ACIDITY AND COMPLEXES OF THE HIGHER PHOSPHATES

DISSERTATION

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By

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GENERAL INTRODUCTION

Statement of the Problem

The problem suggested by Dr. James I. Watters was a study of the acidity and complexes of the higher phosphates. This was to include the determination of the acid dissociation constants of triphosphoric and pyrophosphoric acids. It also comprised the determination of the formation constants of sodium, potassium, lithium, calcium and magnesium complexes which may form with the triphosphate and pyrophosphate ions.

Extension of the Problem

Since numerous phosphate acids and salts were to be studied, various ion exchange methods were investigated to find simple and flexible means of preparation. The first part of the problem involved studies to determine characteristics of various ion exchange resins, columns and modes of use. A rather complete system of various ion exchange resins was constructed which facilitated the preparation of all the compounds under investigation. The final results are described in the section covering experimental work.
Another problem was the preparation of pure, carbonate-free tetramethylammonium hydroxide. Spectroscopic observations indicated that the classical method in which hydrous silver oxide reacts with tetramethylammonium chloride yielded a product contaminated with silver ion. Furthermore, the complete exclusion of carbon dioxide of the air during all phases of this preparation was exceedingly difficult. The use of ion exchange resins was investigated, and the method finally developed is described in detail in the experimental section.

After the acid dissociation constants and the complex formation constants for both tri- and pyrophosphoric acids had been determined, it was suggested that the orthophosphate ion also be studied. This would permit a true comparison of the acidity and complexing ability of the $H_{n+2}P_nO_{3n+1}$ series.
THE ACIDITY OF TRIPHOSPHORIC ACID AND
THE COMPLEXES OF TRIPHOSPHATE ION

Introduction

In recent years, a large number of investigations have been made on the condensed phosphates. A wide variety of applications range from "water softeners" and biochemical yeast studies to phosphors.

Triphosphate is classed as a condensed phosphate and although sodium triphosphate is available in commercial quantities, there have been few published studies on the strength of the acid. This is in part due to the tendency of triphosphate ion to form complexes with most metal ions including the alkali group and also to its rather rapid rate of hydrolysis, forming pyrophosphoric and orthophosphoric acids.

Before 1900, Schwarz\textsuperscript{1} suggested the existence of

\begin{enumerate}
\item E. Schwarz, Z. anorg. Chem., 9, 249 (1895).
\end{enumerate}

*the compound Na\textsubscript{5}P\textsubscript{3}O\textsubscript{10}. Some 40 years later, Andress and Wust\textsuperscript{2}, through X-ray and cooling-curve data, verified its existence.*
Treadwell and Leutwyler\(^3\) proposed the structure


From X-ray analysis of crystalline phosphates, Van Wazer and Holst\(^4\) have set up a general hypothesis of phosphate structure. They suggest the structure to be


where three PO\(_4^4\) tetrahedra are connected linearly through bridging oxygens.
Rudy and Schloesser\textsuperscript{5} published titration curves for triphosphoric acid but did not attempt to calculate the acidity constants since they were aware of complex formation. Incidental to an anion exchange study of condensed phosphates, Buekenkamp, Rieman, and Lindenbaum\textsuperscript{6} calculated the thermodynamic acidity constants by the application of the Debye-Huckel equation to data obtained in the titration of the acid with potassium hydroxide. They mentioned several limitations on the accuracy of their constants which were satisfactory for their purpose. Their values were $pK_3^a = 2.79$, $pK_4^a = 6.47$ and $pK_5^a = 9.24$. Van Wazer and Holst\textsuperscript{11} have stated that "A careful determination of the ionization constants of both pyro- and triphosphoric acids in the absence of metallic cations will be necessary to obtain correct values free from the confusing effects of complex ion formation."

Quimby\textsuperscript{7} has reviewed the properties of the

\begin{itemize}
\item \textsuperscript{5}H. Rudy and H. Schloesser, Ber., 73, 484 (1940).
\item \textsuperscript{7}O. T. Quimby, Chem. Rev., 40, 141 (1940).
\end{itemize}
condensed sodium phosphates in great detail. Bell\(^8\)


investigated the hydrolysis of several phosphates and found that in water solution all phosphates except orthophosphates are thermodynamically unstable. He proposed several reactions showing the decomposition of these phosphates to orthophosphates.

\[
\begin{align*}
\text{Na}_6\text{P}_6\text{O}_{18} + 3\text{H}_2\text{O} & \rightleftharpoons \text{Na}_3\text{P}_3\text{O}_9 + 3\text{NaH}_2\text{PO}_4 \\
\text{Na}_3\text{P}_3\text{O}_9 + 3\text{H}_2\text{O} & \rightleftharpoons 3\text{NaH}_2\text{PO}_4 \\
\text{Na}_5\text{P}_5\text{O}_{10} + \text{H}_2\text{O} & \rightleftharpoons \text{Na}_3\text{HP}_2\text{O}_7 + \text{Na}_2\text{HPO}_4 \\
\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} & \rightleftharpoons 2\text{NaH}_2\text{PO}_4 \\
\text{Na}_3\text{HP}_2\text{O}_7 + \text{H}_2\text{O} & \rightleftharpoons \text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4 \\
\text{Na}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} & \rightleftharpoons 2\text{Na}_2\text{HPO}_4
\end{align*}
\]

Products on the right hand side of the equations continue to react until there is complete conversion to the orthophosphate. Crowther and Westman\(^9\) concluded that in the


pH range of 2-12, the hydrolysis of both pyrophosphoric and triphosphoric acids was first order and acid catalyzed. However, only the hydrolysis of triphosphoric acid was base
catalyzed. McGilvery and Crowther\textsuperscript{10} derived a general rate equation and suggested a mechanism for the hydrolysis of pyro- and triphosphoric acids. Friess\textsuperscript{11} found that

tri phosphoric acid hydrolyzes about six times faster than pyrophosphoric acid.  

Van Wazer and Campanella\textsuperscript{12} investigated the metal ion complexes of several condensed phosphate glasses. They calculated values of log $K$ for the lithium, sodium and potassium complexes of 1.5, 1.3 and 0.7, respectively. Their results indicate that the dissociation constants for both the magnesium and calcium complexes are similar to those of Fe\textsuperscript{2+} and Mn\textsuperscript{2+}. According to Monk\textsuperscript{13}, the first formation constant for the sodium complex was about $10^{2.5}$. During a study of the dissolving effect of sodium
triphosphate on calcium soaps, Rudy\textsuperscript{14} observed the
decrease in pH when calcium ion is added to a sodium
triphosphate solution. This effect was also observed
during a study of Marseille soap dissolution\textsuperscript{15}.

Frankenthal\textsuperscript{16} studied the change in pH on addition of
magnesium, calcium, manganese and aluminum salts to a
solution of sodium triphosphate. He suggested that a
possible explanation for this effect was polyvalent com­
plex formation with sodium triphosphate. Monnier, Bonnet,
and Brard\textsuperscript{17} studied the calcium and magnesium phosphate
complexes in body fluid. Gosselin and Coghlan\textsuperscript{18} state

\textsuperscript{(14)} H. Rudy, Angew. Chem., 54, 447 (1941).

\textsuperscript{(15)} H. Rudy, H. Schloesser, and R. Watzel, Angew. Chem.,
53, 525 (1940).


\textsuperscript{(17)} A. M. Monnier, V. Bonnet, and R. Brard, Arch.
Intern. Physiol., 54, 188 (1946).

\textsuperscript{(18)} R. E. Gosselin and E. R. Coghlan, Arch. Biochem.
Biophys., 45, 301 (1953).
that the toxicity of polyphosphates is due to the reduction in the level of ionized calcium in vivo. Incidental to a study of a copper complex with triphosphate, Loughran


investigated the alkali metal complexes with that ligand. His results showed that for complexes of the type MeP$_3$O$_{10}^{4-}$, where Me represents the alkali metal, the order of decreasing stability is lithium $>$ sodium $>$ potassium. This order agrees with that found by use of ion exchange membranes$^{20}$. Bobtelsky and Kertes$^{21}$ studied the composition of the alkaline earth metal complexes formed with pyro- and triphosphoric acids by turbidity, pH and conductivity measurements. They stated that the complexes formed seemed to be of an electrostatic type. Martell and Schwarzenbach$^{22}$ determined the formation constants of the


calcium and magnesium complexes with triphosphate. Their values were obtained by titrating the acid in a solution containing 0.1 N KCl with a standardized sodium hydroxide solution in the presence of the desired salt. Neglecting potassium and sodium complexes, they reported log 

\[ K_{\text{CaP}_3\text{O}_10^{3-}} = 4.95, \quad \log K_{\text{CaHP}_3\text{O}_10^{2-}} = 3.1, \quad \log K_{\text{MgP}_3\text{O}_10^{3-}} = 5.80 \text{ and } \log K_{\text{MgHP}_3\text{O}_10^{2-}} = 3.7. \]

Rogers and Reynolds\(^\text{23}\)

showed that the condensed phosphates formed complexes with a great number of metal ions. Quimby\(^\text{24}\) discussed experiments by Grey and Lemmerman\(^\text{25}\) in which conductivity measurements were performed according to Jobs method of continuous variations. This evidence indicated a 1:1 complex for the complex of calcium ion with triphosphate having a dissociation constant of the order of \(3.1 \times 10^{-7}\) at 30°. Quimby indicates that the evaluation of the

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\(^\text{25}\) J. A. Grey and K. E. Lemmerman, Unpublished experiments, Research Department, Chemical Division, Proctor and Gamble Co., Miami Valley Laboratory, Cincinnati 31, Ohio.
complexity constants for calcium with triphosphate has been hampered by the limited range of solubility.

**Experimental**

Four ion exchange columns were constructed to prepare the various compounds under investigation. These columns provided a simple yet highly efficient means of preparing any desired compound from another containing one of the desired ions.

By use of the hydrogen cycle, a convenient indicator was available to measure the efficiency of the initial charging since complete charging could be recognized by the absence of hydrogen ion in the effluent. The phosphate salts which were basic served as their own indicator. Incomplete exchange or leakage of alkali and alkaline earth metal ions could easily be detected by spectroscopic methods or spot tests. This provided the knowledge of how efficient the final exchange was.

The completeness of the exchange was finally tested spectrographically using the 1.5 meter Applied Research Laboratory Grating Spectrograph to determine whether the ion to be exchanged could be found in the effluent. After the method proved satisfactory, periodic
checks were made on the effluent viewed in a flame with a small visual spectroscope. Incomplete exchange of cations in phosphates could also be detected by observing the number of equivalents of acid or base required to reach the different end points on the titration curve.

The cation exchange columns were fitted with Pyrex water jackets through which ice water was constantly circulated during the exchange. This was done in order to prevent appreciable hydrolysis of the phosphate solutions passed through the column.

Column 1 was a 90 cm by 2 cm Pyrex column filled to a height of 50 cm with Dowex 50-X12 cation exchange resin, 100-200 mesh, low porosity, supported on a Pyrex glass wool plug. The column was fitted with a Pyrex water jacket, 4 cm in diameter, through which ice water was constantly circulated by means of a Sigmamotor pump. The column resembled a Liebig condenser, Fig. 1, differing in that it had a stopcock on the lower end and a rubber stopper fitted with an ascarite bulb and a tube to facilitate the entry of nitrogen at the top.

(26) Sigmamotor; Middleport, New York.
Fig. 1. - Diagram of The Ion Exchange Column Used To Prepare The Triphosphoric Acid Solutions
Automatic feed keeps liquid at this level

- Solution to be exchanged
- Nitrogen gas bubbled through solution
- Ice water (out)
- Water jacket
- Solution to be exchanged
- Ion exchange resin
- Ice water from pump (in)
- Pyrex glass wool
- Nitrogen gas bubbled through effluent
- Ice and water
- Effluent
The column was initially converted to the hydrogen ion form by passing through it a 15% solution of hydrogen chloride. It was then rinsed with distilled water until the effluent did not produce an acidic color with Alkacid Test Ribbon\(^2\). Two more liters of distilled water were then passed through. The circulating pump was started, and when the water in the column reached about 3°C, the liquid level was lowered until it was only slightly above the resin.

To prepare the triphosphoric acid solution, a solution of the sodium salt having a concentration approximately twice that finally desired was added to the column. The flow rate was then adjusted to 2 ml per minute.

The effluent was periodically checked, and when it became slightly acidic, a volume equal to 5% of the original salt solution added was collected and discarded. Then 85% of the original volume was collected under nitrogen in an erlenmeyer flask immersed in an ice bath. The last fraction was discarded and the column rinsed until the effluent was no longer basic. This middle fraction of the eluted acid was warmed to 25 ± 0.1°C.
diluted to the desired concentration and immediately titrated with standardized, carbonate-free tetramethylammonium hydroxide containing the same concentration of triphosphate as the solution titrated. The inclusion of the triphosphate in both solutions eliminated the dilution of the triphosphate during the titration.

The number of equivalents which could theoretically be exchanged on the column was found as follows: with the column initially in the hydrogen form, a 5% solution of sodium hydroxide was passed through and all of the acid effluent collected. This volume of acid was measured and an aliquot was titrated with standardized sodium hydroxide. The number of equivalents used was a measure of the number of equivalents on the column.

During the use of all columns, nitrogen was constantly swept through the top of the column. All water was purged with nitrogen gas to remove the dissolved carbon dioxide. Extreme care was taken to prevent the level of liquid from falling below that of the resin.

Titrations were performed in a stoppered Berzelius beaker with a stream of nitrogen flowing through the solution. The beaker was immersed in a constant-temperature bath kept at $25 \pm 0.1^\circ$. The solution was stirred by the stream of nitrogen after each addition of
reagent. pH measurements were made with the Beckman Model G pH meter. The Beckman All Purpose Glass electrode and the Beckman reference electrode were inserted directly in the solution.

Column 2 was a 90 cm by 3 cm Pyrex column filled to a height of 50 cm with Dowex 50-X2, 100-200 mesh, high porosity, cation exchange resin, supported on a Pyrex glass wool plug. It was fitted with a Pyrex water jacket and resembled column 1 in most respects.

This column was used to prepare tetramethylammonium triphosphate. Due to the large ion size, it was necessary to use a high-porosity resin and the column diameter was increased from 2 to 3 cm due to the lower flow rate through this resin. The tetramethylammonium triphosphate was prepared in a manner similar to that for the acid, the salt serving as its own indicator. The eluted salt was warmed to $25 \pm 0.1^\circ$, diluted to the desired concentration, and immediately titrated with standardized hydrochloric acid in the manner described above.

Column 3 was a 100 cm by 4 cm Pyrex column filled to a height of 60 cm with Dowex 50-XL2 cation exchange resin, 100-200 mesh, low porosity, supported on a Pyrex glass wool plug. This column was also fitted with
a Pyrex water jacket and except for its larger size resembled both previously described columns.

Preparation of potassium and lithium triphosphate was accomplished through the use of column 3. The method used was essentially that of passing a solution of the sodium salt through the column containing the resin in the desired metal form. The manner of preparation was similar to that of the acid. To prevent any hydrogen ion leakage, the column which was initially in the hydrogen form was charged by using a 10% solution of the desired metal chloride containing just enough of the desired metal hydroxide to make the solution slightly basic. The inclusion of base insured the complete replacement of hydrogen ion. Next a 15% solution of the chloride was passed through the column, after which it was rinsed with double distilled, demineralized water. All solutions to be used on the columns were transferred to a separatory funnel which was then tightly stoppered. The stem was inserted into the column at the desired liquid level. Once set, this feed mechanism automatically maintained the desired level of liquid above the resin.

The sodium triphosphate was prepared from Monsanto technical grade anhydrous sodium triphosphate by
recrystallizing four times to yield a 99.9% pure product according to a procedure developed by P. G. Arvan\textsuperscript{28} in the

\begin{flushright}
(28) R. A. Ruerwein, private communication, Monsanto Chemical Company, Dayton, Ohio.
\end{flushright}

Monsanto Laboratory.

