STUDIES OF SOME HEAVY METAL PHOSPHATE COMPLEX COMPOUNDS

By

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SUMMARY
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The complex species present in solutions of tervalent aluminium, iron and titanium in aqueous orthophosphoric acid have been studied by ion exchange and other techniques.

In one series of batch experiments the sign and size of the charge on the complex ions was established in all cases, and it was shown that the complexes were always singly or doubly charged anionic species with a ligand : metal ratio of 3:1. Ion exchange procedures were used to show the presence of anionic complexes and the absence of cationic complexes. Solvent extraction procedures were used to show the probable absence of neutral complexes. Whenever applicable, visible and ultra violet spectra were obtained as additional evidence.

Further ion exchange experiments were carried out in the case of iron and titanium orthophosphates using trace quantities of metal and very carefully controlled conditions of pH and ionic strength and, from the results, values have been calculated for the stability constants of the complex ions present in the solutions. The calculations and
the justification for the simplifications and assumptions involved are discussed in detail.

Analytical procedures for the metals at very low concentrations and for the metals and orthophosphate in the presence of each other are described.
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"ONE MAY NOT DOUBT THAT, SOMEHOW, GOOD
SHALL COME OF WATER AND OF MUD;
AND, SURE, THE REVERENT EYE MUST SEE
A PURPOSE IN LIQUIDITY."

Rupert Brooke
CONTENTS

Abstract ... ... ... ... ... ... ... ... ... ... ... ... ... 3
Contents ... ... ... ... ... ... ... ... ... ... ... ... ... 7

PART I

Introduction

I.1. Historical Survey ... ... ... ... ... ... ... ... ... 10
I.2. Purpose of the work ... ... ... ... ... ... ... ... ... 15

PART II

Techniques

II.1. Ion Exchange Techniques ... ... ... ... ... ... ... 17
II.2. Analytical Techniques ... ... ... ... ... ... ... ... ... 43
II.3. Spectrophotometric Methods ... ... ... ... ... ... ... 50

PART III

Preparations

III.1.1. Preparation of Aluminium(III) Salts ... ... ... ... ... ... 54
III.1.2. Preparation of Iron(III) Salts ... ... ... ... ... ... ... ... 57
III.1.3. Preparation of Titanium(III) Salts ... ... ... ... ... ... ... 58

contd....
PART IV

Experimental

IV.1. Ion exchange to determine the sign and size of complex species ... ... 68

IV.2. Ion exchange to determine the stability constants of the complex species ... 93

IV.3. Spectrophotometric Experiments ... 112

IV.4. Discussion ... ... ... ... ... 125

PART V

References ... ... ... ... ... ... 143
PART I

INTRODUCTION

I.1. Historical Survey

I.2. Reasons For Undertaking The Present Work
I.1. HISTORICAL SURVEY

The complexing of transition metals with orthophosphoric acid has long been recognised. Dupré (1), showed that ferric thiocyanate solutions were decolorised by addition of orthophosphoric acid, and by 1882, the decolorising action of orthophosphoric acid on ferric ion was used extensively in analytical chemistry. Weinland (3) and Ensgraber (4) considered that the complexes were ferriphosphoric acids such as $\text{H}_3[\text{Fe(PO}_4\text{)}_2]$ and $\text{H}_6(\text{Fe(PO}_4\text{)}_3]$. They reported salts of these acids such as $\text{Na}_3[\text{Fe(PO}_4\text{)}_2]$. Carter and Clews (5) found that sulphur dioxide, while reducing ferric chloride to ferrous chloride, would not reduce the ferric phosphate complex to a ferrous form. In fact, the ferrous phosphate complex was oxidised by sulphur dioxide, whereas ferrous chloride was not. Bonner and Romeyn (6) thought the complex, or complexes, could not be stoichiometrically formulated.

In the presence of chloride ion, Dede (7), Ricca and Meduri (8) deduced that the acid $\text{H}_3[\text{Fe(PO}_4\text{)}\text{Cl}_3]$ was formed. Ricca and Meduri reported the formation of salts of this acid such as $\text{Ag}_3[\text{Fe(PO}_4\text{)}\text{Cl}_3]$. Jensen (9) interpreted his own work on solubility to mean that only ferric-phosphate complexes
were formed in solution, even in the presence of chloride ion. He explained the work of Dede, Ricca and Maduri as evidence for the existence of the \([\text{FeH}_2\text{PO}_4]^{2+}\) ion. The decrease in colour of solutions of ferric nitrate and sodium thiocyanate, on addition of differing amounts of orthophosphoric acid, was studied by Lanford and Kiehl\(^{(10)}\). They assumed only one thiocyanate complex, \(\text{FeCNS}^{2+}\), was formed. The maximum decolorisation of ferric thiocyanate occurred at a \(\text{PO}_4^{3-}:\text{Fe}\) ratio of 1:1, from which it was concluded that the complex formed was \([\text{FeHPO}_4]^{+}\). Bannerjee\(^{(11)}\) questioned the results of Lanford and Kiehl on the grounds that the constitution of the ferric thiocyanate complex varies with the concentration of thiocyanate present. He carried out thermometric, colorimetric and conductimetric titrations, on mixtures of ferric chloride and orthophosphoric acid. From breaks in the titration curves, he determined the complexes to be \([\text{FeHPO}_4]^{+}\) and \([\text{Fe(HP0}_4]_2^{-}\).

Thoms and Gantz\(^{(12)}\), compared the effects on the optical transmission curve of adding various ligands to solutions of ferric chloride. By this means the stability of each complex was compared with that of other ferric
complexes. The order of stabilities was cyanide $\text{CN}^-$ $\succ$ citrate $\succ$ oxalate $\succ$ tartrate $\succ$ acetate $\succ$ orthophosphate $\succ$ fluoride $\succ$ thiocyanate $\succ$ tetraborate $\succ$ sulphate $\succ$ chloride $\succ$ bromide $\succ$ nitrate. Salmon and Jameson$^{(13)}$ showed the existence of the $[\text{Fe(PO}_4^2\text{)}_3]^{6-}$ and $[\text{Fe(HPO}_4^2\text{)}_3]^{3-}$ ions in solutions containing iron and phosphate only, by ion-exchange experiments. In equimolar mixtures of ferric chloride and orthophosphoric acid, the $[\text{FeHPO}_4^+\text{]}$ ion was found. When ferric nitrate was substituted for ferric chloride similar results were observed, i.e. suggesting that $[\text{FeHPO}_4^+\text{]}$ is absorbed. Only in solutions containing a large excess of chloride ions was any trace of ferric chloro-phosphate ions found. Belluco, Busulini and Barbieri$^{(14)}$ used radiochemical, paper chromatographic and spectrophotometric studies to establish a structure for ferric phosphate complexes in hydrochloric acid of $\text{H}_2\text{Na}[\text{Fe(PO}_4^2\text{)}_3]$. Recently Galal-Gorchev and Stumm$^{(15)}$ investigated the ferric-orthophosphate system spectrophotometrically and potentiometrically. In dilute acid systems they established the existence of $[\text{Fe(H}_2\text{PO}_4^2\text{)}]^{2+}$ and $[\text{Fe(HPO}_4^2\text{)}]^+\text{ ions.}$ The stability of these complexes was determined at $25^\circ\text{C.}$
Aluminium reacts similarly. It is strongly complexed by orthophosphoric acid. Dede\(^7\) measured the specific conductivity of aluminium chloride with orthophosphoric acid. He found it was higher than the sum of the individual conductivities and concluded that complexing must have occurred.

