop rate of one drop per second. Care was taken always to keep the surface of the solution in the column above the resin surface. When half of the solution added had descended the column the tap was shut and 10 ml. water added to the top of the column. Elution was then continued at the same drop rate. When the liquid surface passed a mark above the resin top the time was noted, and taken as the start of the reaction. Washing was conducted by twice filling the space above the resin with water and dropping through at 5 drops/ second. 15 ml. water was added to the pH meter cell before the pyrophosphorous acid solution was run in. Exchange was virtually complete.

Expt. 2 5 ml. portions of a $2.846.10^{-2}$M $Na_2H_2P_2O_5$ freshly made up solution were exchanged. The pH of the eluted solutions was 3.2. After hydrolysis for various lengths of time the solutions were titrated. The termination of the hydrolysis reaction was taken at pH c.4.5. The curves are shown, Fig.11.

Expt. 3 10 ml. portions of a $3.522.10^{-2}$M solution of $Na_2H_2P_2O_5$, freshly made up were exchanged, the pH was 2.2.

Ratio 1st./2nd end point	Time of hydrolysis
1.088	37m. 35 s.
1.095	3m. 50 s.
1.136	8m. 20 s.
1.462	77m. 25 s.
1.860	21h.
2.012	24h.

Expt. 4 A freshly made up $4.63.10^{-2}$M $Na_2H_2P_2O_5$ solution was exchanged, 5 ml. portions being employed.

Ratio 1st./2nd e.p.	Time
1.082	2m. 30 s.
1.124	3m. 15 s.
1.133	6m. 20 s.
1.211	14m. 50 s.
1.436	58m. 5 s.
1.536	85m. 13 s.

Expt. 5 Exchange of 5 ml. portions of a 0.2388M $Na_2H_2P_2O_5$ solution was studied.

Ratio 1st./2nd e.p.	Time
1.219	36m. 50 s.
1.241	45m. 33 s.
1.226	44m. 45 s.
1.362	88m. 20 s.
1.442	122m. 40 s.

Expt. 6 A $1.93.10^{-2}$M solution of $Na_2H_2P_2O_5$ was taken in 5 ml. portions and 1 ml. 0.1 N HCl added with 50 ml. H_2O. The reaction was now stopped by adding 1 ml. 0.1 N NaOH solution, and then titrated.

Ratio 1st./2nd e.p.	Time
1.140	10m.
1.180	19m.
1.280	22.5m.
1.226	25m.
1.282	33m.
1.378	44m.
1.462	74.5m
1.498	85m.
2.046	24h.

Expt. 7 The alkaline hydrolysis of sodium pyrophosphite was studied. 1 ml. of 0.1N NaOH was added to a solution containing 5 ml. of a $3.46.10^{-2}M$ $Na_2H_2P_2O_5$ solution. The pH was 10.7. The reaction was stopped by adding 1 ml. 0.1N HCl solution.

Ratio 1st./2nd e.p.	Time
1.107	12m.
1.127	17m.
1.140	25m.
1.225	74m.
1.276	220m.
1.267	246m.
1.291	157m.

Several experiments were carried out on the hydrolysis of $Na_2H_2P_2O_5$ in this way. Frequently the results, on plotting against time showed maxima in the graphs. In these cases since no attempt was made to buffer the solution, pH changes accompanied hydrolysis. Perhaps the results are to be explaied as being due to small differences in pH in this range producing markedly different rates. Such differences in pH from solution to solution could arise by volume errors in pipetting the 1 ml. quantities of NaOH.

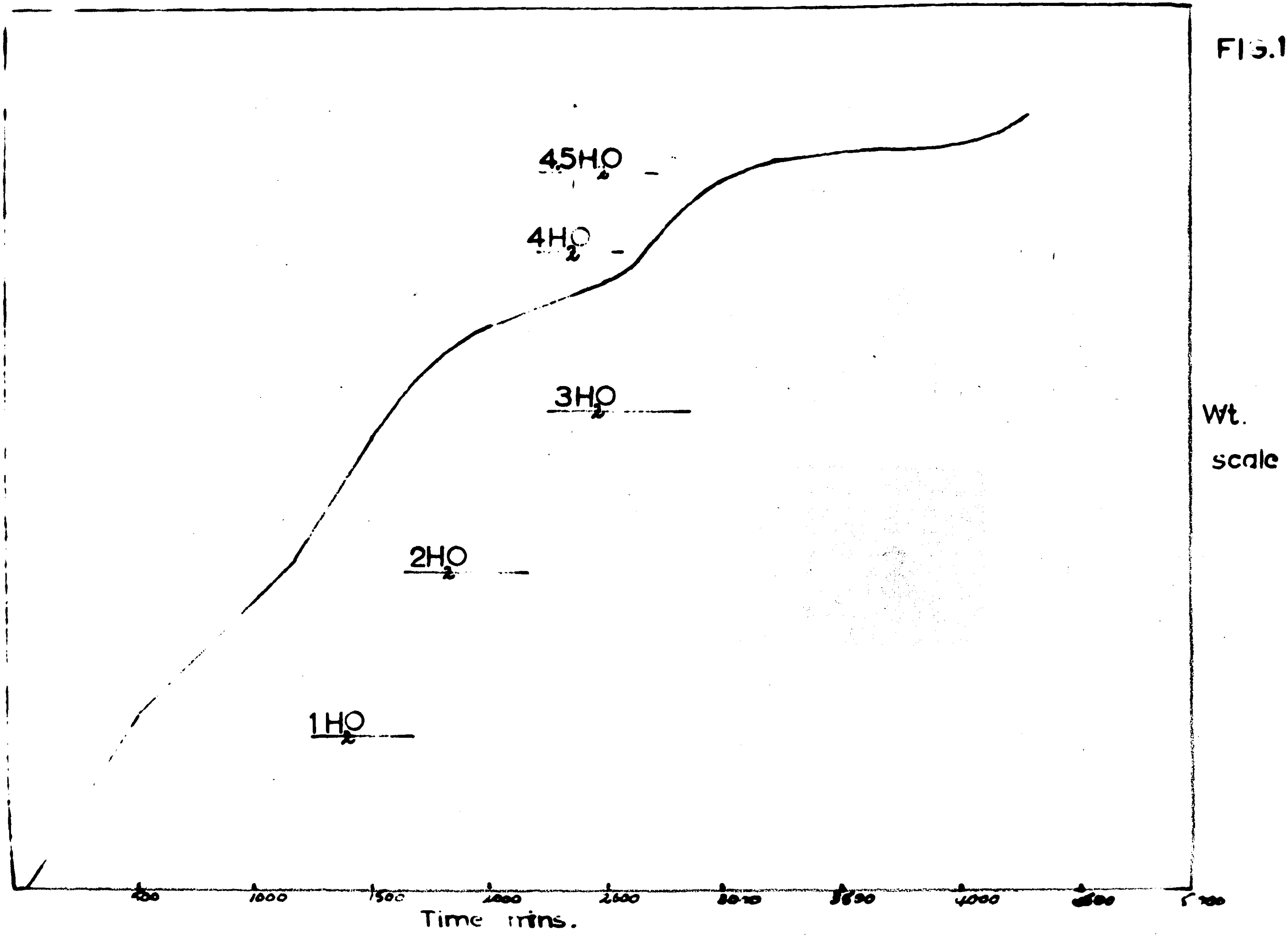
Expt. 8 The hydrolysis of the pyrophosphite bond in 4N sulphuric acid solution was studied to determine whether a simple hydrolysis to ortho phosphite was occurring in this case; the reaction would have been expected to be very rapid. $Na_2H_2P_2O_5$ solutions were added to 4N sulphuric acid solutions and hydrolysis allowed to proceed finally neutralising the sulphuric acid with a similar concentration of sodium hydroxide, then titrating with a 0.1 N NaOH solution. The accuracy of the results is now less.

Ratio 1st./2nd e.p.	Time
1.85	4.5 m.
2.06	14.5m.
2.00	23.7m.
2.15	30.0m.

Information has been gathered on the stability of the pyrophosphite anion in the pH range near 7 by observation of the intensity of the chromatographic spot due to the pyrophosphite anion on the basic chromatograms, as a solution containing pyrophosphite and various other phosphorus oxyanions was allowed to stand over several months. Day to day observations of the pyrophosphite present were made. The spot intensities were estimated visually by comparison with spots which did not change in intensity with time.

Expt. 9 In a solution containing $NaH(HPO_3)$, $8.24.10^{-3}$M $Na_4P_2O_7$ $5.53.10^{-3}$M KH_2PO_2 $1.25.10^{-2}$M, NaH_2PO_4 $6.5.10^{-3}$M and a pyrophosphite concentration of $6.13.10^{-3}$ the pyrophosphite concentration fell by a factor of 25% in 8 days. Complete

FIG.12


4.5H_2O
4H_2O
3H_2O
2H_2O
1H_2O
Wt.
scale
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Time mins.

hydrolysis had occurred by 14 weeks. The initial pH was 4.5 and as hydrolysis proceeded the hydrogen ion concentration increased.

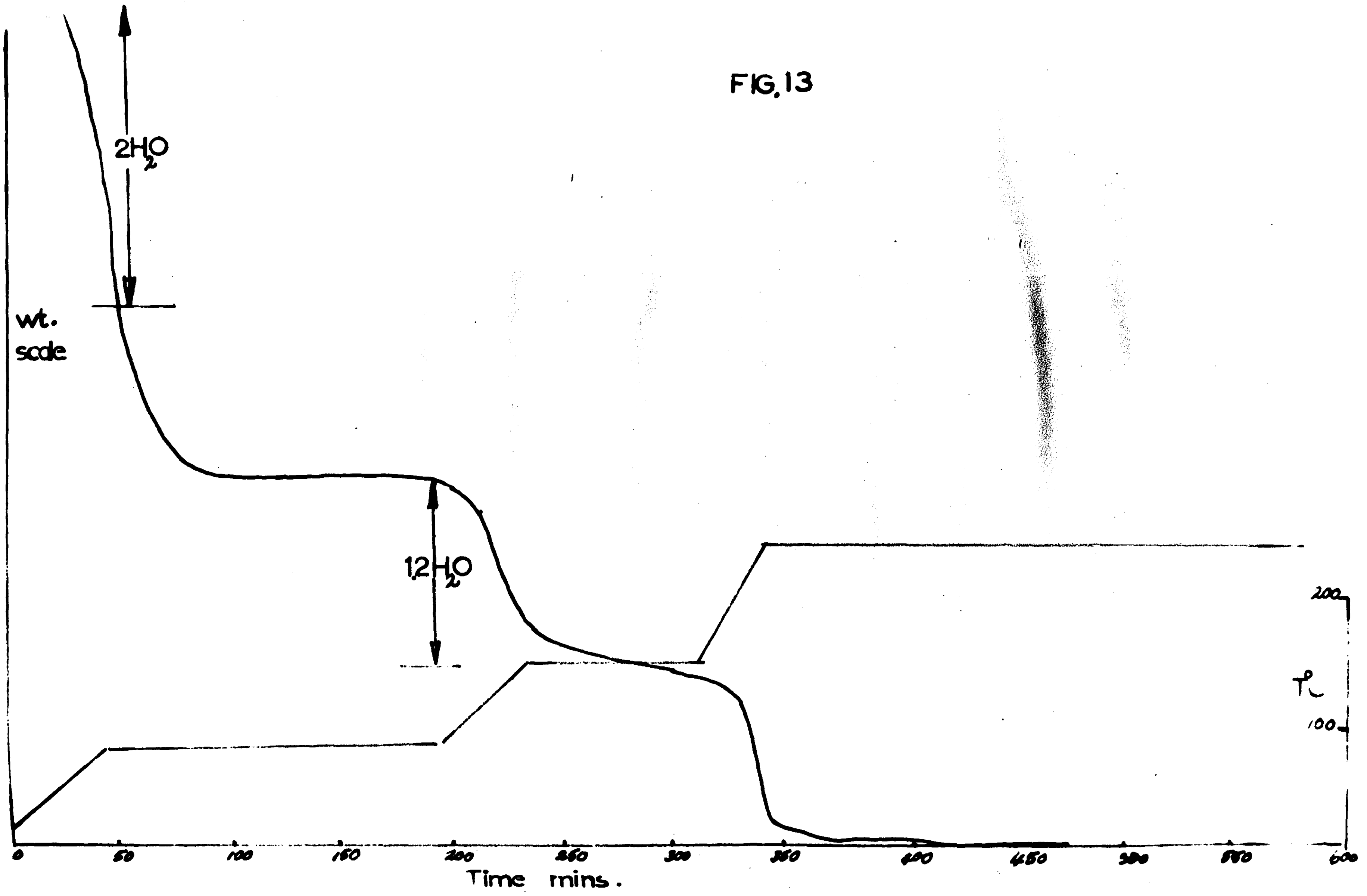
Expt. 10 In a solution with the following concentrations Na_2HPO_3 $4.2.10^{-2}$, $Na_4P_2O_7$, $2.2.10^{-2}M$, KH_2PO_2 $5.0.10^{-2}M$, Na_2HPO_4 $2.9.10^{-2}M$, $Na_4P_2O_6$ $1.9.10^{-2}M$, and a pyrophosphite concentration of $4.1.10^{-2}M$, the concentration of the pyrophosphite decreases by about 80% in 30 days. The initial pH was 9, and the reaction shows a minimum rate at pH close to 7, as observed from the little change in the pyrophosphite concentration at this level, as before the pH decreases as the hydrolysis proceeds. The pyrophosphite concentration decreased to virtually zero after 130 days.

The Uptake of Water by Pyrophosphorous Acid

Thermobalance and analytical experiments were conducted. The sample of pyrophosphorous acid used was obtained from vacuum dehydration of ortho phosphorous acid. Details of this method of preparing the acid have been dealt with recently by Ebel and Hossenlopp, (183).

A controlled humidity nitrogen stream, (6mm H_2O partial pressure) was flowed over the pyrophosphorous acid contained in a platinum crucible, at 20°, on a standard Stanton thermobalance with a silica muffle fitted to the furnace, c.f. Fig. 21b. p.173. Equilibrium wright was reached after 63 hours,

FIG.13



2H$_2$O
wt.
scale
12H$_2$O
200
T°C
100
0
50
100
150
200
250
300
350
400
450
500
550
600
Time mins.

the starting sample weight was 0.4986g. A number of linear stages were observed on the weight plot, the change in the rate between these stages was rather abrupt. The factor which varied during this process was the H_2O : $H_4P_2O_5$ ratio, and changes in this stoicheometry changes the rate of hydration.

Stages observed		Linear rate, mg./500 mins.	
a	10.6mg.	48	
b	50.6mg.	63	
c	25.8mg.	40	
d	19.6mg.	36	
e	45.9mg.	59	54.6mg=
f	36 mg.	varies	1 $H_2O/H_4P_2O_5$
g	21.2mg.	14	
h	41.6mg.	44	

This is shown graphically in Fig. 12.

Dehydration of the Hydrate

This was studied by raising the temperature above 20°, keeping moist nitrogen stream flowing through the furnace. This is shown graphically, Fig. 13. Weight loss was found to occur at relatively low temperatures. A discontinuity occurred at loss of 114.4 mg. equivalent to the loss of 2.09 H_2O, at about 100°; on maintaining at this temperature a further 65.7 mg. was lost; and on heating to 170° no weight change was found. Oxidative breakdown occurs at 230° by which time the mixture is about 39% H_3PO_3 (calculated assuming that the difference between the weight level and the starting weight, 20 mg. at 210°, was due to P-O-P bond hydrolysis, probably at the elevated temperature studied). The temperature increase required to remove the last of the hydration water may be such as to facilitate attack on the P-O-P bond. The "explosion" step at 230° showed a loss of 64.4mg. The temperature reading was confirmed by insertion of a thermometer. The weight was allowed to come to constancy at 270°, this required 85 mins.

47.67mg. of this final product was dissolved in 31.5 ml. of water and titrated using a pH meter, giving a curve with a number of inflexions.

Step height pH	pH e.p.	Equivalent weight
0.16	2.60	150.9
1.96	4.28	86.82
0.19	5.9	78.02
0.08	6.2	74.13
infl.	8.7	54.79
about 2.0	10.5	45.48

The curve shows one strong end point followed by a slow pH increase, indicative of numerous buffer levels, corresponding to many different K values. This is as expected for a mixture of condensed phosphoric acids. Since there is one strong OH/P in these condensed phosphoric acids it is possible to obtain the average molecular weight per phosphorus atom from the first strong OH dissociation (ignoring the lower inflexion for the moment), at pH 4.5. The equivalent weight at this point is 86.8. An equation for the explosive degradation of phosphorous acid can be set up viz.

$$4H_4P_2O_5 \rightarrow H_{10}P_6O_{20} + 2PH_3$$

the strong OH equivalent of the mixture of higher oxy-acids produced here is about 86.0. This equation requires 11.6% weight loss as phosphine. The experimental value was 12.9%. In actual fact it is expected that this equation will only be an approximation, in the present case also since some of the pyrophosphorous acid is hydrolysed to the ortho state. Consideration shows that the pyrophosphorous acid undergoes the "explosive" degradation reaction without the loss of water. Phosphorous acid on the other hand loses about $\frac{1}{2}$ H_2O/ H_3PO_3 in this reaction with the formation of P-O-P bonds. However with pyrophosphorous acid P-O-P bonds are already formed, rearrangement of the P-H bonds to produce condensed phosphoric acids and phosphine occurs. That no condensation of the phosphite unit beyond the pyrophosphite stage occurs, is borne out by these results; at least it can be said with certainty that any such further condensed $\overset{?}{P}$ units are totally different energetically from the pyro and ortho phosphorous acids.

A ceriometric analysis of this product showed that the remaining P-H, or P-P bonds present were of negligible amount, (e.w. about 2000).

The Crystals obtained from the Auger Reaction

On storage of the viscous reaction product of this reaction crystals were observed to grow. Initially the viscous liquid analyses as pyrophosphorous acid. The growth of crystals is accompanied by the uptake of water from the surroundings of the reaction product, when the procedure given by Auger,(25) is adhered to. Storage is carried out in a vacuum desiccator over potassium hydroxide and phosphorus pentoxide.

During the analytical studies which were carried out on these crystals all manipulations were carried out in a drybox where contact between the crystals and the air was necessary.

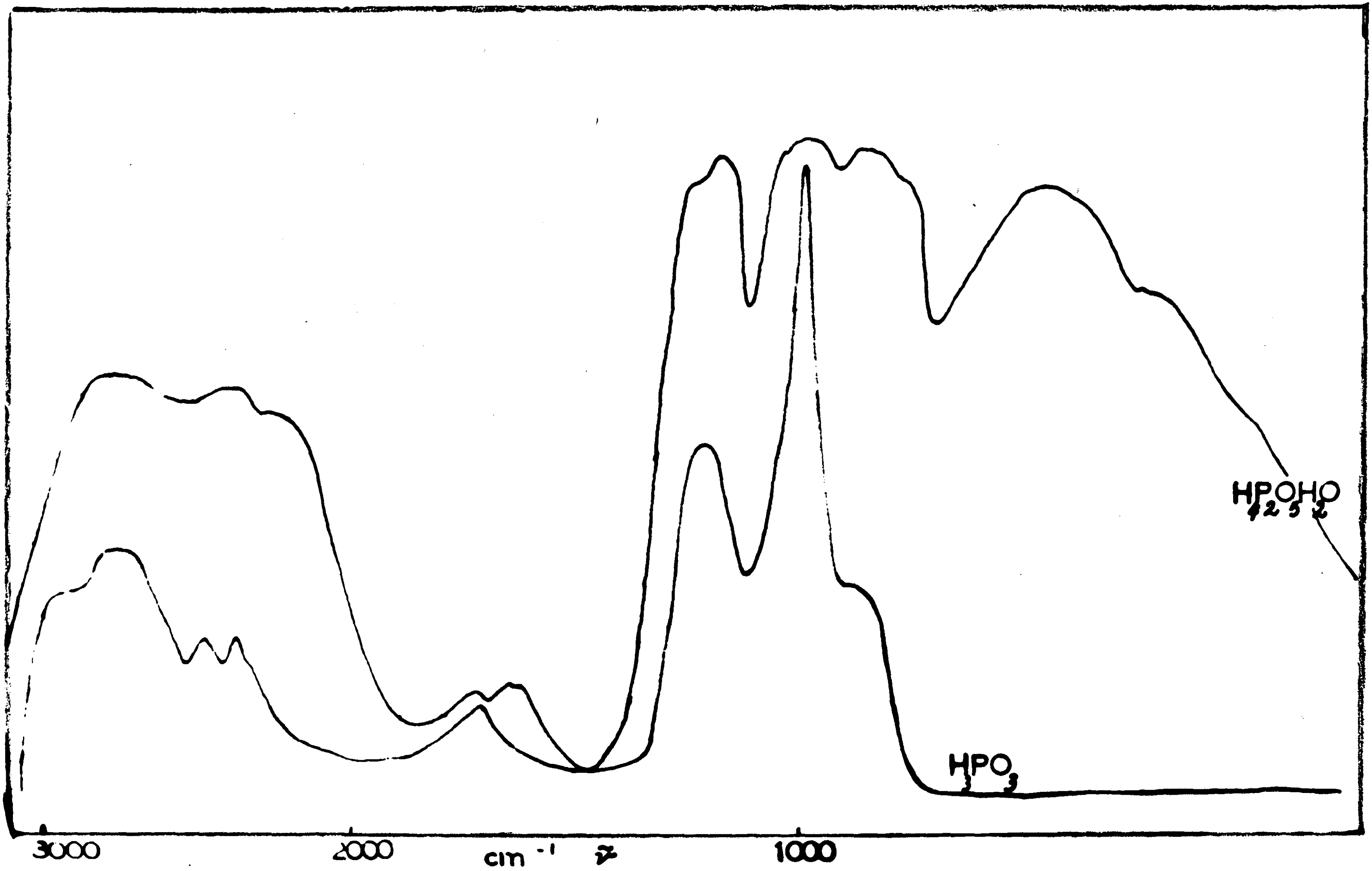
Ceriometric analysis gave an equivalent weight of 40.2±0.1, this was conducted by oxidising different weighed quantities of the crystals and then calculating the equivalent weight from the slope of the line obtained when the reacted cerium (IV) is plotted against the weight taken. This method of analysis gives the correct equivalent weight of 41.0 for phosphorous acid. Ceriometric oxidation of the mother liquor showed that the oxidation equivalent was 38.1. During dissolution in water crystals were formed at first indicating the presence of P-O-P bonds in the liquid. It has been observed in general that where pyrophosphorous acid dissolves in water it does so by the initial separation of a different phase, rationalised as being ortho-phosphorous acid. When the crystalline material being discussed is dissolved in water no complications are observed.

pH titrations were studied. The crystals give a titration curve very similar to that of phosphorous acid, e.w.pH 4.3,83.6; pH 7.8 e.w. 41.3. For phosphorous acid the values 82.0 and 41.0 are required. In the present case the e.w. calculated from the volume between the two end points was 81.2. The mother liquor gave the following values, pH,4.53 e.w. 76.1; pH 8.58 e.w. 40.2. The ratio of the end points was 1:1.893, indicating that 89% hydrolysis of $\overset{3}{P}$-O-$\overset{3}{P}$ had occurred on dissolution.

When a solution of the crystals was studied by paper chromatography the major anion present was seen to be phosphite. Small amounts of other species were also indicated, in particular hypophosphite and pyrophosphite.

When studied on the thermobalance, under atmospheric conditions, a similar pyrolysis plot to phosphorous acid was obtained. Initially on heating a weight increase occurred, decreasing again above 120^{o}. Little weight decrease took place before a large "explosion" step, where the evolution of phosphine took place, after which the melt exhibited a brownish colour. The weight loss up to 260^{o} was 18.5%. The explosive oxidation step became rapid at 230^{o}-240^{o}.