9.2 pounds of sodium tripophosphate were dissolved in 5 gallons of distilled water. The solution was filtered and the filtrates were treated with 7 liters of methyl alcohol. The addition of the alcohol was accompanied by vigorous stirring. The sodium tripophosphate hexahydrate which was precipitated was collected on a filter, sucked as dry as possible, and allowed to air dry over night.

The sodium tripophosphate hexahydrate obtained in this first crystallization was then dissolved in sufficient distilled water to give a 13% solution on a dry weight basis. The solution was filtered and the filtrates were treated with methyl alcohol, 25 to 30\% by volume of methyl alcohol being used for this precipitation. The sodium triphosphate hexahydrate which was precipitated was again collected on a filter, sucked as dry as possible, and allowed to dry over night.

2200 grams of the twice recrystallized sodium triphosphate hexahydrate was slurried with one liter of
distilled water. The slurry was separated by filtration and the filtrates were discarded. The damp filter cake was then dissolved in one liter of distilled water and filtered. The filtrates were treated with two liters of methyl alcohol. The precipitate was collected on a filter, sucked as dry as possible. The damp filter cake was slurried with one liter of distilled water and filtered. The filtrates were discarded. The filter cake was dissolved in 3.5 liters of distilled water and the solution was filtered. The filtrates were treated with one liter of methyl alcohol. The precipitate was collected on a filter, sucked as dry as possible and allowed to air dry over night.

According to Quimby$^{24}$, the commercial 85 to 94\% anhydrous salt can be made 99\% pure by three to five re-crystallizations from water with ethanol added to the extent of 25\% by volume.

Another method used to prepare smaller amounts of triphosphate was obtained from E. J. Griffith$^{29}$ of the

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(29) E. J. Griffith, private communication, Monsanto Chemical Company, Dayton, Ohio.

Monsanto Chemical Company. An aqueous solution was saturated with approximately twice the quantity of
triphosphate required. The solution was filtered with vacuum, and the residue discarded. Acetone (or alcohol) was slowly added to the filtrate with vigorous stirring until precipitation just commenced. The suspension was filtered and the crystalline material discarded. Acetone was then added to the filtrate until the precipitation of hexahydrate was complete. About 30 minutes was required to precipitate one pound of sodium triphosphate from solution. The supernatant liquid was decanted and the sample was slurried with a volume of 40% acetone - 60% water equal to the volume of the precipitate. The above dissolution, precipitation, and slurry steps were repeated five times, and then the sodium triphosphate hexahydrate was filtered from the slurry. The hexahydrate was washed with an 80% solution of acetone and air was drawn through the crystals for about one hour. The latter treatment was used in order to minimize the surface dehydration of sodium triphosphate hexahydrate which occurred on drying. The sample was air dried over night and stored for use.

This procedure usually yielded about 50% of the phosphate originally present as sodium triphosphate hexahydrate. Redistilled, carbonate-free water was used for all of the dilutions.

The tetramethylammonium chloride, used for the adjustment of ionic strength and for charging the column,
was prepared from the Matheson Coleman and Bell 99+\% product which was further purified by recrystallization from a solution containing methanol and acetone. About 10 grams of the salt is dissolved in 100 ml of hot 25\% methanol in acetone. The hot solution is filtered, 100 to 110 ml of acetone is added and the solution is allowed to cool. The crystalline material is filtered and dried in a vacuum desiccator. The yield of salt of sufficient purity for use as a supporting electrolyte in aqueous media is 60-65\%\(^{30}\).

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The potassium and sodium hydroxide solutions were prepared carbonate-free from Baker's Analyzed pellets and stored in paraffin-lined bottles. The metal chlorides and magnesium and calcium oxides used were Mallinckrodt reagent-grade salts. The lithium hydroxide was obtained from Fisher Scientific Company. The alkali and alkaline earth metal chloride solutions were standardized against AgNO\(_3\) using dichloroflourescein as an indicator. The tetramethylammonium sulfate was prepared by neutralization of H\(_2\)SO\(_4\) with (CH\(_3\))\(_4\)NOH. Solid CaSO\(_4\) was prepared by reacting CaCl\(_2\) with ((CH\(_3\))\(_4\)N)\(_2\)SO\(_4\). Flame photometric
measurements were made with the Beckman Flame Photometry Attachment used in conjunction with the Beckman Model DU Spectrophotometer.

The method finally adopted for the preparation of tetramethylammonium hydroxide required more time than the classical method in which tetramethylammonium chloride reacts with hydrous silver oxide.

A Pyrex column 135 cm in height and 6 cm in diameter was coated throughout the interior with paraffin and filled to a height of 95 cm with Dowex 2-X7.5, 20-50 mesh, medium porosity anion exchange resin supported on a Pyrex glass wool plug. The top of the column was fitted with a two-hole rubber stopper containing an ascarite bulb and a tube to permit the introduction of nitrogen gas. At the bottom of the column was a Pyrex stopcock.

To automatically feed the distilled water a spout 3 inches long and 1.5 cm in diameter was sealed to a 5 gallon Pyrex carboy near the bottom and tilted downward to prevent trapping of air bubbles.

A new unopened 5 pound bottle of reagent-grade sodium hydroxide pellets was used to prepare a saturated, carbonate-free solution of sodium hydroxide in a Pyrex bottle. Approximately 1/2 pound of sodium hydroxide and
any sodium carbonate present\textsuperscript{31} remained undissolved. This


solution was filtered with vacuum through an asbestos mat into the 5 gallon Pyrex carboy filled almost completely with distilled water. The spout at the bottom of the carboy was fitted with pure gum rubber tubing and clamped off during the filtering operation. After all the sodium hydroxide solution was transferred, the carboy was tightly stoppered.

Five liters of distilled water was passed through the ion exchange column. The column was fitted with a two-hole stopper at the top. One hole was used for the entry of nitrogen gas, while the second was fitted with either an ascarite drying tube or with a Pyrex tube which could be connected to the Pyrex carboy.

After passing the 5 liters of water through the column, it was connected to the Pyrex carboy containing the sodium hydroxide solution and this solution permitted to pass into the column.

The flow rate was regulated by the stopcock on the bottom to obtain 5 ml of effluent per minute. The
level of solution above the resin was adjusted by lowering or raising the Pyrex tubing. As the solution passed out of the column, the level of solution above the resin was lowered below the Pyrex tubing permitting nitrogen gas to flow into the carboy displacing the sodium hydroxide solution. The sodium hydroxide solution flowed into the column raising the level of the liquid above the end of the Pyrex tubing and stopping further flow of liquid.

After all the sodium hydroxide solution passed through the column, it was rinsed in the same manner with 5 gallons of distilled water. After this rinsing, the volume and concentration of a \((\text{CH}_3)_4\text{NCl}\) needed to obtain approximately the desired concentration of \((\text{CH}_3)_4\text{NOH}\) was passed through the column.

The pH of the effluent was checked at regular intervals, and when it became slightly basic, a volume equal to approximately 5-10% of the original volume of the \((\text{CH}_3)_4\text{NCl}\) used was collected and discarded. The next fraction, approximately 85% of the original volume, was collected in a polyethylene container which had been flushed with nitrogen gas and fitted with a drying tube containing ascarite.

The column was then rinsed until the effluent did not appear basic, rinsed with 5 more liters of
distilled water, then shut off, sealed with a rubber stopper on top, and set away for later use. Testing with barium chloride verified the absence of carbon dioxide.

Using 2 liters of approximately 1 M \((\text{CH}_3)_4\text{NCl}\), the yield obtained was approximately 1700 ml of approximately 0.8 M \((\text{CH}_3)_4\text{NOH}\). A second 900 ml fraction approximately 0.4 M was also collected. Double distilled, demineralized water which was purged with nitrogen gas to remove dissolved carbon dioxide was used for all column operations.

**Nomenclature and Definitions**

The determination of equilibrium constants involved in complex formation is of considerable importance. Two methods of expressing the equilibria involved will be considered here.

The method used by Bjerrum\(^{32}\) considers the

\(^{32}\) J. Bjerrum, "Metal Amine Formation in Aqueous Solution", P. Hasse and Son, Copenhagen (1941).
the ligand, A, as shown below. For simplicity ionic charges are omitted from the following equations and expressions.

\[
\begin{align*}
M + A & \rightarrow MA \\
MA + A & \rightarrow MA_2 \\
MA_2 + A & \rightarrow MA_3 \\
MA_{N-1} + A & \rightarrow MA_N
\end{align*}
\]

The stepwise equilibria or more commonly the stepwise formation constants are expressed as:

\[
\begin{align*}
K_1 &= \frac{(MA)}{(M)(A)} & (1) \\
K_2 &= \frac{(MA_2)}{(MA)(A)} & (2) \\
K_3 &= \frac{(MA_3)}{(MA_2)(A)} & (3) \\
K_N &= \frac{(MA_N)}{(MA_{N-1})(A)} & (4)
\end{align*}
\]

where parentheses are used to express the concentrations of the species in solution. The \( K_1 \)'s indicated are also referred to as consecutive or successive formation constants.

The second method commonly used to express the equilibria involved gives rise to the term complexity
constant. Considering the general equilibria between a central metal ion, M, and a ligand, A, as follows:

\[
\begin{align*}
M + A & \rightleftharpoons MA \\
M + 2A & \rightleftharpoons MA_2 \\
M + 3A & \rightleftharpoons MA_3 \\
M + NA & \rightleftharpoons MA_N
\end{align*}
\]

the consecutive or successive complexity constants are:

\[
\begin{align*}
\beta_1^{(3)} &= \frac{(MA)}{(M)(A)} \\
\beta_2^{(3)} &= \frac{(MA_2)}{(M)(A)^2} \\
\beta_3^{(3)} &= \frac{(MA_3)}{(M)(A)^3} \\
\beta_N^{(3)} &= \frac{(MAN)}{(M)(A)^N}
\end{align*}
\]

The consecutive complexity constants are easily obtained from the products of the consecutive formation constants, so that

\[
\begin{align*}
\beta_1^{(3)} &= K_1 \\
\beta_2^{(3)} &= K_1 K_2 \\
\beta_3^{(3)} &= K_1 K_2 K_3 \\
\beta_N^{(3)} &= K_1 K_2 K_3 \cdots K_N
\end{align*}
\]
The complexity constant for the highest complex is called the over-all or total complexity constant. It is the product of all of the consecutive formation constants. In this dissertation, the constants will be expressed as stepwise formation constants or complexity constants.

The formula for triphosphoric acid is $H_5P_3O_{10}$. Its consecutive dissociation constants, $K^a$, are:

$$K_1^a = \frac{(H^+)(H_4P_3O_{10}^-)}{(H_5P_3O_{10}^-)} \quad (13)$$

$$K_2^a = \frac{(H^+)(H_3P_3O_{10}^{2-})}{(H_4P_3O_{10}^-)} \quad (14)$$

$$K_3^a = \frac{(H^+)(H_2P_3O_{10}^{3-})}{(H_3P_3O_{10}^{2-})} \quad (15)$$

$$K_4^a = \frac{(H^+)(HP_3O_{10}^{4-})}{(H_2P_3O_{10}^{3-})} \quad (16)$$

$$K_5^a = \frac{(H^+)(P_3O_{10}^{5-})}{(HP_3O_{10}^{4-})} \quad (17)$$

When expressing formation constants, a subscript will be used to indicate the complex referred to; for example, the reaction for the first sodium complex with triphosphate ion may be expressed:

$$Na^+ + P_3O_{10}^{5-} \rightleftharpoons NaP_3O_{10}^{4-}$$
The formation constant will be expressed as

$$K_{NaTP} = \frac{(NaP_3O_{10}^{4-})}{(Na^+)(P_3O_{10}^{5-})}$$  \hspace{1cm} (18)$$

For the second complex with sodium ion

$$Na^+ + HP_3O_{10}^{4-} \rightleftharpoons NaHP_3O_{10}^{3-}$$

and

$$K_{NaHTP} = \frac{(NaHP_3O_{10}^{3-})}{(Na^+)(HP_3O_{10}^{4-})}$$  \hspace{1cm} (19)$$

For convenience, formation constants are usually expressed as $pK$ or $-\log K$.

Titration curves are plotted with pH values on the ordinate versus "a" values on the abscissa, where "a" is the number of equivalents of acid or base used per mole of ligand.

The Method of Bjerrum\textsuperscript{32}

Bjerrum defines the quantity, $\overline{n}$, as the average number of ligands bound per central metal ion, M. Then\textsuperscript{33}

\begin{equation}
\overline{n} = \frac{\sum_{i=1}^{N} i(MA_i)}{\sum_{i=1}^{N} i(MA_i) + N} \hspace{1cm} (20)
\end{equation}

where the denominator is the total central ion concentration, $C_M$. The total ligand concentration, $C_A$, is

$$C_A = (A)^{+} \sum_{i=1}^{N} i(MA_i^+)$$  \hspace{1cm} (21)

The formation function, $\bar{n}$, can be written

$$\bar{n} = \frac{(MA) + 2(MA_2) + 3(MA_3) + \cdots + N(MA_N)}{(M) + (MA) + (MA_2) + (MA_3) + \cdots (MA_N)}$$  \hspace{1cm} (22)

Substituting for the values of $(MA)$, $(MA_2)$, etc., in terms of their stepwise formation constants and eliminating $(M)$, $\bar{n}$ may be expressed as

$$\bar{n} = \frac{K_1(A)^{-} + 2K_1K_2(A)^{2} + 3K_1K_2K_3(A)^{3} + \cdots + NK_1K_2K_3\cdots K_N(A)^{N}}{1 + K_1(A) + K_1K_2(A)^{2} + K_1K_2K_3(A)^{3} + K_1K_2K_3\cdots K_N(A)^{N}}$$  \hspace{1cm} (23)

or in terms of stepwise complexity constants as

$$\bar{n} = \frac{\beta_1(A) + 2\beta_2(A)^{2} + 3\beta_3(A)^{3} + \cdots + N\beta_N(A)^{N}}{1 + \beta_1(A) + \beta_2(A)^{2} + \beta_3(A)^{3} + \cdots + \beta_N(A)^{N}}$$  \hspace{1cm} (24)

Rearranging, yields

$$\bar{n} + (\bar{n}-1)\beta_1(A) + (\bar{n}-2)\beta_2(A)^{2} + (\bar{n}-3)\beta_3(A)^{3} + \cdots + (\bar{n}-N)\beta_N(A)^{N} = 0$$  \hspace{1cm} (25)

If one is able to determine the concentration of free ligand, $(A)$, $\bar{n}$ may be evaluated from equation (26) and the constants of the system can readily be calculated.

$$\bar{n} = \frac{C_A - (A)}{C_M}$$  \hspace{1cm} (26)
An expedient solution to equation (25) is by use of determinants where N experiments have been performed. N equations of the type of equation (25) can then be easily solved. Care must be exercised to be sure that the solution of the determinant is unique, i.e., if the absolute value of the determinant is not zero, there is one and only one solution for a set of N equations in N unknowns. This is essentially Cramer's rule\(^3^4\). A modified form of equation (25) was used in the evaluation of the acidity constants of triphosphoric acid. This equation is discussed in a later section.

Bjerrum's method is discussed in his original work\(^3^2\) or a recent review\(^3^5\). Sullivan and Hindman\(^3^3\) adopt Bjerrum's formation function to determinants. Carlson et al.\(^3^6\) and Martell and Calvin\(^3^7\) describe the method in detail.