Bjerrum and Dahn\(^16\) made conductivity and pH measurements on solutions of aluminium chloride and sodium dihydrogen orthophosphate. They found evidence for complexes such as 
\[
[\text{Al}(\text{H}_2\text{PO}_4)^+]^{2+}, [\text{Al}(\text{HPO}_4)^+]^+, [\text{Al}(\text{H}_2\text{PO}_4)_2]^+, [\text{Al}(\text{HPO}_4)_2]^{-},
\]
\[
[\text{Al}(\text{HPO}_4)_2]^{3-}, \text{ and } [\text{Al}(\text{H}_2\text{PO}_4)_3].
\]
Jensen\(^9\) found the solubility of aluminium phosphate in solutions containing phosphate and chloride ions to be independent of the chloride-ion concentration, but dependent on the phosphate concentration. He inferred from this behaviour that only pure aluminium phosphate complexes existed in solution. Jameson and Salmon\(^17\) carried out anion exchange experiments on solutions containing aluminium and phosphate ions only. They concluded that the main complex ion in solution was \([\text{Al}(\text{HPO}_4)_3]^{3-}\). This would be expected by analogy with the ferric-phosphate system. Their
work compared well with that of Bjerrum and Dahm, but since Bjerrum and Dahm carried out their work on solutions containing chloride and phosphate ions, it was felt little purpose would be served by carrying out further comparisons.

Oxygen sensitive titanium(III) complexes strongly with orthophosphoric acid. Genge and Salmon studied the removal of titanium(III) from cation-exchange resins by orthophosphoric acid and other acids. They concluded that titanium(III) formed anionic complexes with orthophosphoric acid in solution. Weissler mentioned that the absorption spectrum of the peroxy-titanyl group is altered by addition of orthophosphoric acid. This would suggest that some complexing occurs.

Wall carried out anion and cation-exchange experiments on solutions of indium and phosphate ions only. His results indicated the \([\text{lnH}_2(\text{PO}_4)_3]^{4-}\) ion and a polynuclear complex \([\text{ln}_3(\text{PO}_4)_2\text{OH}]^{2+}\). Brownlow, Salmon and Wall by ion exchange experiments and pH titrations, inferred the extent of complex formation between various anions and indium was in the order: \(\text{HF} > \text{H}_3\text{PO}_4 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4\).

Brownlow reported the existence of both cationic and anionic complexes of gallium and orthophosphate ion.
I. 2. **REASONS FOR UNDERTAKING THE PRESENT WORK**

Although much effort has been directed towards the elucidation of the composition of the complex species present in aqueous solutions of iron(III) orthophosphate and aluminium(III) orthophosphate, considerable confusion exists about the complexes present especially those of iron(III). Little work has been carried out on the composition of the complexes present in aqueous solution of titanium(III) orthophosphate. It was decided to attempt to ascertain the nature and composition of the species present in aqueous solutions of titanium(III) orthophosphate, iron(III) orthophosphate and aluminium(III) orthophosphate. The stability constants of the complexes would be determined by a simplified version of the cation exchange method of Fronaeus. The stabilities of the metal complexes would be compared with each other to determine any trend in stability of the complex formed with ionic size and electronegativity of the central metal ion. The stabilities of the iron(III) orthophosphate complexes would be compared to the work of Carpenter\(^{23}\) on the stability of similar iron(III) hypophosphite complexes to observe any change in stability with
the orthophosphate ion acting as a ligand. Orthophosphate ions, acting as a bidentate ligand will form a four membered ring and hypophosphate ion will form a five membered ring.

Titanium(III) forms a purple-brown aqueous solution as opposed to the purple coloured solution of the titanium(III) hexaquo ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, it was decided to investigate the visible and ultra violet spectra of titanium(III) orthophosphate solution and solutions containing titanium hexaquo ion.
II.1. ION EXCHANGE EQUILIBRIA INVOLVING A COMPLEXING ANION

1. The determination of the sign and size of charge on complex ions.
2. The determination of the stability constants of the complex ions
   (a) iron(III) - orthophosphate system
   (b) titanium(III) - orthophosphate system.

1.1. THE DETERMINATION OF THE SIGN AND SIZE OF CHARGE ON COMPLEX IONS

Previous experiments had established that aluminium(III), iron(III) and titanium(III) ions were complexed by orthophosphoric acid (13,19), so column equilibria experiments merely to show whether or not complexing occurred, were not carried out. Before formulae may be assigned to these complexes, it is necessary to determine the sign and size of the charge on them. Salmon and co-workers (13) have developed ion exchange methods for this purpose, which can be used to study both anionic and cationic complexes.
Cation-exchange equilibria in the presence of a complexing anion

It is assumed that the total exchange capacity of the resin may be accounted for by the sorption of free metal ions and complex ions only. Consider a solution containing a complexing acid $H_xL$ and a cation $M^{m+}$ left in contact with a cation exchanger in the hydrogen form. If at equilibrium any $H_xL$ is found on the resin, then cationic complex species are present in solution.

Consider the equilibria that occur in solution to produce cationic complex species, in general if only monomeric species are formed:

$$H_xL \rightleftharpoons H_{x-z}L + zH^+ \quad \text{................................. (1)}$$

$$a H_{(x-z)}L^{2-} + M^{m+} \rightleftharpoons MH_y L_a^{(m+y-ax)^+} + [a(x-z)-y]H^+ \quad \text{...... (2)}$$

If at equilibrium, the total number of moles of $M^{m+}$, both free and complexed, sorbed per equivalent of exchanger is $N_M$ and the number of moles of $H_xL$ sorbed per equivalent of exchanger is $N_L$, then for the sorption of $MH_y L_a^{(m-y-ax)^+}$ together with $M^{m+}$ for one equivalent of resin:

Moles complex sorbed $= N_L$

Moles free $M^{m+}$ sorbed $= N_M - N_L$

(continued on next page)
Equivalents complex sorbed = \( (N_L^m) (m+y-\alpha x) \)

Equivalents free \( M^{n+} \) sorbed = \( n(N_M^m-N_L) \)

Total equivalents sorbed = \( 1 = (m+y-\alpha x)N_L^m+n(N_M^m-N_L) \)

\[
= \frac{mN_M^m+N_L^m(y-\alpha x)}{........(3)}
\]

\( N_M, N_L, m \) and \( x \) are known or can be determined practically and hence, by assuming all possible values of 'a' depending upon the co-ordination of \( M^{n+} \) and the nature of the ligand \( H_xL \), corresponding values of 'y' may be determined. A non-integral value of 'y' indicates sorption of a mixture of complexions.

Anion exchange equilibria in the presence of a complexing anion

Salmon and co-workers (13) have used anion exchange studies similar to those employed for cationic studies to determine the sign and size of charge of complexes. In this case resin exchange capacity is accounted for in terms of the free ligand and anionic complexes sorbed.

If the equilibria that occurs in solution producing anionic complex species is considered:

\[
H_L^{x+y} \rightleftharpoons H^+ + H_L^{x-3}
\]

\[
a H_{\frac{x+y}{2}}^Z + M^{n+} \rightleftharpoons MH_L^{y-a}(ax-m-y)^- + [a(x-z)-y]^{+} \quad ........(4)
\]
If any $M^{3+}$ is found to be present on the resin at equilibrium, then anionic complexes are present in solution.