FIG14



Differences between this substance and phosphorous acid although apparently real, are not great.

From the results which are presented above it might be considered that the crystalline material is simply ortho phosphorous acid. Such impurities as are present can be considered to have arisen by the inclusion of mother liquor in the solid, the oxidation equivalent weight for example being slightly lower than that of phosphorous acid for this reason.

The infra-red spectrum of the crystals, in Nujol, is totally different from that of phosphorous acid. Although small differences are observed in spectra of phosphorous acid in Nujol, as has been mentioned, arising from "concentration" factors no rationalisation of the differences between the product being discussed and phosphorous acid are possible from this point of view. The presence of a P-O-P bond is indicated, Fig. 14. The presence of $H_4P_2O_5H_2O$, where the hydrate water is not easily removed by heating is indicated.

SECTIONS (III)a(ii), (III)b(i),(ii),(iii)

NOTE ON REAGENTS EMPLOYED

The thermobalance experiments were carried out using a variety of phosphites obtained by straightforward methods, employing solutions of phosphorous acid which had been standardised using the acid base titration, ceriometric and iodometric methods. Solids which were obtained were analysed by similar oxidation-reduction and acid base methods as well as analysis for elemental phosphorus, in certain cases.

Unless otherwise specified the crucibles used were of silica. No appreciable differences have been noted between thermobalance results obtained using platinum and silica crucibles, for the substances studied.

(III)

b)

(ii) The Formation of $\overset{3}{P}-O-\overset{3}{P}$ Bonds

$NaH(HPO_3).2.5H_2O$

Expt. 1 1.2298g. was studied on the thermobalance by raising the temperature until weight loss occurred then keeping the temperature constant until weight loss ceased at this temperature, as far as was practicable.

Stage	Wt. loss corresponding to,	Temp.
a	1.2 H_2O	95°
b	to 1.5 H_2O	100°
c	to 2.0 H_2O	120°, finished at 135°
d	to 0.65H_2O left/H_2PO_3	140°
e	to 0.0 H_2O " "	"
f	to $Na_2H_2P_2O_5$	finished at 240°

The stages a-d are first order reactions, half life values at the temperatures studied are, a, 3.2; b, 5.2; c, 5.2, d, 1.8, all hours. 10^{-1}. Process e becomes linear, i.e. zero order. The final process, the large scale formation of P-O-P bonds is not a simple first order process.

Expt. 2 0.1517g. was studied at a constant temperature. Again several breaks in the dehydration curve were noted. Dehydration was studied for 23 hours at 105°. In this time loss of 2.57 $H_2O/NaH(HPO_3).2.5H_2O$ occurred. Even at the low temperature used some P-O-P bond formation takes place on prolonged heating. After 2.5 hours a discontinuity was found at the $NaH(HPO_3)1.5H_2O$ hydration stage and several discontinuities were apparent after this at longer times of heating. It seems that an equilibrium between the ortho and pyrophosphite may occur in the solid phase. Generally with phosphites the P-O-P bonded form does not arise from the ortho anion until higher temperatures than are studied here are employed; however the special factor of prolonged heating times may be important here. With change in the environment of the P-OH groups the ease of P-O-P bond formation will change. The previous experiment showed that process e was linear. This suggests that at this stage a decrease occurs in the energy of water loss from the solid.

Expt. 3 3.0015g. was studied by raising the temperature slowly over the temperature range 100°-200°, at 1°/min. Only a little weight increase occurred up to 100°, ($0.097H_2O/(HPO_3)$ being lost). A discontinuity occurred at this temperature and rapid weight decrease took place, until the stoicheometry $NaH(HPO_3)0.085H_2O$ was reached. After this the rate of weight loss became slower, there being a slight discontinuity at the "anhydrous" stoicheometry. The temperature was maintained at 180°, at this point and the weight loss plot was observed to become linear.

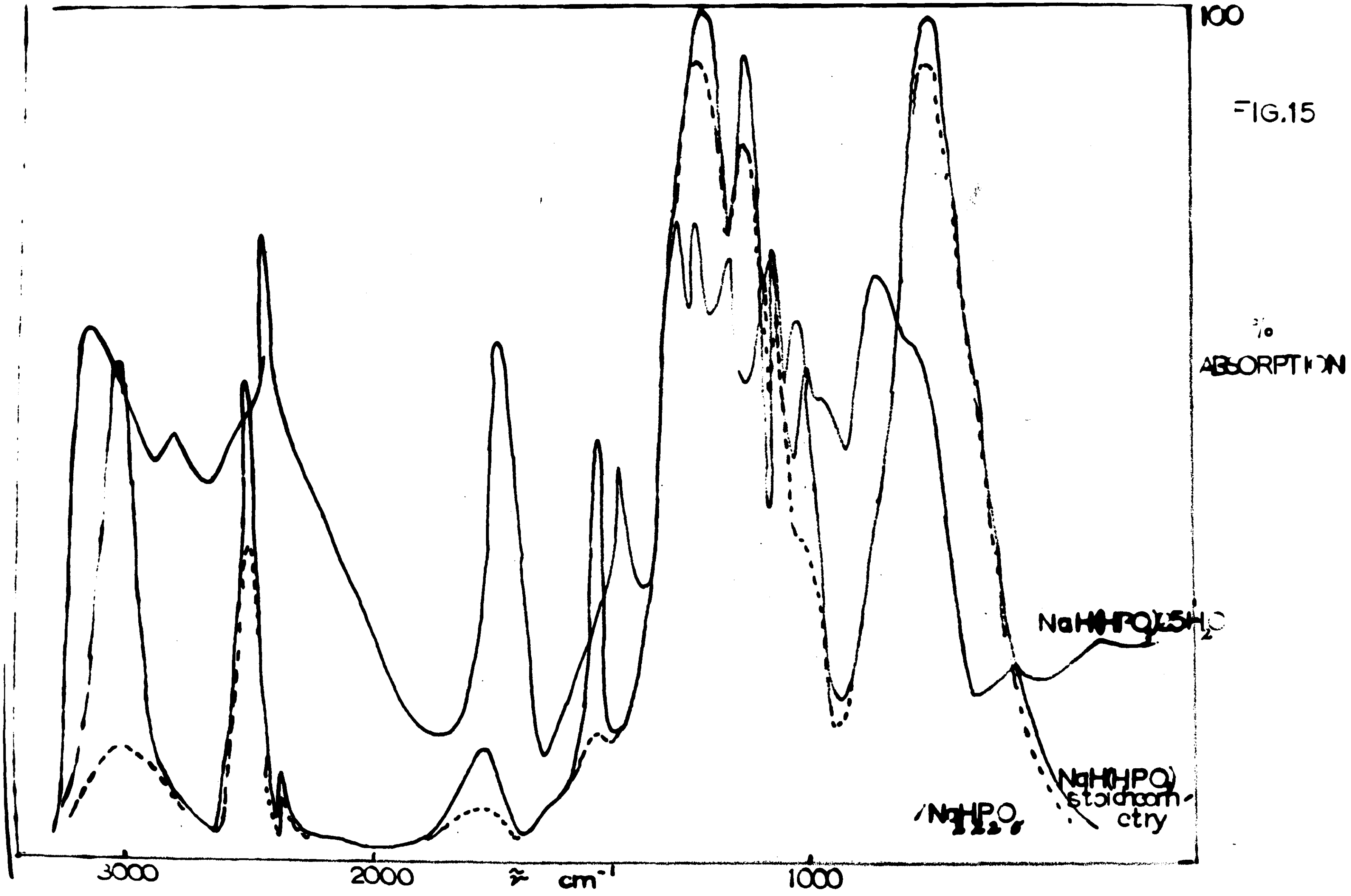
The temperature was allowed to decrease as the weight plot was continued. Further weight loss occurred, beyond the anhydrous stoicheometry, formation of P-O-P bonds still proceeding although at decreasing rate, as the temperature dropped back to room temperature. The total weight loss was 2.68 $H_2O/NaH(HPO_3).2.5H_2O$. This was a larger sample than employed in expt. 1. The major difference was the single process nature of the main loss of water from $NaH(HPO_3).2.5H_2O$. However redrawing the thermobalance graph on a different scale showed that two processes could be distinguished in the large weight loss step, the first up to the $NaH(HPO_3).1.25H_2O$ stage and, with a slightly greater temperature coefficient, another first order reaction beyond this half dehydration stage. The last part of the dehydration proceeding as described above linearly at constant temperature. There may be some special structural significance of the occurrence of a reaction rate change at the loss of half the total water of hydration.

<u>Expt. 4</u> A dehydration of 0.3208g. was studied this time, using a linear temperature increase.

Stage	Weight loss corresponding to	Temp.
a	0.16 H_2O	60°
b	to 0.5 H_2O	98°
c	to 0.72 H_2O	105°
d	to 1.0 H_2O	120°
e	to 2.45 H_2O	160°

Each of these stages corresponds to a discontinuity in the weight plot. A sharp discontinuity is found at the $NaH(HPO_3).1.5\ H_2O$ stage this time. The linear temperature being studied is faster than used before, it is now 3°/ min.

FIG.15


100
% ABSORPTION
3000
2000
$\tilde{\nu}$ cm^{-1}
1000
$NaH(HPO)2.5H_2O$
$NaH(HPO)$ stoichiometry
$Na_2H_2P_2O_6$

General Discussion of the Weight Plots for the Dehydration of $NaH(HPO_3).2.5H_2O$

These results demonstrate that the kinetics of water loss and the different hydration levels indicated depend on the manner in which the study is made. The three methods which have been employed namely the increasing of the temperature by stagesm allowing weight to become virtually constant at each stage; the pyrolysis at constant temperature and the study of a linear temperature increase over the whole dehydration stage reveal that different processes of weight loss occur according to the conditions. This dependence of the process on the manner of heating was been noted previously in thermogravimetric studies, (195). In experiment one, it was reported that the individual processes noted were first order. This is found to be valid if the asymptote which is used to plot the logarithm of the weight is taken to be the level value at the particular temperature used. This indicates that each of these stages is kinetically separate, if the asymptote necessary to fit the data were found to be the anhydrous level then only one process would have been indicated, the effect of temperature merely increasing the rate at each of the temperatures studied.

Infra-Red Study of the Spectra of the Products

The presence of P-O-P bonding in products obtained by heating $NaH(HPO_3).2.5H_2O$ may be determined by the broad band (P-O-P deformation) at 887cm.$^{-1}$.

An absorption due to P-OH at 906cm.$^{-1}$ becomes replaced by the P-O-P absorption as P-O-P bonds are formed. The spectra of samples at the "$NaH(HPO_3)$" stoicheometry when compared with the spectrum of $NaH(HPO_3).2.5H_2O$ and that of sodium pyrophosphite, $Na_2H_2P_2O_5$ suggested that the pyrophosphite anion was a major constituent of the product after loss of only 2.5 H_2O/ starting unit. The only significant difference between the spectra of "$NaH(HPO_3)$" obtained as described above and $Na_2H_2P_2O_5$ was the presence of a strong absorption at 3110cm.$^{-1}$ in the former case. This is to be attributed to hydrate water. It appears that as the heating process continues, P-O-P bonding present is not related directly to the weight loss which has occurred. Hydrated pyrophosphite anions are formed first and then loss of this water of hydration takes place. In confirmation of this idea it was found that when samples which appeared, from a weight point of view to be mixtures of $NaH(HPO_3)$ and $Na_2H_2P_2O_5$ were heated just above room temperature weight loss occurred. This is most likely to be due to the loss of hydrate water rather than to P-O-P bond formation.

Paper Chromatography of the Products

The presence of pyrophosphite was indicated in samples where the weight loss did not suggest this, in substantial agreement with the spectral correlatins. Traces of other products were also indicated however, some oxidation of the phosphite may occur, but this is only a minor reaction.

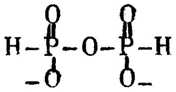
Iodometric Analysis of the Products

Kiehl and Moose demonstrated that the rate of oxidation of pyrophosphite in neutral solution is much less than that of oxidation of the orthophosphite.

Attempts were made to obtain analytical data from samples which, from a weight point of view were mixtures of hydrated ortho phosphite. When dissolved in a phosphate buffer at pH7 and compared with the iodine uptake of samples dissolved in water and then heated to hydrolyse $\overset{3}{\mathrm{P}}\text{-}\mathrm{O}\text{-}\overset{3}{\mathrm{P}}$ bonds present differences were found in the amount of oxidisable phosphorus present in the two cases. However the differences were not as great as would have been expected for the spectral differences. Hydrolysis of the $\overset{3}{\mathrm{P}}\text{-}\mathrm{O}\text{-}\overset{3}{\mathrm{P}}$ bonds may be occurring as dissolution proceeds in the present case. The material also appears to be heterogeneous, when ground up in a mortar in a dry-box prior to analysis uniform results were obtained. A sample with the $NaH(HPO_3)$ stoicheometry gave several analyses suggesting that 77% ortho phosphite was present. A sample with the $NaH(HPO_3)1.6H_2O$ stoicheometry appeared to have 87% ortho phosphite present.

$LiH(HPO_3)$

0.3245g. $LiH(HPO_3)$ was studied with a linear temperature increase of 3°/min. Weight loss began at 205° and dehydration proceeded to the pyrophosphite stage over $1\frac{1}{4}$ hours, the temperature being held at 205°. The weight loss curve approximates to a logarithmic one, half life 16 mins.

The spectrum of $Li_2H_2P_2O_5$ is different from that of $Na_2H_2P_2O_5$ in the P-O-P region. Three strong absorptions are observed here 967(s), 970(s, broad), and 721(s)cm^{-1} absorptions being present. Analysis by ceriometric oxidation and cation exchange to pyrophosphorous acid however showed that the material is lithium pyrophosphite, the  $H{-}\overset{O}{\underset{-O}{P}}{-}O{-}\overset{O}{\underset{O-}{P}}{-}H$ anion being present.

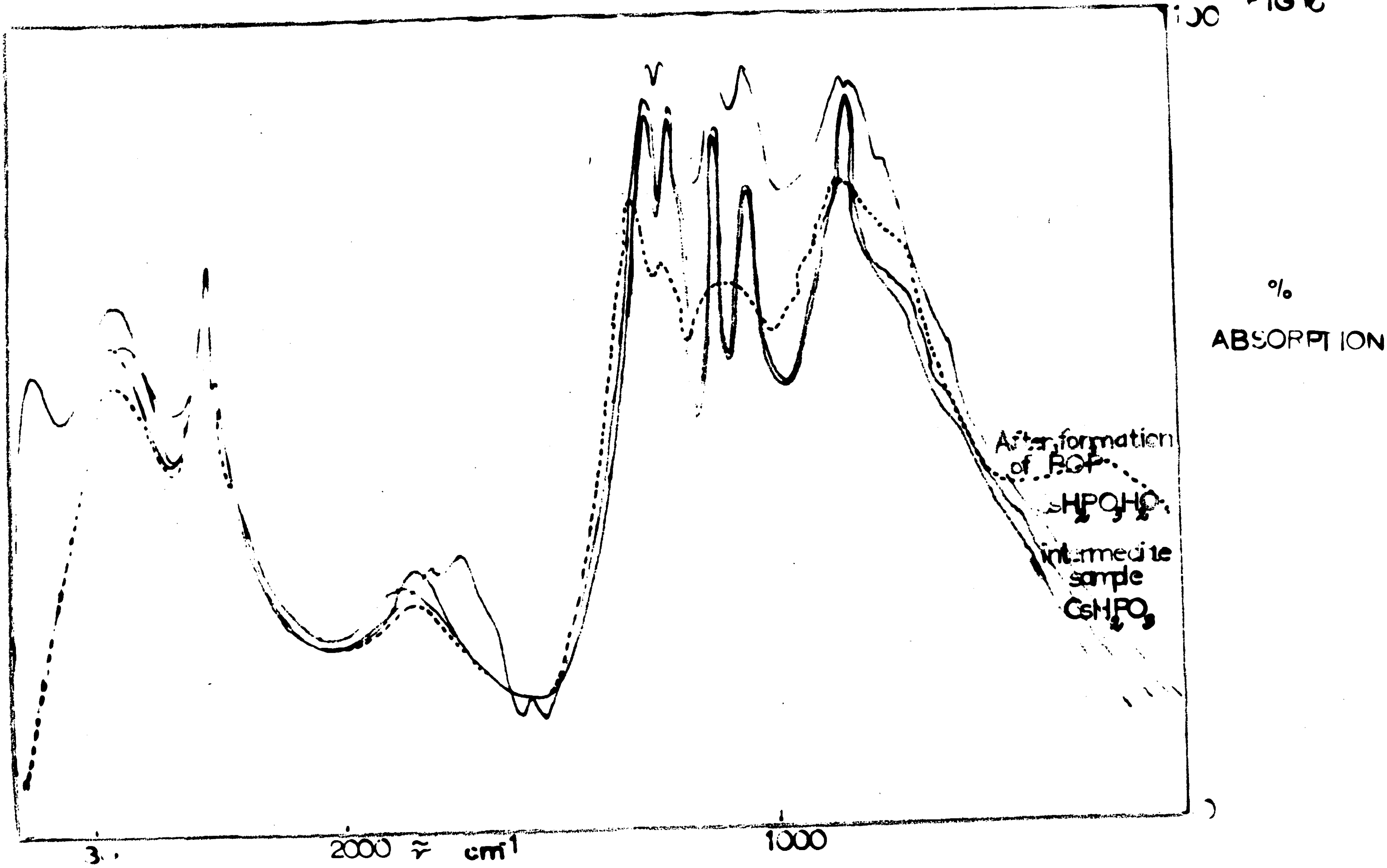
$KH(HPO_3)$

Numerous thermobalance studies have been carried out on this compound. Oxidative breakdown preceds the formation of the potassium pyrophosphite at atmospheric pressure. The results have been reported, (142), and the spectral correlations discussed, p.91-93

$RbH(HPO_3)$

In this case also oxidation-reduction reactions tend to proceed simultaneously with the formation of P-O-P bonds,however

FIG 16


100
%
ABSORPTION
0
3.
2000
$\tilde{\nu}$ cm^{-1}
1000
After formation of RbF
$CsH_2PO_3H_2O$
intermediate sample
CsH_2PO_3

oxidation products are not formed as easily with this salt as they are with the potassium salt.

The rate of formation of $\overset{3}{P}-O-\overset{3}{P}$ bonds becomes appreciable at 220°. Dehydration proceeds with exponential rate, half life, ± 4 mins. at this temperature, until $\overset{3}{P}-O-\overset{3}{P}$ bond formation is 75% complete on the weight basis. Thereafter gradual weight loss proceeds, as the pyrophosphite stoicheometry is approached the evolution of phosphine begins, slowly at first but becoming faster beyond the pyrophosphite stage. A melt is present at this temperature in the system, this may be correlated with the ease of the oxidative breakdown reaction. Beyond the oxidation step condensed phosphate units are present as the results of paper chromatographic studies show. With this salt being studied the same thermobalance behaviour was found for two different sample weights, suggesting an independence of the reactions which are occurring on the sample size.

$CsH(HPO_3)H_2O$

Using the method of increasing the temperature in steps, 3.2409g. was studied. Similar phenomena were observed to those described for the dehydration of $NaH(HPO_3).2.5H_2O$, in that a number of different weight levels were found at different temperatures used. In the present case however the oxidation reduction reaction overlaps the $\overset{3}{P}-O-\overset{3}{P}$ bond forming reaction. As with the Rb and K salts a melt is present as this occurs.

Stage	Wt. loss corresponding to	temp.
a	0.08 H_2O	75°
b	0.463 H_2O	170°
c, discont.	0.56 H_2O	190°
d	0.78 H_2O	253°
e, discont.	1.04 H_2O	280°
f	1.14 H_2O	"
g	1.42 H_2O	305°

This shows that the hydration levels $CaH(HPO_3)\frac{1}{2}H_2O$ and $CaH(HPO_3)$ can be distinguished. Ceriometric analysis showed that the final product was 44% oxidised to the $\overset{5}{P}$ stage. A gradual loss of P-H bonds may occur during the process, probably becoming faster as the temperature is increased.

Infra-red spectral studies were made on samples removed during this experiment, at points b, d and g and compared with the spectrum of the starting product. It seems that all the spectra show the same anion present except the last one. From the starting product to b the only difference is the disappearance of an absorption at $3360cm.^{-1}$ due to the removal of the "free" water of hydration at this stage. The spectrum shows a total change in the final stage g however. A broad P-O-P band at $894cm.^{-1}$ has been formed, replacing other bands in this region due to P-OH. No evidence of the formation of P-O-P bonds prior to the final dehydration stage is therefore indicated from this data. At stage f the ceriometric equivalent of the product was 211.5, the theory for no oxidation was 210.5. The spectra are shown in Fig. 16.

$NH_4H(HPO_3)$

Studies have been undertaken both under nitrogen and in atmospheric conditions. Some loss of ammonia occurs here as the temperature is raised, the equilibrium

$$\mathrm{P{-}O^-} \quad \mathrm{NH_4^+} \rightarrow \quad \mathrm{P{-}OH} \quad + \quad \mathrm{NH_3}$$

being possible. Volatilisation of the ammonia drives the equilibrium to the right hand side. However data which have been collected suggests that this reaction is only of secondary importance at the temperature where $\overset{3}{\mathrm{P}}{-}\mathrm{O}{-}\overset{3}{\mathrm{P}}$ bond formation begins.

<u>Expt 1</u> Using atmospheric conditions and raising the temperature at 3°/min. 1.0327g. was studied. The temperature was kept constant when appreciable weight loss began, at 100°. Initially the exponential curve for the reaction P-OH + HO-P P-O-P + H_2O, is followed, half life 2.7h. When this process became about 66% complete the weight loss became less than required for this reaction. After weight loss corresponding to 85% $\overset{3}{\mathrm{P}}{-}\mathrm{O}{-}\overset{3}{\mathrm{P}}$ bond formation, the temperature was increased and a fast oxidative breakdown observed at 180°. It appears that as the P-O-P bond formation proceeds other reactions leading to oxidative breakdown become more important. The substance is liquid at 100°.

<u>Expt. 2</u> Another experiment was carried out using a smaller sample, 0.6003g., using the same approach as before. The

temperature was increased to 105° and maintained here until the weight loss corresponded to the complete formation of the pyrophosphite anion. The dehydration plot in the interval, however, showed a number of discontinuities. The exponential weight loss to the pyro stage was followed up to 50% of the P-O-P bond formation. Thereafter the weight loss became slower than this. Raising the temperature above the apparent pyrophosphite stoicheometry caused the oxidative breakdown reaction to occur.

Expt. 3 Using the nitrogen stream with a controlled humidity of 6mm. H_2O partial pressure, 0.7620g. was studied, using the same temperature increase method.

Stage	Wt. loss corresponding to	Temp.
a	0.25 H_2O	134°
b	to 0.75 H_2O	240°
c	0.25 PH_3 + some ammonia	260°
d	0.5 H_2O	490°

Stage a is approximately logarithmic, a number of discontinuities occur along its course, but the general trend is exponential, half life $6.4.10^{-1}$ hours at 134°. At 250° another smooth reaction occurs associated with the rearrangement of P-H bonds producing gaseous phosphine and possible other products. This oxidation step does not proceed with increasing rate as for the case of phosphorous acid previously discussed; the present reaction is exponential half life at 260°, $4.75.10^{-1}$ h.

Expt. 4 A closed dry nitrogen flow system, described on page was used, 0.7118g, being taken.

Stage	Wt. loss corresponding to	Temp.
a	0.51 H_2O	215-225
b	0.56 H_2O	320°
c	0.16 PH_3 0.25 NH_3	364°

Expt. 5 The same method of study was used as in the above experiment, using

Stage	Wt. loss corresponding to	Temp
a	0.5 H_2O	180-210°
b	0.3 NH_3 0.2 PH_3	to 375°
c	0.5 H_2O	490°

Analysis of the Products

Ceriometric analysis of the product present after the oxidation step showed that there was no oxidisable phosphorus present. Difficulties occur due to the precipitation of the cerium (IV) by species present in the product. This is characteristic of the behaviour of condensed phosphates.