Calculation of Formation Constants

Use of the Apparent Acidity Constant

If an acid can be titrated in the presence of a relatively large excess of metal ion without precipitate formation, it is possible to investigate complex formation by the lowering of the pH. When the inflections at the various equivalence points persist for the stepwise addition or removal of hydrogen ions, the calculations are greatly simplified. In this case, it is evident that each ligand adds one hydrogen ion in a stepwise way even though it may also be bound to a metal ion. Under these conditions it is expedient to define a function which is called the apparent acidity constant for this stepwise addition of hydrogen ion. This method is similar to one used by Martell and Schwarzenbach\textsuperscript{22}. Using triphosphate ion as an example, consider the general expressions for the equilibria involved:

\[ H^+ + H_{n}P_3O_{10}^{(5-n)-} \rightleftharpoons H_{n+1}P_3O_{10}^{(4-n)-} \]

\[ k_a^{3-n} = \frac{[H^+][H_nP_3O_{10}^{(5-n)-}]}{[H_{n+1}P_3O_{10}^{(4-n)-}]} \]  \hspace{1cm} (27)
The general expression for the apparent acidity constant, $K_{5-n}'$, is given by

$$K_{5-n}' = \frac{\left[H^+\right] \sum q(M_{m}H_{n}P_{3010}q_q(5-n-m))}{\sum (M_{m}H_{n}P_{3010}q_q(4-n-m))}$$

(29)

where brackets indicate activities and parentheses concentrations.

Combining equation (29) (where $n = 0, 1, q = 1$, and $m = 1$) with the expressions for the stepwise formation constants for the sodium complexes

$$K_{NaTp} = \frac{(NaP_{3010}^1-)}{(Na^+)(P_{3010}^5^-)}$$

(18)

$$K_{NaHTp} = \frac{(NaHP_{3010}^3^-)}{(Na^+)(HP_{3010}^4^-)}$$

(19)

and also with the acid dissociation constants

$$K_{a}^4 = \frac{\left[H^+\right] (HP_{3010}^4^-)}{(H_{2}P_{3010}^3^-)}$$

(16)

$$K_{a}^5 = \frac{\left[H^+\right] (P_{3010}^5^-)}{(HP_{3010}^4^-)}$$

(17)
the following equations are obtained:

\[
K_5' = \frac{[H^+][\text{P}_3\text{O}_{10}^{5-}+(\text{NaP}_3\text{O}_{10}^{4-})]}{[\text{HP}_3\text{O}_{10}^{4-}]+(\text{NaHP}_3\text{O}_{10}^{3-})} = \frac{K_5^a + K_{\text{NaTP}}K_5^a(\text{Na}^+)}{1 + K_{\text{NaHTp}}(\text{Na}^+)}
\]  

(30)

\[
K_4' = \frac{[H^+][\text{HP}_3\text{O}_{10}^{4-}+(\text{NaH}_2\text{P}_3\text{O}_{10}^{3-})]}{[\text{H}_2\text{P}_3\text{O}_{10}^{3-}]} = \frac{K_4^a + K_{\text{NaHTp}}K_4^a(\text{Na}^+)}{}
\]  

(31)

Knowing the acid dissociation constants, the concentration of metal ion, (Na\(^+\)), and by obtaining the apparent acidity constant from its respective point on the titration curve, the values for \(K_{\text{NaTP}}\) and \(K_{\text{NaHTp}}\) are easily calculated.

The Method of Schwarzenbach, Kampitsch, and Steiner\(^{38}\)

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Using triphosphate as an example, one proceeds directly from the basic stoichiometric equations involved. The general expressions for the equilibria involved are equations (27) and (28).

Consider the titration of \(\text{H}_2\text{P}_3\text{O}_{10}\) with (CH\(_3\))\(_4\)NOH in the presence of excess sodium ion (where TP represents
$P_3O_{10}^{5-}$, $M$, the metal ion, and leaving off charges for simplicity), between the regions $a = 3$ and $a = 5$

\[ K_5^a = \frac{[H]}{(HTp)} \quad , \quad K_4^a = \frac{[H]}{(H_2Tp)} \quad (17,16) \]

\[ K_{MTp} = \frac{(MTp)}{(M)(Tp)} \quad , \quad K_{MHTp} = \frac{(MHTp)}{(M)(HTp)} \quad (18,19) \]

Combining these equations with the equations for the conservation of species $C_p$, $C_M$ and the electroneutrality equation, the following reduced equations are obtained:

\[ (Tp) = \frac{C_pK_4^aK_5^aK_{MTp}K_{MHTp}}{Den} \quad (32) \]

\[ (HTp) = \frac{C_p[H]K_4^aK_{MTp}K_{MHTp}}{Den} \quad (33) \]

\[ (H_2Tp) = \frac{C_p[H]^2K_{MTp}K_{MHTp}}{Den} \quad (34) \]

\[ (MTp) = \frac{C_p(M)K_4^aK_5^aK_{MHTp}}{Den} \quad (35) \]

\[ (MHTp) = \frac{C_p(M)[H]K_4^aK_{MTp}}{Den} \quad (36) \]

where $\text{Den} = K_4^aK_5^aK_{MTp}K_{MHTp} + [H]K_4^aK_{MTp}K_{MHTp} + [H]^2K_{MTp}K_{MHTp} + (M)K_4^aK_5^aK_{MHTp} + (M)[H]K_4^aK_{MTp}$

$C_p$ is the total phosphate concentration, and $C_M$ is the total metal ion concentration. Substituting these values into the electroneutrality condition,

\[ aC_p + [H] + (M) = (A) + [OH]^3 + 5(Tp) + 4(HTp) + 3(H_2Tp) + 3(MHTp) + 4(MTp) \quad (37) \]
and eliminating (M) and (A) which are present in large excess and therefore remain constant, one obtains

\[ \alpha C_p + [H] - [OH] = \frac{5C_pK_{1}K_{5}K_{MTp}K_{MHTp}}{\text{Den}} + \frac{4C_p[H]K_{4}K_{MTp}K_{MHTp}}{\text{Den}} + \frac{3C_p(M)[H]K_{4}K_{MTp}}{\text{Den}} + \frac{4C_p(M)K_{4}K_{5}K_{MHTp}}{\text{Den}} \]

(38)

Collecting terms and dividing through by \([H]K_{MTp}K_{MHTp}\), the final result is

\[
\frac{1}{K_{MHTp}} \left[ \left\{ (a-3)C_p + [H] - \frac{K_{W}}{[H]} \right\} (M)K_{4} \right] + \\
\frac{1}{K_{MTp}} \left[ \left\{ (a-4)C_p + [H] - \frac{K_{W}}{[H]} \right\} (M)K_{4}K_{5} \right] = \\
\left[ \frac{K_{W} - 1}{[H]} \right] \left[ \frac{K_{4}K_{5}a}{[H]} + [H]K_{4}a + [H]^2 \right] - \\
\alpha a C_p \left[ (a-5)\frac{K_{4}K_{5}}{[H]} + (a-4)K_{4}a + (a-3)[H] \right]
\]

(39)

All terms except \(K_{MTp}\) and \(K_{MHTp}\) are known or can be experimentally determined. By simultaneously solving pairs of equations at various "a" values, taking the \([H]\) from the titration data corresponding to the value of "a" used, \(K_{MTp}\) and \(K_{MHTp}\) may be evaluated.
Discussion of Results and Conclusion

Acidity Constants

Curve 1, Fig. 2, was obtained for the titration of 0.00919 M \((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}\) with a solution containing 0.0543 M HCl and exactly the same concentration of \(\text{H}_5\text{P}_3\text{O}_{10}\) as the solution titrated. Curve 2, Fig. 2, was obtained for the titration of 0.00943 M \(\text{H}_5\text{P}_3\text{O}_{10}\) with a solution containing 0.0528 M \((\text{CH}_3)_4\text{NOH}\) and exactly the same concentration of \((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}\) as the solution titrated. All solutions contained sufficient \((\text{CH}_3)_4\text{N})_4\text{NCl}\) to produce an ionic strength of 1.0. The ordinate, "a", is the number of equivalents of acid or base added per mole of triphosphate ion.

Spectroscopic observations and spot tests with magnesium uranyl acetate\(^{39}\) indicated that sodium was quantitatively removed in the column. Any remaining sodium ion would decrease the number of equivalents required to reach the first equivalence point in titrating the acid. Any unavoidable hydrolysis in the column or during the early portion of the titration should not
Fig. 2. - Curves for The Titration of Tetramethylammonium Triphosphate with Hydrochloric Acid and The Titration of Triphosphoric Acid with Tetramethylammonium Hydroxide

Curve 1 - 0.00919 M (CH$_3$)$_4$N$_5$P$_3$O$_{10}$ titrated with a solution 0.0543 M in HCl and 0.00919 M in H$_5$P$_3$O$_{10}$. Both solutions contained sufficient (CH$_3$)$_4$NCl to produce $\mu = 1.0$.

Curve 2 - 0.00943 M H$_5$P$_3$O$_{10}$ titrated with a solution 0.0528 M in (CH$_3$)$_4$NOH and 0.00943 M in ((CH$_3$)$_4$N)$_5$P$_3$O$_{10}$. Both solutions contained sufficient (CH$_3$)$_4$NCl to produce $\mu = 1.0$. 

39
affect the first end point appreciably in the acid titration since ortho-, pyro- and triphosphoric acids all contain one moderately highly ionized hydrogen ion per phosphorus atom with an acidity constant of the order of $10^{-2}$ or larger. The number of equivalents in the $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ to $\text{HP}_3\text{O}_{10}^{4-}$ range would increase by one in both the acid and salt titrations if hydrolysis were complete since both ortho- and pyrophosphoric acids contain hydrogen ions with acidity constants to replace the one of triphosphoric in this range. The number of equivalents in the $\text{HP}_3\text{O}_{10}^{4-}$ to $\text{P}_3\text{O}_{10}^{5-}$ range should not increase much in the acid titration since essentially only the last hydrogen of pyrophosphoric acid and not that of orthophosphoric acid would be titrated in this range.

One cannot apply previously calculated hydrolysis rate constants since these were made in the presence of alkalis. Furthermore, the extent of hydrolysis on the exchange resin is not known. However, it was observed from the ratio of the amounts of base required to reach the three end points in the acid titration that appreciable hydrolysis did occur if the acid solution was left at room temperature for a few hours or even if it were stored at 0°C for several days. The determination of various phosphates in mixtures on the basis of the several end
points is discussed by Gerber and Miles\(^{40}\) as well as by


Van Wazer and Holst\(^{14}\) indicate that the last two dissociation constants for triphosphoric acid are close to those of pyrophosphoric acid with the weakest hydrogen ion being slightly more dissociated in the triphosphoric acid case. This will be explained in the section on comparison of the acid dissociation constants.

Since the pH in the range of "a" values between zero and three for the acid and between three and five for the salt titration is close to that for concentrated hydrochloric acid having a concentration three times that of the triphosphate, the first three ionization constants must have values in the order of \(10^{-2}\), or larger. Due to the high degree of dissociation and the possibility of the constants having similar values, Bjerrum's method was applied in a manner described by Sullivan and Hindman\(^{33}\). The constants may be expressed as stepwise complexity constants, thus

\[
\beta_n = \frac{\left(\text{H}_n\text{P}_{30}^{10\,(5-n)-}\right)}{[\text{H}^+]^n \left(\text{P}_{3}^{0\,10\,5-}\right)}
\]  \((40)\)
where parentheses indicate concentrations and brackets indicate activities. In this case the latter were obtained from pH readings. To calculate $n$, the average number of bound hydrogen ions per triphosphate, the total number of bound hydrogen ions per triphosphate, the total number of millimoles of triphosphate and hydrogen ion (bound as well as dissociated) were obtained from the titration data. The concentrations of dissociated hydrogen ions were assumed to be equal to the known concentrations of hydrochloric acid having the same pH in the presence of the same concentration of indifferent electrolyte. It was found that the $p$H values were $0.10 \pm 0.02$ units smaller than the measured pH values. The corresponding activity coefficient, 0.80, is consistent with the results of Harned and Ehlers. Their values were found valid for


known solutions of hydrochloric acid in which the ionic strength was adjusted with $(\text{CH}_3)_4\text{NCl}$ instead of the acid itself. The titration data for $((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}$ with HCl are given in Table I.
Table I

APPLICATION OF BJERRUM'S METHOD TO THE TITRATION CURVE FOR TRIPHOSPHORIC ACID

The titration of 25 ml of a solution of 0.0388 M \(((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}\) with a solution 0.4043 M in HCl and 0.0388 M in \(((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}\) at 25°C. All solutions contained sufficient \((\text{CH}_3)_4\text{NCl}\) to produce an ionic strength of 1.0.

<table>
<thead>
<tr>
<th>a</th>
<th>pH</th>
<th>(n_{\text{theory}})</th>
<th>(n_{\text{experiment}})</th>
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<td>0.92</td>
<td>3.60</td>
<td>3.66</td>
</tr>
</tbody>
</table>
Bjerrum's formation function may be written in the following form.

\[ \bar{n} = (1-n)/1 \left[ H^+ \right] + (2-n)/2 \left[ H^+ \right]^2 + (3-n)/3 \left[ H^+ \right]^3 + \\
(4-n)/4 \left[ H^+ \right]^4 + (5-n)/5 \left[ H^+ \right]^5 \]  

(41)

Because two hydrogen ions were associated throughout the range the equation was modified in the actual calculations by defining \( n^* \) as the average number of hydrogen ions combined with \( H_2P_3O_{10}^{3-} \) and \( \beta_n^* \) as the corresponding complexity constants. Thus \( \beta_n^* = \beta^*/\beta_2 \) and \( n^* = \bar{n}-2 \)

\[ n^* = (1-n^*)/3 \left[ H^+ \right] + (2-n^*)/4 \left[ H^+ \right]^2 + \\
(3-n^*)/5 \left[ H^+ \right]^3 \]  

(42)

The simultaneous solution of equations in groups of three established that only two constants, having magnitudes in the order of \( \log/\beta_3^*=2 \) and \( \log/\beta_4^*=3 \) were required to account for all the data. By successive substitutions of these constants into the formation function, the values finally obtained were \( \log/\beta_3^*=2.11 \pm 0.05 \) and \( \log/\beta_4^*=3.17 \pm 0.10 \). Converting to the usual stepwise acidity constants the \( p \) values are \( pK_2^a = 2.11 \pm 0.05 \), \( pK_2^a = 1.06 \pm 0.10 \) and \( pK_1^a = \infty \) at an ionic strength adjusted to unity with tetramethylammonium chloride. The satisfactory agreement between \( \bar{n}_{\text{experimental}} \) and \( \bar{n}_{\text{theoretical}} \) is shown in Table I.
It is observed that \( n \) varied from 2 to 3.5, thus the predominant equilibrium might be anticipated to involve \( K_3^a \), as is evident from the relative values of the constants. The value of \( pK_3^a \) is therefore believed to be very reliable. The value of \( pK_2^a \) is somewhat less reliable since the equilibrium becomes significant only at the low pH range approaching unity where the error in hydrogen ion concentration becomes large relative to the total triphosphate concentration. The thermodynamic value of \( K_3^a \) was obtained by extrapolation to infinite dilution for \( a = 2.5 \). The constant was calculated as before, using hydrogen ion activity coefficients given by Harned and Ehlers\(^{40}\) for similar ionic strengths. The results are shown in Fig. 3. In calculating \( K_3^a \), the most dilute solutions were too dilute for accuracy. At an ionic strength of 0.1, the value of \( pK_3^a \) was 2.15, while the graphic extrapolation to infinite dilution yielded \( pK_3^a = 2.30 \).