Quantitatively, if no other sorbable anions are present in solution and the pH of the solution is below that at which hydroxyl ions would be sorbed, then the capacity of the resin may be accounted for in terms of $\text{MH}_yL^{(ax-m-y)-} + \text{free } H_{x-z}L^z^-$. If, at equilibrium, the number of moles of $M^{3+}$ sorbed as complex per equivalent of exchanger is $N_M$ and the total number of moles of $L$ sorbed per equivalent of exchanger, both free and complexed, is $N_L$, and if under identical experimental conditions but in the absence of $M^{3+}$, $L$ is sorbed as $H_{x-z}L^z^-$, then for one equivalent of exchanger:

- Moles of complex sorbed = $N_M$
- Moles of free $H_{x-z}L^z^-$ sorbed = $N_L - aN_M$

```
\implies \text{Equivalents of complex sorbed} = (ax-y-m)N_M

\implies \text{Equivalents of free } H_{x-z}L^z^- \text{ sorbed} = z(N_L - aN_M)

\implies \text{Total equivalents sorbed} = 1 = z(N_L - aN_M) + aN_M(ax-y-m)

= \frac{1}{N_M} = \frac{[a(x-z) - y - m]N_M + zN_L}{N_M} \quad \text{.... (5)}
```
The value of 'z', the charge on the free ligand sorbed is determined from a blank experiment. By assuming values of 'a' corresponding values of 'y' may be obtained.

Any neutral complex species in solution, will not be sorbed by either the anion or cation exchangers. The neutral species will not thus invalidate equations (4) and (5). These experiments, however, will not indicate the absence or otherwise of such species in solution.

II.1.2. THE DETERMINATION OF STABILITY CONSTANTS OF
THE COMPLEXES FORMED IN (a) THE IRON(III) ORTHO-
PHOSPHATE SYSTEM (b) THE TITANIUM(III) ORTHO-
PHOSPHATE SYSTEM

Measurements of the stability constants of complex systems using synthetic ion exchangers have been carried out by Samuelson (23) and Schubert and co-workers (24). However, their work was concerned principally with the complexes formed between bivalent metals and organic acid ligands; and their methods of calculation involved restrictive assumptions, in particular, that only anionic or neutral species were formed.
Schubert also assumed that only a single complex was formed. Fronaeus\(^{(25)}\) has developed a much more general approach taking into consideration all possible complex species, anionic, neutral cationic, monomeric and polymeric, between a complexing acid and a metal. The following deviation for orthophosphoric acid, a tribasic acid is from the work of Carpenter\(^{(26)}\), which was based on Fronaeus's approach to the problem but with some simplifications which can be applied to the systems studied in this work. No attempts were made to account for species other than anionic, as previous experiments had shown that only anionic species were present in solution: Organic extractions of the aqueous solutions with chloroform and other solvents gave negative results, indicating the absence of any neutral species. No trace of orthophosphate ion could be found on the cation exchanger in the sign and size of charge experiments showing the absence of any cationic complex species. The presence of polymeric species is very unlikely in these experiments as only trace concentrations of metal are used. The structure of anionic complex species is known prior to the experiments to determine
stability constants. The stability constants are determined from cation exchange equilibria measurements with trace concentrations of metal both in the resin and aqueous phases in varying large excesses of complexing acid.

The ligand studied in the present work, orthophosphoric acid is tribasic and of the dissociation of such an acid $H_3L$ is considered, if it may be represented by the following equilibria.

\[
\begin{align*}
H_2^+L & \rightleftharpoons k_1 H_2L^- + H^+ \quad \text{............... 1.} \\
H_2L^- & \rightleftharpoons k_2 HL^2- + H^+ \quad \text{............... 2.} \\
HL^2- & \rightleftharpoons k_3 L^3- + H^+ \quad \text{............... 3.}
\end{align*}
\]

As the acidity of the solution rises the concentration of the lower charged species will increase and as it falls the concentration of the higher charged species will increase. All studies in this work were carried out at or below pH 1.1. Hence since $k_3 = 4.8 \times 10^{-13}$ (27), the $L^3-$ ion was neglected.
(a) **Iron(III) Orthophosphate System**

For the equilibria 1, 2.

\[
\begin{align*}
    k_1 &= \frac{[H_2L^-][H^+]f_{H^+}f_{H_2L^-}}{[H_3L]} \\
    k_2 &= \frac{[H^+][HL^2-]f_{H^+}f_{H_2L^-}}{[H_2L^-] f_{H_2L^-}}
\end{align*}
\]

\[ \text{.................(5)} \]

\[ \text{.................(6)} \]

If it is assumed that:

\[ f_{H_2L^-} = f_{H^+} = f_1 \]

and \[ f_{HL^2-} = f_2 \]

where \( f_i \) is the activity correction for the ionic species \( i \)

as expressed approximately by the Davies Equation (28),

and \([A]\) is the concentration of any species \( A \).

\[ \text{From 4 and 5} \]

\[
\begin{align*}
    [H_3L] &= \frac{[H_2L^-][H^+]f_{H^+}^2}{k_1} \\
    [HL^2^-] &= \frac{[H_2L^-]k_2}{[H^+]f_2}
\end{align*}
\]

\[ \text{.................(7)} \]

\[ \text{.................(8)} \]
If the total concentration of the complexing acid is \( C \)

\[
C = [H_3L] + [H_2L^–] + [HL^{2–}] \quad \text{.................. (9)}
\]

Substituting from 6, 7.

\[
C = \frac{[H_2L^–][H^+]}{k_1} + \frac{[H_2L^–]}{[H^+]f_2} + k_2\frac{[H_2L^–]}{[H^+]f_2}
\]

\[
= [H_2L^–]\left[ \frac{[H^+]f_2}{k_1} + 1 + \frac{k_2}{[H^+]f_2} \right] \quad \text{.................. (10)}
\]

The expression \( \frac{[H^+]f_1^2}{k_1} + 1 + \frac{k_2}{[H^+]f_2} \) is constant for solutions of constant pH and ionic strength.

\[ \therefore \text{Let} \quad \frac{[H^+]f_1^2}{k_1} + 1 + \frac{k_2}{[H^+]f_2} = \alpha \text{ and} \]

\[ \therefore \quad [H_2L^–] = \frac{C}{\alpha} \quad \text{.................. (11)} \]

\[ \therefore \text{Substituting 10. into 6. and 7.} \]
\[ [H_3L] = \frac{[H^+]f_1^2}{k_1} \cdot \left( \frac{C}{\alpha} \right) \] ..........................(12)

\[ [HL^{2-}] = \frac{k_2}{[H^+]f_2} \cdot \frac{C}{\alpha} \] ..........................(13)

Hence in this aqueous solution of \( H_3L \), theoretically there are three species \( H_3L \), \( H_2L^- \), \( HL^{2-} \) all of which could complex with \( M^{n+} \), either separately or together. The equilibrium may be represented by the equation:

\[
(2r+q-am)^{+} aM^{n+} + p(H_3L)+q(H_2L^-)+r(HL^{2-}) \rightleftharpoons M_a(H_3L)_p(H_2L^-)_q(HL^{2-}) \] ..........................(14)

For an anionic complex, \( 2r+q - am \), \( p=0, 1, 2 \ldots \), \( q=0, 1, 2 \ldots \), \( r=0, 1, 2, 3 \ldots \).

If the Law of Mass Action is applied to equation 13 then,

\[
\sum \beta = \frac{K_a[H_3L]_p[H_2L^-]_q(HL^{2-})_r}{[M]^a[H_3L]^p[H_2L^-]^q[HL^{2-}]^r} \] ..........................(14a)

where \( \beta \) is the stability constant.