The products from expts. 1 and 2 were investigated by pH titration. This showed that dissolution of the glassy product and then rapidly titrating produced some P-OH (strong) groups, (e.w., pH 4.8=222). These could arise either by hydrolysis of branched $\overset{5}{\mathrm{P}}\mathrm{-O-}\overset{5}{\mathrm{P}}$ chains or from P-OH groups present in the glass. In either case such strongly ionised hydroxyl groups must have arisen by the loss of ammonia. Cation exchange of the glass gave an e.w. of 97 at pH 4.8, that required for the general formula of the product NH_4PO_3 is 96, and it is seen that the overall stoicheometry required for the metaphosphate formulation is found.

The infra-red spectrum of the glass is poorly resolved. On storage over silica gel some crystallisation is observed to occur and the infra-red spectrum of this product is interpretable in terms of NH_4 and condensed phosphate units being present. The occurrence of an absorption in the P-H region may indicate that some P-N-H is present, although it must be admitted that although such bonds being present is not ruled out, spectral correlations of this sort are open to question.

The product obtained from expt. 4 was studied by paper chromatography. The presence of ortho, pyro-, tripoly- and probably trimeta- as well as more condensed phosphates was indicated.

Expt. 6 A vacuum pyrolysis of the compound was studied, taking 0.9927g., heating in a vessel attached to a vacuum system, up to a temperature of 190° for 45 minutes. At about 140° melting occurred and the formation of bubbles began as soon as this happened. A weight loss of 120.1 mg. occurred, The volatiles produced were condensed in a trap and pressure measurements made to estimate the phosphine produced, the most volatile fraction of the condensed products. 32 mg. was found to be present. Loss of 90mg. would be required for the formation of the pyrophosphite unit and it is seen that the observed weight loss can be accounted for by the loss of $H_2O/2$ + 32mg. phosphine. Kiehl and Moose studied the dehydration of this compound in vacuo and found that the initial loss of $\frac{1}{2}H_2O$/phosphite unit occurred, (89). That only phosphine is liberated in addition to water, under the present conditions was confirmed by vapour density measurements.

$NH_4H(HPO_3)$ General Discussion

It appears from the foregoing experiments that three stages can be distinguished in the pyrolysis of this compound.

1. formation of the pyrophosphite unit
2. oxidative breakdown of the P-H bonds
3. further condensation of the phosphate units produced in stage 2.

In addition some loss of ammonia will occur at the higher temperatures, leading to the formation of P-OH groups which subsequently form branched $\overset{5}{P}-O-\overset{5}{P}$ chains.

$TlH(HPO_3)\ 0.25H_2O$

This substance is hygroscopic. A 0.3646g. sample was studied.

Stage	Wt. loss corresponding to	Temp.
a	0.25 H_2O	115-200°
b	0.5 H_2O	200-355°

The weight loss is linear with linear temperature increases over stage b. Stage a showed a gradually increasing rate with the temperature increase. After the pyrophosphite stage is reached oxidative breakdown was observed to occur, some phosphine being liberated. The sample was present as a melt above 200°.

$BeH_2(HPO_3)_2xH_2O$

1.9275g. of the viscous solution containing this stoicheometry was studied. Up to 170° rapid weight loss occurred 1.686g. being lost. The following stages were observed after this;

Stage	Wt. loss corresponding to	Temp.
a	0.23 H_2O	200°
b	0.46 H_2O	260°
c	0.79 H_2O	300°

The method of raising the temperature in stages was used. At stage a the product was colourless, at stage b it had a greenish colour and a slight odour of phosphine was detected. At stage c the product was glass like and has a brownish hue. It appears that alongside the P-O-P bond forming reaction there is an oxidation reaction proceeding possibly with the formation of P-P bonds, the "colour" of the melt increased as the process was continued. However the weight loss data suggests that the formation of P-O-P bonds is actually occurring. This case is analgous to the pyrolysis of Ca and Rb hydrogen phosphites already dealt with. The pyrolysis was continued above 300°. Further weight loss occurred above 400°, (wt. equiv. $0.5H_2O$). The temperature was increased up to 690°, the weight being constant above 480°. The sample was swollen up in the crucible and the "colour" had diminished on account of oxidation of P-P bonds which were present at lower temperatures.

Expt. 2 A viscous liquid containing the $BeH_2(HPO_3)_2xH_2O$ stoicheometry was allowed to come to equilibrium at room temperature on the thermobalane. Initially 0.9369g. was present. On standing for 4.6 h. a weight loss of 0.1080g. was obtained; on increasing the temperature above room temperature, c.19°, further weight loss was observed.

	Stage	Wt. loss corresponding to	Temp.
	a	0.2 H_2O	100°-105°
$BeH_2(HPO_3)_2$	b	1.5 H_2O	-170°
	c	0.46 H_2O	200°
	d	0.15 H_2O	230°
	e	0.15 H_2O	260°
$BeH_2P_2O_5$	f	0.23 H_2O	290°
	g	cor. 0.14 H_2O	300°

After stage b the product was colourless, whereas after stage f it was greenish. The pyrolysis was carried further. On raising the temperature rapidly to 350° gas evolution occurred (wt. equiv. 0.25 H_2O). Oxidative breakdown of the P-H bonds had occurred, a smell of phosphine was detected.

$MgH_2(HPO_3)_2xH_2O$

A syrupy product was obtained with this stoicheometry, 1.6922g. was taken. Equilibrium was allowed to occur in the thermobalance furnace over 17 h. at room temperature. On raising the temperature the following results were obtained.

	Stage	Wt. loss corresponding to	Temp.
	room temp.	0.3 H_2O	19°
	a	4.28 H_2O	160°
$MgH_2(HPO_3)_2$	b	1.86 H_2O	to 205°
	c	0.336 H_2O	to 232°
	d cor.	0.385 H_2O	to 415°

Oxidative breakdown occurs in the last stages of the $\overset{3}{P}-O-\overset{3}{P}$ bond forming reaction. Above about 250° coloured material is formed.

Expt. 2 A crystalline product was obtained eventually from the above viscous solution. This was $MgH_2(HPO_3)_2 3.5H_2O$

Stage	Wt. loss corresponding	Temp.
a	3.5 H_2O	100-180°
b	0.5 H_2O	180°
c	0.5 H_2O	230°

Little further weight loss occurred up to 520°, although there were some fluctuations in the weight. The final product was coloured bright red. The discontinuity noted at half the loss for formation of $\overset{3}{P}-O-\overset{3}{P}$ corresponds to the phase $MgH_2(HPO_3)_2MgH_2P_2O_5$.

$CaH_2(HPO_3)_2 6H_2O$

The crystals obtained were moist, a 1.6628g. sample was taken. The temperature was increased rapidly to 100° and thereafter it was slowly increased to 184°.

	Stage	Wt. loss corresponding to		Temp.
$CaH_2(HPO_3)_2$	a	5.2	H_2O	155°
	b	0.89	H_2O	184°
	c	0.48	H_2O	to 380°

During stage c the smell of phosphine was noted although the sample was still a white powder. At 380° a sudden weight increase occurred due to the breakdown of the P-H structure. It seemed that as the P-O-P bond forming reaction proceeds oxidative breakdown also occurs.

$SrH_2(HPO_3)_2$

In this case a simple P-O-P bond forming reaction with no complications is observed. A linear temperature increase up to 223°, (3°/min) was used and thereafter the temperature was maintained here until the weight became constant. No further stage occurred up to 370°, the material remaining unaltered.

	Stage	Wt. loss corresponding to		Temp.
$SrH_2P_2O_5$	a	0.03	H_2O	150-200°
	b	0.47	H_2O	223°

The first weight loss step is probably related to crystal surface effects, those P-OH groups which are nearer the surface of the crystal may be able to form P-O-P bonds at lower temperatures than those in the inside of the crystal. Although it must be admitted that this effect is quite general however there is always some doubt as to the possibility of surface moisture being present on the crystal surface. With

$SrH_2(HPO_3)_2$ the crystals are anhydrous and non-hygroscopic, the formation of $\overset{3}{P}-O-\overset{3}{P}$ bonds at this lower temperature being unambiguous in this case.

In this case also the kinetics of the main dehydration stage are interesting. When the curve is plotted on semi log paper, plotting the logarithm of the weight position taking the pyrophosphite stage as the asymptote, against time the process was found to be one of slightly different first order reactions, a number of straight lines are obtained. The change from one of these "sub processes" to the next is rather abrupt. It appears that this situation will be caused by rearrangement of the units in the crystal possibly by change of hydrogen bonding between phosphite, pyrophosphite and water units.

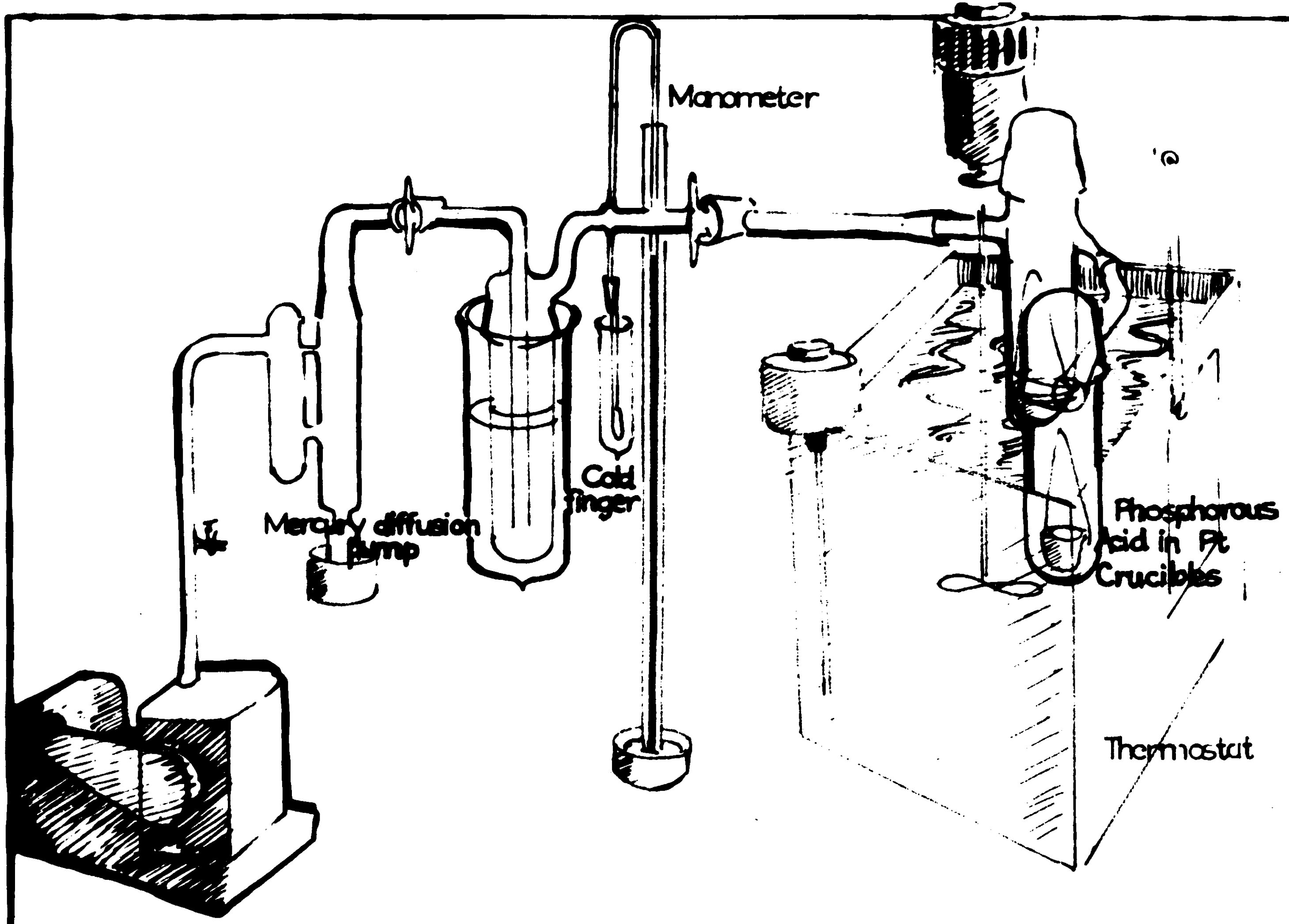
$BaH_2(HPO_3)_2 1.5\ H_2O$

1.0964g. was studied. The material lost no weight at room temperature on the thermobalance. Heating at a steady temperature increase of 3°/min. was employed.

	Stage	Wt. loss corresponding to		Temp.
$BaH_2(HPO_3)_2$	a	1.46	H_2O	30-170°
	b	0.70	H_2O	228°

Stage b is accompanied by an oxidation process. The plot becomes irregular and a weight increase is observed after the weight loss given above. The formation of $\overset{3}{P}-O-\overset{3}{P}$ is superseded by the breakdown of the P-H bonds. The temperature was increased up to 640° at the same rate, the weight remained nearly unaltered above 500°. The product was rather strikingly coloured red, this colour persisted even at highest temperature studied, although some change was noted due to the probable oxidation of P-P bonds to colourless products.

FIG. 7



SET UP FOR VACUUM PYROLYSIS OF H_3PO_3

(III)

b)

(i) Vacuum Pyrolysis of Phosphorous Acid

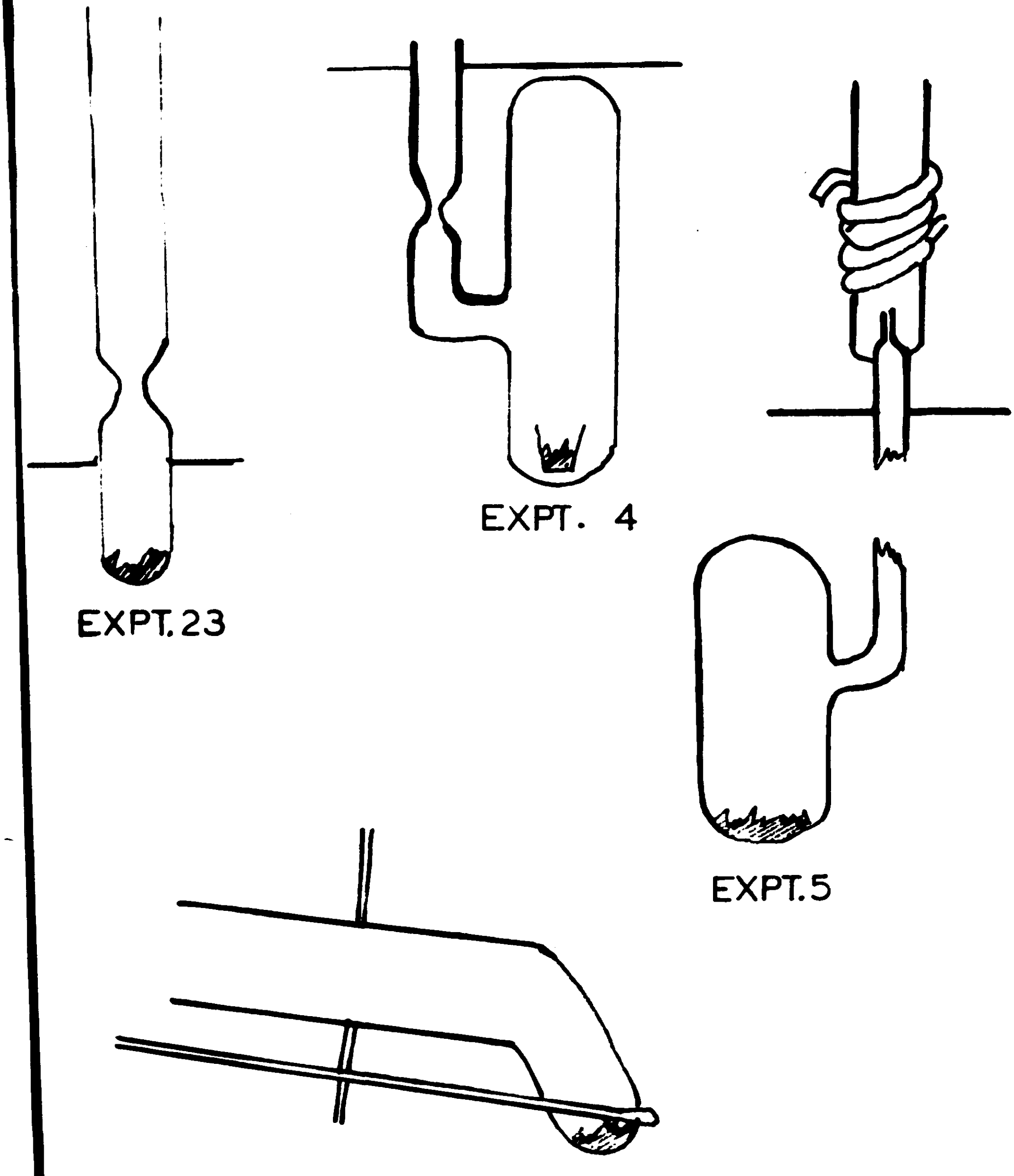
Samples of phosphorous acid which had been dried by storage over silica gel at atmospheric pressure were heated under vacuum, (10^{-4}mm.Hg), using a rotary pump, "Speedvac", model No. ISC50B, and a mercury diffusion pump, Edwards type GM2. Wide bore tubing, 1.2cm. internal diameter, with the appropriate taps were employed to allow maximum pump efficiency.

Expt. 1 Two platinum crucibles containing phosphorous acid samples were placed in suitable vessels attached to the small vacuum system shown, Fig. 17, and heated in a thermostatically controlled oil bath. 0.5896g. and 0.4983g. samples were used. It was appreciated that, owing to the hygroscopic nature of phosphorous acid and its pyrolysis products, that accurate weighing could only be carried out if the crucibles were weighed rapidly and the time of exposure to the atmosphere noted. In this way it was possible to treat each case in the same way, and to make corrections for the uptake of moisture from the atmosphere.

After standing in the evacuated vessels for 6 and one third hours the samples showed no sensible change in weight at 19°. Small increases in weight observed, 0.6mg. were due to exposure to the atmosphere during weighing. After a further 16 hours (evacuated) the weight had decreased by only 0.1 mg. This lack of weight change under vacuum at room temperature demonstrated the very small tendency for P-O-P bonds to be formed at this temperature.

On taking manometer readings at different temperatures after having evacuated the vessels at room temperature and isolating this part of the apparatus, the partial pressure of water vapour over phosphorous acid at the different temperatures was obtained. On plotting the water pressure against temperature, a break was found corresponding to the melting point of phosphorous acid, (70°). At this point the formation of P-O-P bonds appears to proceed. On cooling and re-heating, a different variation of water pressure with temperature was found; P-OH bonds are not readily formed from P-O-P bonds by the addition of water in this system. Equilibrium between these two structures will be slow. However since recrystallisation does not occur readily with phosphorous acid the different physical factors on reheating the viscous liquid may play a part in the phenomena observed.

The system including a liq. nitrogen trap was evacuated and the loss of weight followed at 117°. The crucibles were weighed from time to time by removal from the system, rapid transfer to a vacuum desiccator, in which they were kept until at room temperature, and then rapidly weighed on an automatic



EXPT. 23

EXPT. 4

EXPT. 5

EXPT. 7,8

Sublimation Vessels used, Sublimation of H_3PO_3.

single pan balance. A weight increase of 0.04mg/sec. was corrected for (due to the uptake of moisture from the atmosphere). The weight of the product present reached a level value at about 6 hours heating time corresponding to $0.47H_2O$ and $0.52H_2O/H_3PO_3$ originally present for the larger and smaller weights studied respectively. An odour of phosphine was apparent from the melt at this stage. Although very small amounts of phosphine can be detected by smell, this phosphine is significant since none was detected before this weight loss level. On further heating evolution of measurable quantities of phosphine took place. It was also noted at the melt composition $H_4P_2O_5$ (loss of $0.5\ H_2O/H_3PO_3$) that traces of a crimson solid were present on the crucible walls, on continuing the pyrolysis at this temperature large amounts of red material are produced.

Expt. 2. Sublimation of colourless crystalline material had been noted to occur when H_3PO_3 is heated in vacuum, (193). To study this process various types of sublimation apparatus were employed, Fig. 18. A glass apparatus consisting of a long tube with a bulb at one end and a constriction immediately above this bulb, which could be sealed off isolating any sublimate for further study, was attached to the vacuum system. 1.4356g. H_3PO_3 was weighed into the bulb and heated under vacuum for 16 hours at 117° (± 0.5°), with constant pumping through a liquid nitrogen trap to catch volatile material.

The product obtained in the bulb was a colourless liquid, weight loss corresponded to a loss of 0.67 H_2O/H_3PO_3 apparently. Traces of "flower patterns were noted on the side of the sublimation area. The residual liquid in the bulb was analysed by ceriometric oxidation and a sample taken for infra-red spectral study. On dissolving the product in water, an odour of phosphine was noted. The material in the trap appeared to be a mixture of water and phosphine. From pressure measurements the weight of phosphine present was found to be about 22 mg. The total trapped material was 0.2041g. The oxidation equivalent of the pyrolysis product was 41.95. From these figures it may be calculated that 14% oxidation from $\overset{3}{P}$ to $\overset{5}{P}$ had taken place during the pyrolysis. The water loss which had occurred was really $0.6H_2O/H_3PO_3$ originally present. From previous observations phosphine loss would have been expected only after loss of $0.5H_2O/H_3PO_3$. Hence pyrolysis of the pyrophosphorous acid formed at this stage would occur by loss of 0.10 $H_2O/H_4P_2O_5$ and phosphine equivalent to 14% loss of the P-H bonds present in the melt. The water loss reaction is equivalent to the forming of $(-\overset{3}{P}-O-)_n$ chains to 20% completion. It is to be expected that the loss of phosphine which occurs is related to the possibility of forming such chains in the melt. The loss of phosphine may then be thought of as being due to a 70% oxidative breakdown of such hypothetical chains, giving polyphosphate units. The quantity of sublimate obtained in this experiment was too small for convenient study.

Expt. 3 Another experiment was conducted in the same apparatus using 1.1661g. H_3PO_3. It was thought that by heating for a longer period of time the amount of sublimate obtained would be greater. After heating for 49 hours at 117° as before, under vacuum, the material in the bulb was coloured bright red, pyrolysis was discontinued after 52 hours. During the experiment the sublimation area was air cooled and insulated from the oil surface by a piece of asbestos. On proceeding up the tube beyond the constriction, differently coloured products were noted. In the lower part red material was present while above this some liquid was present and further up, corresponding to the level of the asbestos sheet there was some white solid.

Measurements showed that the loss of water in this case was $0.7H_2O/H_3PO_3$ and the loss of phosphine was that required for the volatilisation of 0.54 PH_3 required by the complete breakdown of $\overset{3}{P}$ to $\overset{5}{P}$.

The formation of this red solid is found at a more highly oxidised state of the bulk product. The formation of P-P bonds is indicated by the colour of the material. The overall oxidation state of the phosphorus atoms present in the product is near 4, as was obtained from ceriometric oxidation data, the equivalent weight of the bulk product was 193.6. The presence of condensed phosphoric acids in the product was indicated by the addition to ceric sulphate solution, a yellow difficulty soluble product was formed. When the mixture present in the reaction product was treated with water most dissolved leaving a small amount of a brownish-red solid. The effect of various reagents on the reaction products was investigated. Slight solubility appeared to take place in ethanol giving a light brown solution (possibly colloidal). On addition of chloroform to this solution extraction into the chloroform layer took place, there being a paricular concentration of reddish material at the interface of the two liquids. The reaction product from the phosphorous acid pyrolysis does not dissolve in chloroform alone. Similarly when treated with water and then chloroform, extraction into the chloroform layer took place. In these cases solvolysis appears to have occurred, and the product of this reaction dissolves in the non-hydroxylic solvent.