If the first hydrogen ion dissociated from a terminal P tetrahedron, there would be two structures having the formula \( \text{H}_3\text{P}_3\text{O}_{10}^{2-} \) and \( K_2^a \) would be an apparent dissociation constant. However, the experimental values of \( K_1^a, K_2^a \) and \( K_3^a \) differ by tenfold or better indicating significantly different acidic strengths for the various \( \text{H}^+ \) ions. A comparison of the first ionization constants
Fig. 3. - Graphic Extrapolations to Infinite Dilution (Triphosphoric Acid)

Curve $K^a_3$ - 10.00 ml of 0.0396 M $H_5P_3O_{10}$ + 11.02 ml of 0.0898 M $(CH_3)_4NOH$ (a = 2.50)

Curve $K^a_4$ - 25.00 ml of 0.05649 M $((CH_3)_4N)_5P_3O_{10}$ + 4.24 ml of 0.4990 M HCl (a = 1.50)

Curve $K^a_5$ - 25.00 ml of 0.05649 M $((CH_3)_4N)_5P_3O_{10}$ + 1.41 ml of 0.4990 M HCl (a = 0.50)
of pyrophosphoric acid and phosphoric acid indicates that
the replacement of an -OH group in phosphoric by the
-OP03H2 of pyrophosphoric acid enhances the acidity by
considerably more than the increase in statistical
probability of 4 to 3. By analogy one would expect that
the single hydrogen ion held by the central P tetrahedron
of triphosphoric acid to be even more acidic. This
argument indicates that the H+ ion held by the central P
tetrahedron is the most highly dissociated. The second ion
can then ionize from either terminal P tetrahedron to yield
identical structures. If this is the case, K2 is a real
equilibrium constant.

Martell and Schwarzenbach22 have suggested that
the high pK4 value of HP3O104− may be explained by a
hydrogen bridging structure, I

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{P} \quad \text{O} \\
\text{P} \quad \text{O} \\
\text{P} \quad \text{O} \\
\text{O} \quad \text{O} \\
\text{I}
\end{array}
\]

whose pK4 value is larger than that of the corresponding
structure II. In the following structures the three
resonating double bonds and the ionic charges are omitted.

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{P} \quad \text{O} \\
\text{P} \quad \text{O} \\
\text{P} \quad \text{O} \\
\text{O} \quad \text{O} \quad \text{O} \\
\text{II}
\end{array}
\]
Structure III then indicates their $\text{H}_2\text{P}_3\text{O}_{10}^{3-}$ ion.

\[
\begin{array}{ccccccc}
0 & 0 & 0 & 0 & H \\
\downarrow & & & & \\
O-P & O & P & O & P & 0 \\
\downarrow & & & & \\
0 & 0 & 0 & 0 & \\
\end{array}
\]

A more detailed discussion of structure will be given in the chapter on comparison of the acid constants.

The calculations of $K_i^a$ and $K_j^a$ were simple since the constants were sufficiently different in magnitude so that the addition of hydrogen ion was stepwise and the degree of dissociation was negligible compared to the concentrations of the triphosphate species involved. Furthermore, the effect of hydrolysis was negligible except in the most dilute solutions near a pH of 9. The hydrolysis correction consists of the addition or subtraction of $K_w/[H^+]$ due to the following type of reaction:

\[
P_{3}O_{10}^{5-} + HCH \rightleftharpoons HP_{3}O_{10}^{4-} + OH^{-}
\]

The values of $K_i^a$ and $K_j^a$ were accordingly calculated by the following general equation for the acid titration:

\[
K_n^a = \frac{[H^+] [(e+1-n)C_p - K_w/[H^+] f + [H^+]/f]}{(n-e)C_p + K_w/[H^+] f - [H^+]/f}
\]

(43)

where $f$ is the activity coefficient of a univalent ion.

Fig. 3 shows the results of graphic extrapolations used to obtain thermodynamic constants.
At an ionic strength adjusted to unity with \((\text{CH}_3)\_4\text{NCl}\), the values of \(pK^a_4\) and \(pK^a_5\) were found to be 5.83 and 8.81. At an ionic strength of 0.1 the values of \(pK^a_4\) and \(pK^a_5\) were found to be 6.00 and 8.73, respectively. Extrapolated to zero ionic strength the values were \(pK^a_4 = 6.50\) and \(pK^a_5 = 9.24\).

**Complex Formation Constants**

When triphosphoric acid was titrated by hydroxide ion in the presence of various alkali metals, it was observed, Fig. 4, that the pH decreased in the range where the last two hydrogen ions were displaced. From the decrease in pH, it was possible to establish the presence of complexes of the type \(\text{MP}_3\text{O}_{10}^{4-}\) and \(\text{MHP}_3\text{O}_{10}^{3-}\) where \(M\) represents the alkali metal. Since there was no precipitation and since the inflections at the various equivalence points did persist for the stepwise addition and removal of hydrogen ion, the method of apparent acidity constants, previously discussed, was used to determine the stability constants of the complexes formed.

The general equation for the apparent acidity constant, \(K_{5-n}'\), is given by equation (29).

\[
K_{5-n}' = \frac{[H^+] \sum q(M\text{mH}_n(\text{P}_3\text{O}_{10})_q q(5-n-m)-) \sum q(M\text{mH}_n+\text{FP}_3\text{O}_{10})_q q(4-n-m)-)}{\sum q(M\text{mH}_n(\text{P}_3\text{O}_{10})_q q(5-n-m)-)} \tag{29}
\]
Fig. 4. - A Comparison of The Effects of Potassium, Sodium and Lithium Ions on The Curve for The Titration of Triphosphate Ion with Hydrochloric Acid

Curve 1 - 0.00371 M $((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}$ titrated with a solution 0.01140 M in HCl and 0.00271 M in H$_5$P$_3$O$_{10}$

Curve 2 - Similar to curve 1, but 0.15 M in K$^+$

Curve 3 - 0.068 M in Na$^+$

Curve 4 - 0.013 M in Li$^+$

All solutions adjusted to $\mu = 1$ with $(\text{CH}_3)_4\text{NCl}$
where \( m, n, \) and \( q \) indicate the number of metal, hydrogen and triphosphate ions in any particular species. Parentheses indicate concentrations and brackets indicate activities. \( n \) has a single value from zero to five if the addition of hydrogen ion is stepwise, while \( m \) and \( q \) may have several values if several complex species and the uncomplexed ligand, as well, are in equilibrium. The general equation for the stepwise addition of hydrogen ion to triphosphate ion and the corresponding acidity constant are:
\[
H^+ + H_nP_3O_{10}^{(5-n)-} \rightleftharpoons H_{n+1}P_3O_{10}^{(4-n)-}
\]
\[
K_{a_{5-n}}^n = \frac{[H^+][H_nP_3O_{10}^{(5-n)-}]}{[H_{n+1}P_3O_{10}^{(4-n)-}]}
\]
(27)
The general equation for the formation of any complex ion and the corresponding complexity constant, \( \beta_{M_mH_nHp_{q}} \), are
\[
mM^+ + qH_nP_3O_{10}^{q(5-n)-} \rightleftharpoons M_m(H_nP_3O_{10})_q^{q(5-n-m)-}
\]
\[
\beta_{M_mH_nHp_{q}} = \frac{(M_m(H_nP_3O_{10})_q^{q(5-n-m)-})}{(M^+)_m(H_nP_3O_{10}^{q(5-n)-})_q}
\]
(28)
where the subscript \( T_p \) indicates the ligand \( P_3O_{10}^{5-} \).

The calculations are further simplified if the maximum values of \( m \) and \( q \) are unity. This assumption can be tested by calculations based on varied concentrations.
and ratios of metal ion and triphosphate ion. In this case, then,

\[ M^+ + H_nP_3O_{10}^{(5-n)} \xrightleftharpoons{K_{MH_nTp}} M_{Hn}P_3O_{10}^{(4-n)}\]

\[ K_{MH_nTp} = \frac{(M_{Hn}P_3O_{10}^{(4-n)})}{(M^+)(H_nP_3O_{10}^{(5-n)})} \]  

A high concentration of an essentially noncomplexing electrolyte such as tetramethylammonium chloride and relatively low concentrations of metal ion and triphosphate ion are used in order to minimize the effect of the varied concentrations of the reacting species on the various activity coefficients. Under these conditions a lowering of the pH in the titration curve indicates complex formation since the presence of metal ion in an acid enhances its acidity. In regions where no pH lowering occurs, one may conclude that complex formation does not occur to an appreciable extent. Since no pH lowering occurred in the triphosphate curves for n values larger than 2, when the concentrations of the reactants were relatively small the following equations were derived by substituting equations having the forms of (27) and (44) into (29) with m and q equal to unity in the metal complex.

\[ K_4' = \frac{[H^+][(HP_3O_{10}^{4-}) + (MHP_3O_{10}^{3-})]}{(H_2P_3O_{10}^{3-})} = K_4a + K_{MHTp}K_4(M^+) \]
\[ K_5' = \frac{[H^+]\left[(P_3O_{10}^{5-}) + (MP_3O_{10}^{4-})\right]}{(HP_3O_{10}^{4-}) + (MHP_3O_{10}^{3-})} = \frac{K_5^\theta + K_{MTp}K_5^\alpha(M^+)}{1 + K_{MTp}(M^+)} \]  

Equation 30

\( K_5^\theta \) and \( K_5^\alpha \) are the acidity constants of triphosphoric acid, while \( K_{MTp} \) and \( K_{MTp} \) are the formation constants of the form in equation (44) for the complexes \( M(P_3O_{10})^{4-} \) and \( M(HP_3O_{10})^{3-} \).

From these equations it follows that the apparent acidity constants are constants if the concentration of unbound metal ion is constant, provided precautions are taken to avoid changes in activity coefficients. The apparent constants can be calculated by the following form of equation (29) for the titration of the triphosphate ion with hydrogen ion.

\[ K_{5-n} = \frac{[H^+](n+1-a)C_p - K_w/H^+ f + [H^+] f}{(a-n)C_p + K_w/H^+ f - [H^+] f} \]  

Equation 45

where "a" is the number of moles of hydrogen added per mole of triphosphate ion present in any form. The symbol, \( f \), indicates the activity coefficient of a univalent ion. If the acid is not too dilute \( pK_{5-n}' \) has the same value as the pH at \( a = n+1/2 \).

Curve 1, Fig. 5, was obtained for the titration of 0.00919 M \((CH_3)_4N)P_3O_{10}\) with a solution containing 0.0543 M \(HCl\) and exactly the same concentration of \(H_5P_3O_{10}\) as the solution titrated. Curves 2, 3, 4 and 5 were
Fig. 5. - The Effect of Various Concentrations of Sodium Ion on Curves for The Titration of Triphosphate Ion With Hydrochloric Acid

Curve 1 - 0.00919 M ((CH₃)₄N)₅P₃O₁₀ titrated with a solution 0.05 M in HCl and 0.00919 M in H₅P₃O₁₀.
Curve 2 - Similar to curve 1, but 0.05 M in Na⁺
Curve 3 - 0.10 M in Na⁺
Curve 4 - 0.25 M in Na⁺
Curve 5 - 1.00 M in Na⁺
All solutions adjusted to μ = 1 with (CH₃)₄NCl
obtained in titrations of solutions containing approximately 0.01 M Na₅P₃O₁₀ and different concentrations of NaCl. The acid solution contained approximately 0.05 M HCl and the same concentrations of NaCl and triphosphate as the solution titrated. Since no complex formation was observed between any of the metal ions and triphosphate ions containing two or more hydrogen ions, equations (29), (27) and (44) were sufficient to calculate the formation constants. The data and results are given in Table II.

The necessity of using a constant large concentration of a noncomplexing electrolyte and relatively low concentrations of complexing species is evident from Fig. 5, curves 4 and 5, for there is a pH lowering when the mean number of bound hydrogen ions exceeds two where no complex formation occurs. In the presence of sodium ions pH lowering occurred for n or "a" values less than 2 for all solutions. In the presence of 0.25 M and 1.00 M salt some pH lowering occurred for larger "a" values as shown in curves 4 and 5. This lowering of pH at larger "a" values is due to the activity effect resulting from the relatively large amount of sodium ion present. The effect did not occur for n > 2 with lower total concentrations but the same ratios of triphosphate to metal ion with sufficient tetramethylammonium chloride
### Table II

**DATA AND RESULTS FOR THE TITRATION OF TRIPHOSPHATE ION WITH HYDROGEN ION IN THE PRESENCE OF VARIOUS ALKALI METAL IONS**

The heading "a" is the number of moles of hydrogen ion added per mole of triphosphate ion. $CT_p \times 10^3$ is the total triphosphate concentration and $CM \times 10^3$ is the total concentration of metal ion. The ionic strength was adjusted to unity with $(CH_3)_4NCl, 25^\circ$.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>$CT_p \times 10^3$</th>
<th>$CM \times 10^3$</th>
<th>log $K_{TP}$</th>
<th>log $K_{NaTP}$</th>
<th>log $K_{LiTP}$</th>
</tr>
</thead>
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<tr>
<td><strong>Potassium</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>0.50</td>
<td>8.69</td>
<td>2.27</td>
<td>13.87</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>8.61</td>
<td>2.27</td>
<td>28.87</td>
<td>1.36</td>
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<tr>
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<td>0.50</td>
<td>8.52</td>
<td>2.27</td>
<td>33.87</td>
<td>1.38</td>
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<td>8.45</td>
<td>2.27</td>
<td>58.87</td>
<td>1.38</td>
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<td>Average</td>
<td>1.39 ± 0.06</td>
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<td>51.00</td>
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<tr>
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<td>9.940</td>
<td>99.70</td>
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<td></td>
<td>Average</td>
<td>1.64 ± 0.06</td>
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<td>8.24</td>
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<td>13.12</td>
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<tr>
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<td>46.04</td>
<td>2.90</td>
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<td>7.87</td>
<td>2.623</td>
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<td>Average</td>
<td>2.87 ± 0.06</td>
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<td></td>
<td>1.50</td>
<td>5.29</td>
<td>3.208</td>
<td>31.04</td>
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<tr>
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<td>5.19</td>
<td>3.208</td>
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<td>1.87</td>
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<tr>
<td></td>
<td>1.50</td>
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<td>61.04</td>
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<td></td>
<td>Average</td>
<td>1.88 ± 0.06</td>
<td></td>
</tr>
</tbody>
</table>
present to adjust the ionic strength to unity. Consequently, all calculations were based on relatively low concentrations of reacting species.