It has been shown\(^{(29)}\) that the amount of cation, at tracer concentration, bound to a definite amount of exchanger at equilibrium, is proportional to the concentration of the
free metal ion in solution over a wide concentration range.

\[
\frac{[M^{m+}]}{[M^{m+}_R]} = \Delta_0 = \frac{C^o_M}{(C_M-C^o_{Md})\frac{v}{w}} \\
\text{ where } [M^{m+}] = \text{concentration of metal ions in solution.}
\]

\[
[M^{m+}_R] = \text{concentration of metal ions bound to exchanger.}
\]

\[
\Delta_0 = \text{distribution coefficient, a constant.}
\]

\[
C^o_M = \text{the concentration of } M^{m+} \text{ in solution in equilibrium with the exchanger.}
\]

\[
C_M = \text{the concentration of } M^{m+} \text{ in solution before the exchanger added.}
\]

\[
d = \text{fractional decrease in the initial volume of solution (d always } \leq 1).\n\]

\[
v = \text{the initial volume of solution.}
\]

\[
w = \text{the weight of ion exchanger.}
\]

If the complexing acid \( H_3L \) is introduced to the above system and complexing occurs, forming anionic species, the
amount of free $M^{m^+}$ in solution will be reduced in proportion to the stability constants of the complexes formed. Since $\Delta \alpha$ is a constant, less $M^{m^+}$ will be sorbed on the resin and a new equilibrium distribution will be set up:

$$\frac{[M^{m^+}]_1}{[M^{m^+}]_R} = \Delta = \frac{\text{Concentration of total } M^{m^+} \text{ in solution}}{\text{Concentration of } M^{m^+} \text{ on resin}} \quad \ldots (16)$$

By measuring the effect of ligand concentration on $\Delta$ it is possible to calculate stability constants for the species in solution. To accomplish this, it is necessary to compare a series of solutions of constant pH, temperature, volume of solution, weight of exchanger and ionic strength, but different concentration of complexing anion. Constant ionic strength is achieved by the addition of corresponding amounts of a strong electrolyte whose anion does not complex with $M^{m^+}$, generally sodium perchlorate. The ligand must not be sorbed by the exchanger and to maintain ionic strength the resin must be previously saturated with the cation of the strong electrolyte.

In order to ensure that only trace concentrations of metal $M^{m^+}$ were sorbed by the resin, only trace concentrations
of metal are introduced into solution. Conveniently this simplifies calculations as the concentration of the metal $M^{m+}$ is negligible compared to that of the complexing anion and the concentration of the complexing anion = $C$ where $C$ is the initial concentration of complexing anion and $d$ $\neq$ 1.

Metal concentrations are generally determined radiochemically using a convenient isotope of $M^{m+}$. However, in the present work none of the metals studied had suitable isotopes and the metal ion concentrations were determined spectrophotometrically, since sufficiently sensitive colorimetric methods were available.

With ligand present 16, may be expressed:

$$\Delta = \frac{[M^{m+}] + \sum [M_a (H_2 L) P (H_2 L^-) q (HL_2^-) r]}{[M^{m+}]}$$

$$\text{Now } [M^{m+}] = \frac{[M^{m+}]}{\Delta o}$$

$$\Delta = \Delta o(1 + \sum a \cdot \beta (H_2 L)^P [H_2 L^-]^q [HL_2^-]^P)$$
Substituting in 19, from 11, 12.

\[ 
A = A_0 (1 + \sum \beta [M^{m+}]^{a-1} \left[ \frac{[H^+]}{k_1} \right]^p \left[ \frac{k_2 X}{[H^+]^2} \right]^q ) \cdots (20) 
\]

Thus by varying the ligand concentration 'C', corresponding values of \( \Delta \) are obtained by measuring the concentration of \( M^{m+} \) initially and at equilibrium. The calculation of \( \Delta \) requires knowledge of \( d \). This was determined by equilibrating the resin (0.5g) with \( \frac{N}{10} \) hydrochloric acid (25.0ml) and measuring the initial and final pH of the solution. 'd' is independent of C at constant ionic strength and it may also be assumed to be independent of \( [M^{m+}] \) at low \( [M^{m+}]_R \). However at a small value of \( \frac{W}{V} \) only an approximate value of \( d \) is required and so it is assumed that \( d \approx 1 - \frac{W}{V} \).

In practice it was found that the relationship between \( \Delta \) and C (Equation 20) was of the form:

\[ 
\Delta = \Delta_0 (1 + AC^3) = F(C) \quad \cdots \cdots \cdots (21) 
\]

where \( \Lambda = a \beta_1 \). 'a' is a constant which can be calculated from a knowledge of \( f_1, f_2, k_1, k_2 \) and \([H^+]\) (section IV.2.1.).
Equation 21 was solved for $\beta_1$ using the method of least squares \((30)\) as follows:

For $i$ values of $C$, $i$ corresponding values of $\Delta$ are obtained and the sum of the squares of error $S$ is equal to

$$\Sigma [\Delta_i - F(C_i)]^2 \quad \text{..................(22)}$$

Differentiating 22.

$$\frac{dB}{dA} = -2 \Sigma [\Delta_i - F(C_i)] \frac{dF(C_i)}{dA} \quad \text{..................(23)}$$

Differentiating 21.

$$\frac{dF(C_i)}{dA} = \Delta_0 C_i^3 \quad \text{..................(24)}$$

\[.\] Combining 21, 23, and 24,

$$\frac{dB}{dA} = 2 \Sigma [\Delta_i - \Delta_0 - \Delta_0 A C_i^3] \Delta_0 C_i^3 \quad \text{..................(25)}$$

For $S$ to be a minimum:

$$\frac{dB}{dA} = 0$$

\[.\] $\Sigma [\Delta_i - \Delta_0 - \Delta_0 A C_i^3] \Delta_0 C_i^3 = 0$

\[.\] $\Sigma [\Delta_i - \Delta_0] \Delta_0 C_i^3 = \Delta^2 A C_i^6$

\[.\] $A = \frac{\Sigma (\Delta_i - \Delta_0) C_i^3}{\Delta_0 \Sigma C_i^6}$

Hence 21. can be solved for $A$ and hence $\beta_1$, the stability constant involved, may be determined.
(b) **Titanium(III) Orthophosphate System**

When experiments are carried out to determine the stability constant of a complex ion in solution, they are normally carried out using solutions of constant ionic strength so as to control the activity coefficients of the electrolytes. This is done either by using a large excess of background electrolyte and determining the stoichiometric stability constant of the complex under the conditions used, or by determining the thermodynamic stability constants using a solution of low but constant ionic strength as in the case of iron(III) (Section II. 1. 2(a)).

To carry out work at constant activity correction, i.e. constant ionic strength a non-complexing anion, normally perchlorate, is needed.

However, in this case a suitable non-complexing anion could not be found. Perchloric acid oxidised titanium(III) to titanium(IV). It was found that freshly prepared solutions of titanium(III) perchlorate oxidised in two or three hours even when perchlorate concentration was low, i.e. 0.1M and oxygen was excluded (Section III. 1.3). The fluoroborate ion behaves similarly to perchlorate and
has been used as a non-complexing anion especially in the study of solid complexes with organic ligands. However, Wamser (31) showed that at room temperature a 0.1M aqueous solution of fluoboric acid is 13% hydrolysed to a mixture of hydrofluoric acid and hydroxyborofluoric acid. It has been reported that titanium(III) complexes with the fluoride ion (32). The use of chloride ion as a means of maintaining ionic strength was not considered possible as titanium chloride complexes have been reported (33), also the possibility of mixed or different orthophosphate complexes similar to those of iron(III) (13) could not be ruled out.

Thus if the stability of titanium(III) orthophosphate complex was to be determined, it would have to be done in solutions of titanium(III) and orthophosphate only, necessitating a high concentration of orthophosphoric acid to give the required pH of 0.805. It was thus necessary to make various assumptions in order to calculate the activities of orthophosphate ion in 1M aqueous solutions of orthophosphoric acid. Orthophosphoric acid is largely undissociated at these concentrations and the ionic strength,
due largely to the $H_2PO_4^-$ ion, is about 0.15M. However, it must be realised that the constants obtained are only approximate, because of the various assumptions made in their calculations. Marcus (34) used a similar technique to determine the activities of orthophosphate ions in aqueous solution in order to measure the approximate stability constant of uranium(VI) orthophosphate complexes. He assumed that:

(a) the measured $pH = -\log a_{H^+}$ where $a_{H^+}$ is the activity of the hydrogen ion, since liquid junction potentials are eliminated to a great extent by the saturated potassium chloride bridges used.