Expt. 4. The effect of the contact between the pyrex glass and the phosphorous acid products in the above pyrolysis route and the formation of sublimate was investigated by carrying out the experiment avoiding contact between the glass of the vacuum vessel and the phosphorous acid. A platinum crucible containing a sample of phosphorous acid was sealed up in a glass vessel, and pyrolysis conducted as before. Again the apparatus was constructed to obtain a sample of sublimate for further study. 2.0035g. phosphorous acid was heated for 73 hours at 120°. The amount of sublimate obtained in this experiment was very small, possibly owing to the apparatus having a rather less favourable shape than in the previous experiments. The total weight loss was estimated in this case as 27% (the previous experiments with the shorter heating time gave less % loss, expt. 3, gave 21% loss). This corresponds to the value expected on comparison with other experiments when the different times of heating are taken into account. The final product was red in colour. No obvious effect of changing the phosphorous acid container from glass to platinum was found. Examination of the platinum crucible however suggested that some chemical reaction with the phosphorous acid pyrolysis product had taken place. A dark coloured residue was present where the melt had contacted the platinum, strongly adhering to the sides of the crucible. After washing and drying in an oven at 110° for 1 day the crucible showed a weight increase over the original weight of 0.5mg. Analysis of the pyrolysis products was carried out. The crucible was washed out with water and the insoluble red material filtered through a weighed sinter glass crucible. Although after filtration the bulk of the red material was large, on drying by storage over silica gel in a vacuum desiccator only a small residue remained. Analysis was carried out by combustion in a flask filled with oxygen followed by precipitation as quinoline phosphomolybdate and titration of this precipitate by NaOH, back titrating with HCl. The results indicated that there was 87% of phosphorus present. The material was however probably heterogeneous, some areas being c90% phosphorus. The weight of red material after drying was c.0.5% of the total weight.

Expt. 5 Since much sublimate had been observed in experiments where no mercury diffusion pump was employed, c.f. (193), it was decided to see if reasonable quantities of sublimate could be obtained using onlt the rotary pump.

An apparatus was constructed with a sample of phosphorous acid sealed in a glass bulb from which a tube emerged. A copper pipe spiral was wound around this tube where it emerged from the oil bath to cool the glass in the sublimation area. 0.9637g. of phosphorous acid was employed. Heating was conducted at 120° for 111 hours, after which time an orange colour was noted in the bulb. The experiment was carried out in a closed system. After having been pumped down by use of the rotary pump the sublimation apparatus connected to a liquid nitrogen trap was shut off. Only a little sublimate was present. The quantity of phosphine in the trap was estimated by pressure measurements. This gave a value for the amount of breakdown $\overset{3}{P} \rightarrow \overset{5}{P}$ as 59%.

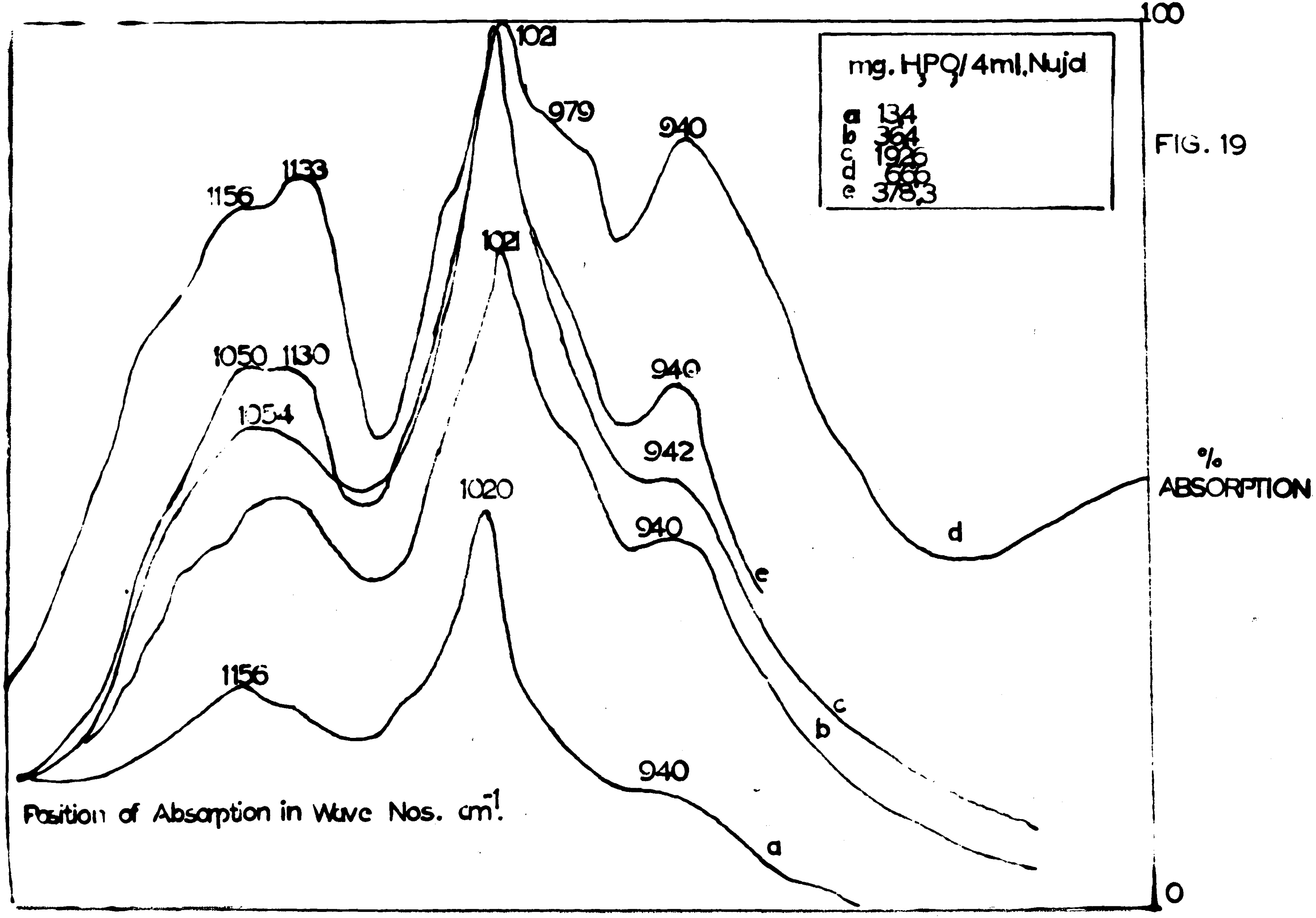
Expt. 6 A similar experiment was carried out with a pressure of 5 mm. air in the apparatus. A simple test-tube with a B19 joint and a tap to allow the sublimation apparatus to be transferred to a dry-box, was employed, immersed partially in the oil bath. After 42 hours the crystalline area had increased in size by a factor of about 2½. When heating had been continued for about 60 hours some liquid material, too, was noted in the sublimation area. Some gas evolution was now suggested by the slow formation of bubbles, indicating that the oxidative breakdown had started, the pyrolysis was terminated at this point. Phosphine pressure measurements were taken and this suggested that the product was 25.2% oxidised. Much larger quantities of sublimate were obtained this time than with previous experiments, it being obtained in the form of colourless crystals. No red product was formed in the vessel.

Expt. 7 An attempt was made to further study the sublimation process by varying the experimental conditions, bearing in mind the reported large scale sublimation observed by previous workers, and trying to duplicate the conditions employed by them. A different rotary pump was used, Metrovac Type SR2. An air thermostat was employed, (this enabled the physical appearance of the sublimate to be more easily noted), the type used was a Towers Simmerstat set at control 78. This apparatus is in the form of an electrically heated tube open at both ends. Asbestos ends were constructed for the tube and a sample of phosphorous acid in a sublimation set-up, inserted through a hole in the asbestos together with a thermometer.

The sample of phosphorous acid, c. 3g. was heated at 128-129° for 4 days. No red material was formed. Considerable quantities of sublimate were produced, in crystalline form.

<u>Expt. 8</u> Another experiment was carried out in the same way, taking 1.1205g. phosphorous acid. The sample was inserted in the thermostat at room temperature and its appearance noted as the temperature was increased to 138°. This indicated that sublimation began as soon as the temperature was raised, although appreciable quantities only could be observed after 45 min. at 120°. The temperature was re-adjusted to this level, and the heating continued for 8 days. It is noted here that this type of pump is not as efficient as the rotary pump employed previously. This sublimation proceeded for 4 days only, at decreasing rate as the process continued. After 5 days red material became visible in the sublimation apparatus. Before this a cloudiness had arisen in the melt. The sublimation was seen to occur only when there was from a weight point of view (using the data from the other experiments), ortho phosphorous acid present in the melt. The rate of

FIG. 19



mg. H_3PO_3/4ml. Nujol
a 13,4
b 36,4
c 192,6
d 66,6
e 378,3
100
0
% ABSORPTION
Position of Absorption in Wave Nos. cm^{-1}.
1021
979
940
1156
1133
1021
1050
1130
1054
940
942
940
1020
1156
940
a
b
c
d
e

sublimation is probably directly related to the proportion of phosphorous acid present. The amount of red material increased in amount from the time when it was first noted to the termination of the experiment. Evolution of phosphine which was correlated with the appearance of bubbles, rose to a maximum rate of evolution at about 6$\frac{1}{2}$ days heating.

Infra Red Spectral Study of Some of the Products obtained from the Pyrolysis of Phosphorous Acid

The precise type of absorption curve obtained depended on the type of technique used to prepare the sample for measurement, there being a difference between the spectrum of phosphorous acid for example as a KCl disc and as a nujol mull. The positions of the P-H stretching and the P-O vibrations are altered. When different amounts of the constituents of the nujol mull are considered, changes are found in the P-O region of absorption. Thus care is necessary in interpretation of phosphorus oxy-acid spectra. The variation with the phosphorous acid concentration is presented in Fig.19.

Infra-Red Spectra of Sublimation

Expt.,

2	3	6,a	6,b	8,a	8,b	8,c
frequency, cm^{-I}						
3287mb	3175w+	3240sh	3175m		3360	3360
2800mb	2800m	2800m	2800m	2800m	2800	2800
242Im		2410w	2421w		2420	2466
2283m+	2288w+	2290m	2292m	2289m-	2290	2293

2	3	6,a	6,b	8,a	8,b	8,c
frequency, cm^{-1}						
1634mb-	1638w+	1643m	1630m	1635m-	1635	1646
1192m+	1206sh				1171	
1135s-	1122s	1147s	1142s	1134s	1161	1154
1096s	1062s	1052sh		1021vs		
1021vs	1020vs	1024vs	1020vs		1020	1021
979vsb	1000sh	1000sh	1000sh	945s	934	937
906vw		946 sh	960 sh			
722m		722 w	716 vw	780w		
663				722w	721	719

Two spectra were obtained from expt. 6 by taking different quantities of sublimate in the Nujol mull, 6,b contains the greater quantity. Spectra 8 a, b and c were obtained by exposing the sublimate to the atmosphere for, in the case of b one minute and c twelve minutes. 8a was obtained without exposure to the atmosphere, as were the other spectra given. Dry-box manipulation was used.

From the study which was made of the variations in the spectrum of phosphorous acid with the amount of crystalline acid ground up in Nujol, a calibration is obtained which was used to interpret the spectra of the sublimates. The material from experiments 6 and 8 is virtually pure phosphorous acid, whereas the sublimate from expts. 2 and 3 appears to be a mixture of phosphorous acid and a smaller amount of a species or species with a different type of absorption at 980cm^{-1}. This may indicate the presence of P-O-P bonding. This arises from decomposition of initially sublimed phosphorous acid, probably under the influence of gaseous phosphine.

Infra-Red Spectra of the Non-Sublimed Residue

With viscous liquids spectra become poorly defined, this is the case with the remaining liquids in these experiments.

Expt. No.

I	2	3	viscous liq. $H_4P_2O_5$ from PCl_3 + H_3PO_3	crystals from this viscous liq. in nujol.
	2800	2769	2800	
2676	2292	2275	2252	2885
2300	2458		2468	2468
2428	1630	1640	1610	2115
1635	1471			1530
1474	1189	1133	1215	1206
1199	1130		1130	1142
1120	1019	1005	1010	1026
	942	948	945	982
938				940
944	901	826		792
984			798	735

These spectra show the same general features. There is also some resemblance to those of the sublimates. They were obtained by the thin film method, except that of the crystalline product. The product from experiment 3 contained red material. It seems likely that no special feature is detectable due to the presence of a red material. The absorptions at about 900 cm^{-1} are considered to be due to P-O-P bonding in the liquid. In addition these spectra exhibit high level absorption at frequencies lower than the maxima positions given, again this is characteristic of the presence of P-O-P bonding.

Comparison with the spectra of products obtained from the reaction of phosphorus trichloride and phosphorous acid is interesting. There is similarity in general profile of the spectra taken as thin films, an example is given. Absorption in the lower regions of the spectrum (frequency) is atributed to the presence of P-O-P bonding. In the cases where there is a variety of different P-O-P bonded species present as in the cases where oxidative breakdown has occurred, maxima are not distinguishable, continuous absorption over a wide range is found. The comparison is also interesting with the product obtained from crystallisation of the initial Auger reaction product. The spectrum is similar to that of the viscous liquid from which the crystals grew. P-O-P bonds are present.

Analytical Data on the Sublimate

The main difficulty in the analysis of the sublimate was the difficulty of obtaining it in large quantities. However it was found that, using sufficient care, satisfactory pH titrations and ceriometric analyses could be carried out. A sample of the sublimate was weighed out, transferring all material as far as possible in a dry-box, then a pH titration was carried out, after which the titrated solution was oxidised by cerium (IV), allowing for the reaction between cerium (IV) and water which also occurs.

Sublimate expt.,	Wt.mg.	Strong POH NaOH e.w.	Weak POH NaOH e.w.	Oxidation e.w.
3, a	1.4(4)	91	37	37.7
3, b	3.1(4)	100	51	39.0
6	6.7(9)	85	41	40
8	10.8(5)	88.9	44.5	43.8
	49.8(7)	85.1	42.3	
H_3PO_3,a	23.7(6)	82.2	40.1	38.8
	16.1(7)	85.3	40.6	41.0
salicylic acid	2.0(7)	136.2		
	15.4(3)	138.2		
H_3PO_3,b	7.5(7)	85.3	42.0	41.0
	61.8(9)	82.1	40.8	41.0
	27.1(0)	81.4	40.6	41.0

Experiment 3, a refers to a sample of sublimate which was found further up the sublimation tube than 3b b. The former was colourless while the latter was yellowish. The analytical method was tested by using samples of phosphorous acid which had been stored over silica gel at atmospheric pressure. It was found that the pH titrations did not yield the expected equivalent weights for phosphorous acid. A test was therefore made with salicylic acid, (e.w. 138.1). The accuracy of the results for this organic acid show that any weighing errors or volume errors in the procedure are negligible. Some special factor appears to be in play with the phosphorus oxy-acid samples. A contributory factor will certainly be the hygroscopic nature of these materials but this alone does not rationalise the lack of symmetry of the pH titration curves. The ratios of the first and second equivalent weights should remain at 1:2 on uptake of water, from the atmosphere. Nor can the presence of dissolved carbon dioxide account for the divergencies from the theoretical equivalent weights. Attempts were made to remove carbon dioxide from the system. Boiled out distilled water was used to obtain 0.IN NaOH (by dilution of B.D.H. concentrated volumetric solution) and the titrations were carried out with a current of nitrogen passing through the pH cell, stirring being carried out by a magnetic stirrer. Since the extent of the variation in the ratio of the first and second end points depends on the weight of phosphorous acid which is taken, it seems as though slight reaction of the acid with the pyrex glass vessels may lead to a partial neutralisation of the phosphorous acid.

It is considered that the sublimate obtained from experiment 6 is pure phosphorous acid, in agreement with the spectral data. The sublimate obtained in the other cases were from pyrolysis where considerably more phosphine was evolved than in experiment 6. Decomposition of the initially sublimed phosphorous acid by evolved phosphine is indicated. The decomposition products appear to have a higher oxidation number on the phosphorus.

FIG. 20

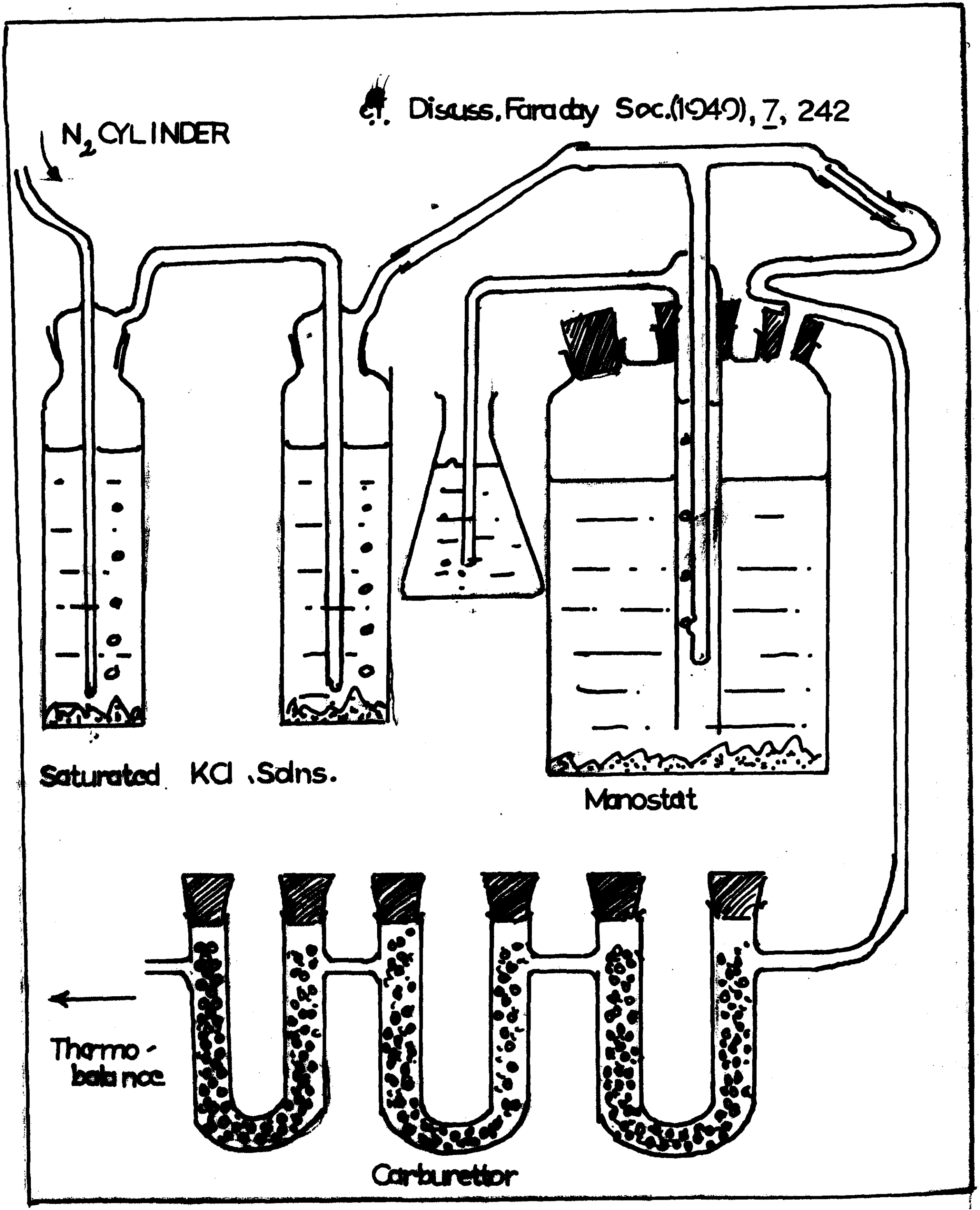
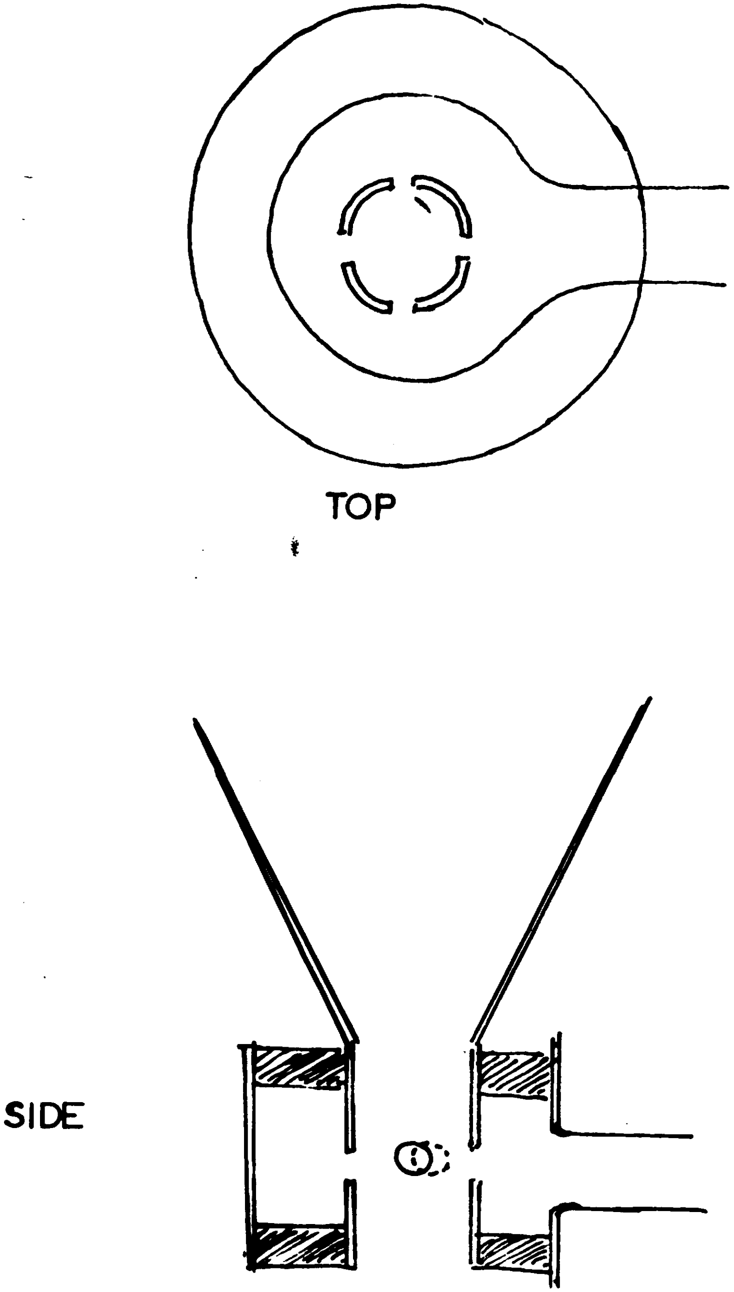

cf. Discuss. Faraday Soc.(1949), 7, 242
N$_2$ CYLINDER
Saturated KCl Solns.
Manostat
Thermo-balance
Carburettor