In the presence of potassium ion a lowering of the pH occurred only for "a" values less than unity, as shown in Fig. 4, curve 2, proving the absence of detectable concentrations of potassium hydrogen triphosphate complexes, so equation (30) reduced to the form

\[ K'_5 = K'_4 + K_{KTP}K'_5(K^+) \]  \hspace{1cm} (46)

The apparent constant, \( K'_5 \), is equal to the pH at the corresponding "a" value of 1/2. The values for the acidity constants of triphosphoric acid in 1.0 M (CH\(_3\))\(_4\)NCl at 25\(^\circ\) taken from the previous section were \( 10^{-5.83} \) for \( K'_4 \) and \( 10^{-8.81} \) for \( K'_5 \). The total concentration of potassium ion was first used for the value of free potassium ion. After obtaining preliminary formation constants a correction was applied for the metal bound in the complex. Substituting these values into equation (46) yields the formation constant, \( K_{KTP} \), for the following reaction:

\[ K^+ + P_3O_{10}^{5-} \rightleftharpoons KP_3O_{10}^{4-} \]

\[ K_{KTP} = \frac{(KP_3O_{10}^{4-})}{(K^+)(P_3O_{10}^{5-})} = 10^{1.39 \pm 0.06} \]

In the presence of sodium or lithium ions pH lowering occurred for n or "a" values less than two for all
of the solutions as shown in Fig. 4, curves 3 and 4. Substituting the individual values for the apparent constant, $K'_4$, the acidity constant, $K^a_4$, and $(M^+)$ into equation (31) yields the values of $K_{LiHTp}$ and $K_{NaHTp}$ given in the last column of Table II for the reactions

\[ \text{Na}^+ + \text{HP}_3\text{O}_{10}^{4-} \rightleftharpoons \text{NaHP}_3\text{O}_{10}^{3-} ; \]

\[ K_{NaHTp} = \frac{(\text{NaHP}_3\text{O}_{10}^{3-})}{(\text{Na}^+)(\text{HP}_3\text{O}_{10}^{4-})} = 10^{0.77 \pm 0.06} \]

\[ \text{Li}^+ + \text{HP}_3\text{O}_{10}^{4-} \rightleftharpoons \text{LiHP}_3\text{O}_{10}^{3-} ; \]

\[ K_{LiHTp} = \frac{(\text{LiHP}_3\text{O}_{10}^{3-})}{(\text{Li}^+)(\text{HP}_3\text{O}_{10}^{4-})} = 10^{1.88 \pm 0.06} \]

Substituting the values for the apparent acidity constant, $K'_5$, the acidity constant, $K^a_5$, the metal concentration, $(M^+)$, and the above metal-hydrogen formation constants into equation (30) yields the values of the metal formation constant given in the last column of Table II for the following reactions:

\[ \text{Na}^+ + \text{P}_3\text{O}_{10}^{5-} \rightleftharpoons \text{NaP}_3\text{O}_{10}^{4-} ; \]

\[ K_{NaTP} = \frac{(\text{NaP}_3\text{O}_{10}^{4-})}{(\text{Na}^+)(\text{P}_3\text{O}_{10}^{5-})} = 10^{1.64 \pm 0.06} \]

\[ \text{Li}^+ + \text{P}_3\text{O}_{10}^{5-} \rightleftharpoons \text{LiP}_3\text{O}_{10}^{4-} ; \]

\[ K_{LiTP} = \frac{(\text{LiP}_3\text{O}_{10}^{4-})}{(\text{Li}^+)(\text{P}_3\text{O}_{10}^{5-})} = 10^{2.87 \pm 0.06} \]
These results establish moderately stable complex formation between triphosphate ion and these alkali metals which should be considered in calculating the stabilities of other metal ions with triphosphate ions. It is probable that the metal ions are members of at least one chelate ring containing two phosphorus and three oxygen atoms, structure I, as suggested by Kolthoff and Watters\(^{42}\) for the manganese (III) complex with pyrophosphate and by Van Wazer\(^{4,12}\) and his co-workers for complexes of higher phosphates. Martell and Schwarzenbach\(^{22}\) have proposed that the triphosphate ion may be tridentate, structures II and III, in the corresponding complexes with calcium and magnesium. A more detailed discussion of structure will be given in the chapter on comparison of the formation constants. In the following structures the three resonating double bonds and the ionic charges are omitted.

\[
\begin{align*}
\text{I} & : \quad \overset{\text{O}}{\text{O}}-\text{P}\sim\text{O}-\text{P}\sim\text{O}-\text{P}\sim\text{O} \\
\text{II} & : \quad \overset{\text{O}}{\text{O}}-\text{P}\sim\text{O}-\text{P}\sim\text{O}-\text{P}\sim\text{O} \\
\text{III} & : \quad \overset{\text{O}}{\text{O}}-\text{P}\sim\text{O}-\text{P}\sim\text{O}-\text{P}\sim\text{O}
\end{align*}
\]

The last four acidity constants of triphosphoric acid and the four acidity constants of ethylenediamine tetraacetic acid are quite similar. It is of interest that this similarity persists in the sodium and lithium complexes of both these ligands.

The results in Table II show the order lithium > sodium > potassium for formation constants of the type $M\text{P}_3\text{O}_{10}^{4-}$. Potassium did not form a complex of the type $M\text{HP}_3\text{O}_{10}^{3-}$ whereas both lithium and sodium did, lithium > sodium as expected.

The principle used in the investigations of alkali metal complexes remained applicable for the magnesium complexes although the pH decrease was much greater. Fig. 6 shows the effect of various concentrations of magnesium ion on the curve for the titration of 0.002700 M $((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}$ with a solution 0.011145 N in HCl and 0.002700 M in $\text{H}_5\text{P}_3\text{O}_{10}$.

A complex having the form $\text{Mg}_2\text{P}_3\text{O}_{10}^-$ was detected in the buffer region below "a" 1.0 and equation (30) was modified to include this species. The existence of this complex is demonstrated if one assumes that only the 1:1 complex exists and then calculates the values for the formation constant, $K_{\text{MgTP}}$, as the ratio of magnesium to triphosphate is increased. One observes that the values
Fig. 6. - The Effect of Various Concentrations of Magnesium Ion on Curves for The Titration of Triphosphate Ion with Hydrochloric Acid

Curve 1 - 0.002700 M \((\text{CH}_3)_4\text{N})_5\text{P}_3\text{O}_{10}\) titrated with a solution 0.01145 N in HCl and 0.002700 M in \(\text{H}_5\text{P}_3\text{O}_{10}\)

Curve 2 - Similar to curve 1, but 0.01 M in \(\text{Mg}^{2+}\)

Curve 3 - 0.02 M in \(\text{Mg}^{2+}\)

Curve 4 - 0.10 M in \(\text{Mg}^{2+}\)

All solutions adjusted to \(\mu = 1\) with \((\text{CH}_3)_4\text{NCl}\)
obtained vary in a regular way with the increase in the magnesium ion concentration. This regular increase indicates that the equilibria proposed were not adequate to account for the data obtained. With the inclusion of the \( \text{Mg}_2\text{P}_3\text{O}_{10}^- \) complex the values obtained for the formation constants, \( \text{K}_{\text{MgTP}} \) and \( \text{K}_{\text{Mg}_2\text{TP}} \), were constant within experimental error. Table III shows the values obtained in this manner. The values obtained for \( \log \text{K}_{\text{MgTP}} \) assuming only the 1:1 complex increase from 6.10 to 6.97 for a tenfold increase in the total magnesium ion concentration.

Modifying equation (30) to include the \( \text{Mg}_2\text{P}_3\text{O}_{10}^- \) complex yields

\[
\frac{[H^+][\text{P}_3\text{O}_{10}^{5-} + (\text{MgP}_3\text{O}_{10}^{3-}) + (\text{Mg}_2\text{P}_3\text{O}_{10}^-)]}{(\text{HP}_3\text{O}_{10}^{1-}) + (\text{MgHP}_3\text{O}_{10}^{2-})}
\]

Comparing curve 1 with 2, 3 and 4, Fig. 6, it is evident that there is a lowering of the pH in the region between \( a = 1.0 \) and \( a = 2.0 \) indicating the presence of an acidic complex. Applying equation (31) together with the individual values for the apparent constant, \( K_i \), the
Table III

FORMATION CONSTANTS FOR THE MAGNESIUM AND CALCIUM COMPLEXES WITH TRIPHOSPHATE

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Stepwise Formation Constant</th>
<th>Calculated Values of log K</th>
<th>Average Value of log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>$K_{Mg_2Tp}$</td>
<td>2.14, 2.12, 2.13 ± 0.06</td>
<td>$2.13 ± 0.06$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sqrt{Mg_2Tp} = 7.96 ± 0.06$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$K_{MgTp}$</td>
<td>5.84, 5.81, 5.85 ± 0.06</td>
<td>$5.83 ± 0.06$</td>
</tr>
<tr>
<td></td>
<td>$K_{MgHTp}$</td>
<td>3.37, 3.30, 3.36 ± 0.06</td>
<td>$3.34 ± 0.06$</td>
</tr>
<tr>
<td>Calcium</td>
<td>$K_{CaTp}$</td>
<td>5.42, 5.41, 5.52 ± 0.15</td>
<td>$5.44 ± 0.15$</td>
</tr>
<tr>
<td></td>
<td>$K_{CaHTp}$</td>
<td>3.08, 3.02, 3.02 ± 0.06</td>
<td>$3.04 ± 0.06$</td>
</tr>
</tbody>
</table>
Table IV

DATA FOR THE TITRATION OF TRIPHOSPHATE ION WITH HYDROGEN ION IN THE PRESENCE OF MAGNESIUM AND CALCIUM IONS

The heading "a" is the number of moles of hydrogen ion added per mole of triphosphate ion, $C_{Tp} \times 10^3$ is the total triphosphate concentration and $C_M \times 10^3$ is the total concentration of metal ion. The ionic strength was adjusted to unity with (CH$_3$)$_4$NCl, 25°C.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>$C_{Tp} \times 10^3$</th>
<th>$C_M \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>0.50</td>
<td>6.08</td>
<td>2.553</td>
<td>9.934</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>5.84</td>
<td>2.710</td>
<td>19.86</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>5.18</td>
<td>2.553</td>
<td>99.34</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>4.50</td>
<td>2.553</td>
<td>9.934</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>3.30</td>
<td>2.710</td>
<td>19.86</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>4.51</td>
<td>2.553</td>
<td>9.934</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.50</td>
<td>6.52</td>
<td>5.530</td>
<td>4.169(1)</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>6.49</td>
<td>5.530</td>
<td>8.316(1)</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>6.41</td>
<td>3.000</td>
<td>4.468</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>4.84</td>
<td>2.765</td>
<td>8.378</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>4.77</td>
<td>2.765</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>4.58</td>
<td>2.765</td>
<td>17.51</td>
</tr>
</tbody>
</table>

(1) These values indicate the free metal concentration.
acidity constant, $K_a$, and the metal ion concentration ($Mg^{2+}$) yields the values of $K_{MgHTp}$ given in Table III for the reactions

$$Mg^{2+} + HP30_{10}^{4-} \rightleftharpoons MgHP30_{10}^{2-}$$

$$K_{MgHTp} = \frac{(MgHP30_{10}^{2-})}{(Mg^{2+})(HP30_{10}^{4-})} = 103.34 \pm 0.06$$

The lowering of the curves in the buffer region below "a" equal 1.0 has been previously discussed. Substituting the values for the apparent acidity constant, $K'_5$, the acidity constant, $K_a$, the metal ion concentration ($Mg^{2+}$) and the value of the formation constant for the metal-hydrogen complex, $K_{MgHTp}$, into equation (47) and solving pairs of equations simultaneously yields the values of $K_{MgTp}$ and $K_{Mg2Tp}$ for the following reactions:

$$Mg^{2+} + P30_{10}^{5-} \rightleftharpoons MgP30_{10}^{3-}$$

$$Mg^{2+} + MgP30_{10}^{3-} \rightleftharpoons Mg2P30_{10}^{-}$$

$$K_{MgTp} = \frac{(MgP30_{10}^{3-})}{(Mg^{2+})(P30_{10}^{5-})} = 105.83 \pm 0.06$$

$$K_{Mg2Tp} = \frac{(Mg2P30_{10}^{-})}{(Mg^{2+})(MgP30_{10}^{3-})} = 10^{2.13} \pm 0.06$$
One also obtains the complexity constant, $\beta_{Mg_2Tp}$, for the reaction

$$2Mg^{2+} + P_{3010^{5-}} \rightleftharpoons Mg_2P_{3010^{-}}$$

$$\beta_{Mg_2Tp} = \frac{(Mg_2P_{3010^{-}})}{(Mg^{2+})^2(P_{3010^{5-}})} = 10^{7.96 \pm 0.06}$$

The data and formation constants obtained are listed in Tables III and IV.

Precipitation occurred during the titration of triphosphate ion with HCl in the presence of excess calcium ion when less than approximately 1.3 equivalents of hydrogen ion per mole of triphosphate ion were added. The method previously used to determine the complex formation constant depends upon obtaining the pH of a solution of triphosphate containing excess calcium ion at an "a" value of 0.50. Because of the solubility limitation the method was modified by equilibrating the triphosphate solution with freshly precipitated calcium sulfate. The solubility of calcium sulfate in such a solution was then determined. By adding a known amount of sulfate, as the tetramethylammonium salt, to the triphosphate solution under investigation and equilibrating with calcium sulfate precipitate one can calculate the free calcium ion concentration. This method permits one to obtain a known concentration of free calcium ion which is less than that required for precipitation.
Under these experimental conditions, a binuclear complex would probably not be detected. Titrations were performed in the presence of solid calcium sulfate to show that the addition of hydrogen ion was stepwise.

The solubility product of calcium sulfate in 1.0 M tetramethylammonium chloride was determined in order to calculate the free calcium ion concentration. Polaro-graphic determination of calcium ion proved ineffective since in aqueous solution, calcium ion gave a sharp undefined maximum which could not be suppressed. Also, the potential for the reduction of calcium ion occurs very close to that for the reduction of the tetramethylammonium ion. An amperimetric titration of calcium ion with versenate ion was unsuccessful due to interference of the chloride anodic wave with the versene anodic wave.

A flame photometric method of determining calcium concentration proved successful. Standard solutions of various concentrations of calcium chloride in 1.0 M tetramethylammonium chloride were used to obtain a working curve from 0.10 to 20.00 ppm of calcium ion. Freshly precipitated calcium sulfate was shaken with solutions 1.0 M in tetramethylammonium chloride and containing various concentrations of sulfate ion added as tetramethylammonium sulfate. The mixtures were filtered
through a glass funnel containing a fritted disc and the filtrate analyzed for calcium ion by the flame photometer. Four independent determinations yielded an average value of \( \text{pK}_{\text{sp}} = 3.16 \pm 0.06 \) for \( \text{CaSO}_4 \). The results are given in Table V.

When "a" was equal to 1.50 no precipitation occurred and the method originally used was applied to the determination of the formation constant, \( K_{\text{CaHTP}} \). Substituting the individual values for the apparent acidity constant, \( K'_4 \), the acidity constant, \( K_a \), and the metal concentration (\( M^{2+} \)) into equation (31) yields the formation constant, \( K_{\text{CaHTP}} \), for the following reaction:

\[
\text{Ca}^{2+} + \text{HP}_3\text{O}_10^{4-} \rightleftharpoons \text{CaHP}_3\text{O}_10^{2-}
\]

\[
K_{\text{CaHTP}} = \frac{(\text{CaHP}_3\text{O}_10^{2-})}{(\text{Ca}^{2+})(\text{HP}_3\text{O}_10^{4-})} = 10^{3.04} \pm 0.06
\]

Under the conditions previously discussed at "a" equal to 0.50 equation (30) can be used to obtain the formation constant, \( K_{\text{CaTP}} \). Substituting the individual values for the apparent constant, \( K_5 \), the acidity constant, \( K_a \), the above metal-hydrogen formation constant, \( K_{\text{CaHTP}} \), and the metal ion concentration (\( M^{2+} \)) into equation (30) yields the formation constant, \( K_{\text{CaTP}} \), for the reaction
### Table V

**DETERMINATION OF K\(_{sp}\) FOR CALCIUM SULFATE IN 1.0 M TETRAMETHYLAMMONIUM CHLORIDE**

<table>
<thead>
<tr>
<th>Concentration of (((\text{CH}_3)_4\text{N})_2\text{SO}_4)</th>
<th>Concentration of (\text{Ca}^{2+} \times 10^3) Determined Experimentally</th>
<th>(pK_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0550 M</td>
<td>10.8</td>
<td>3.23</td>
</tr>
<tr>
<td>0.1100 M</td>
<td>6.32</td>
<td>3.16</td>
</tr>
<tr>
<td>0.1375 M</td>
<td>5.01</td>
<td>3.16</td>
</tr>
<tr>
<td>0.2000 M</td>
<td>4.18</td>
<td>3.08</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td><strong>3.16 ± 0.08</strong></td>
</tr>
</tbody>
</table>

between calcium ion and triphosphate ion. Tables III and IV give the data and formation constants obtained.

\[
Ca^{2+} + P_{3}O_{10}^{5-} \rightleftharpoons CaP_{3}O_{10}^{3-}
\]

\[
K_{CaTp} = \frac{(CaP_{3}O_{10}^{3-})}{(Ca^{2+})(P_{3}O_{10}^{5-})} = 10^{5.44 \pm 0.15}
\]

As predicted earlier no complex \(Ca_{2}P_{3}O_{10}^{-}\) was detected.
THE ACIDITY OF PYROPHOSPHORIC ACID AND
THE COMPLEXES OF PYROPHOSPHATE ION

Introduction

Prior to 1930 a number of investigations were made on the strength of pyrophosphoric acid. The classic conductivity measurements of Abbott and Bray\(^{43}\) yielded reliable values for the acidity constants of pyrophosphoric acid, particularly the first and second constants. In a study of the hydrolysis of ammonium salts of pyrophosphoric acid by a distribution method, they obtained the following values for the acid dissociation constants at 18°:

\[
\begin{align*}
K_1^a &= 1.4 \times 10^{-1}; \\
K_2^a &= 2.9 \times 10^{-7}; \quad \text{and} \\
K_4^a &= 3.6 \times 10^{-9}.
\end{align*}
\]

Kolthoff and Bosch\(^{44}\) obtained excellent values for the third and fourth ionization constants extrapolated to infinite dilution. Applying the Debye-Hückel relationship to data obtained using a hydrogen electrode, their final constants at 18° were

\[
K_3^a = 2.1 \times 10^{-7} \quad \text{and} \quad K_4^a = 4.06 \times 10^{-10}.
\]

---


\(^{44}\) I. M. Kolthoff and W. Bosch, Rec. trav. chim., 47, 826 (1928).
During a biochemical investigation of buffer mixtures by pH measurements, Morton obtained values of

\[ K_3^a = 1.98 \times 10^{-7} \text{ and } K_4^a = 1.32 \times 10^{-10} \]

for pyrophosphoric acid at 30°. Recently McGilvery and Crowther, studying the hydrolysis of condensed phosphates, determined the acid dissociation constants at 65.5°. Substituting the data obtained by electrometric titrations into the basic stoichiometric equations, they obtained values of

\[ K_1^a = 0.107, K_2^a = 7.58 \times 10^{-2}, K_3^a = 1.45 \times 10^{-6} \text{ and } K_4^a = 9.8 \times 10^{-9} \]

for the second and final approximation.