(b) activity coefficients of monovalent ions are equal.

\[ i.e. \ fH^+ = fH_2PO_4^- = f1 = fNa^+ \ldots \ldots \ldots \ldots (26) \]

\[ k_1 = \frac{(a_{H^+} + a_{Na^+}) (a_{H_2PO_4^-})}{a_{H_3PO_4}} \]

Since it is assumed that $fH^+ = fH_2PO_4^- = fNa^+$ and at this $pH = 0.805$, concentration of positive ions = concentration of $H_2PO_4^-$ ions. \[ k_1 = 7.85 \times 10^{-3} \] \[ k_2 = 7.99 \times 10^{-8} \]
\[ k_1 = \frac{(a_{H_2PO_4}^-)^2}{a_{H_3PO_4}} \]
\[ k_2 = \frac{(a_{H_2PO_4}^-)}{k_1} \]
\[ a_{H_3PO_4} = \frac{(a_{H_2PO_4}^-)^2}{k_1} \]

Where \( f_0 \) is the activity correction of the uncharged species

\[ \log f_0 = 0.68[H_2PO_4^-] \]

0.68 is the salting out constant for orthophosphoric acid.

\( f_1 \) was determined by use of the relationship: (due to Lugg)

\[ -2 \log f_1 = \frac{[H_2PO_4^-]}{1+\sqrt{[H_2PO_4^-]}} \]

The values of \([H_3PO_4^-] \) and \([H_2PO_4^-] \) are not initially known, but are determined by successive approximination, assuming \( f_1 = 1 \)

\[ k_2 = \frac{(a_{H_2PO_4}^-)}{k_1} \]

\[ a_{H_3PO_4} = \frac{(a_{H_2PO_4}^-)^2}{k_1} \]
Consider equations 15 and 16, (Section II.1.2(a)).

\[
\Delta_o = \frac{C_0^M}{(C^M_0 - C^M_d)Y \frac{w}{m}} \quad (15)
\]

\[
\Delta = \frac{\text{Total amount of metal in solution}}{\text{Total amount of metal sorbed on resin}} \quad (16)
\]

Equation 15 represents a system consisting of uncomplexed titanium(III) ions in equilibrium with a cation-exchanger. Considering the addition of orthophosphoric acid to this system, complexing occurs forming anionic species and thus the amount of free titanium(III) in solution will be reduced in proportion to the stability constants of the complexes formed. This equilibrium is represented by equation 16.

Thus by measuring the effect of ligand activity on \( \Delta \) it is possible to calculate stability constants for the species in solution. To accomplish this a series of solutions of constant \( \text{pH}, \) temperature, volume of solution and weight are compared.

The activity of an ion is approximately directly proportional to its concentration, in solutions up to
Consider the reaction:

\[
\text{Ti}^3^+ + \text{H}_3\text{PO}_4^- \xrightarrow{\beta} \text{complex(es) of Ti}^{3+} + \text{H}_3\text{PO}_4^-
\]

Where \( \beta \) is an approximate stability constant for the complex formed.

Thus, for a fixed amount of titanium(III), as the concentration ratio \( \text{H}_3\text{PO}_4^- : \text{Ti(III)} \) the amount of free titanium(III) in solution decreases and the amount of free titanium(III) on the resin decreases. The stability constants are determined by plotting \( \Delta \) against the activity of the complexing anions. If the \( \text{Ti} : \text{H}_3\text{PO}_4^- \) ratio is too small then curve fitting would have to be carried out using section AB to define the total curve.
This is very difficult and inaccurate. The concentration of orthophosphoric acid in solution was fixed by the need to have solutions of a constant pH. Thus, in order, to decrease the $H_3PO_4 : Ti(III)$ concentration ratio, it was necessary to use higher than trace concentrations of titanium(III) in solution. But even so, in order to increase the amount of titanium(III) on the resin, the amount of Zoo Karb 225 used was increased from the normal 0.5g to 2.0g. As in the case of iron, the metal concentration in solution was determined spectrophotometrically as titanium has no suitable radioactive isotope and the usual radiochemical method was not possible.

Equation 16 may be expressed:

$$\Delta = \frac{[Ti^{3+}] + \sum [Ti^{3+}]_S (H_3PO_4) (H_2PO_4^-) (HPO_4^{2-})}{[Ti^{3+}]_R} \ldots (30)$$

Where the subscript 'R' indicates the resin phase, and 'S' the solution phase.

From 15.

$$\Delta_0 = \frac{[Ti^{3+}]_S}{[Ti^{3+}]_R} \ldots .................. (31)$$

$$\therefore [Ti^{3+}]_R = \frac{[Ti^{3+}]_S}{\Delta_0} \ldots .................. (32)$$
In this solution of orthophosphoric acid, theoretically, three species $H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$, can complex with titanium(III) either separately or together.

The equilibrium may be represented by the equation:

$$a Ti^3+ + p(H_3PO_4) + q(H_2PO_4^-) + r(HPO_4^{2-}) \rightleftharpoons [Ti_3^{(3+)}]^a(H_3PO_4)^p(H_2PO_4^-)^q(HPO_4^{2-})^r]^{(2r+q-3a)-}$$

where $2r+q - 3a, p = 0, 1, 2, 3 \dots, q = 0, 1, 2 \dots, r = 0, 1, 2 \dots$.

Applying the Law of Mass Action to equation 33.

$$\Sigma \beta = \Sigma \frac{[Ti_3^{(3+)}]^a(H_3PO_4)^p(H_2PO_4^-)^q(HPO_4^{2-})^r]}{[Ti_3^{(3+)}]^a(H_3PO_4)^p(H_2PO_4^-)^q(HPO_4^{2-})^r]} \quad \quad (34)$$

Where $\beta$ is total stability constant of the titanium(III) orthophosphate complexes.

Hence from 30, 32, and 34

$$\Delta = \frac{[Ti_3^{(3+)}] + \Sigma \beta[ti^{(3+)}]^a(aH_3PO_4)^p(aH_2PO_4^-)^q(aHPO_4^{2-})^r]}{[Ti_3^{(3+)}]} \quad \quad (33)$$

$$= \Delta_0(1 + \Sigma \beta(aH_3PO_4)^p(aH_2PO_4^-)^q(aHPO_4^{2-})^r)$$
Substituting from 28 and 29

\[ \Delta = \Delta_0 (1 + \sum \beta \left( \frac{[T_i^{3+}]^{n-1}(a_{H_2PO_4}^-)^2(a_{H_2PO_4}^-)^q(z_2)}{K_1^2} \right)) \ldots (35) \]

Hence by varying the activities of the ions in solution, corresponding values of \( \Delta \) may be obtained.

Let \( a_{H_2PO_4}^- = a \) ......................... (36.)

In practice it was found that equation 35 was of the form:

\[ \Delta = \Delta_0 (1 - Da + Ea^2) = F(a) \text{(say)} \ldots \ldots \ldots (37) \]

\( \Delta_0, D \) and \( E \) were not known. \( D \) and \( E \) are constants such that \( \beta_2 d = D, \beta_3 e = E. \) With knowledge of \( K_1 \), the stability constants \( \beta_2 \) and \( \beta_3 \) may be calculated. (See Section IV. 2. 2.) It has not been possible to determine \( \Delta_0 \), as a non-complexing anion could not be used. \( \Delta_0 \) is the distribution coefficient in the absence of ligand.