FIG. 21a

FLOWING SEAL DEVICE Constructed using Pyrex Glass



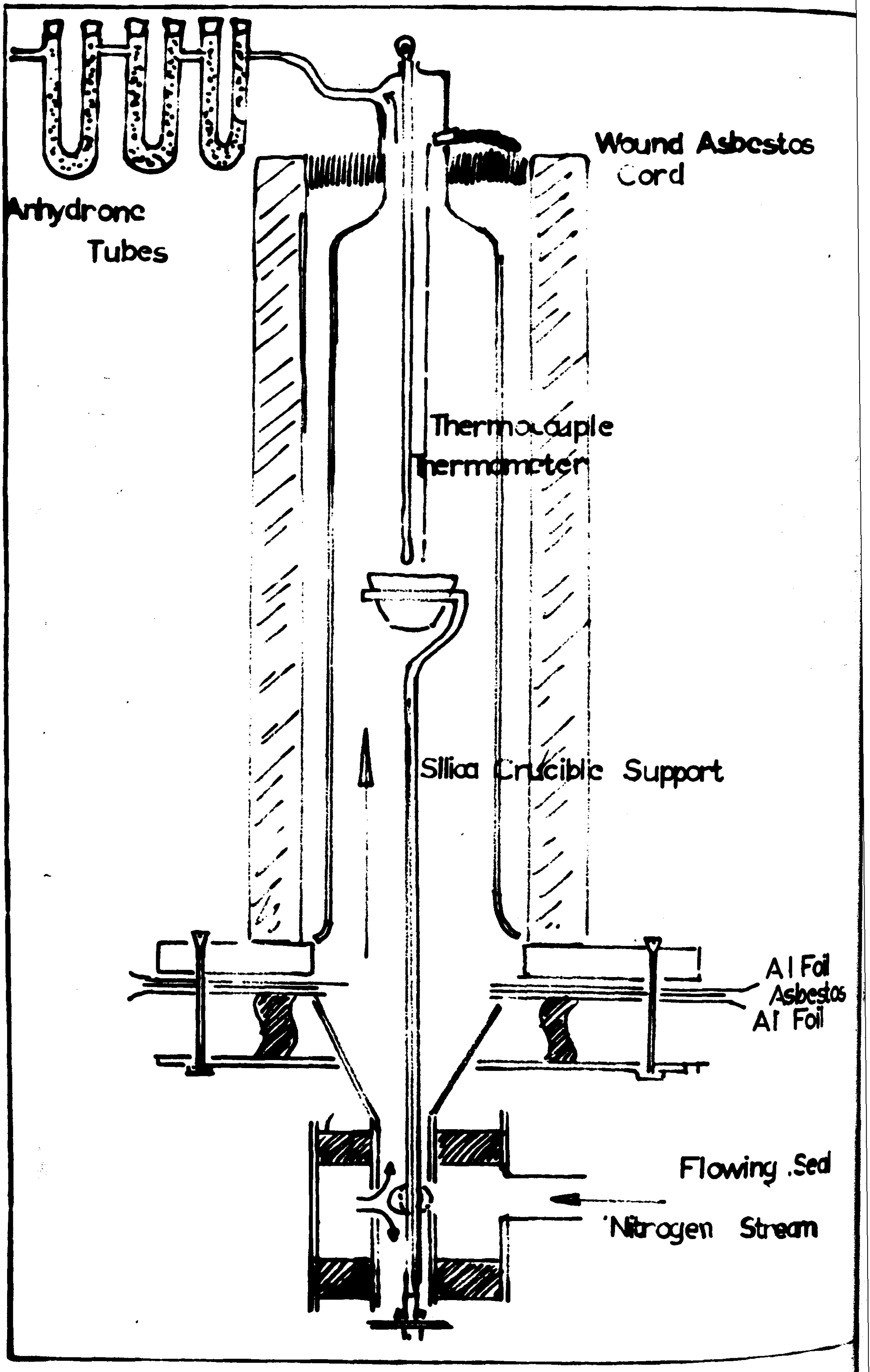

Anhydrone Tubes
Wound Asbestos Cord
Thermocouple Thermometer
Silica Crucible Support
Al Foil
Asbestos
Al Foil
Flowing Seal
Nitrogen Stream

FIG. 21b.

(III)

(b)

(ii) Pyrolysis of Phosphorous Acid at Atmospheric Pressure

Experiments were conducted on a thermobalance, with dry and moist nitrogen flows and under atmospheric conditions. The samples of phosphorous acid studied, both B.D.H. and Hopkins and Williams preparations were used, were stored over silica gel at atmospheric pressure. The acid was analysed by acid-base titrations, ceriometric and iodometric oxidation methods, as well as paper chromatography, and shown to contain no impurities. The commercial acid contains about 1% water. Initial experiments were with an unmodified Stanton thermobalance; later a silica muffle supplied by the manufacturers was fitted inside the furnace through which a steady flow of nitrogen (B.O.C. white spot grade) descended the furnace at a controlled flow rate obtained by employing a flow regulator, Fig. 20. A further improvement in this type of arrangement was achieved by using an upward flow of nitrogen, passing from the furnace to a liquid nitrogen trap whereby volatile material could be condensed out of the nitrogen stream and used for further study. It was necessary to devise a "flowing-gas seal" to allow the crucible support to pass out of the nitrogen atmosphere to the balance mechanism, Fig. 21,a and b.

<u>Expt. 1</u> Using 1.6630g. phosphorous acid, the atmospheric pyrolysis was studied. On raising the temperature at 3°/min. a weight increase occurred reaching a maximum at about 100° and decreasing to the starting weight at 136°. The temperature was maintained at 170° until the weight loss at this temperature had become slow, thereafter the temperature was raised to 230° a rapid temperature increase took place at this point, the maximum was reached after anout 1 minute, at 250°. The weight was allowed to reach constancy at 230°, on increasing the temperature further weight decrease took place, becoming linear with linear increase in temperature, 3°/min.

Stage		Wt. loss corresponding to		Temp.
a		0.14	H_2O	to 230°
b	cor.	0.5	H_2O	
	to	0.19	PH_3	230°
c	approach	0.5	H_2O	360°

The pyrolysis process appears to be describable in terms of initial $\overset{3}{P}-O-\overset{3}{P}$ bond formation to 28% completion after which oxidative breakdown becomes apparent. During the oxidative rearrangement phosphine is lost, this burns exothermically in the furnace, water is also lost at this stage. On continued pyrolysis the build up of $\overset{5}{P}-O-\overset{5}{P}$ bonds ensues, the product at about 360° contains mixtures of condensed phosphoric acids.

<u>Expt. 2</u> This was carried out using a nitrogen stream. The partial pressure of water vapour in the furnace was 6mm. Hg. As before the weight increased initially at low temperatures up to a maximum at 108°, decreasing again to the starting

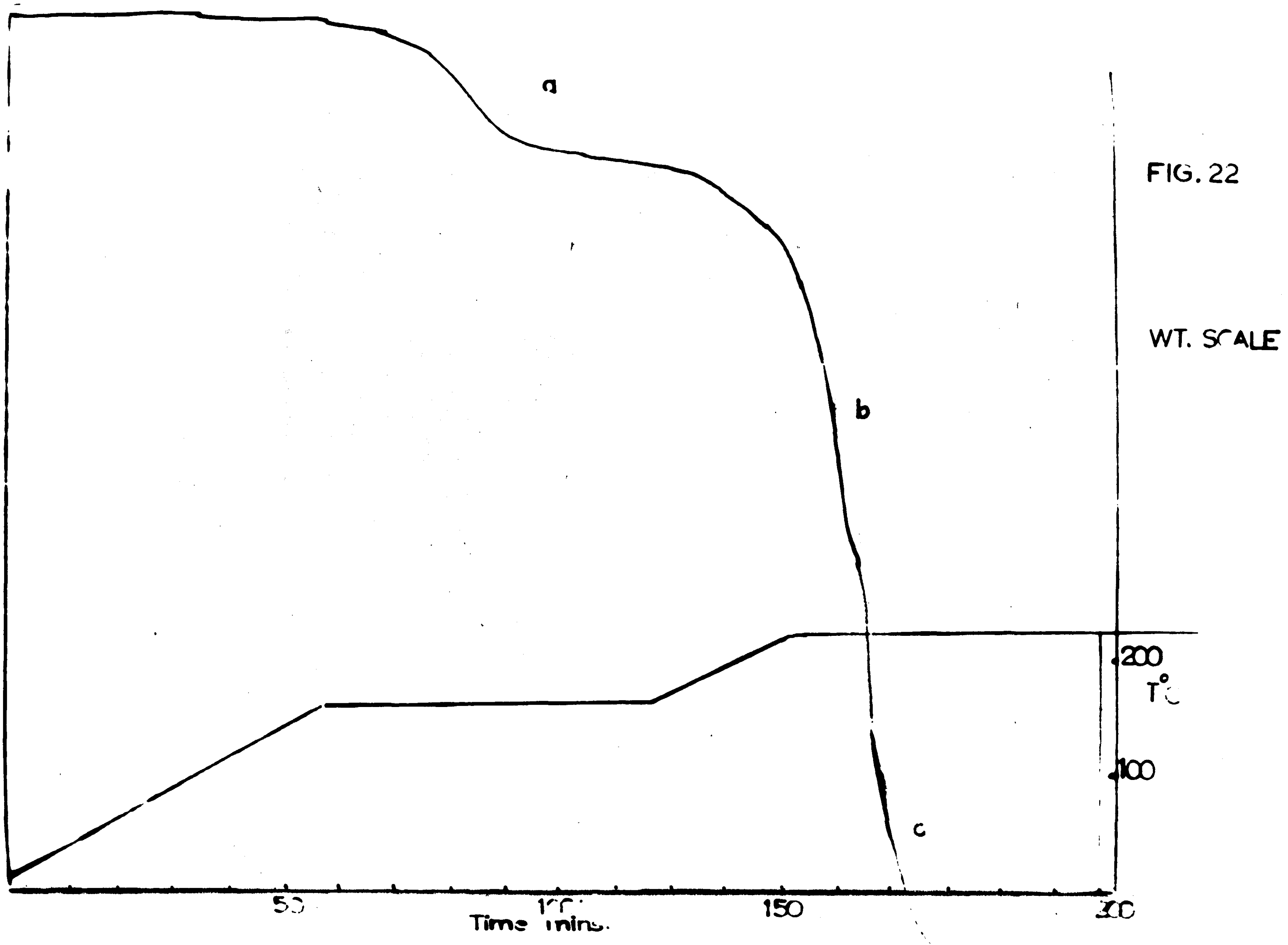
weight, 0.9000g. at 175°. The height of the maximum in this type of experiment employing fast temperature increases, (3°/min.), is small in terms of the water stoichbeometry, here it was 0.054 H_2O/H_3PO_3 initially present. The temperature was held ay 170° until the weight loss at this temperature had become constant. The temperature was raised linearly to 230°, at which temperature rapid weight loss took place; no increase in temperature was observed at this point now, no combustion of the evolved phosphine took place in the furnace. After this fast loss of weight the product was brought to constant weight at this temperature. The temperature allowed to reach equilibrium.

Stage	Wt. loss corresponding to		Temp.
a	0.086	H_2O	170°
b	0.4	H_2O	230°
	0.2	PH_3	
c	0.5	H_2O	400°

This last step, c is a one stage process (the step c was obtained by raising the temperature to 290°, keeping it at this level for 35 mins. and then raising the temperature to 400°. When plotted on semi-log paper the two weight losses at constant temperature obeyed first order kinetics for the same asymptote- the constant weight at 400°). The change in weight over step c was that required for the loss of water from pyrophosphoric acid to produce the metaphosphoric acid stoicheometry. It appears that the stage b proceeds by loss of phosphine and some hydrogen as well as water, leaving the equilibrium product at this temperature, pyrophosphoric acid, as the residue (at least the pyrophosphoric acid stoicheometry). It is found in this type of experiment that the oxidation equivalent of the melt increases sharply at the oxidative rearrengement step. Little lower oxy-acid residue remains. The loss of phosphine required to remove all P-H bonds is greater than the observed loss if the product after stage b is of pyrophosphoric acid stoicheometry. Thus with the present case the weight loss required for the equation $8\ H_3PO_3 \rightarrow 3\ H_4P_2O_7 + 3\ H_2O + 2\ PH_3$ is 167mg., the observed weight loss was 151mg. The difference may be due to the loss of hydrogen gas during the fast reaction, if so in the present case about 10% of the initially present P-H bonds give rise to hydrogen.

<u>Expt. 3</u> An experiment was conducted in a platinum crucible, with 2.2744g. phosphorous acid. The same type of nitrogen stream as was employed before was used. Initial weight increase occurred up to about 110°, the temperature being increased at a rate of 3°/min. The weight loss required by the above equation for the equilibrium weight loss at 230° is 422.6mg.; the value found here was 411.7 mg. This would indicate that about $3\frac{1}{2}$% loss of reduction equivalent as hydrogen takes place.

FIG. 22



Expt. 4 In a platinum crucible 1.1218g. phosphorous acid was studied; the weight loss was allowed to come to equilibrium at 300° and then the temperature increased to 400°. Again the same type of nitrogen stream was used. The weight loss was 309mg., the theoretical loss for the equation,

$$4\ H_3PO_3 \rightarrow 3\ HPO_3 + 3H_2O + 2PH_3 \text{ is}$$

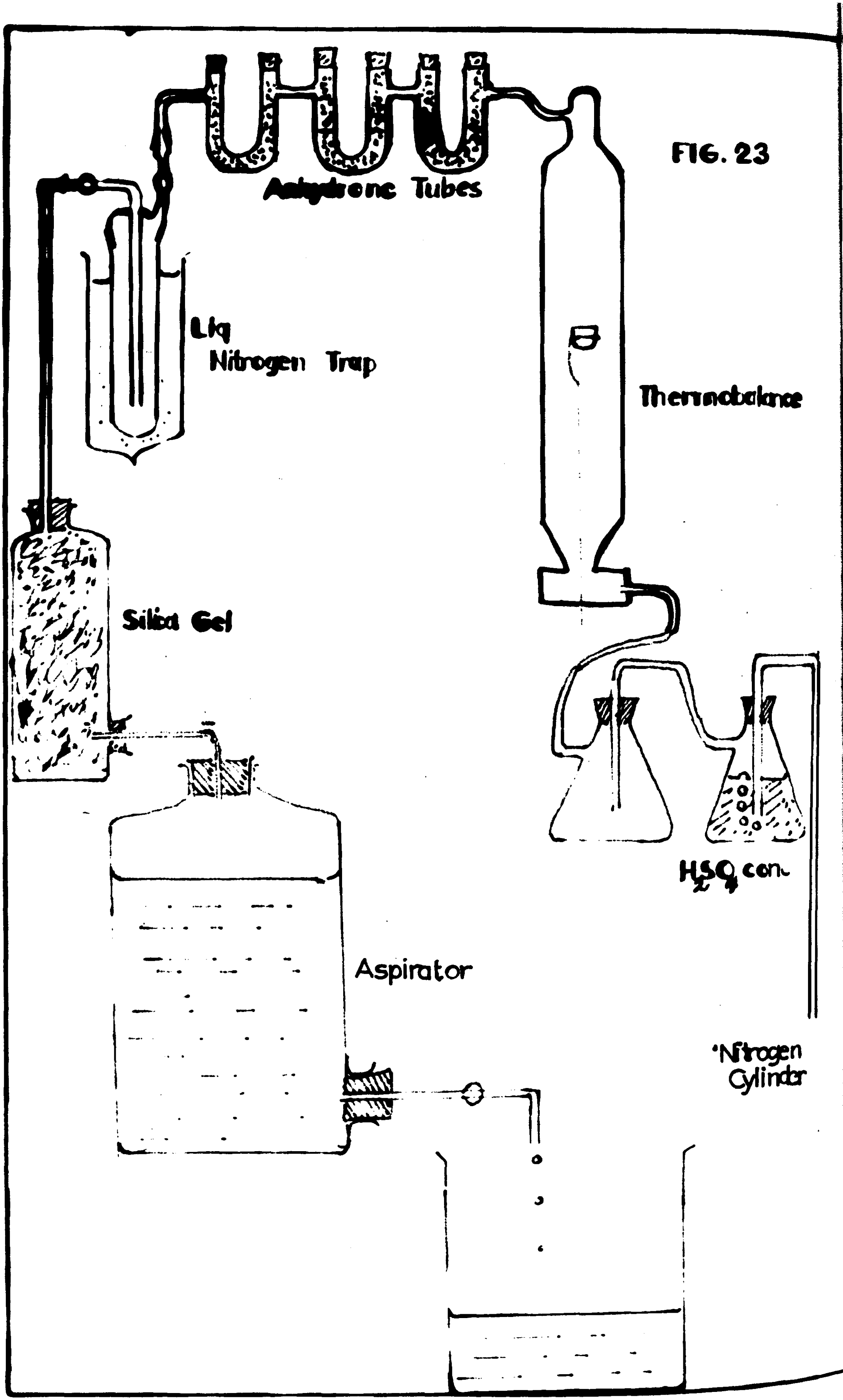
300mg.

Expt. 5 A dry nitrogen stream was used now, the nitrogen flow was passed directly through silica gel and phosphorus pentoxide columns. No weight increase of 1.0710g. phosphorous acid studied occurred. On raising the temperature (3°/min.) weight loss began at 100°, very slowly, more rapidly at 130°, the equilibrium at this temperature is 0.12 H_2O / H_3PO_3. At 218° another process begins, phosphine is evolved. The temperature was held constant at 220°. Two stages in the fast reaction occurring at this temperature can now be recognised, the curve is shown in Fig. 22. A platinum crucible was also used in this experiment.

Stage		Wt. loss corresponding to			Temp.
a		0.12	H_2O		130°
b	to	0.375	H_2O	inflexion	220°
c		0.22	PH_3		220°
d		0.5	H_2O		to 360°

The two stages of the fast reaction appear to be rationalisable by the occurrence of $\overset{3}{P}\text{-O-}\overset{3}{P}$ bond formation almost to the pyro stage before oxidative breakdown takes place; however the two

FIG. 23


Anhydrone Tubes
Liq
Nitrogen Trap
Thermobalance
Silica Gel
H_2SO_4 con.
Aspirator
Nitrogen
Cylinder

reactions run into each other and it is doubtful if this method could be used to prepare pyrophosphorous acid. The weight loss up to the equilibrium value at 220° is 184mg. and that required by the stoicheometry $H_4P_2O_7$ at this point is 198.4mg. This suggests that about 8% of the P-H bond rearrangement reaction product is hydrogen. The weight loss continues at higher temperatures as studied to about the HPO_3 stoicheometry.

Expt. 6 The above experiments were conducted with a downward flow of nitrogen through the furnace, the volatile pyrolysis products passed into the atmosphere. Since the thermobalance was situated where toxic gases could not be removed (for efficient thermobalance operation air currents in the surrounding atmosphere are to be avoided), and since the measurement of the phosphine which was evolved would enable a more accurate estimate of the hydrogen evolved in this sort of experiment to be made, a special method had to be devised to trap the emitted phosphine. This was done by passing the nitrogen up the furnace cavity into which a glass sleeve had been inserted, the crucible support passed through the flowing nitrogen seal described, the whole set-up is shown in Fig. 23.

Using 1.1535g. phosphorous acid the weight loss at 220° was 193mg. For the $H_4P_2O_7$ stoicheometry at this point a weight loss of 212.9mg. is required. Consideration of this weight loss, in the same way as carried out before, suggests that about 10% loss of P-H bonds as gaseous hydrogen occurs during the rearrangement step. The water absorption tubes, attached to the top of the furnace increased in weight by 98mg. (theory for the process suggested 94.3mg). It was found that the absorption tubes increased in weight by a few mg. on standing in air over the length of time used in these experiments, due to slight porosity of the connecting tubing employed to link the U-tubes.

Expt. 7 Using the same nitrogen flow arrangement 0.4752g. of phosphorous acid was studied. The weight loss was now 87.0mg. over the rearrangement step. That required for the formation of the pyrophosphoric acid stoicheometry was 88.4mg. During this experiment phosphine measurements were carried out and the technique of measurement of the amount evolved studied. The values obtained were not accurate however on account of absorption of the phosphine by tap grease and mercury decomposition products in the vacuum system used. These factors were removed in the next experiment.

Expt. 8 The same method of study was used, with 0.699g. phosphorous acid. The temperature was raised to 280°. The weight loss up to this temperature was 143mg. This corresponds to a dehydration stage intermediate between the pyrophosphoric and metaphosphoric stoicheometries, (about half way between). A weight of phosphine evolved of 59mg. was indicated by pressure measurements. The water absorption tubes had increased in weight by 87.4mg. The sum of these two weights is 3.4mg. greater than the observed weight decrease, rationalised by the extra uptake of moisture by the Anhydrone tubes mentioned above. Loss of phosphine in this case then appears to be 88% of the reaction involving the complete breakdown of the P-H bonds to phosphine. The oxidation equivalent of the final product is rather high (analysis of the final products are discussed later), being 2000, only 2% of the starting reduction equivalent is present, probably as P-P bonds. Again the results indicate the formation of a quantity of hydrogen of the order of magnitude of 10%, from the breakdown of P-H bonds.

Expt. 9 The reaction at 220° was allowed to come to completion, 1.0014g. phosphorous acid was studied, using the same nitrogen flow method.

Expt. 10. After the reaction at 220° the temperature was raised to 300°, and the weight allowed to come to constancy. The same flow method was used with 1.0901g. of phosphorous acid. 214mg water and 50mg. phosphine were evolved. This sample of phosphorous acid was obtained from a different source. It had not been stored over silica gel, and contained about 1% water. These results indicate that some differences may occur in the pyrolysis reaction in this case. Loss of all P-H bonds as phosphine requires the loss of 112.8mg. phosphine.

Analytical Data on the Products of the Pyrolysis of Phosphorous Acid at Atmospheric Pressure

Products obtained in the preceding experiments were studied by oxidation analysis, (using the ceriometric method, (194). pH titrations and paper chromatographic studies were also carried out.

The products were dissolved in water and transferred to standard flasks from which volumes were withdrawn for the three analytical approaches studied.

Volumetric Analyses

Expt.,	Equiv. Wt. strong P-OH	Equiv. Wt. weak P-OH	Ceriometric equiv. wt.
2			1938
4			very high
6	89.2	45.2	1438
7	88.8	43.9	2180
8	89.3	47.4	3760
9	89.3	44.5	216
10	86.7	50.4	6080

The strongly dissociated P-OH equivalent weight of pyrophosphoric acid is 89.0. This corresponds to the pyrophosphoric acid stoicheometry at the 220° equilibrium weight loss from phosphorous acid, confirming the previously made postulates. In these experiments the amount of heating beyond the rearrangement step varied. A direct relationship between this and the oxidation equivalent weight is found.

Experiment 9 is not quite in line since the value obtained is much lower than in the other cases. Here the presence of red colour was noted in the pyrolysis product, and a strong odour of phosphine was noted on dissolution of the material in water. Heating was continued only for a short time after the rearrangement step in this case.

The shape of the pH titration curves varied from product to product consistent with the formation of more complex mixtures of polyphosphates as the heating continued, as expected. The curve obtained from the product of experiment 9 gives the best definition of individual buffer regions, there being levels on the curve at pH 6.5, 7.2, 7.8 and II. This indicates the presence of several oxy-anions in the melt as would be expected.

Paper chromatograms were run on the various products from experiments 6-10. Again variations in the nature of the spots obtained depend on the length of time after the rearrangement step for which the sample was heated. The build up of condensed phosphate units is indicated, the product consists of mixtures of polyphosphates, the molecular weight of the species present increasing with the time and temperature of heating.

Paper Chromatography of the Products

The method employed was essentially that of Ebel, (99). Isopropanol solvents were used, with one dimensional elution and the running of a standard solution containing various phosphorus oxy-anions parallel to the unknown solution on the same paper. Both Schleider and Schull and treated Whatman No. 1 paper were used. The pretreatment method of Hanes and Isherwood as used by Ebel was employed for the latter paper.

Chromatograms were run of the pyrolysis products after standing at room temperature for various lengths of time in order to see if any of the spots initially present disappeared with time. This would have suggested the presence of easily hydrolysed $\overset{3}{P}-O-\overset{3}{P}$ bonds. The pH of the solutions was about I.