The existence of alkali metal complexes with pyrophosphate ion was not considered before Monk, during a conductance study of the acidity of pyrophosphoric acid, found evidence of complex formation with sodium ion and calculated a dissociation constant of \(10^{-2.45}\) for the complex, \(\text{NaP}_2\text{O}_7^{3-}\). He reported the acid dissociation
constants of pyrophosphoric acid to be $K_{4}^a = 2.4 \pm 0.2 \times 10^{-7}$ and $K_{3}^a = 2.7 \times 10^{-7}$ at $25^\circ$. Complex formation of pyrophosphate with alkali metal ion is of considerable importance since alkali metal ions are usually added to adjust ionic strength or as a source of pyrophosphates. The tendency of pyrophosphate to form complexes with many metals through chelate ring formation has been the subject of numerous studies.(12,21-23,42,46-50).

---


In the present study the acidity constants of pyrophosphoric acid were evaluated at various ionic strengths in the presence of tetramethylammonium chloride with alkali metal ions absent.

Experimental

The source of pyrophosphate ion for most of the experiments was Na$_4$P$_2$O$_7$·10H$_2$O, Mallinckrodt analytical reagent grade. The pyrophosphoric acid was prepared from sodium pyrophosphate by the use of the acid form of the ion exchange resin Dowex 50-X12, 100-200 mesh, low porosity, in a manner exactly analogous to that described previously for the preparation of triphosphoric acid. Potassium pyrophosphate was prepared by heating anhydrous dipotassium hydrogen phosphate at 500 to 700 for 3 hours. Lithium pyrophosphate was prepared in the same manner as lithium triphosphate in the previous section using the ion exchange resin Dowex 50-X12 charged with lithium ions. All other reagents and the general experimental procedure are described in the previous section.

The titrations were performed in an aqueous thermostat adjusted to $25 \pm 0.1^\circ$ using the Beckman model G pH meter equipped with the "all purpose" glass electrode.
The $H_4P_2O_7$ or $((CH_3)_4N)_4P_2O_7$ solutions obtained from the columns were tested for removal of sodium ion as previously described. The extent of hydrolysis of tetramethylammonium pyrophosphate was tested by titration and found to be negligible after periods of one week if the solution was stored in a freezer at $-15^\circ$. Crowther and Westman\(^9\) studied the hydrolysis of pyrophosphoric acid


and found it to be acid catalyzed but not base catalyzed. In the present study no appreciable hydrolysis was observed if the tetramethylammonium pyrophosphate solution was left at room temperature for one hour.

**Discussion of Results and Conclusion**

**Acidity Constants**

Since all previous studies of the acidity of pyrophosphoric acid at large ionic strength were made in the presence of alkali metal ions, the acidity constants were re-evaluated using tetramethylammonium chloride to adjust the ionic strength but with alkali metal ions absent.

Curve 1, Fig. 7, was obtained for the titration of 0.02968 M $((CH_3)_4N)_4P_2O_7$ with a solution containing
Fig. 7. - Curves for the Titration of Tetramethylammonium Pyrophosphate with Hydrochloric Acid and the Titration of Pyrophosphoric Acid with Tetramethylammonium Hydroxide; A Comparison of the Effects of Potassium, Sodium and Lithium Ions on the Curve for the Titration of Pyrophosphate Ion with Hydrochloric Acid.

Curve 1 - 0.02968 M \((\text{CH}_3)_4\text{N})_4\text{P}_2\text{O}_7\) titrated with a solution 0.2805 M in HCl and 0.62968 M in H_4P_2O_7.

Curve 2 - Similar to curve 1, but 0.12 M in K\(^+\).

Curve 3 - 0.12 M in Na\(^+\).

Curve 4 - 0.12 M in Li\(^+\).

Curve 5 - 0.04524 M \(\text{H}_4\text{P}_2\text{O}_7\) titrated with a solution 0.08901 M in \((\text{CH}_3)_4\text{NOH}\).

All solutions adjusted to \(\mu=1\) with \((\text{CH}_3)_4\text{NCl}\).
0.2805 M HCl and the same concentration of H₄P₂O₇ as the solution titrated. Curve 5, Fig. 7, was obtained for the titration of 0.04524 M H₄P₂O₇ with 0.08901 M (CH₃)₄NOH. All solutions contained sufficient (CH₃)₄KCl to produce an ionic strength of unity. The ordinate "a" is the number of equivalents of acid or base added per mole of pyrophosphate present in any form. The titration curves for pyrophosphoric acid indicate that the first two hydrogen ions are highly dissociated and that the values for their ionization constants are not widely separated. Therefore, Bjerrum's method was used to evaluate these constants in the same manner as for triphosphoric acid.

The expression for the stepwise complexity constant is

\[ \beta_n = \frac{[\text{H}_n\text{P}_2\text{O}_7^{(1-n)^-}]}{[\text{H}^+]} \frac{1}{(\text{P}_2\text{O}_7^{4^-})} \]

(40)

where parentheses indicate concentrations and brackets indicate activities.

Due to the absence of appreciable concentrations of the species P₂O₇⁴⁻ and HP₂O₇³⁻ at pH values below 3, Bjerrum's formation equation was modified by defining \( n^* = \bar{n} - 2 \), so that \( \beta_n = \beta \sqrt{2} \) and

\[ n^* = (1-n^*) \beta_3^* [\text{H}^+] + (2-n^*) \beta_4^* [\text{H}^+]^2 \]

(48)

Simultaneous solution of equations in groups of two yielded the values of \( \log \beta_3^* = 1.81 \pm 0.05 \) and
\[ \log f^*_{4+} = 2.63 \pm 0.05. \] Converting to the usual stepwise acidity constants the values are \( pK_{2}^a = 1.31 \pm 0.05 \) and \( pK_{1}^a = 0.82 \pm 0.05 \). Table VI shows the agreement between the experimental and theoretical.

The acidity constants were also evaluated at infinite dilution. The values of \( K_3^a \), \( K_4^a \) and \( K_2^a \) at concentrations approaching infinite dilution were calculated using equation (43) which contains terms for the degree of hydrolysis and dissociation. The activity coefficients of Harned and Ehlers\(^1\) were used. The \( p \) values of \( K_3^a \) and \( K_4^a \) at an ionic strength of unity were \( pK_{3}^a = 6.13 \) and \( pK_{4}^a = 8.93 \). At an ionic strength of 0.1, the values of \( pK_{2}^a \), \( pK_{3}^a \) and \( pK_{4}^a \) were 2.22, 6.36 and 9.11, respectively. The graphic extrapolations to infinite dilution, Fig. 8, yielded \( pK_{2}^a = 2.64 \), \( pK_{3}^a = 6.76 \) and \( pK_{4}^a = 9.42 \). It is of interest to observe that the last two constants for \( K_3^a \) and \( K_4^a \) were quite similar to the values \( pK_{3}^a = 6.679 \) and \( pK_{4}^a = 9.391 \) obtained by Kolthoff and Bosch using a hydrogen electrode with sodium ion added as the pyrophosphate salt. It is evident from the magnitude of the sodium complexes constant that the latter should not affect their result at infinite dilution.
Table VI
APPLICATION OF BJERRUM'S METHOD TO THE TITRATION CURVE FOR PYROPHOSPHORIC ACID

The titration of 20 ml of a solution of 0.02968 M \((\text{CH}_3\text{)}_4\text{N})_4\text{P}_2\text{O}_7\) with a solution 0.2805 M in HCl and 0.02968 M in \(\text{H}_3\text{PO}_4\). Both solutions contained sufficient \((\text{CH}_3\text{)}_4\text{N})_4\text{Cl}\) to produce an ionic strength of 1.0.

<table>
<thead>
<tr>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>(\bar{n}) theory</th>
<th>(\bar{n}) experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.10</td>
<td>2.93</td>
<td>2.07</td>
<td>2.06</td>
</tr>
<tr>
<td>2.24</td>
<td>2.61</td>
<td>2.14</td>
<td>2.14</td>
</tr>
<tr>
<td>2.37</td>
<td>2.42</td>
<td>2.22</td>
<td>2.22</td>
</tr>
<tr>
<td>2.50</td>
<td>2.25</td>
<td>2.29</td>
<td>2.32</td>
</tr>
<tr>
<td>2.63</td>
<td>2.13</td>
<td>2.35</td>
<td>2.34</td>
</tr>
<tr>
<td>3.03</td>
<td>1.89</td>
<td>2.53</td>
<td>2.51</td>
</tr>
<tr>
<td>3.41</td>
<td>1.73</td>
<td>2.64</td>
<td>2.68</td>
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<td>3.75</td>
<td>1.61</td>
<td>2.75</td>
<td>2.79</td>
</tr>
<tr>
<td>4.08</td>
<td>1.52</td>
<td>2.83</td>
<td>2.88</td>
</tr>
<tr>
<td>4.93</td>
<td>1.31</td>
<td>3.00</td>
<td>3.00</td>
</tr>
<tr>
<td>5.84</td>
<td>1.15</td>
<td>3.05</td>
<td>3.11</td>
</tr>
</tbody>
</table>
Fig. 8. - Graphic Extrapolations to Infinite Dilution (Pyrophosphoric Acid)

Curve $K_2^a$ - 20.00 ml of 0.03962 M $(\text{CH}_3)\text{N}_4\text{P}_2\text{O}_7 + 4.95$ ml of 0.3992 M HCl ($a = 2.50$)

Curve $K_3^a$ - 20.00 ml of 0.03962 M $(\text{CH}_3)\text{N}_4\text{P}_2\text{O}_7 + 2.97$ ml of 0.3992 M HCl ($a = 1.50$)

Curve $K_4^a$ - 20.00 ml of 0.03962 M $(\text{CH}_3)\text{N}_4\text{P}_2\text{O}_7 + 0.99$ ml of 0.3992 M HCl ($a = 0.50$)
Complex Formation Constants

As in the previous section on triphosphate complexes with alkali metal ions the lowering of the apparent acidity constants of pyrophosphoric acid in the presence of an excess of various alkali metal ions was used as a means of evaluating the extent of complex formation. The equation for the apparent acidity constant, $K_{a-n}$, is

$$K_{a-n} = \frac{[H^+] \sum q(M_mH_n(P_2O_7)_q q^{(4-n-m)-})}{\sum q(M_mH_{n+1}(P_2O_7)_q q^{(3-n-m)-})}$$

(49)

where $m$, $n$ and $q$ indicate the number of metal, hydrogen and pyrophosphate ions in any particular species. Parentheses indicate concentrations and brackets indicate activities. The number of bound hydrogen ions, $n$, has a single value from zero to four if the addition of hydrogen is stepwise, while $m$ and $q$ may have several values if several complex species, and the uncomplexed ligand, as well, are in equilibrium. The general equation for the stepwise addition of hydrogen ion to pyrophosphate ion and the corresponding acidity constant are:

$$H^+ + H_nP_2O_7^{(4-n)-} \rightleftharpoons H_{n+1}P_2O_7^{(3-n)-}$$

$$K_{a-n} = \frac{[H^+] \left[H_nP_2O_7^{(4-n)-}\right]}{\left[H_{n+1}P_2O_7^{(3-n)-}\right]}$$

(50)
The general equation for the formation of any complex ion and the corresponding complexity constant, $\beta_{mM^n_{n}P_{y}q}$, are

$$mM^+ + qH_nP_2O_7^{q(4-n)-} \rightarrow M_m(H_nP_2O_7)_q^{q(4-n-m)-}$$

$$\beta_{mM^n_{n}P_{y}q} = \frac{(M_m(H_nP_2O_7)_q^{q(4-n-m)-})}{(M^+)^m(H_nP_2O_7^{q(4-n)-})^q} \quad (51)$$

where the subscript $Py$ indicates the ligand $P_2O_7^{4-}$.

The equations used to calculate the complex formation constants were derived by substituting equations having the forms of (50) and (51) into (49) with $m$ and $q$ assumed to be equal to unity.

$$K_3' = \frac{[H^+][\text{HP}_2O_7^{3-}] + (\text{MHP}_2O_7^{2-})}{(\text{HP}_2O_7^{2-})} = K_3^a + K_{MPy}K_3^a(M^+) \quad (52)$$

$$K_4' = \frac{[H^+][\text{P}_2O_7^{4-}] + (\text{MP}_2O_7^{3-})}{(\text{HP}_2O_7^{3-}) + (\text{MHP}_2O_7^{2-})} = K_4^a + K_{MPy}K_4^a(M^+) \quad (53)$$

$K_3^a$ and $K_4^a$ are the acidity constants of pyrophosphoric acid, while $K_{MPy}$ and $K_{MHPy}$ are the formation constants for the complexes $\text{M}(\text{P}_2\text{O}_7)^{3-}$ and $\text{M}(\text{HP}_2\text{O}_7)^{2-}$.

From these equations it follows that the apparent acidity constants are constants if the concentration of unbound metal ion is constant, provided precautions are taken to avoid changes in activity coefficients. A high concentration of an essentially noncomplexing electrolyte
and relatively low concentrations of metal ion and pyrophosphate ion were used for this purpose. For the titration of pyrophosphate ion with hydrogen ion in the absence of metal ions the acidity constants can be calculated by the following form of equation (45). In the presence of metal ions $K_{4-n}^{'b}$ is calculated by the same equation

$$K_{4-n}^{'b} = \frac{[H^+] [(n+1-a)C_p - K_w / [H^+] f] [H^+] / f]}{(a-n)C_p + K_w / [H^+] f - [H^+] / f}$$

(54)

where "a" is the number of moles of hydrogen added per mole of pyrophosphate ion present in any form. The symbol, $f$, indicates the activity coefficient of a univalent ion. If the acid is not too dilute the constants have the same value as the pH at $a = n + 1/2$.