Initially the method of least squares was applied in an attempt to determine the value of \( \Delta_0, D \) and \( E. \) Although
the method gave these simultaneous equations:

\[ \Sigma (aA - aAo - AoDa^2 - AoEa^3) = 0 \]
\[ \Sigma (a^2A - a^2Ao - AoDa^2 - AoEa^4) = 0 \]
\[ \Sigma [(1 + Da + Ea^2)^2Ao - \Delta] = 0 \]

It was not possible to determine three unknowns because of the complexities of the equations.

A graphical treatment was then applied, based on the work of Sillén (38). It was found to be impossible to fit the points, determined from practical work, to the calculated curves by eye with any accuracy.

It was decided to use the method of least squares, estimating an approximate value of Ao in order to calculate corresponding values of D and E. Then F(a) was calculated for a series of values of a and these were plotted against a. The approximate value of Ao was gradually refined, in this way, to give the best fit to the experimental results.

An approximate value of Ao was obtained from the work of Genge (39) on the elution of titanium(III) from titanium(III) form cation-exchanger using perchloric acid.
Applying the method of least squares to equation 37:-

Consider, the sum of the square of error, S, in equation 37.

\[ S = \sum (\Delta - F(a))^2 \] .......................... 38.

Partial differentiation of 38, w.r.t. D and E:

\[ \frac{\delta S}{\delta D} = -2 \sum (\Delta - F(a)) \frac{F(a)}{D} , \quad \frac{\delta F(a)}{\delta D} = \sum_{a} \Delta_{o} \] .......................... 39.

\[ \frac{\delta S}{\delta E} = -2 \sum (\Delta - F(a)) \frac{\delta F(a)}{\delta E} , \quad \frac{\delta F(a)}{\delta E} = \sum_{a}^{2} \Delta_{o} \] .......................... 40.

For S to be a minimum, \( \frac{\delta S}{\delta D} = 0, \frac{\delta S}{\delta E} = 0, \)

\[ \therefore \sum (\Delta_{a} - \Delta_{oa} - \Delta_{oDa}^{2} - \Delta_{oEa}^{3}) = 0 \] .......................... 41.

\[ \therefore \sum (\Delta_{a}^{2} - \Delta_{oa}^{2} - \Delta_{oDa}^{3} - \Delta_{oEa}^{4}) = 0 \] .......................... 42.

Rearranging:

\[ (\Delta_{o} \sum_{a} \Delta_{a}^{2}) D + (\Delta_{o} \sum_{a} \Delta_{a}^{3}) E = \sum a (\Delta - \Delta_{o}) \] .......................... 43.

\[ (\Delta_{o} \sum_{a} \Delta_{a}^{3}) D + (\Delta_{o} \sum_{a} \Delta_{a}^{4}) E = \sum a^{2} (\Delta - \Delta_{o}) \] .......................... 44.

These two equations may be solved to give values of D and E, hence \( \beta_{2} \) and \( \beta_{3} \).
2.1 ANALYSIS OF ALUMINIUM

Aluminium was determined gravimetrically as the "oxine" (8-hydroxy quinolate). The sample was transferred to a 400ml. beaker; stabilized with 60% perchloric acid (5ml.) and 20% sodium hydroxide solution added until the precipitate that formed just dissolved. The solution was warmed to 70-80°C and a 5% oxine solution in 2N acetic acid (5mls.) added. 10% ammonium acetate solution (25mls.) was added and the solution boiled, until precipitation was complete. If the supernatant liquor was yellow, sufficient oxine solution had been added. The solution was allowed to stand for at least two hours, then filtered on a weighed sintered glass crucible; the precipitate was dried to constant weight at 135°C and weighed as Al(C^6H^8O^N^3)^3.

2.2 ANALYSIS OF IRON(III)

Iron(III) was determined colorimetrically by means of the bathophenanthroline method. The sample solution was pipetted into a 60ml. separating funnel and sufficient iron free water added to make its volume up to 20mls.
10% Hydroxylamine hydrochloride solution (2ml.), 10% sodium acetate solution (4ml.) and 0.01M bathophenanthroline (4mls.) were added and the solutions mixed. n-Hexanol (6ml.) was added and the separating funnel shaken well. The liquids were allowed to separate and the lower aqueous layer run off and discarded. The hexanolic layer was collected in a 10ml. graduated flask and the separating funnel was washed out with two aliquots (1ml.) of ethanol. The solution was adjusted to the mark with ethanol. The absorbancy of the solution was measured on a Unicam S.P.500 spectrophotometer at 533m\textmu. A blank was made up using distilled water (20ml.) as sample solution.

A calibration curve (Fig. 1) was made up by the use of A.R. Ferrous ammonium sulphate hexahydrate. The colour of the blank was decreased by purifying the hydroxylamine hydrochloride and sodium acetate solutions; reacting the solutions with bathophenanthroline and extracting the colour with n-hexanol. It has been reported\cite{41} that the presence of orthophosphate ion can cause errors in the determination of iron by this method. No evidence for this interference was found. The calibration curves were the same in the presence and absence of orthophosphate ion.
Figure (1) shows a plot of concentration of iron vs. optical density.
2.3 ANALYSIS OF TITANIUM(III)

Titanium(III) was analysed volumetrically (a) and colorimetrically (b).

(a) Volumetric Analysis of Titanium(III)

An aliquot of titanium(III) solution was transferred to a conical flask containing a five-fold excess of sulphuric acid. Titanium dioxide was immediately precipitated. The solution was titrated with potassium permanganate solution. If the normality of the potassium permanganate solution was less than 0.02M, two drops of the redox indicator ferrous-1.10 orthophenanthroline were used. Solutions of less than 0.02M potassium permanganate were made up as required by dilution of 0.1M potassium permanganate solution. The potassium permanganate solutions were standardised against sodium oxalate.
(b) Colorimetric Analysis of Titanium(III)

Although usually the determination of titanium(III) was conveniently carried out by titration with potassium permanganate solution, at the much lower concentrations used in the determination of stability constants, the method was not practicable. A colorimetric method (42) using hydrogen peroxide and sulphuric acid was adopted. The procedure was: 3% hydrogen peroxide (5ml.) and 6M sulphuric acid (10ml.) were added to a titanium sample in a 25ml. graduated flask. The solution was made up to the mark with distilled water and the optical density of the solution measured at 410nm on a S.P.500 spectrophotometer. A calibration curve, Fig. 2, was prepared using previously standardised titanium(III) chloride solution. The presence of orthophosphate ion did not cause interference.

It has been suggested by P.J. Elving and E.C. Olsen (43) that a colorimetric method based on the chloroform extraction of titanium cupferrate would provide an accurate analysis of trace concentrations of titanium. This method was investigated and found not to be successful.
concentration of titanium $x \times 10^6$ M

- Optical density

- Concentration of titanium $x \times 10^6$ M

- Fig. (2)
2.4 **ANALYSIS OF PHOSPHATE**

Phosphate was determined, colorimetrically, by the ammonium molybdophosphato vanodate method (44). Two solutions were made up for use in the analysis:

**Solution A** - This was prepared by dissolving A.R. ammonium molybdate (8g.) in water (100ml.). The solution threw a slight precipitate on standing, but this did not affect its properties.

**Solution B** - This solution was made up by dissolving A.R. ammonium metavanadate (0.4g.) in a mixture of 60% perchloric acid (60mls.) and water (40mls.). This solution was stable.

The sample was pipetted into a 25ml. graduated flask. Solution B (1ml.) and then solution A (1ml.) were added and was made up to the mark with distilled water. The solutions were left for five minutes to allow full colour development. For solutions containing iron, titanium or aluminium, a blank solution was made up, concurrently, containing the sample solution and solution B (1ml.). This effectivity removed the interference of iron, titanium or aluminium. For solutions free from interfering ions, the blank was made up by adding both solutions A and B and making the solutions up to the mark with distilled water.
A calibration curve was made up, by dissolving A.R. potassium dihydrogen phosphate (0.67 g.), dried over night at 105°C, in water (1,000 mls.). Aliquots of this solution were used to plot calibration curves: in the presence of aluminium, iron and titanium and in their absence. Titanium(III) was oxidised to titanium(IV) before carrying out the determination, otherwise titanium(III) reduced the molybdate ion yielding molybdenum blue. The calibration curve is shown in Fig. 3.