Product from expt. 6 ,	Time in soln.,	Rf value,	Solvent	Rf standard	
	40 mins.	.82	acid	.80	$\overset{3}{P},\overset{5}{P}\ \overset{1}{P}$
		.75			
		.50			
				.39	$\overset{5}{P}-O-\overset{5}{P}$
				.37	$\overset{4}{P}-\overset{4}{P}$
	"		basic	.70	$\overset{1}{P}$
				.56	$\overset{3}{P}-O-\overset{3}{P}$
		.42		.38	$\overset{3}{P}$
		.27		.24	$\overset{5}{P}$
				.19	$\overset{5}{P}-O-\overset{5}{P}$ $\overset{4}{P}-\overset{4}{P}$

Product from expt. 6 ,	Time in soln.,	Rf value,	Solvent	Rf standard
	2 days		basic	.66 $\overset{1}{P}$
				.55 $\overset{3}{P}-O-\overset{3}{P}$
		.40		.41 $\overset{3}{P}$
		.34		
		.29		.34 $\overset{5}{P}$
		.24		.26 $\overset{5}{P}-O-\overset{5}{P}$
		.19		.17 $\overset{4}{P}-\overset{4}{P}$
		.77	acid	.81 $\overset{4}{P}$ $\overset{5}{P}$ $\overset{1}{P}$
		.68		.74
				.67
		.47		.38 $\overset{5}{P}-O-\overset{5}{P}$
		.20		.29 $\overset{4}{P}-\overset{4}{P}$
			basic	.70 $\overset{1}{P}$
				.58 $\overset{3}{P}-O-\overset{3}{P}$
		.43		.40 $\overset{3}{P}$
		.36		.34 $\overset{5}{P}$
		.27		.28 $\overset{5}{P}-O-\overset{5}{P}$
		.23		.19 $\overset{4}{P}-\overset{4}{P}$
		.16		
	2 days	.75	acid	.81 $\overset{1}{P}$
				.75 $\overset{3}{P}$
				.69 $\overset{5}{P}$
		.56		
		.50		.50 $\overset{5}{P}-O-\overset{5}{P}$
		.41		.40 $\overset{4}{P}-\overset{4}{P}$
		.29		.30
		.21		
			basic	.67 $\overset{1}{P}$
				.54 $\overset{3}{P}-O-\overset{3}{P}$

contd.,

Time in soln.,	Rf value	Solvent	Rf standard
	.44		.41 $\overset{3}{P}$
	.38		.34 $\overset{5}{P}$
	.32		.27 $\overset{5}{P}-O-\overset{5}{P}$
	.26		.19 $\overset{4}{P}-\overset{4}{P}$
	.22		
	.17		
8 days	.85	acid	.85 $\overset{1}{P}$
	.78		.81 $\overset{3}{P}$
	.70		.73 $\overset{5}{P}$
	.53		.67
	.48		.47 $\overset{5}{P}-O-\overset{5}{P}$
	.41		
	.36		.36 $\overset{4}{P}-\overset{4}{P}$
	.27		
"		basic	.74 $\overset{1}{P}$
			.69 $\overset{3}{P}-O-\overset{3}{P}$
			.61 $\overset{3}{P}$
			.53 $\overset{5}{P}$
	.53		.41 $\overset{5}{P}-O-\overset{5}{P}$
	.51		.31 $\overset{4}{P}-\overset{4}{P}$
	.46		
	.41		
	.35		
	.30		

Similar experiments were carried out with the other pyrolysis products from experiments 7-10; these will not be dealt with in full. In the above series of chromatograms the solution contained 961mg. of pyrolysis product/50ml., lots of 5.10^{-3}ml. were applied to the paper from a micrometer syringe. The series shown at 2 days dissolution were run with different quantities of the unknown solution on the papers. As shown the pairs of acid and basic elutions were increased by 5.10^{-3}ml. unknown solution. It is seen that the Rf values observed tend to increase as the quantity of solution taken increases, also the numbers of distinguishable species increase.

The results indicate that there is a distribution of spots on the basic papers between phosphite and hypophosphate, while on the acid papers the distribution is not parallel to the standard spot distribution, especially in the occurrence of a well defined spot between phosphate and pyrophosphate Rf values. This, as far as is known, does not correspond to any of the so far characterised phosphorus oxy-acids. In the freshly made-up solution there is probably ortho, pyro, tri and tetra polyphosphate present; there may also be some phosphite or a species difficult to distinguish from this, like $\overset{3}{P}-O-\overset{5}{P}$ present. In addition there is the unknown species mentioned, present as a major constituant, (Rf, c.0.5, acid solvent). With the runs on the solution which had been allowed to stand for some time the amount of condensed phosphate units present appears to decrease, the spot at Rf. c. 0.5, however, remains of undiminished or possibly increased intensity. It is unlikely that there is an easily hydrolysed P-O-P bond present in this species. The presence of a P-P bond is suggested by the manner of formation of this mixture of product, the lack of hydrolysis and the presence of some oxidisable phosphorus in the solution.

The results which were obtained from the other reaction products studied may be mentioned.

From expt. 7 the chromatograms were similar to those obtained from expt. 6, except that there is more condensed phosphate species present. The spots extended to the origin of the chromatogram. No spot was detected in advance of phosphate on the basic chromatogram. The spot at acid Rf value 0.5 was also present here.

From expt. 8 the pattern was again similar except that the intensity of the spot at acid Rf. 0.5 was now less.

From expt. 9 five acid and five basic elutions with different amounts of freshly made up pyrolysis product solution were studied. On the acid chromatograms there were three groups of spots only, present, viz. the most advanced spot, which became resolved into two or three differently coloured spots at the higher phosphorus concentration studied, pyrophosphate and the unknown spot. Most of the phosphorus appeared to be present around the phosphate Rf (initially present pyrophosphate would have hydrolysed under the conditions used producing some phosphate). Some phosphite was also indicated. From expt. 10, a similar series of acid and basic chromatograms to the previous experiment were examined. The same type of distribution of spots as the earlier pyrolysis product solutions discussed, was noted. Much high molecular weight polyphosphate was present as well as the usual ortho phosphate and acid Rf. c5 spot.

Discussion of the Chromatographic Results

In general the type of product obtained as suggested by the chromatographic evidence is in keeping with the expected products of phosphite oxidative rearrangement. The molecular weight distribution present depends on the time and temperature of the pyrolysis after the rearrangement step. The more the oxidation product is heated the more $\overset{5}{P}-O-\overset{5}{P}$ bonds that are formed.

The presence of the spot at acid Rf. 0.5 may be correlated with the presence of oxidisable phosphorus in the product, albeit in small amounts. The equivalent weight of 6000 for example would suggest one $\overset{3}{P}$ / 12000 molecular weight units, or one $\overset{4}{P}$ / 6000 molecular weight units, or one $\overset{4}{P}-O-\overset{5}{P}$ for about 3000 m.w.u. ; $\overset{5}{P}-O-\overset{4}{P}-O-\overset{5}{P}$ / 1500 m.w.u. etc. Since the chromatographic Rf value can be used to obtain molecular weight data when homologous series are considered, there being for example a simple relationship between the Rf values of a series of polyphosphate anions or metaphosphate ring anions, an attempt may be made in the present case to consider this acid Rf 0.5 spot. The anions containing several P-P and P-O-P units have been studied in the basic chromatographic medium by Blaser and co-workers. Decomposition often seems to occur in the acid medium employed for chromatography. On the basic papers these species are lower than, or about the same Rf as the well known $\overset{4}{P}-\overset{4}{P}$ anion. The unknown spot on the acid papers is in advance of the $\overset{4}{P}-\overset{4}{P}$ anion, being intermediate between $\overset{5}{P}$ and $\overset{5}{P}-O-\overset{5}{P}$. The $\overset{4}{P}$ series, to judge from the present state of the subject is lower in Rf than the $\overset{5}{P}-O$ series, while the $\overset{3}{P}$ and $\overset{3}{P}-O-\overset{3}{P}$ anions are found in advance of the $\overset{5}{P}$ anion in the basic chromatograms. Incidentally the presence of pyrophosphite on the chromatogram, being in advance of ortho phosphite demonstrates the breakdown of the simple idea of decreasing Rf with molecular weight for a homologous series. This case of the advancement of pyrophosphite has been discussed by Ebel in terms of the correlation between the observed position of pyrophosphite and the expected position using the same approach as is employed with the polyphosphate or metaphosphate series; pyrophosphite lies where "metaphosphite" HPO_2 would have been expected to lie. He also claims to have observed the pyrophosphite spot on the acid chromatograms but this is unlikely since hydrolysis would occur here, however hydrolysis may not have taken place during the initial part of the elution, leading to an apparent small difference between the Rf value of the pyrophosphite and phosphite,(99). It seems that the best explanation of the advancement of pyrophosphite is the distinct difference between phosphite and pyrophosphite, this difference is much greater than between phosphate and pyrophosphate. Pyrophosphite is at the end of a series, as far as can be concluded from the present work and the real comparison in the phosphate series is between orthophosphate and metaphosphate. Confirming this similarity in the two series $\overset{3}{P}$ and $\overset{5}{P}$ the trimeta and tetrameta anions lie in advance of ortho phosphate in the basic chromatogram. Perhaps the present unknown spot is something like $\overset{2}{P}-\overset{4}{P}-O-\overset{5}{P}$, which has not been mentioned in the literature yet. A reduction in the overall oxidation number of the phosphorus atoms probably increases the Rf relative to some other structurally similar species. The $\overset{2}{P}-\overset{4}{P}$ might not be expected to be hydrolysed under the conditions used and the $\overset{4}{P}-O-\overset{5}{P}$ bond would be expected to be next to $\overset{5}{P}-O-\overset{5}{P}$ in hydrolytic stability, the series $\overset{3}{P}-O-\overset{3}{P}$, $\overset{3}{P}-O-\overset{5}{P}$, $\overset{4}{P}-O-\overset{5}{P}$ and $\overset{5}{P}-O-\overset{5}{P}$ probably showed increasing hydrolytic stability in this order, (other types of P-O-P bonds can, of course, be envisaged). The presence of $\overset{3}{P}-O-\overset{5}{P}$ in the pyrolysis products is difficult to ascertain by chromatographic studies since the anion decomposes on the acid paper to phosphate and phosphite while on the basic elution it gives one spot at the same position as ortho phosphite, although the spot is of a different colour, (196). The results obtained certainly do not rule out the formation of $\overset{3}{P}-O-\overset{5}{P}$ in the rearrangement products of phosphorous acid. The formation of this type of unit is perhaps to be expected when it is considered that the pyrolysis seems to show the initial formation of the $\overset{3}{P}-O-\overset{3}{P}$ acid which then undergoes a rearrangement of the P-H bonds, under certain conditions.

(III)

b)

(iii) Some Salts of Phosphorous Acid, (Phosphites)

The thermobalance pyrolysis of hydrogen phosphites has already been dealt with in the section on the formation of P-O-P bonds. Experimental data and some discussion of the individual pyrolysis experiments on normal and acid phosphites will now be considered.

Normal Phosphites

$Li_2HPO_32H_2O$

1.0726g. was studied. This salt was found to lose weight at room temperature (the actual stoicheometry at the start of the thermobalance run was for this reason slightly less than the 2.H_2O formulation).

Stage	Wt. loss corresponding to	Temp.,
a	1.16 H_2O	30°
b	0.72 H_2O	167°

The temperature was held at 210° while this last stage was proceeding and the rate was found to be only roughly exponential with a half life of about 22 mins. The initial part of the dehydration was zero order and the rate increased by a factor of 3.5 for a 10° rise in temperature.

0.6551g. of the sample of Li_2HPO_3 obtained here was taken for further pyrolysis. On raising the temperature to

340° an exothermic reaction took place with an accompanying weight increase (44mg. or 0.40 / HPO_3^{2-}). This will be due to the oxidative breakdown of the P-H bonds. A weight decrease rapidly followed this (+ 19mg. from the Li_2HPO_3 level). On raising the temperature above 490° a further 6mg. was lost. Since there are no P-OH bonds present now the simplest type of oxidation of the P-H bonds, in the atmosphere, to P-OH which at the temperature employed would lose H_2O to form P-O-P bonds leading to an overall process thus,

$$2\ Li_2HPO_3 + O_2 \rightarrow Li_4P_2O_7 + H_2O\ .$$

In the present case this leads to the requirement for the increase of weight of 49mg; the weight process found indicates the formation of only 26% P-O-P bonds in this way. The formation of P-P- bonds in the final product or the volatilisation of some material is indicated by these figures. 5% volatilisation up to 600° would account for the observed weight changes, if the non-volatile residue is present in the fully oxidised form. The final residue was analysed by ceriometric oxidation and the oxidation equivalent of $c. 2.10^3$ found, suggesting about 5% $\overset{4}{P}$ in the product. Volatilisation of material is suggested by these results.

$Na_2HPO_3\ 5H_2O$

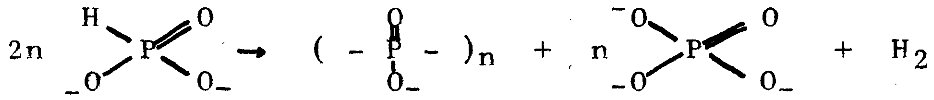
2.3562g. was studied with stepwise increases in temperature at 3°/min.

Stage	Wt. loss corresponding to	Temp.,
a	0.3 H_2O	60°
b	0.25 H_2O	"
c	0.25 H_2O	"
d	4.0 H_2O	118°
e	0.25 H_2O	138°

The first three stages are zero order being continuous each having a slightly different linear rate. The difference between stage a and b is the more marked. Perhaps after initial loss to stage b the structure of the 5 H_2O hydrate breaks down forming the phase $Na_2HPO_3.4.25H_2O$ and free water in the crystal, then this water escapes by a simple evaporation process involving zero order kinetics. Such different hydration levels as are suggested will probably reflect hydrogen bonding possibilities in this system. Changes occur with "4" units. About $\frac{3}{4}$ H_2O are lost initially forming a phase which loses 4 H_2O. The phase produced here is $4Na_2HPO_3H_2O$.

The pyrolysis was continued to higher temperatures. Little weight change took place at 400°. The weight increased slowly and was brought to eqilibrium at 500°. The residue was coloured brown. The actual weight increase was 90% of that required for pyrophosphate formation. A ceriometric analysis was carried out on the product and an oxidation equivalent weight of about 1400 found. If the oxidation equivalent weight is due to the presence of P-P bonds produced by the loss of hydrogen during the breakdown of the P-H structure, then the ratio of P^4 / P^5 in the product obtained from this c.I.10, is in agreement with the weight increase data. No volatilisation of sodium oxy-phosphorus units is indicated here in contrast to the results for the lithium salt.

The formation of colour in these cases by the build up of P-P bonds, involving reorganisation of the anions must be accompanied by the formation of ortho phosphate to maintain electrical neutrality c.f.



There is another possibility in general that of formation of P-M bonds. Phosphides could conceivably be produced in these reactions, as has been generally considered to be the case by other earlier workers.

K_2HPO_3 $0.67H_2O$

This phase was obtained by evaporating a solution containing the normal potassium phosphite stoicheometry at 60°, until solidification occurred. The material is hygroscopic at room temperature.

0.6132g. was studied on the thermobalance, weight loss became rapid above 100°, a discontinuity being found at c. $K_2HPO_3 0.4H_2O$ and anhydrous at 150°. On continuing the pyrolysis weight increase occurred gradually being noticeable at

250°. Up to 360° the weight had only increased by 0.16%, at this temperature the material was coloured brown and a slight smell of phosphine was detectable.

Rb_2HPO_3

0.1363g. was taken and the temperature increased linearly at 3°/min. to 420°, and maintained at this temperature for 7.8 hours. Little change in weight occurred during the process as studied. The final product appears to have the same crystal form as the starting material, although somewhat discoloured. No apparent change whatsoever appeared to have occurred at 280°. An infra-red study of the pyrolysis product and the starting product is given:

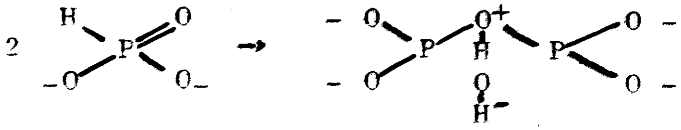
frequency, cm.$^{-1}$	Starting product		Final product	
	3329	s	3308	m
	2770	m	2770	m
	2360	m	1646	w
	2283	sh	1288	sh
	1644	m	1271	vs
	1158	s+	1142	sh
	1070	s	1107	sh
	1015	s	1091	s
	976	m	1008	m
	934	m	873	vs
	858	sh	801	m
	773	w	721	sh
	720	m	720	m

These spectra were obtained in nujol mulls.

A total change in the symmetry of the anion present in the final and starting product is observed. The frequency ascribable to P-H at 2360 cm.$^{-1}$ in the starting product is not present in the final product; here the strong absorption at 873 cm.$^{-1}$ is characteristic of the P-O-P bond; this is present as a major constituant of the product.

A study was made of the oxidation equivalent of the final product. Surprisingly it dissolved readily in water and the resulting solution was analysed giving an oxidation equivalent of about 140, the starting product had a value of 125. This indicates that although the P-H bonds have been removed from the product, the oxidation equivalent has only been reduced by 11%. Chromatograms suggested the presence of phosphite and other species with Rf values around P^{4}-P^{4} in the basic elution. Hydrolysis of the solid product will have taken place on dissolution.

The rationalisation of the results would seem, on the face of it to suggest some rearrengement of the P-H bond of the product to the non P-H bonded form, some oxidation of the product by atmospheric oxygen will have occurred leading to the equivalent weight of the product being greater than that of the starting material. Perhaps the data can be rationalised by the main reaction occurring on heating as follows:



This rationalisation should be regarded as provisional only at present.

Cs_2HPO_3 $2.5H_2O$

3.2409g. was studied. The temperature was held at 123° for 21 hours, during which time the weight continued to alter, the rate of change becoming slower as time progressed. The asymptote tended toward was the $Cs_2HPO_2 2H_2O$ stoicheometry. On raising the temperature to 160° rapid weight loss took place. A rather surprising odour was apparent over the crucible, perhaps rearrangement to some extent had proceeded leading to volatilisation of some unknown product. This point was not studied further.

The oxidation of Cs_2HPO_3 in air is a slow process, weight became constant after 23 hours at 320°. The final product was largely tetra caesium pyrophosphate. The oxidation process was followed by removal of samples and studying infra-red spectra and pH titrations on the acid obtained on passing the pyrolysis product through a cation exchange column. The final product had a ceriometric equivalent weight of 3600 and the infra-red spectrum of this product as well as the weight change which had occurred in its formation were as expected for the pyrophosphate formulation. In this case then the oxidative rearrangement which takes place is straightforward.

The pH titrations, infra-red spectra and oxidation equivalents of the three samples which were studied, viz. the final and starting products and one corresponding to a minimum weight, in the weight curve, may be compared

Product	Oxidation Equiv. wt.	pH Equiv wt. (Cs replaced by H^+)	pH step	Frequency cm^{-I}
Start	174.4	146.2	8.4	3960 sb
		235	6.2	2353 w
		248	6.1	2245 w+
		348	4.9	1660 mb
		410	4.1	1110 vs
				1095 s
				980 s
				940 vw,b
				967 vw
Mid	212.0	156.5	9.7	3260 sb
		234	7.2	2370 vw
		245	7.1	2265 w+
		299	6.3	1660 mb
		321	5.9	1206 ws
		353	5.3	1088 vs
				979 m
				888-901 wb
				703-731 vwb
Final	3595	170	9.4	3260 sb
		180.3	8.9	2471 vw
		184.7	8.7	2275 vw+
		198.3	8.2	1660 mb
		213.8	7.4	1220 m-
		344	5.3	1118 vs
		385	4.8	1021 m-
		414	4.4	968 m+
				896 sb
				703-716 mb
				671 vw

Note, the formula weight of Cs_2HPO_3 is 346.

These results show the change on heating from the P-H bonded form to the P-O-P bonded form. The P-H absorption in the infra-red at about 2250 cm^{-I} disappears as the formation of the P-O-P bond occurs, the absorption due to this latter unit is at about 703 cm^{-I}. These pH titrations were carried out after cation replacement by H^+, the complexity of the material increases as the pyrolysis was continued.

$BeHPO_3H_2O$

0.2151g. was studied. On heating a discontinuity occurred in the weight plot corresponding to the $BeHPO_30.5H_2O$ hydration level, at 165°. After the anhydrous stage continuation of the heating produced little change in the weight. The colour however becomes orange and the material swells up, the final product was of low bulk density. Heating was continued up to 525°. The final product had a ceriometric equivalent weight of 390, this would correspond to $\overset{4}{P}:\overset{5}{P}$ of 1:4-5, the infra-red spectrum of the final product does not show the P-H stretching absorption. The oxidisable phosphorus may then be reasonably assumed to be due to P-P bonding. Again the orange colour will be an indication of this. The spectra of $BeHPO_3H_2O$ and the pyrolysis product are rather interesting apart from the P-H absorption range; the starting product exhibits fewer absorption positions than any other similar phosphite met with in these studies.

$BeHPO_3H_2O$ frequency cm^{-I}		Pyrolysis product frequency cm^{-I}	
3220	m	3175	vw
2403	w+	2281	vw
2293	w	1651	w
1643	w	1183	w
1107	vs	983	sb
720	mb	894	s

These spectra were obtained in Nujol mulls. In the beryllium phosphite monohydrate the P-O region exhibits only one absorption at 1107 cm^{-1}. This peak is broad and symmetrical. It is as though the customary degeneracy of the absorptions had been removed and all the P-O absorptions come together. This will be due to the polarising nature of the Be^{2+} cation. The symmetry of the phosphite oxygens will be increased by the highly charged small cation, discrete P=O and $P-O^-$ units can be no longer distinguished in the anion. This difference from the other salts studied where the cation is not so highly polarising will be reflected in the differences in the nature and course of the pyrolysis reactions which are found with such different cations. There may be a higher tendency for P-P bonded forms to be stabilised to atmospheric oxidation when the electrons are attracted to a polarising central metal ion from the P-O bonds.

Paper chromatography was used to study the reaction products. The orange solid is insoluble in water; however on standing some time in contact with hot water, some phosphate and polymeric zero Rf material is detected on the chromatograms. Treatment with HCl produces a variety of high molecular weight material. One of the major snags to the identification of the units present in solution is the presence of Be^{2+} which interferes in the elution by complexing with the phosphorus oxy-anions on the paper. When the solution of the products which can be obtained by the action of concentrated HCl on the orange solid, is passed through a cation exchange resin, some Be appears to be unexchanged. This will be due to the presence of complex ions in solution containing Be which are anionic, and therefore cannot be exchanged for H^+ in the resin.

The chromatographic results are however in line with the idea of the formation of orthophosphate in a matrix of poly-units, containing P-P and P-O-P bonds; the equation written on page 195 for the rearrangement of the HPO_3^{2-} anion producing phosphate and condensed units is valid here. It was noted that the coloured material in HCl solution remained at the origin in paper chromatography, this tends to confirm the idea that the oxidisable phosphorus is present as polymeric units, it being assumed that the presence of colour indicates the presence of oxidisable species.

$MgHPO_3$ 5 H_2O

1.1803g was studied. On preparation of magnesium phosphites bulky precipitates are obtained; when they are filtered these appear to increase in bulk, due to the crystallisation of hydrates during the filtration process. One such product was taken and the weight loss allowed to come to constancy, roughly at room temperature. On raising the temperature to 60° immediate weight loss ensued. When the thermobalance weight plot was transferred to semi-log paper, using the final constant weight at 60° as asymptote, a number of linear sections appeared corresponding to successive dehydration stages of the starting compound. From the straight thermobalance plot the following sections may be distinguished,

Stage	Wt. loss corresponding to	Temp.,
a	4 H_2O	60°
b	0.5 H_2O	80°
c	0.17 H_2O	180°
d	0.33 H_2O	235-340°

The last stage verges onto the region of oxidative breakdown of the P-H bond, in this system. On the logarithmic plot of the first stage the following stages may also be distinguished loss of 1, 2, 3 and 3.5 H_2O. Towards the end of this, several more stages may be present. At the temperature of 350° oxidative breakdown occurs. During this stage the sample was noted to become brown in colour. The weight increase registered was only about 1%, whereas that required for the simple oxidation to the pyrophosphate stage is about 7%.