Curves 2, 3 and 4, Fig. 9, illustrate the pH lowering effect due to the presence of approximately 0.10 M potassium, sodium and lithium in the titration of approximately 0.03 M $((CH_3)_{14}N)_4P_2O_7$ with a solution containing approximately 0.28 M HCl and the same concentration of $H_4P_2O_7$ as the solution titrated. Since curves 1 to 4 coincide at "a" values beyond 2, it is evident that no complex formation occurs between any of the alkali metal ions and $H_2P_2O_7^{2-}$ or $H_3P_2O_7^-$. Furthermore, the reactants
Fig. 9. - A Comparison of The Effects of Potassium, Sodium and Lithium Ions on The Curve for The Titration of Pyrophosphate Ion with Hydrochloric Acid

Curve 1 - 0.02968 M \((\text{CH}_3\text{N})_4\text{P}_2\text{O}_7\) titrated with a solution 0.2805 M in HCl and 0.02968 M in H\text{P}_2\text{O}_7

Curve 2 - Similar to curve 1, but 0.12 M in K\(^+\)

Curve 3 - 0.12 M in Na\(^+\)

Curve 4 - 0.12 M in Li\(^+\)

All solutions adjusted to \(\mu=1\) with \((\text{CH}_3)_4\text{NCl}\)
are sufficiently dilute so there is no measurable effect on the activity coefficients. Consequently the pH lowering at "a" values below 2 must be due to complex formation.

Comparing curves 2 and 3, Fig. 9, obtained in the presence of potassium, a lowering of the pH occurred only for "a" values less than unity proving the absence of detectable concentrations of potassium hydrogen pyrophosphate complexes, so equation (53) reduced to the form

\[ K_{4}^{'} = K_{4}^{a} + K_{\text{py}} K_{4}^{a} (K^{+}) \]  

(55)

Using the acidity constants of pyrophosphoric acid taken from the previous section and estimating the concentration of the free potassium ion to be the total concentration less the concentration of pyrophosphate ion, one obtains a temporary complexity constant. More accurate values of \( (K^{+}) \) were obtained on the basis of the temporary constant.

\[ K^{+} + P_{2}O_{7}^{4-} \rightleftharpoons KP_{2}O_{7}^{3-} \]

\[ K_{\text{py}} = \frac{(KP_{2}O_{7}^{3-})}{(K^{+})(P_{2}O_{7}^{4-})} = 10^{0.80 \pm 0.06} \]

As shown in curve 3 obtained in the presence of sodium ion the pH was lowered only for "a" values less than unity proving the absence of detectable concentrations of acidic
sodium complexes. Substituting the values of \( k'_4 \) and the free sodium ion into equation (53) as before, one obtains

\[
Na^+ + P_2O_7^{4-} \rightleftharpoons NaP_2O_7^{3-}
\]

\[
K_{NaPy} = \frac{(NaP_2O_7^{3-})}{(Na^+)(P_2O_7^{4-})} = 10^{1.00 \pm 0.06}
\]

As shown in curve 4, Fig. 9, obtained in the presence of lithium ions, pH lowering occurred for or "a" values less than 2 proving the presence of complexes of lithium ion with both \( P_2O_7^{4-} \) and \( HP_2O_7^{3-} \). Substituting the individual values for the acidity constant, \( k^a_3 \), and \( (Li^+) \) into equation (52) yields the values of \( KLiHPy \) given in Table VII for the reaction

\[
Li^+ + HP_2O_7^{3-} \rightleftharpoons LiHP_2O_7^{2-}
\]

\[
KLiHPy = \frac{(LiHP_2O_7^{2-})}{(Li^+)(HP_2O_7^{3-})} = 10^{1.03 \pm 0.06}
\]

Substituting the values for the apparent acidity constant, \( k'_4 \), the acidity constant, \( k^a_4 \), the metal concentration, \( (Li^+) \) and the above metal-hydrogen formation constants into equation (53) yields the values of the metal formation constant given in the last column of Table VII for the following reaction:

\[
Li^+ + P_2O_7^{4-} \rightleftharpoons LiP_2O_7^{3-}
\]

\[
KLiPy = \frac{(LiP_2O_7^{3-})}{(Li^+)(P_2O_7^{4-})} = 10^{2.39 \pm 0.06}
\]
Table VII

Data and results for the titration of pyrophosphate ion with hydrogen ion in the presence of various alkali metal ions

The heading "a" is the number of moles of hydrogen ion added per mole of pyrophosphate ion, \( C_{py} \times 10^3 \) is the total pyrophosphate concentration and \( C_{M} \times 10^3 \) is the total concentration of metal ion. The ionic strength was adjusted to unity with \((CH_3)_4NCl, 25^\circ\).

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>( C_{py} \times 10^3 )</th>
<th>( C_{M} \times 10^3 )</th>
<th>( \log K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \log K_{Kpy} )</td>
</tr>
<tr>
<td>0.50</td>
<td>8.71</td>
<td>27.16</td>
<td>109.9</td>
<td></td>
<td>0.78</td>
</tr>
<tr>
<td>0.50</td>
<td>8.87</td>
<td>19.87</td>
<td>20.01</td>
<td></td>
<td>0.82</td>
</tr>
<tr>
<td>0.50</td>
<td>8.72</td>
<td>10.11</td>
<td>100.31</td>
<td></td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
<td>0.80 ± 0.06</td>
</tr>
<tr>
<td>Sodium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \log K_{NaPy} )</td>
</tr>
<tr>
<td>0.50</td>
<td>8.87</td>
<td>2.175</td>
<td>16.20</td>
<td></td>
<td>0.98</td>
</tr>
<tr>
<td>0.50</td>
<td>8.84</td>
<td>2.200</td>
<td>28.80</td>
<td></td>
<td>1.02</td>
</tr>
<tr>
<td>0.50</td>
<td>8.80</td>
<td>2.180</td>
<td>36.38</td>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
<td>1.00 ± 0.06</td>
</tr>
<tr>
<td>Lithium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( \log K_{LiPy} )</td>
</tr>
<tr>
<td>0.50</td>
<td>8.13</td>
<td>3.667</td>
<td>30.21</td>
<td></td>
<td>2.38</td>
</tr>
<tr>
<td>0.50</td>
<td>8.08</td>
<td>3.667</td>
<td>39.80</td>
<td></td>
<td>2.36</td>
</tr>
<tr>
<td>0.50</td>
<td>7.98</td>
<td>3.667</td>
<td>50.41</td>
<td></td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
<td>2.39 ± 0.06</td>
</tr>
<tr>
<td>1.50</td>
<td>6.00</td>
<td>3.667</td>
<td>30.21</td>
<td></td>
<td>1.02</td>
</tr>
<tr>
<td>1.50</td>
<td>5.97</td>
<td>3.667</td>
<td>39.80</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>1.50</td>
<td>5.91</td>
<td>3.667</td>
<td>50.41</td>
<td></td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Average</td>
<td>1.03 ± 0.06</td>
</tr>
</tbody>
</table>
The method previously employed was used to determine the formation constants for the complexes of magnesium with pyrophosphate. In Fig. 10, curves 2 and 3 can be compared to curve 1 to show the effect of 0.01 M and 0.02 M Mg$^{2+}$ on the curve for the titration of pyrophosphate ion. Approximately 0.0028 M ((CH$_3$)$_4$N)$_4$P$_2$O$_7$ was titrated with a solution 0.014 M in HCl and containing the same concentration of pyrophosphate ion as the solution titrated. The pH decrease is comparable to that obtained for triphosphate in the presence of magnesium ion. Since there was a decrease in the buffer region between $a = 1$ and $a = 2$, equation (31) was used to determine the value of the formation constant, $K_{\text{MgHPy}}$, for the acidic complex. Substituting the individual values for the apparent acidity constant, $K_3^{'}$, the acid dissociation constant, $K_3^a$, and the metal ion concentration ($M$) into equation (52) yields the value of the formation constant, $K_{\text{MgHPy}}$, for the following reaction:

$$\text{Mg}^{2+} + \text{HP}_2\text{O}_7^{3-} \rightleftharpoons \text{MgHP}_2\text{O}_7^{-}$$

$$K_{\text{MgHPy}} = \frac{(\text{MgHP}_2\text{O}_7^{-})}{(\text{Mg}^{2+})(\text{HP}_2\text{O}_7^{3-})} = 10^{3.06 \pm 0.06}$$
Fig. 10. - The Effect of Various Concentrations of Magnesium Ion on Curves for The Titration of Pyrophosphate Ion with Hydrochloric Acid

Curve 1 - 0.002820 M ((CH₃)₄N)₄P₂O₇ titrated with a solution 0.01367 N in HCl and 0.00280 M in H₄P₂O₇.

Curve 2 - Similar to curve 1, but 0.01 M in Mg²⁺.

All solutions adjusted to μ = 1 with (CH₃)₄NCl.

All solutions adjusted to μ = 1 with (CH₃)₄NCl.
The data and formation constants obtained are listed in Tables VIII and IX.

In the buffer region below \( p = 1 \), a complex \( \text{Mg}_2\text{P}_2\text{O}_7 \) was detected. When equation (53) was used without including the species \( \text{Mg}_2\text{P}_2\text{O}_7 \), the value for the complexity constant, \( K_{\text{MgPy}} \), increased from \( 10^{5.79} \) to \( 10^{6.08} \) with a twofold increase in the total magnesium ion concentration. These variations which are much greater than the experimental deviation of \( 10^{\pm 0.06} \), can only be accounted for by the presence of a \( \text{Mg}_2\text{P}_2\text{O}_7 \) complex. Including this species in equation (53) and solving pairs of equations simultaneously for both complexity constants yielded constant values. Equation (53) then became

\[
K'_{4} = \frac{[\text{H}^+] [\text{P}_2\text{O}_7^{4-}] + (\text{MgP}_2\text{O}_7^{2-}) + (\text{Mg}_2\text{P}_2\text{O}_7)]}{(\text{HP}_2\text{O}_7^{3-}) + (\text{MgHP}_2\text{O}_7^{2-})}
\]

\[
K_{4} + K_{4}K_{\text{MgPy}}(\text{Mg}^{2+}) + K_{4}K_{\text{MgPy}}K_{\text{Mg}_2\text{Py}}(\text{Mg}^{2+})^2 = 1 + K_{\text{MgHPy}}(\text{Mg}^{2+})
\]

Substituting the individual values for the apparent acidity constant, the corresponding acid dissociation constant, the metal ion concentration and the value for the formation constant, \( K_{\text{MgHPy}} \), into equation (56)
Table VIII
FORMATION CONSTANTS FOR THE MAGNESIUM AND CALCIUM COMPLEXES WITH PYROPHOSPHATE

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Stepwise Formation Constant</th>
<th>Calculated Values of log K</th>
<th>Average Value of log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>K${<em>{\text{Mg}</em>{2}\text{Py}}}$</td>
<td>2.32, 2.36, 2.34 (\beta)</td>
<td>2.34 ± 0.06, 7.75 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>K${_{\text{MgPy}}}$</td>
<td>5.14, 5.38, 5.40</td>
<td>5.41 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>K${_{\text{MgHPy}}}$</td>
<td>3.08, 3.08, 3.02</td>
<td>3.06 ± 0.06</td>
</tr>
<tr>
<td>Calcium</td>
<td>K${_{\text{CaPy}}}$</td>
<td>5.52, 5.52</td>
<td>5.55 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>K${_{\text{CaHPy}}}$</td>
<td>2.27, 2.29</td>
<td>2.28 ± 0.15</td>
</tr>
</tbody>
</table>
Table IX

DATA FOR THE TITRATION OF PYROPHOSPHATE ION WITH HYDROGEN ION IN THE PRESENCE OF MAGNESIUM AND CALCIUM IONS

The heading "a" is the number of moles of hydrogen ion added per mole of pyrophosphate ion, $C_{py} \times 10^3$ is the total pyrophosphate concentration and $C_M \times 10^3$ is the total concentration of metal ion. The ionic strength was adjusted to unity with $(CH_3)_4NCl$, 25°.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>&quot;a&quot;</th>
<th>pH</th>
<th>$C_{py} \times 10^3$</th>
<th>$C_M \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>0.50</td>
<td>6.24</td>
<td>2.950</td>
<td>9.934</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>6.20</td>
<td>2.900</td>
<td>9.934</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>5.93</td>
<td>2.950</td>
<td>19.87</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>5.08</td>
<td>2.950</td>
<td>9.934</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>5.12</td>
<td>2.968</td>
<td>9.934</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>4.76</td>
<td>2.950</td>
<td>19.87</td>
</tr>
<tr>
<td>Calcium</td>
<td>0.50</td>
<td>6.05</td>
<td>5.136(1)</td>
<td>4.170(1)</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>5.91</td>
<td>5.136(1)</td>
<td>5.012(1)</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>5.89</td>
<td>2.568(1)</td>
<td>4.170(1)</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>5.79</td>
<td>2.568(1)</td>
<td>5.012(1)</td>
</tr>
</tbody>
</table>

(1) These values were for the solutions equilibrated with solid CaSO_4.
and solving pairs of equations simultaneously yielded the
values of the formation constants for the following
reactions:

\[ \text{Mg}^{2+} + \text{P}_2\text{O}_7^{4-} \rightleftharpoons \text{MgP}_2\text{O}_7^{2-} \]

\[ \text{Mg}^{2+} + \text{MgP}_2\text{O}_7^{2-} \rightleftharpoons \text{Mg}_2\text{P}_2\text{O}_7 \]

\[ K_{\text{MgPy}} = \frac{\text{MgP}_2\text{O}_7^{2-}}{\text{Mg}^{2+}(\text{P}_2\text{O}_7^{4-})} = 10^{5.41} \pm 0.06 \]

\[ K_{\text{Mg}_2\text{Py}} = \frac{\text{Mg}_2\text{P}_2\text{O}_7}{\text{Mg}^{2+}(\text{MgP}_2\text{O}_7^{2-})} = 10^{2.34} \pm 0.06 \]

One also obtains the complexity constant, \( \beta_{\text{Mg}_{2}\text{Py}} \), for the
reaction

\[ 2\text{Mg}^{2+} + \text{P}_2\text{O}_7^{4-} \rightleftharpoons \text{Mg}_2\text{P}_2\text{O}_7 \]

\[ \text{Mg}_2\text{Py} = \frac{(\text{Mg}_2\text{P}_2\text{O}_7)}{(\text{Mg}^{2+})^2(\text{P}_2\text{O}_7^{4-})} = 10^{7.75} \pm 0.06 \]

Due to the limited solubility as was discussed
in the section dealing with the calcium complexes of
diphosphate, the method of determining the formation
constants was slightly modified for studying the calcium
complexes of pyrophosphate. The method of equilibrating
the solution with freshly precipitated CaSO₄, and measuring
the pH yielded the values of the formation constants
given in Table VIII. Titrations of pyrophosphate ion with
hydrogen ion in the presence of equivalent concentrations of calcium and pyrophosphate ion were performed in order to show that the addition of hydrogen ion remained stepwise and also to determine in what regions a pH decrease occurred. The pH was found to be lowered in all regions below \( a = 2 \).