3. SPECTROPHOTOMETRIC METHODS

When no chemical reaction occurs in solution between two solutes, the absorption of light of a particular wavelength is a function of concentration as a consequence of the Lambert-Beer Law. It is a limiting Law and its upper limit of validity is usually taken to be of the order of 0.1M. If a reaction was occurring in solution, a deviation from the linear relationship would be expected. This technique, known as the method of continuous variation, was first applied quantitatively to complex formation by Job (45). Although the deviating property measured has
usually been optical absorption, other colligative properties of the solution have been used and, for example, constants have been calculated from calorimetric measurements for the copper(II) - ammonia system. Job assumed that only one complex was present in solution, but, as Woldbye has pointed out it is extremely unlikely that only a single complex will be present in solution under any given conditions. Moreover, the method of continuous variation does not readily show whether or not several complexes are present and although attempts have been made to extend Job's treatment to systems in which two or more complexes are formed, except in a few instances are of limited applicability giving results which can be interpreted only with extreme caution. Accordingly, the data obtained have been interpreted in the light of the known limitations of the method, and in general in conjunction with data obtained by the other methods used.
PART III

PREPARATIONS

1.1. Aluminium Salts
1.2. Iron Salts
1.3. Titanium Salts

2.1. Conditioning of Ion Exchange Resins
(a) 10% sodium hydroxide solution was added dropwise to a solution of ammonium aluminium sulphate (50g.) in water (500ml.) which contained syrupy orthophosphoric acid (10ml.) until a precipitate was just visible. The solution was filtered, then heated on a steam bath. Because of its negative solubility coefficient, aluminium orthophosphate was precipitated. After about six hours the precipitate became granular. The supernatant liquor was decanted off and replaced by a solution of syrupy orthophosphoric acid (5ml.) in water (400ml.), then heated for six hours. Two further treatments with water, followed by washing with boiling water on a Buchner pad yielded a white solid, free from sodium to the flame test. Yield of product was about 10g. Typical analysis given below.

<table>
<thead>
<tr>
<th></th>
<th>%</th>
<th>Al</th>
<th>PO₄</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical for AlPO₄H₂O</td>
<td></td>
<td>19.27</td>
<td>67.85</td>
<td>12.87</td>
</tr>
<tr>
<td>Found</td>
<td></td>
<td>19.28</td>
<td>67.90</td>
<td>-</td>
</tr>
</tbody>
</table>
III.1.1(b) PREPARATION OF ALUMINIUM PERCHLORATE

A.R. Hydrated aluminium sulphate (40g.) in water (100ml.) was allowed to trickle down a column of hydrogen form ZeoKarb 225 ion exchange resin. The resin was washed with deionised water until no trace of sulphate ion could be detected in the effluent solution, by the barium chloride test. The resin was eluted with 2M perchloric acid. The effluent solution was evaporated until crystals separated out and dried under vacuum. The solid was filtered off at the pump and stored under vacuum. The crystals obtained were colourless and hygroscopic.

III.1.2(a) PREPARATION OF FERRIC ORTHOPHOSPHATE

A.R. ammonium ferric sulphate (60g.) was dissolved in water (300ml) to which concentrated A.R. sulphuric acid (20ml.) had been added. A 17% solution (400ml) of A.R. sodium dihydrogen orthophosphate was added dropwise with constant mechanical stirring, yielding a white precipitate. After heating on a steam bath for six hours, the precipitate assumed a granular nature and was pink in colour.
The supernatant liquor was decanted off. The precipitate was mixed with a solution of A.R. orthophosphoric acid (3ml.) in water (500ml.) and heated on a steam bath for six hours. The supernatant liquor was then replaced with water (500mls.) and the heating repeated. This was followed by a further treatment with water. The precipitate was filtered at the pump from hot solution washed with boiling water and allowed to dry in air. The product was a pale pink amorphous solid. Typical analyses are given below. Iron(III) was analysed using a Jones Reductor and subsequent titration with potassium permanganate solution. Orthophosphate was determined spectrophotometrically by the ammonium molybdophosphato vanadate method.

Theoretical % given below are for \((\text{FePO}_4)_{2.5\text{H}_2\text{O}}\).

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>PO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>28.51</td>
<td>48.49</td>
</tr>
<tr>
<td>Found</td>
<td>28.5</td>
<td>48.3</td>
</tr>
</tbody>
</table>
III.1.2. Preparation of Iron(III) Perchlorate

A.R. ferric sulphate (20g.) was dissolved in dilute A.R. sulphuric acid and made just alkaline with A.R. ammonium hydroxide solution to precipitate ferric hydroxide. The precipitate was back-washed up a sintered glass column until the effluent solution was free of sulphate ions when treated with barium chloride solution. The precipitate was filtered at the pump, transferred to a large beaker and A.R. 60% perchloric acid added until the pH of the solution was 2.0. The mixture was left overnight and by morning yielded a brown solution. This was filtered and evaporated. The colour of the solution changed from brown to pink. When crystals separated out, they were filtered at the pump and dried under vacuum over calcium chloride, to yield very hygroscopic pink crystals of iron(III)- perchlorate.

III.1.3. Preparation of Titanium(III) Salts.

Titanium(III) is very oxygen sensitive and all preparations and manipulations were carried out under a pure nitrogen atmosphere.
III.1.3(a) Preparation of Pure Nitrogen

Commercial "oxygen-free" nitrogen contains at least 0.05% of oxygen and pure nitrogen was prepared as follows:

Using the apparatus shown in Fig. 4 B.O.C. "white spot" nitrogen was passed up a column, electrically heated to 170°C, packed with alternate layers of copper turnings and copper deposited on keiselguhr. This apparatus removed oxygen to a concentration lower than 10^-4% \(^4\).

The copper deposited on keiselguhr was prepared as follows: kieselguhr (250g.) was mixed with a copper sulphate solution (250g. CuSO₄ in 2L. water) and the mixture boiled. While the solution was boiling, 40% sodium hydroxide solution (500ml.) was added. The mixture was boiled for a further ten minutes to ensure complete precipitation of copper hydroxide. The supernatant liquor was decanted off and the solid material was filtered at the pump. The solid material was dried in an oven at 110°C and then broken up and ground to a fine powder.

Copper turnings and copper oxide on keiselguhr was packed, in alternate layers into the column, already
wound with nichrome wire, such that the internal temperature was 170°C. Nitrogen was then passed up the column to remove any air present and then hydrogen was passed up the column and the column heated to 170°C. This reduced the copper oxide present to copper.

To further purify the nitrogen it was bubbled through a chromous sulphate bubbler. The bubbler was filled with M chrome alum solution in 2M sulphuric acid over zinc amalgam. Initially the solution was deep green, but on standing for two days it was reduced to a lighter blue. As normally the copper oven removed most of the oxygen present in the nitrogen, this bubbler was a useful indicator of the efficiency of the copper oven. On reaction with a small amount of oxygen, the light blue solution turned dark green.