$CaHPO_3H_2O$

Expt. 1 Using 0.2812g. of a product an initial weight loss was found to be detectable at 218°, there was a possible discontinuity at 248° on linearly increasing the temperature. On increasing the temperature a slight weight increase began at 294° and stopped probably at 380°. The highest temperature studied was 521°.

Expt. 2 Using 0.2932g. of a different product $CaHPO_3H_2O$ obtained by precipitating from a solution containing excess phosphorous acid (where the Ca; phosphite was 1 : 2), two stages may be distinguished in the weight loss curves. The weight was allowed to come to equilibrium at 185°, the value obtained was 0.68 H_2O loss at this temperature. On heating up to 230° the dehydration was completed.

As is the normal case on pyrolysis of normal phosphites no phosphine is evolved from the product. On raising the temperature above this, weight increase was noted to begin at 430°. The weight increased by 58% of that required for the pyrophosphate formation. No weight increase occurred above 517° although the temperature was increased to 580°.

Differences in the infra-red spectra of the substance studied in expts. one and two above were noted. The spectra of the starting products in expts. one and two as well as the spectrum of the intermediate dehydration product of expt. two are shown:

Expt. 1		Expt. 2		Intermediate dehydration product.	
3305	s	3350	s	3360	m+
2416	m	2303	m	2481	m-
2298	w	1660	m	1633	m
1663	m	991	s	1130	vs
1130	s+	864	w	1074	vs
1060	vs			989	s
1024	w			864	vwb
990	s			740	wb

Two main points of difference emerge from these spectra, differences in the P-H region and those in the P-O region. In expt. 1 and expt. 2 intermediate product, the P-H absorption is split whereas in the starting material for expt. 2 it is a singlet. Also the strongest vibration group in the P-O region is single or split the same as the P-H in these cases. The differences will be structural ones. The splitting of these absorptions denotes a decrease in symmetry on the anion in the crystal structure. It is noted that the P-O region shows increasing discreteness from the product used in expt. 2 to the intermediate product in expt. 2 to the starting product of expt. 1.

$SrHPO_3H_2O$

Similar studies were carried out on samples with this formulation. Again differently prepared samples showed variations in the dehydration curves and in the infra-red spectra.
Expt. 1 Two experiments were conducted with a sample obtained from a solution to which excess phosphorous acid was added. 0.1361 and 0.6688g. samples were studied. Weight loss starts at 78° and becomes rapid at 113°, in both cases.

At 330° a weight increase was found, ceasing when the temperature was brought below this value and starting up again on reheating above it. Weight increase was studied up to 460° and a weight increase indicative of 80.7% pyrophosphate formation found. The final product was brownish coloured.

Expt. 2 Another sample was obtained by the straightforward precipitation of Sr by one equivalent of phosphite, and the thermobalance plot showed that weight loss occurred at somewhat higher temperatures than found in the previous experiment. Weight loss became rapid at c. 180°, and remained unaltered to about 350°. The oxidation of the P-H bonds became more noticeable at 400°, a weight increase of 5.3mg. was recorded indicating 56% pyrophosphate formation.

The infra-red spectra may be compared,

Expt. 1		Expt. 1 dehydrated		Expt. 2			
3264	s	3306	m	3259	s+		
2381	m	2395	s-	2371	s		
2294	w	1620	wb	1679	m		
1675	w	1350	vwb	1215	m	967	m
1118	vs-	1132	vs	1128	vs-	747	m
1062	vs	1080	vs	1070	vs	708	m
1010	w	984	s	1062	vs	694	m
993	s	761	vwb	1015	m		
				992	s		

Again in this case it was noted that there was a tie-up between the splitting of the P-H absorption and the resolution of the P-O region, this was most noticeable for products from expt. 1. The number of absorptions, which are well resolved, found in the product used for expt. 2 is surprisingly large.

$BaHPO_3x\ H_2O$

This product was investigated in the same way. Two samples obtained as for the previous two salts discussed were found in this case to be identical. Both the P-H region and the strong absorption in the P-O region were singlets.

Expt. 1 Taking 0.6965 and 0.3965g. weight loss was found to occur in the temperature range 350-400° consistent with a value of x of 0.14 in the above formulation. Simon has rationalised this weight loss as being due to the migration of the P-H unit producing some P-OH bonds, but with barium salts it is difficult to be sure of this since the formation of basic salts and ill-defined hydrates appears to be common. The infra-red spectra are given

Starting product		Pyrolysis product	
3330	w	3360	w
2386	m	2283	vw
1088	vs	2243	vw
1026	m-	1660	wb
1010	m-	1182	m
977	s .	1142	s+
		1115	s
		1051	m
		1018	s
		977	s
		748	w

Weight increase had been observed at 477°, the weight becoming constant above 600°. This suggested 25% pyrophosphate formation, some P-O-P bond absorption is indicated in the infra-red spectrum of the final product.

Tl_2HPO_3

0.6131g. was taken and the temperature increased at 3°/min. to 380° and after a period at this temperature this was increased to 500°, slowly. Little change in the weight over the whole process may be distinguished, however slight weight increase occurred above 340°. The crucible was examined at various points. At 350° the colour of the melt present was greenish with some bubbles present. A slight odour of phosphine was detected. At 400° the phase present was a viscous glass with some entrapped bubbles and this appearance was also observed at 500°. On cooling the material became solid. The reaction possibilities are increased in this case by the possibility of the existence of the two oxidation states of the Tl ion, viz. (I) and (III).

The residue from this experiment was dissolved in water and made up to 25ml. The ceriometric equivalent was 140, indicating about 13% oxidation of the starting material, this, however, is not in agreement with the weight increase observed although this is rather small, and possible subject to the thermobalance weighing errors.

Chromatograms were run using the solution. On the acid paper there were a series of spots in the pyrophosphate-hypophosphate region, in the basic elution most of the phosphorus in the pyrolysis product appeared to migrate to below the hypophosphate level. If it is considered that the presence of Tl in solution (the oxidation results indicate that this is present largely as Tl(I)) unlike the presence of the alkaline earth ions will not perturb the migration of the anion as compared to a solution which does not contain this cation, then these results indicate the presence of lower oxy-anions of phosphorus in solution, possible based on the P-P-P type of unit.

The infra-red spectrum of the final product is rather simple, frequency cm.$^{-I}$

1062	vsb
991	m
878	sb
727	wb
693	m

There is an indication of the presence of condensed units, and some P-O-P bonding is indicated.

$(NH_4)_2HPO_3H_2O$

0.2679g. was taken, and the total weight loss up to 660° was 251.6mg. or 94.2% of the original weight. From 20-30° the material was found to increase in weight by uptake of moisture from the atmosphere. As the temperature was raised slowly to 90° a number of linear sections were obtained in the dehydration curve. At 100° weight loss became more rapid and the evolution of ammonia and later phosphine was noted. Above 550° weight loss again became rapid, this proceeding linearly with a linear temperature increase. The weight loss came to a stop at 620°. There was found to be some difficulty in distributing the observed weight loss between ammonia phosphine and water but the data obtained are in agreement with the initial loss of hydration water followed above 100° by the loss of one molecule of ammonia per phosphite unit, this gives essentially the mono ammonium hydrogen phosphite already dealt with. Above 235°, at a similar temperature to that observed with the oxidative breakdown of phosphorous acid, the evolution of phosphine became apparent.

Stage	Wt. loss corresponding to	Temp.,
a	H_2O	to 90°
b	NH_3	to 290°
c	0.2 PH_3	from 235°
d	H_2O	to 590°

It is expected that as the large scale volatilisation of the residue above 590° occurs decomposition of the largely ammonium metaphosphate stoicheometry at this stage will take place producing gaseous ammonia and phosphorus pentoxide as well as water vapour. However the formation of N-P-O material in the gaseous phase cannot be ruled out.

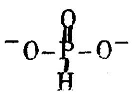
These results are in agreement with published data c.f (82).

$CdHPO_3$

0.6711g. was studied. Little weight loss was found to occur up to 330°. The weight loss registered was found to be 0.4%. Samples were withdrawn during the pyrolysis run and the ceriometric equivalent weight obtained. This showed that, as the heating progressed, the amount of oxidisable material fell to zero. It seems that loss of reduction equivalent is best rationalised in this case by the loss of hydrogen, since the weight change observed is so small. In actual fact two simultaneous weight loss and gain processes may be occurring.

That no weight loss occurs is somewhat surprising in light of the infra-red spectrum, which is rather anomalous.

Starting material	3142	sb	1103	vs
	2387	m	1040	vs
	2314	vw	975	vs
	2291	w	859	m
	1745	m	721	m
	1642	w		
	1534	m-		
	1447	s		
	1418	m+		
	1296	m		

The presence of the strong broad absorption at 3142 cm^{-I} is indicative of the presence of O-H stretching as in hydration water and is different from that of the P-OH stretching at 2880 cm^{-I}. However the analysis of the salt by the ceriometric method gives the correct equivalent weight for the $CdHPO_3$ formulation. The remainder of the spectrum is also as required by the presence of the  $^{-}O-\overset{O}{\underset{H}{\overset{\|}{P}}}-O^{-}$ anion. Unusual absorptions do however occur which are not normally obtained with this type of salt, viz. 1534 and 1437 and 859 (this latter one is sharp) cm^{-I}. The results might be indicative of the presence of "migrated P-H" forms of the phosphite anion, although this can only be taken as a provisional rationalisation at the present.

$ZnHPO_3 2 H_2O$

Stage	Wt. loss corresponding to	Temp.,
a	0.66 H_2O discont.	105°
b	to 1.50 H_2O	105°
c	to 2.00 H_2O	186°

On increasing the temperature above the level studied, above weight increase occurred. This became rapid at 255°. The sample was odourless. The colour of the material became black during this stage. The weight increase is really only a small amount, about 20% of the weight increase required for the pyrophosphate formation.

Ceriometric analysis of samples withdrawn from the crucible after appropriate times showed that the initial dehydration proceeded without loss of P-H bonds but that heating for 2.8 hours at 230° before the weight increase had occurred lead to a loss of c.60% of the reduction equivalent. This shows that the loss of hydrogen occurs here.

$PbHPO_3$

0.6879g was studied. Little weight change occurred on heating although above 303° some slight increase occurred. This was equivalent to 21% of the weight increase required for the formation of pyrophosphate. An interesting observation was made during the low temperature pyrolysis before the weight increase. An odour, not unpleasant, was detected over the sample. The final product had a ceriometric equivalent weight of 780 or the ratio of $P^4 : P^5$ in the product was 1 :1.8, (the sample had been heated at 342° for 3 hours). The infrared spectrum showed that there was no P-H absorption present, the spectrum may be compared with that of the starting product

Starting product		Pyrolysis product	
frequency cm^{-1}			
3280	vw	3233	w
2463	w		
2309	m		
1620	vw	1620	vw
1076	vs	1109	vs-
988	s	1072	vs
963	s	1021	s
		944	s
		732	shm-
		716	mb

The presence of condensed products with some P-O-P bonding is indicated.

$SnHPO_3$

(The sample was kindly supplied by Mr. Moser and Mr. Simpson, Aberdeen). 0.1658 g. was taken. Little change in weight occurred on heating. As with the other cases studied a colour change became apparent. A slight grey colour was noted at 320° while the colour was black by 460°.

$MnHPO_3.0.67H_2O$

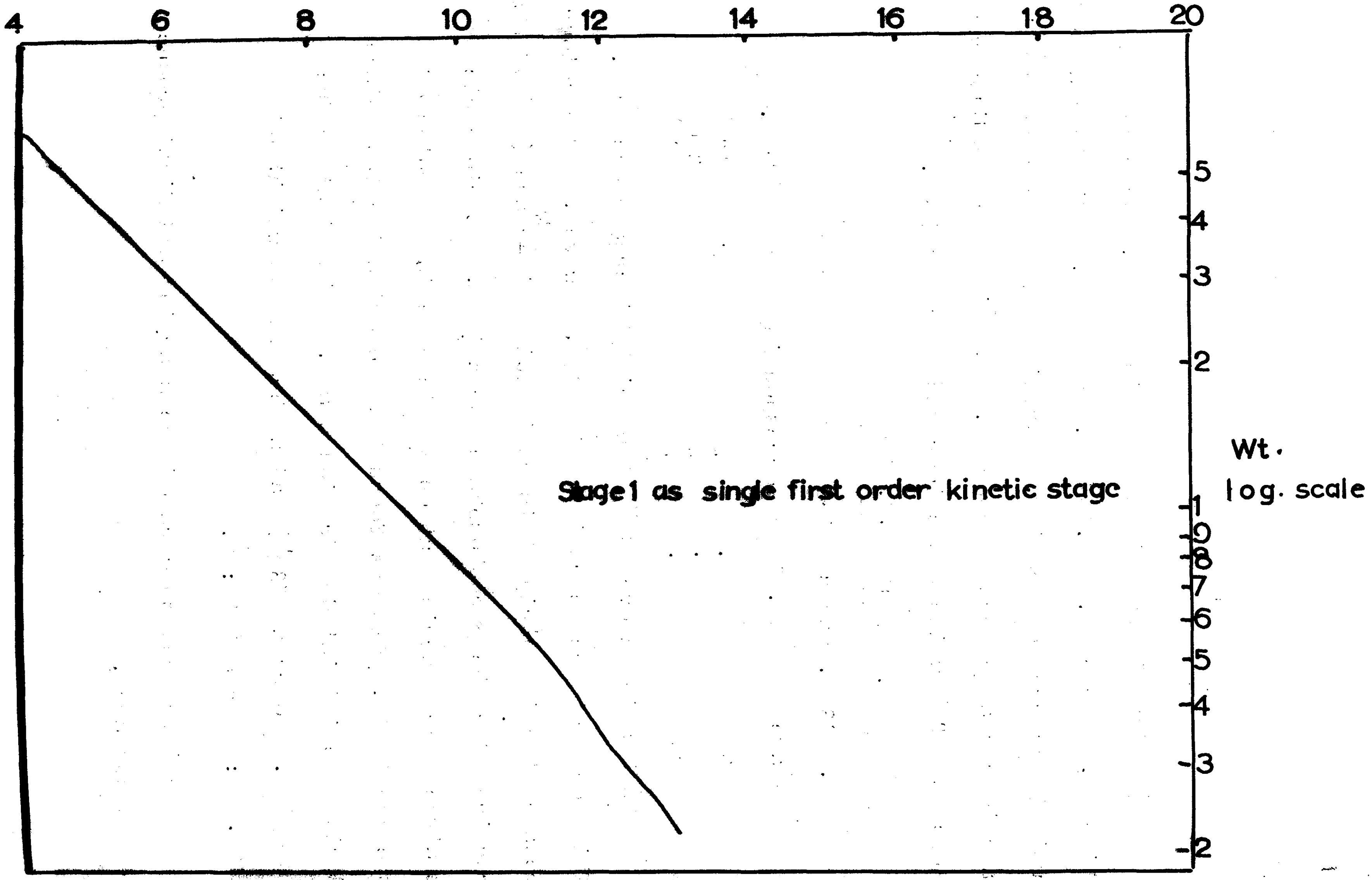
0.4833 g. was studied

Stage	Wt. loss corresponding to		Temp.
a	0.50	H_2O	135°
b	0.1	H_2O	260°
c	0.06	H_2O	338°

On heating above 338° slow weight increase occurred. This does not become rapid until 534°, however. The colour became blackish during this rapid weight increase (59% of that required for the pyrophosphate formation). Ceriometric analyses were carried out on the intermediate samples of the pyrolysis. It was found that no oxidation took place during the initial dehydration stage. The final product (about 1.7 hours at 536°) had an equivalent weight of 1220, $P^4 : P^5$ about 1 : 9.

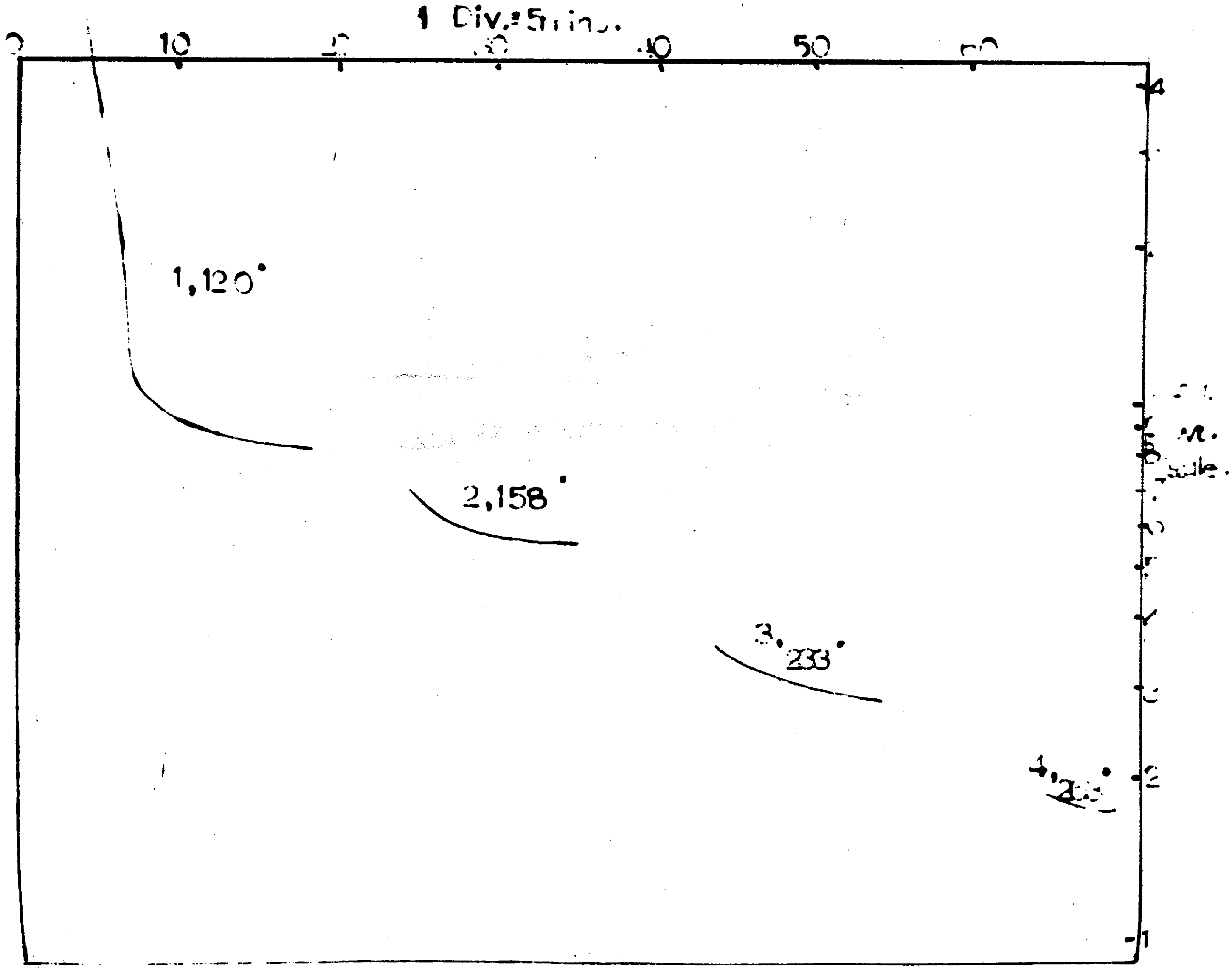
The infra-red spectra of the starting and final product may be compared,

FIG.24


1 Div= 5mins.
4
6
8
10
12
14
16
18
20
5
4
3
2
1
9
8
7
6
5
4
3
2
Wt.
log. scale
Stage1 as single first order kinetic stage

Stages in Dehydration of $NiHPO_3.2.5H_2O$

FIG. 24a



frequency cm.$^{-I}$

Starting product		Final product	
3200	sb	3367	sb
2388	m	2305	w
1633	m	2264	w
1088	vsb	1645	m
984	s	1244	sb
		1097	vsb
		965	vs-
		923	s
		721	mb

Some P-H appears to remain in the final product, the presence of condensed units with P-O-P bonding present is also indicated.

$FeHPO_3$ IO H_2O

0.3920 g. was studied.

Stage	Wt. loss corresponding to	Temp.,
a	9 H_2O	75-135°
b	I H_2O	170°

On heating above this level a slow weight increase occurred accompanied by a colour change. Oxidation of Fe(II) to Fe(III) is indicated. The starting colour was greenish, as was the colour after stages a and b.

$CoHPO_3$ I.5 H_2O

Stage	Wt. loss corresponding to		Temp.,
a	0.2 H_2O	purple	128°
b	0.57 H_2O	blue	136°
c	0.66 H_2O	blue	250°

The distinction between stages b and c is not sharp. At 380° the weight showed an increase, decreasing momentarily after this as the temperature was raised. The temperature was held at 545° for 2 hours ; the increase over this time was 54% of that required for the pyrophosphate formation. The final colour was dark green-blue, no odour was detected at any time during the process.

The ceriometric equivalent weight of the final product was about 550 indicating a ratio of $P^{4}:P^{5}$ of I:2.9.

$NiHPO_3 2.5\ H_2O$

0.6678 g. was studied.