Equation (52) was used to determine the formation constant for the acidic complex present in the buffer region between \( a = 1 \) and \( a = 2 \). Substituting the known values for the acid dissociation constant, \( K^a \), the apparent constant, \( K'_3 \), and the metal ion concentration (M) into equation (52) yielded the value for the formation constant for the following reaction:

\[
\text{Ca}^{2+} + \text{HP}_2\text{O}_7^{3-} \rightleftharpoons \text{CaHP}_2\text{O}_7^{-}
\]

\[
K_{\text{CaHPy}} = \frac{(\text{CaHP}_2\text{O}_7^{-})}{(\text{Ca}^{2+})(\text{P}_2\text{O}_7^{4-})} = 10^{2.28 \pm 0.15}
\]

As predicted, where an excess of metal ion was not present, a complex of the type \( \text{Ca}_2\text{P}_2\text{O}_7 \) was not detected. Equation (53) was used to obtain the value for the formation constant, \( K_{\text{CaPy}} \). Substituting the values for the apparent acidity constant, the acid dissociation
constant, the metal ion concentration and the value obtained for the metal-hydrogen formation constant, $K_{\text{CaHPy}}$, into equation (52) yielded the value given in Table VIII for the following reaction:

$$\text{Ca}^{2+} + \text{P}_{2}\text{O}_{7}^{4-} \rightarrow \text{CaP}_{2}\text{O}_{7}^{2-}$$

$$K_{\text{CrPy}} = \frac{\text{[CaP}_{2}\text{O}_{7}^{2-}]}{\text{[Ca}^{2+}][\text{P}_{2}\text{O}_{7}^{4-}]} = 10^{6.55 \pm 0.15}$$
THE ACIDITY OF ORTHOPHOSPHORIC ACID AND THE COMPLEXES OF ORTHOPHOSPHATE ION; A COMPARISON OF THE ACIDITY AND COMPLEXING ABILITY OF ORTHO-, PYRO-, AND TRIPHOSPHORIC ACIDS

Introduction

A study of the acidity and alkali metal complexes of orthophosphoric acid logically followed similar studies of pyro- and triphosphoric acids. The acidity and complexing ability of the $H_{n+2}PnO_{3n+1}$ series was compared and a general hypothesis of structure for these acids and complexes was proposed.

One of the earlier investigations on the strength of orthophosphoric acid was that of Abbott and Bray\(^{43}\) who studied the hydrolysis of ammonium salts of orthophosphoric acid by conductivity and by distribution of phosphate salts between chloroform and an aqueous solution of ammonia. They reported $pK_1^a = 1.96$, $pK_2^a = 6.71$ and $pK_3^a = 12.44$ at $18^\circ$. Jowett and Millet\(^{51}\) report $pK_1^a = 2.10$


and \( pK_2^a = 7.13 \) at 25° calculated from data obtained using the hydrogen electrode. Britton and Robinson\(^{52}\) during a study of the glass electrode reported \( pK_1^a = 2.00 \), \( pK_2^a = 6.93 \) and \( pK_3^a = 11.75 \) at 18°. In 1933 and 1934 Nims\(^{53}\)


using cells without liquid junction obtained the values \( pK_1^a = 2.124 \) and \( pK_2^a = 7.206 \) at 25°. Bates and Acree\(^{54}\)


report \( pK_2^a = 7.198 \pm 0.0010 \) and Bates\(^{55}\) reports \( pK_1^a = 2.148 \)


at 25°. Their data were obtained by use of cells of the type \( \text{Pt}(H_2)/\text{phosphate solution}/HCl/AgCl;Ag \) without liquid junction.

Orthophosphate ion has long been known to form complexes with the transition metals and numerous
applications of this fact have been made in analytical chemistry. A calcium complex with orthophosphate ion has been reported without literature reference by Van Wazer\(^56\). However, many difficulties are encountered in studying the calcium-orthophosphate system due to low solubility and slow attainment of equilibrium.

**Experimental**

The phosphoric acid solution was prepared by diluting concentrated (85\%) Baker Analyzed phosphoric acid to the desired volume. This solution was then boiled for about 10 minutes in order to completely hydrolyze any higher phosphates that might be present. The Na\(_3\)PO\(_4\) and K\(_3\)PO\(_4\) used were Mallinckrodt Analytical Reagent Grade salts.

The preparation and standardization of the tetramethylammonium hydroxide solution and the alkali metal chloride solutions were described in an earlier section. Tetramethylammonium orthophosphate was prepared by an ion exchange method similar to that for tetramethylammonium triphosphate.

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Discussion of Results and Conclusion

Curve 1, Fig. 11, was obtained by the titration of 0.001818 M \((\text{CH}_3)_4\text{N})_3\text{PO}_4\) with a solution 0.01451 M in \(\text{HCl}\) and 0.001818 M in \(\text{H}_3\text{PO}_4\). Curve 2 was obtained by the titration of 0.001912 M \(\text{H}_3\text{PO}_4\) with a solution 0.01465 M in \((\text{CH}_3)_4\text{NOH}\) and 0.001912 M in \((\text{CH}_3)_4\text{N})_3\text{PO}_4\). Identical curves were obtained in the presence of 0.100 M \(\text{K}^+, \text{Na}^+\) and \(\text{Li}^+\) ions proving the absence of detectable concentrations of alkali metal complexes with the orthophosphate ion.

A Comparison of The Acidity and Complexing Ability of Ortho-, Pyro- and Triphosphoric Acids

The thermodynamic ionization constants of \(\text{H}_3\text{PO}_4\), \(\text{H}_4\text{P}_2\text{O}_7\) and \(\text{H}_5\text{P}_3\text{O}_{10}\) are given in Table X. Since no complexes of orthophosphate ion with the alkali metals were detected and since the acidity of orthophosphoric acid has been extensively studied, the values for these constants were taken from the literature. A comparison of the first ionization constants of orthophosphoric acid and pyrophosphoric acid indicates that the replacement of an \(-\text{OH}\) group in orthophosphoric acid by the \(-\text{OPO}_3\text{H}_2\) group of pyrophosphoric acid enhances the acidity by considerably more than the increase in
Fig. 11. - Curves for the Titration of Tetramethylammonium Orthophosphate with Hydrochloric Acid and the Titration of Orthophosphoric Acid with Tetramethylammonium Hydroxide

Curve 1 - 0.001818 M \((\text{CH}_3)_4\text{N})_3\text{PO}_4 \) titrated with a solution 0.01451 M in HCl and 0.001818 M in H\(_3\)PO\(_4\).

Curve 2 - 0.001912 M \(\text{H}_3\text{PO}_4\) titrated with a solution 0.01465 M in \((\text{CH}_3)_4\text{N})_4\text{OH}^−\) and 0.001912 M in \((\text{CH}_3)_4\text{N})_3\text{PO}_4\). Identical values were obtained in the presence of 0.10 M K\(^+\), Na\(^+\) and Li\(^+\) ions.

All solutions adjusted to \(\mu = 1\) with \((\text{CH}_3)_4\text{N})\text{Cl}\).
Table X

THERMODYNAMIC IONIZATION CONSTANTS

<table>
<thead>
<tr>
<th>Acid</th>
<th>$H_3PO_4$ (l)</th>
<th>$H_4P_2O_7$</th>
<th>$H_5P_3O_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pK^a_1$</td>
<td>2.15</td>
<td>$\infty$</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$pK^a_2$</td>
<td>7.20</td>
<td>2.64</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$pK^a_3$</td>
<td>12.44</td>
<td>6.76</td>
<td>2.30</td>
</tr>
<tr>
<td>$pK^a_4$</td>
<td>-</td>
<td>9.42</td>
<td>6.50</td>
</tr>
<tr>
<td>$pK^a_5$</td>
<td>-</td>
<td>-</td>
<td>9.24</td>
</tr>
</tbody>
</table>

(1) For $H_3PO_4$ $pK^a_1$ was determined by Bates$^{55}$, $pK^a_2$ by Bates and Acree$^{54}$ and $pK^a_3$ by Abbott and Bray$^{43}$. The constants for $H_4P_2O_7$ and $H_5P_3O_{10}$ were determined in this study.
statistical probability from 1 to 3 for the dissociation of a hydrogen ion. One would expect this inductive effect to be even greater for the central P tetrahedron of triphosphoric acid. This argument indicates that the hydrogen ion held by the central P group of triphosphoric should be the most highly dissociated. The second hydrogen ion can then ionize from either terminal P group to yield identical structures.

Structure I depicts the $\text{H}_3\text{P}_3\text{O}_{10}^{2-}$ ion. Hydrogen bonding is indicated in this structure. The possibility of strong bonding of a hydrogen ion to one or two oxygen atoms of a single phosphorus atom is evident from the small second and third acid dissociation constants of orthophosphoric acid. Studies by Simon and Schultz\(^\text{57}\)


indicate considerable hydrogen bond formation in orthophosphoric acid. The analogous $\text{H}_3\text{P}_2\text{O}_7^{1-}$ ion is shown in structure IV. The similarity between the values of $pK_2^a$, $pK_3^a$ and $pK_4^a$ of pyrophosphoric acid and $pK_2^a$, $pK_3^a$ and $pK_5^a$ of triphosphoric acid indicate a possibility that the hydrogen ions may dissociate from similar structures.
Structures I through VI depict the similarity involved. In the following structures the resonating double bonds and the ionic charges are omitted.

I

II

III

IV

V

VI
Table XI compares the values of the formation constants obtained for the alkali metal complexes of pyro- and triphosphoric acids.

Regarding the structure of the complexes $\text{MP}_2\text{O}_7^{-}$ and $\text{MP}_3\text{O}_{10}^{3-}$, the most pertinent information is the fact that no alkali metal complexes were obtained with orthophosphate ion even though the latter has a greater affinity than pyrophosphate or triphosphate ion for the first associated hydrogen ion. Bjerrum has pointed out a general relationship between hydrogen ion affinity and complex forming tendency. This, then, eliminates the possibility that the metal ion is associated with one or two oxygen atoms of a single phosphorus tetrahedron in the pyrophosphate and triphosphate complexes. For the $\text{MP}_2\text{O}_7^{3-}$ complex it is probable that the metal ion is a member of a six membered ring, structure VII, which can be formed without strain. If this structure persists for the acidic complex $\text{MHP}_2\text{O}_7^{2-}$ which forms with lithium ion, it seems probable that the hydrogen ion is bonded to one oxygen atom, structure VIII, possibly with some hydrogen bonding to the other available oxygen atom bonded with the same phosphorus atom, since two six membered rings involving both phosphorus atoms cannot be formed without some strain. The possibility of strong bonding of a hydrogen ion to one
Table XI

A COMPARISON OF THE STABILITIES OF THE PYROPHOSPHATE AND TRIPHOSPHATE COMPLEXES WITH VARIOUS ALKALI METAL IONS

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Ligand</th>
<th>log K(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K⁺</td>
<td>P₂O₇⁴⁻</td>
<td>log KKPₚ 0.80 ± 0.06</td>
</tr>
<tr>
<td>K⁺</td>
<td>P₃O₁₀⁵⁻</td>
<td>log KKₚ 1.37 ± 0.06</td>
</tr>
<tr>
<td>K⁺</td>
<td>HP₂O₇³⁻</td>
<td>not detected</td>
</tr>
<tr>
<td>K⁺</td>
<td>HP₃O₁₀⁴⁻</td>
<td>not detected</td>
</tr>
<tr>
<td>Na⁺</td>
<td>P₂O₇⁴⁻</td>
<td>log KNaₚ 1.00 ± 0.06</td>
</tr>
<tr>
<td>Na⁺</td>
<td>P₃O₁₀⁵⁻</td>
<td>log KNaₚ 1.64 ± 0.06</td>
</tr>
<tr>
<td>Na⁺</td>
<td>HP₂O₇³⁻</td>
<td>not detected</td>
</tr>
<tr>
<td>Na⁺</td>
<td>HP₃O₁₀⁴⁻</td>
<td>log KNAHTₚ 0.77 ± 0.06</td>
</tr>
<tr>
<td>Li⁺</td>
<td>P₂O₇⁴⁻</td>
<td>log KLiₚ 2.39 ± 0.06</td>
</tr>
<tr>
<td>Li⁺</td>
<td>P₃O₁₀⁵⁻</td>
<td>log KLiₚ 2.87 ± 0.06</td>
</tr>
<tr>
<td>Li⁺</td>
<td>HP₂O₇³⁻</td>
<td>log KLiₚHₚ 1.03 ± 0.06</td>
</tr>
<tr>
<td>Li⁺</td>
<td>HP₃O₁₀⁴⁻</td>
<td>log KLiₚHₚ 1.88 ± 0.06</td>
</tr>
</tbody>
</table>

(1) Complex formation constants were obtained at an ionic strength adjusted to unity with (CH₃)₄NCl, 25°C.
or two oxygen atoms of a single phosphorus atom has been
previously discussed. In the following structures the
resonating double bonds and the ionic charges are omitted.

\[
\begin{align*}
\text{VII} & \quad \text{VIII} \\
0 \quad 0 \\
\text{O-P-O-P-O} \\
0 \quad 0 \\
\text{M} \\
0 \quad 0 \\
\text{O-P-O-P-O} \\
0 \quad 0 \\
\text{M} \\
\end{align*}
\]

\[
\begin{align*}
\text{IX} & \quad \text{X} \\
0 \quad 0 \\
\text{O-P-O-P-O-P-O} \\
0 \quad 0 \\
\text{M} \\
0 \quad 0 \\
\text{O-P-O-P-O-P-O} \\
0 \quad 0 \\
\text{M} \\
\end{align*}
\]

\[
\begin{align*}
\text{XI} & \quad \text{XII} \\
0 \quad 0 \\
\text{O-P-O-P-O-P-O} \\
0 \quad 0 \\
\text{M} \\
0 \quad 0 \\
\text{O-P-O-P-O-P-O} \\
0 \quad 0 \\
\text{M} \\
\end{align*}
\]

A comparison of the stabilities of the pyrophosphate and triphosphate complexes with alkali metals, shown in Table XI, is interesting. In general, the constants of the triphosphate complexes are \(10^{0.56 \pm 0.1}\) larger than those of pyrophosphate. As suggested by Martell and
Schwarzenbach for the calcium triphosphate complex, this may be due to a tridentate structure involving two six membered rings containing oxygens bound to all three phosphorus atoms, structures IX and X. Hershfelder-Taylor models indicate that the bonding of the metal ion to the two terminal phosphate tetrahedra and to the center tetrahedron as well can occur without strain. However, the following factors may also be responsible: The statistical probability of complex formation with triphosphate ion and one metal ion is greater by a factor of 2 if the metal ion enters at a chelating position or by a factor of $8/6$ if the metal enters the complex at a single oxygen position. Thus, the statistical factor may account for $10^{0.3}$ or about half of the difference. Furthermore, the triphosphate ion has a total negative charge of five while pyrophosphate has a total negative charge of four which may be partially localized in the vicinity of the metal ion. Consequently, there is a possibility that the structure of the triphosphate complexes with alkali metal ions, structures IX and X, may be similar to those of the pyrophosphate complexes, structures VII and VIII. However, the bonding with the alkali metal ions is probably essentially electrostatic rather than covalent in nature so that the exact position of the metal ion as a part of
a chelate ring may be more a function of field strength than of bond direction. On this basis it is probable that neither structure IX or XI uniquely describes the actual situation.

The formation constants of the acidic complexes with either $\text{HP}_2\text{O}_7^{4-}$ or $\text{HP}_2\text{O}_7^{3-}$ are about $10^{1.2 \pm 0.2}$ smaller than those with hydrogen ion absent. This is consistent with the fact that no detectable concentrations of the acid complexes of potassium with either $\text{HP}_2\text{O}_7^{4-}$ or $\text{HP}_2\text{O}_7^{3-}$ and sodium with $\text{HP}_2\text{O}_7^{3-}$ were found since their constants would probably be of the order of unity or smaller.

The stabilities of the pyrophosphate and triphosphate complexes with magnesium and calcium ions were compared in Tables III and VIII.
I, Sheldon Marvin Lambert, was born in Cleveland, Ohio, on September 27, 1930. I received my secondary education in the public schools of Cleveland, Ohio, and Lyndhurst, Ohio, graduating from Charles F. Brush High School, Lyndhurst, Ohio, in June, 1948. I received my B. S. in Chemistry from The Ohio State University in June, 1953, and entered the graduate school of this university in October, 1953. From October, 1953 until October, 1955, I served alternately as a teaching assistant and a research assistant in the Department of Chemistry. From October, 1956, until the time of my graduation in June, 1957, I was a Kettering Foundation Fellow.