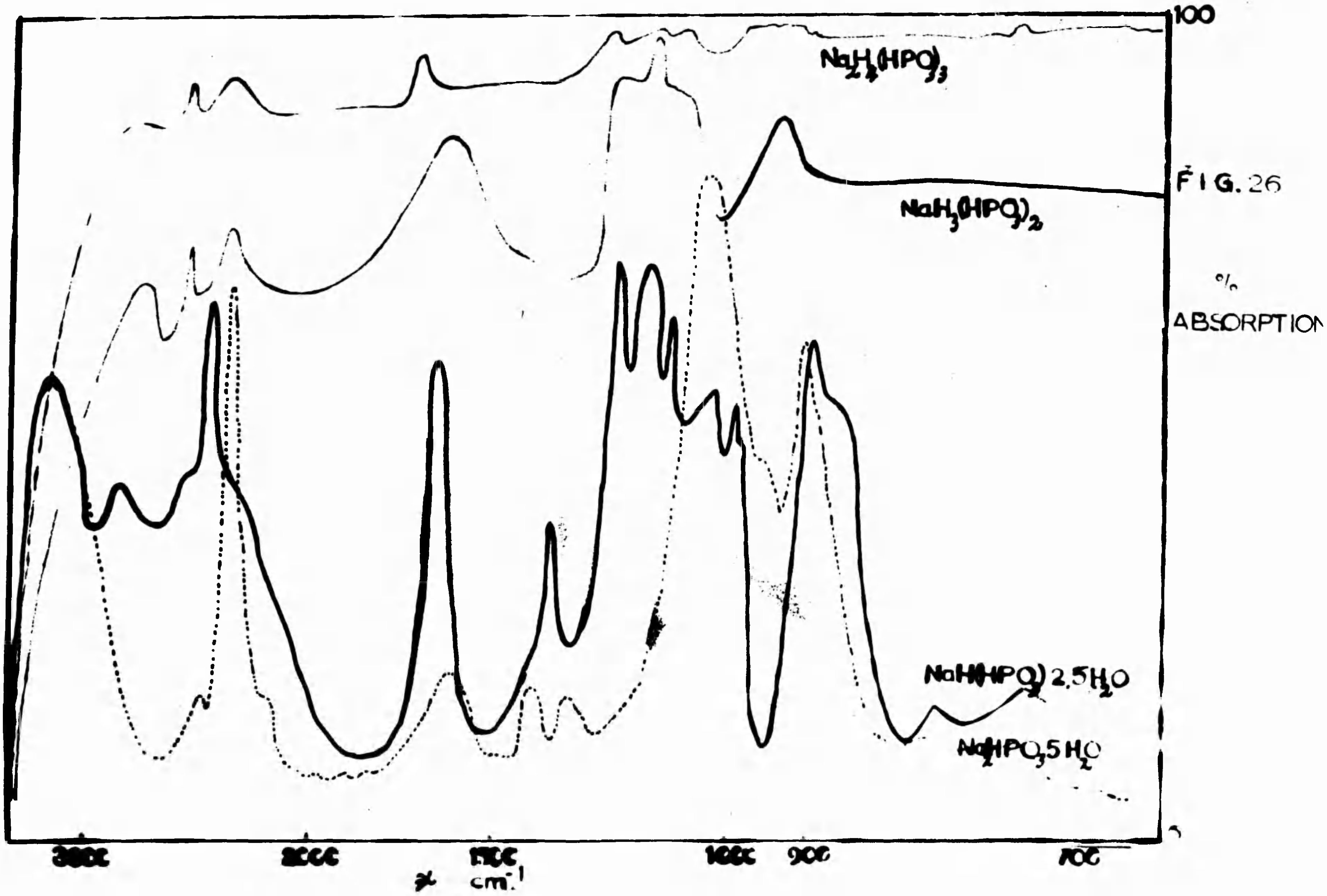
Stage	Wt. loss corresponding to			Temp.,
a	I	H_2O	light green	45°
b	0.5	H_2O	" "	124°
c	0.5	H_2O	Darkens	168°
d	0.5	H_2O		239°

The oxidation reaction overtakes the final dehydration reaction, the colour is found to darken. The weight reached a constant level at 360° which does not alter sensibly as the temperature is raised to 575°. A small weight increase may have taken place during the dehydration process, the data suggests that the weight increase was as required by about 50% pyrophosphate formation. The steps in the above process have straightforward kinetics, stages a and b being first order. They correspond to distinct kinetic processes having different asymptotic levels. The semi-log. plot is shown in Fig. 24.

$(Hg(I)_2)HPO_3$

This substance was found to possess a number of interesting properties. When heated rapidly up to 230° violent explosion occurs, with loud detonation. Drops of metallic mercury are produced in this reaction. When heated slowly volatilisation took place at c.74°. 0.1214g. was studied in this experiment, and at this temperature a weight increase of IImg. had taken place, the sudden decrease was 55 mg. Metallic mercury and phosphorus containing residue remained in the crucible. It appears that oxidation-reduction reactions occur here with the production of volatile mercury compounds and metallic mercury. Paper chromatographic results on the phosphorus material showed the presence of phosphate but no phosphite.

It was observed that the starting product decomposed on standing, studies by ceriometric oxidation where Hg(I) and Hg(II) can be distinguished, c.f. (197), showed that the reaction $\text{Hg-Hg(I)} \rightarrow \text{Hg(II)} + \text{Hg(0)}$, which is common with mercurous compounds, had occurred.



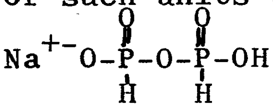
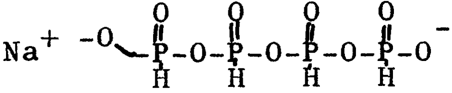
100
% ABSORPTION
$Na_2H_2(HPO_3)_3$
$NaH_3(HPO_3)_2$
$NaH(HPO_3)\ 2.5H_2O$
$Na_2HPO_3\ 5H_2O$
3000
2000
1500
1000
900
700
ν cm^{-1}

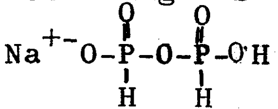
FIG. 26

	I.R. ABSORPTION	H BOND O:H	H_2O loss, stages Thermobalance		$\overset{3}{P}\rightarrow\overset{5}{P}$ T°C
			A	B	
$Na_2HPO_35H_2O$	Discrete	1:1·25	0·75,4,0·25	-	(250°
$NaH_2(HPO_3)2\frac{1}{2}H_2O$	Discrete	1:1·09	1,0·5,1	0·5	330°
$NaH_3(HPO_3)_2$	Continuous areas	1:0·50	-	0·25,0·3, 0·5	265°
$Na_2H_4(HPO_3)_3$	Continuous	1:0·44	-	1	240°
$KH(HPO_3)$	Discrete	1:0·33	-	0·25	220°
$KH_3(HPO_3)_2$	Continuous	1:0·50	-	0·5	220°
$K_2H_4(HPO_3)_3$	(Continuous)	1:0·44	-	0·5	268°
H_3PO_3	Discrete	1:0·6	-	0·04	220°

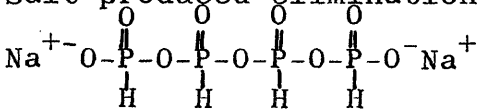
Fig. 25 thermobalance and spectral results for a series of acid phosphites

Acid Salts of Na^+ and K^+

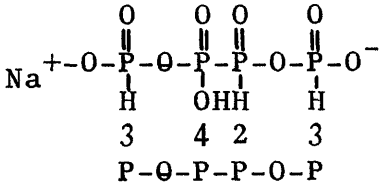
Since these salts behave essentially as mixtures of the appropriate hydrogen phosphite and phosphorous acid the pyrolyses of which have been discussed the results for these acid salts will be presented in tabular form, Fig. 25. Data on other salts have been added for completion. The infra-red spectra display the phenomena often found for acid salts namely that of continuous absorption in the infra-red region. The spectra of the sodium salts, are presented, those of the potassium salts are similar, Fig. 26. On Fig. 25 the formation of $\overset{3}{P}-O-\overset{3}{P}$ bonds is indicated under the heading B, A refers to loss of hydrate water. Solutions of the reaction product before the oxidative breakdown step ($\overset{3}{P} \rightarrow \overset{5}{P}$ T^oC), show the presence of pyrophosphite on the chromatograms. No further condensed phosphite units are formed in these experiments. Oxidative breakdown occurs after the formation of $M_2^+H_2P_2O_5$ (the disodium pyrophosphite appears to form as a separate phase during the pyrolysis of $NaH_3(HPO_3)_2$), in the melt. If polyphosphite units were thermodynamically stable it would be expected that during the pyrolysis of these salts formation of such units would occur. Reaction schemes like  $Na^{+-}O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-OH$  $Na^+ \; {}^-O\!\frown\!\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O^- Na^+$, involving successive elimination of water between P-OH groups, can be envisaged. The possibility of such water elimination reaction occurring has been investigated by formation of the salt



$Na^{+-}O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-OH$ from methanolic solution where the easy $_{3\ \ 3}$ hydrolysis of the P-O-P bond does not occur. Heating of this salt produced elimination of water to give



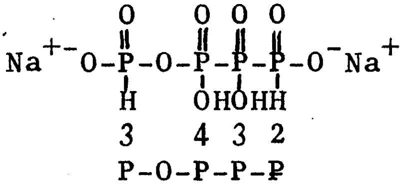
$Na^{+-}O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O-\overset{O}{\underset{H}{P}}-O^-Na^+$, at least initially, on dissolution in water hydrolysis to orthophosphite occurred, the ceriometric oxidation equivalent and thermobalance weight loss suggested that this reaction had occurred. However the infra-red spectrum, the cells being prepared in a dry-box, showed the presence of absorptions undoubtedly due to P-OH, so it appears that rearrangement of the initially formed P-H compound to either



$Na^{+-}O-\overset{O}{\underset{\substack{H\\3}}{P}}-O-\overset{O}{\underset{\substack{OH\\4}}{P}}-\overset{O}{\underset{\substack{H\\2}}{P}}-O-\overset{O}{\underset{\substack{H\\3}}{P}}-O^-Na^+$

P-O-P-P-O-P

or



$Na^{+-}O-\overset{O}{\underset{\substack{H\\3}}{P}}-O-\overset{O}{\underset{\substack{OH\\4}}{P}}-\overset{O}{\underset{\substack{OH\\3}}{P}}-\overset{O}{\underset{\substack{H\\2}}{P}}-O^-Na^+$

P-O-P-P-P

has occurred. As mentioned, dissolution in water produces only ortho phosphite. pH titrations cannot therefore be used to distinguish these possibilities. The experiments which have been conducted on acid salts and hydrogen pyrophosphites cannot be dealt with here, further. The findings are however in line with the principles of lower oxy-acid chemistry which have been discussed in the preceding pages.

The infra-red spectra are analogous to those reported by Speakman et al. for acid salts in other systems, c.f. (164)

APPENDIX

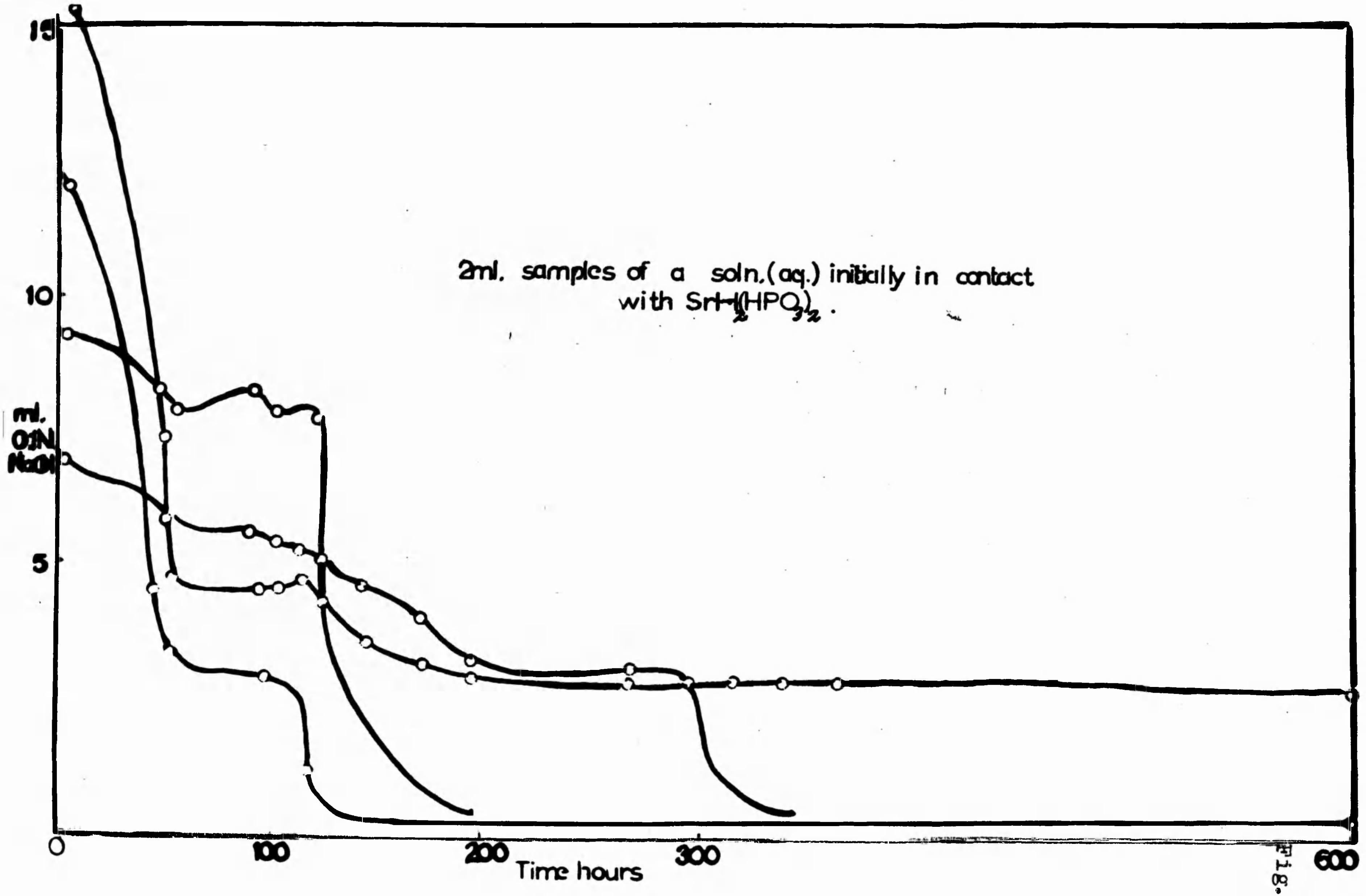

2ml. samples of a soln.(aq.) initially in contact with $SrH_2(HPO_3)_2$.
ml. 0.1N NaOH
15
10
5
0
100
200
300
600
Time hours

Fig. 27

Appendix (I)

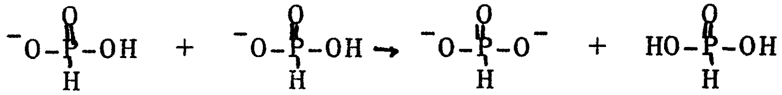
The Hydrolysis of $SrH_2(HPO_3)_2$

Ebert has published the solubilities of the alkaline earth phosphites, (79). Although solubility experiments can be made to give these results true solubility has not been observed in these systems. The hydrolysis of $SrH_2(HPO_3)_2$ has been studied by us in some detail. The solubility equilibrium at $20^o \pm 0.1^o$ was attempted from both under and supersaturated solutions, obtained by adding crystals to water at 20^o and allowing dissolution to take place, and by total dissolution of crystals at 50^o and allowing crystallisation to proceed. The solutions in contact with solid were continuously rotated in a thermostat, and samples were removed at intervals through a filter arrangement. Titration of these samples with O.IN NaOH was carried out, and the plot of this titre against time is shown for a typical experiment in Fig.27. A series of pseudo eqilibria were found. Comparison with one experiment to another suggested that the change from one pseudo equilibrium level to the next was related to many factors, such as the solid interface present and the speed of rotation. At intermediate time intervals the ratio of Sr : HPO_3 in the solution phase is about I : I.5. Analyses were carried out for oxidisable phosphorus in the samples removed by the ceriometric technique. Analyses for Sr were conducted in some cases only, by precipitation as the $Sr(NO_3)_2$ salt.

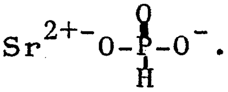
Indications are that this type of hydrolysis phenomenon is met with quite generally for the alkaline earth phosphites. The different phases $CaHPO_3H_2O$, two forms and $SrHPO_3H_2O$ two forms, which have been discussed are produced by this type of hydrolysis.

The question arises as to the formulation of $SrH_2(HPO_3)_2$. From infra-red spectra and thermobalance data the presence of the hydrogen phosphite anion is indicated. It is also noted in this context that the material is insoluble in acetone which reagent may be used to remove excess phosphorous acid in preparations of this Sr hydrogen phosphite by the method used by Ebert, (79).

However the possibility arises, as for this type of hydrogen phosphite generally, of the rearrengement of the anionic structure viz.



$$^{-}O-\overset{O}{\underset{H}{P}}-OH + {}^{-}O-\overset{O}{\underset{H}{P}}-OH \rightarrow {}^{-}O-\overset{O}{\underset{H}{P}}-O^{-} + HO-\overset{O}{\underset{H}{P}}-OH$$

Such rearrangements will occur in solution, and the results of the hydrolysis experiments will be due to this. Precipitation of the sparingly soluble normal Sr phosphite will occur from such solutions,  $Sr^{2+}\,{}^{-}O-\overset{O}{\underset{H}{P}}-O^{-}$.

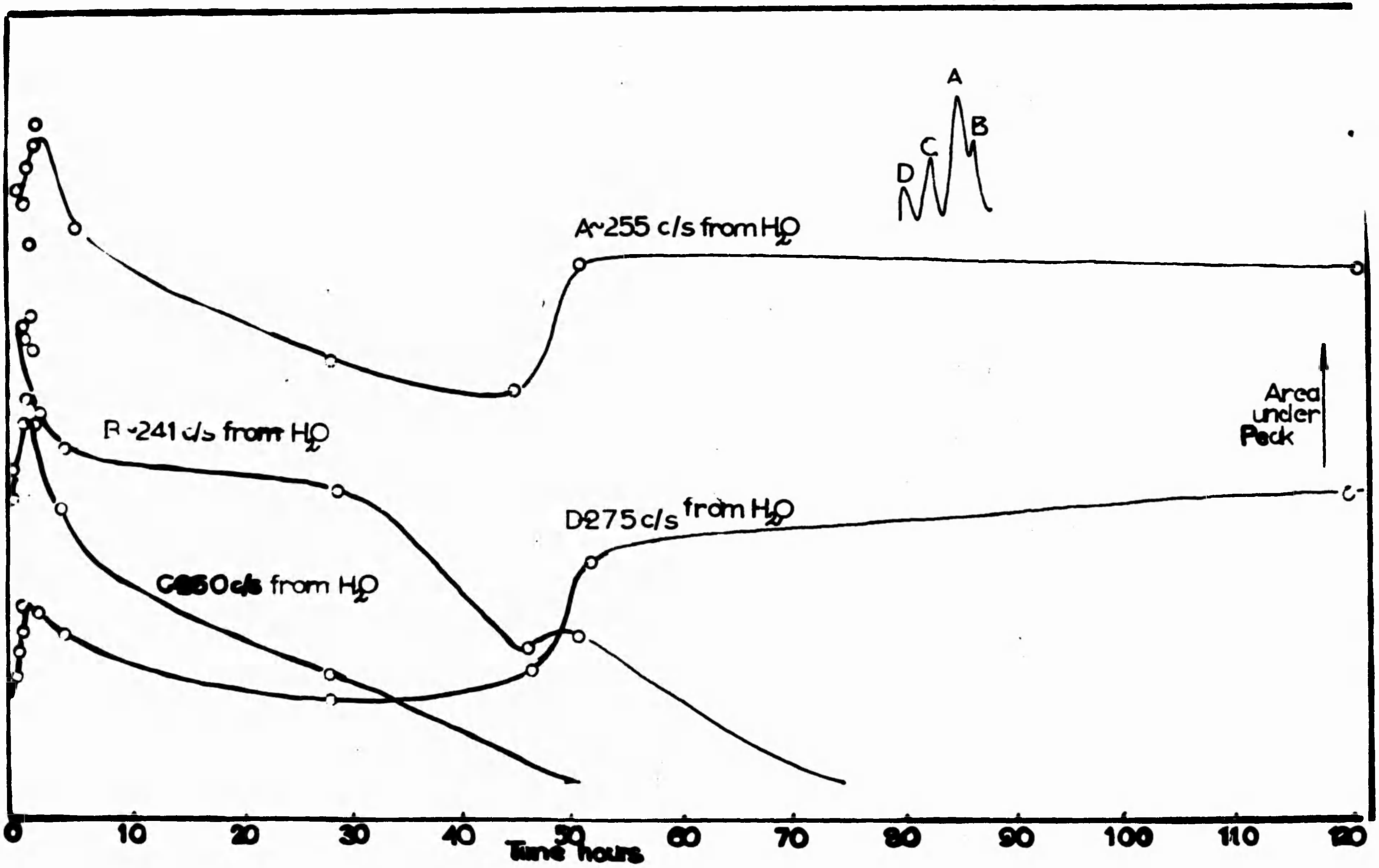
However the situation is not as simple as this. Hydrolysis of the Sr^{2+} cation may also occur. The insoluble material finally found is not simply the normal phosphite, although it approximates to this formulation.

Appendix (II)

The Question of Acetyl Phosphite

During studies on the preparation of $\overset{3}{P}$-O-$\overset{3}{P}$ bonds by use of chemical dehydration, when acetic anhydride was used it was found that although dehydration occurred when mixtures of phosphorous acid and acetic anhydride were rotated in a thermostat at 50°, chemical reaction between the phosphorous acid and the acetic anhydride also took place. The nature of the final product which is obtained after removal of the solvent acetic anhydride was found to vary with the ratio of acetic anhydride to phosphorous acid which had been used. With large excesses of acetic anhydride red products were obtained. Over a range of ratios of moderate excess acetic anhydride, however, the product was colourless (sometimes discoloured in places), and the weight suggested the formation of monoacetyl phosphite. Analysis of this product was carried out by cerimetric, acid-base titrations (after hydrolysis), infra-red and paper chromatographic techniques. The results suggested that the material was approximately rationalisable as being mono acetyl phosphite from the oxidation analyses and acid base titrations, the results of the paper chromatographic investigations and infra-red spectral investigations suggested however, that this was not the case. The material appeared to be much more complex.

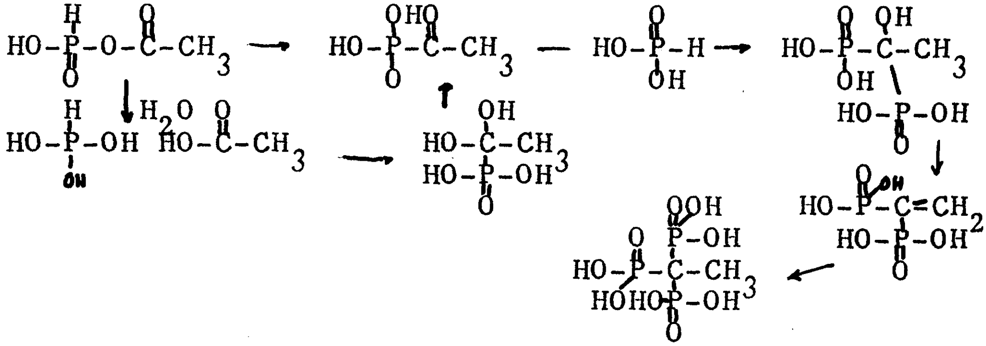
FIG. 28


A~255 c/s from H_2O
B~241 c/s from H_2O
C~250 c/s from H_2O
D275 c/s from H_2O
A
B
C
D
Area under Peak
0
10
20
30
40
50
60
70
80
90
100
110
120
Time hours

Although the preparation of acetyl phosphite has been reported, a genuine sample of this compound has never been prepared, (198). The substance which is readily prepared by the reaction of phosphorous acid and acetyl chloride in acetic anhydride solvent was compared with the product of the acetic anhydride reaction. It appeared to be similar. Cade has recently reported a short study of this material, coming to the conclusion that it was a mixture of acetyl phosphite and acetyl phosphonate, produced by migration of the P-H bond in the initially produced material, (199). It appears that although this rationalisation is valid it does not account for all the observations which we have made on the similar product from the direct reaction product of phosphorous acid and acetic anhydride.

On hydrolysis no phosphite is produced on the chromatogram as required by the presence of a $\overset{3}{P}-O-C$ in the reaction product. The presence of several types of P-O-C and P-C bonds is indicated in the infra-red spectra.

Proton N.M.R. spectra were studied of a concentrated aqueous solution of the product, (c.7M). No proton ascribable to the presence of a P-H bond was found in solution, although several different types of methyl groups were present. The spectra changed with time indicating that rearrangement reactions were occurring in the solution. The variation in the area under the peaks is shown in Fig. 28. It seems that breaking and reforming of $CH_3-\overset{O}{\overset{\|}{C}}-O-P$ bonds with the formation of acetic acid on solution, occurs. The formation of CH_3-P or CH_2-P units is also indicated by the results, present after about 7 days in solution. It must be admitted that although there does not seem to be P-H bonded material present in solution of this product this does not rule out the possibility that such bonds could have been present in the solid product. Dissolution in water might proceed by the reaction of these P-H groups for example with the carbonyl groups of the acetyl unit. Some hypothetical reaction sequences may be written:



Such reaction of carbonyl groups with P-H bonds is well known. The presence of polymeric and relatively high molecular weight material is indicated on the chromatograms, although the bulk of the material present migrates at the same rate, roughly as pyrophosphate.

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