The nitrogen then passed through a liquid air trap, to prevent splash over of chromous sulphate and remove any further impurities. It was then either, further dried by passing up a column packed with magnesium perchlorate (anhydrous) and this dry nitrogen used in preparations, or passed through a pair of wash bottles and used in the ion exchange batch experiments.
3.1.3(b) Preparation of Titanium(III) Orthophosphate

Titanium(III) orthophosphate was prepared by an ion exchange technique from titanium(III) chloride. Titanium(III) is easily oxidised and experiments involving this ion were carried out under nitrogen, with precautions to exclude any trace of atmospheric oxygen. Solid titanium(III) chloride was dissolved in deoxygenated IN hydrochloric acid, under nitrogen in a glove box to yield a purple solution. Deoxygenation was carried out by alternately evacuating the vessel and filling with nitrogen. This process was carried out three times. The titanium(III) chloride in hydrochloric acid solution was transferred to the dropping funnel of the apparatus shown in Fig. 5. The column of the apparatus was packed with hydrogen form Zeo Karb 225. Purified nitrogen was continually passed through the apparatus, during the course of the preparation while the titanium solution was allowed to trickle down over the resin. As the titanium(III) displaced hydrogen ion on the ion exchanger, the resin darkened to a deep purple. The resin was never allowed to run dry; it was washed with de-oxygenated de-ionised water.
fig (5)
until no trace of chloride could be detected in the effluent solution by the silver nitrate test; it was then eluted with deoxygenated 2M orthophosphoric acid. As the orthophosphoric acid band front passed down the resin, its colour darkened to a deep purple. This purple-brown effluent solution was collected, immediately deoxygenated and was stored under nitrogen.

III.1.3(c) Attempts to Prepare Titanium(III) Perchlorate

The preparation of titanium(III) perchlorate was attempted using these methods: (a) Ion Exchange, using the same apparatus as for preparing titanium(III) orthophosphate (Section III.1.(b)). Solid titanium(III) chloride was dissolved in deoxygenated 1N hydrochloric acid, under nitrogen in a glove box. The solution was deoxygenated and transferred to the dropping funnel of the apparatus shown in Fig. 5. The column of the apparatus was packed with hydrogen form Zeo Karb 225. Purified nitrogen was continually passed through the apparatus during the course of the preparation and the solution was
allowed to trickle down over the resin. As titanium(III) displaced hydrogen on the resin, it darkened to a deep purple. The resin was never allowed to run dry and was then washed with deoxygenated deionised water until no trace of chloride ion could be detected in the effluent solution by the silver nitrate test. It was then eluted with 1.5M perchloric acid. This was the most dilute acid that eluted the resin to any extent. The purple effluent solution was collected, deoxygenated and stored under nitrogen, overnight. In all cases, by morning the solution had become colourless, i.e. titanium(III) had been oxidised to titanium(IV). The technique of batch elution of the resin was tried using more dilute, M/10 perchloric acid. Aliquots (100ml.) of perchloric acid being allowed to come to equilibrium and run off, but this failed to elute the resin.

(b) Precipitation of titanium(III) oxide and subsequent dissolution of the precipitate in perchloric acid. The titanium(III) oxide was precipitated from titanium(III) chloride solution by the use of 0.88 ammonium hydroxide solution and transferred to a column.
where it was washed with hot deoxygenated deionised water, until no trace of chloride ion could be detected in the effluent solution by the silver nitrate test. All attempts to dissolve the titanium(III) oxide resulted in oxidation to titanium(IV) oxide.

(c) By solution of the pure metal in dilute perchloric acid. All attempts to dissolve titanium metal in perchloric acid produced a titanium(IV) solution and ultimate precipitation of titanium dioxide.

3.2.1. Conditioning of Hydrogen Form Cation Exchanger

The cation exchanger Zeo Karb 225 with nominal 8% cross linking and 20-50 mesh bead size was used throughout this work. To avoid errors due to differences in various batches of resin, all samples used were taken from the same large batch of resin, treated as described below. The resin, when supplied commercially contains a considerable amount of iron and is in the sodium form. To convert it to the hydrogen form and remove iron and other impurities, the resin was mixed with water and transferred as a slurry to a glass column. The resin was eluted with 2M
hydrochloric acid, until no trace of iron could be detected by the use of ammonium thiocyanate solution. It was then washed with deionised water, until no trace of chloride could be detected in the effluent by the silver nitrate test. The resin was filtered at the pump and dried in air. Oven dried resins are hygroscopic and unstable. It was stored in a screw top jar.

3.2.2. Conditioning of Orthophosphate Form Resins

The anion exchanger used throughout this work was orthophosphate form Deacidite FF. This resin when supplied commercially is in the chloride form and to convert it to the orthophosphate form the following method was used: The column was packed as described for cation exchanger and the resin was washed with 2M orthophosphoric acid, until no trace of chloride ion could be detected in the effluent solution by the silver nitrate test. It was then washed with deionised water until no trace of orthophosphate ion could be detected in the effluent solution by the ammonium molybdate test. Finally the resin was filtered at the pump and air dried.
PART IV

EXPERIMENTAL

IV.1. Ion Exchange Experiments to determine the sign and size of charge on complex species in solution.

IV.2. Determination of the stability constants of the complex species.


IV.4. Discussion.
IV.1. ION EXCHANGE EXPERIMENTS TO DETERMINE
THE SIGN AND SIZE OF CHARGE ON COMPLEX SPECIES
IN SOLUTION

IV.1.1. Preparation of complex solutions.
IV.1.2. Determination of the capacity of ion exchange resins.
IV.1.3. Batch Experiments.
IV.1.4. Results.
IV.1.5. Discussion.

Previous experiments \textsuperscript{13,18} gave evidence of the complexing action occurring between orthophosphoric acid and aluminium, iron(III) and titanium(III). Batch experiments were carried out to determine the sign and size of charge of the complex species in solution. The results obtained agreed with those obtained by Jameson and Salmon \textsuperscript{13} and confirmed those of Genge and Salmon \textsuperscript{13}.

IV.1.1. Preparation of Complex Solutions
(a) Batch Anion Exchange Experiments
   (i) Aluminium

Solid aluminium(III) orthophosphate, prepared as described in Section III.1.1., was dissolved in concentrated
orthophosphoric acid and the solution diluted to the
required concentration with water. The salt was sparingly
soluble in concentrated orthophosphoric acid and dissolved
on shaking for about an hour on a mechanical shaker.

(ii) **Iron(III)**

Solid iron(III) orthophosphate (prepared as
described in Section III.1.2.) is sparingly soluble in
concentrated orthophosphoric acid and thus was shaken with
this concentrated acid until a clear pink solution was
obtained. This was diluted as required with water.

(iii) **Titanium(III)**

Titanium(III) orthophosphate solution was prepared
by ion exchange as described in Section III.1.3.

(b) **Batch Cation Exchange Experiments**

Because of the low solubilities of aluminium and
iron(III) orthophosphate in orthophosphoric acid, the
concentration of orthophosphate in these solutions was high.
Spurious high concentrations of orthophosphoric acid were
found on the cation exchanger, probably due to the
adsorption of uncharged orthophosphoric acid by the ion
exchange resin. Thus the iron(III) and aluminium orthophosphate batch experiments were carried out using the metal perchlorate, perchloric acid and orthophosphoric acid. It was considered that perchloric acid would not complex with aluminium or iron(III) to any extent.

(i) Aluminium

Moist crystals of aluminium perchlorate were easily dissolved in dilute perchloric acid and dilute orthophosphoric acid was added as a ligand. The solution was diluted as required with water.

(ii) Iron(III)

Iron(III) perchlorate was very soluble in dilute perchloric acid - orthophosphoric acid mixture.

(iii) Titanium(III)

As reported in Section III.1.3, it was impossible to prepare titanium(III) perchlorate, but because titanium(III) orthophosphate solutions were prepared by ion exchange rather than by dissolution of a sparing soluble solid, the titanium: orthophosphate ratio was not as low as in the case of iron(III) and aluminium. The effects of physical adsorption were minimal.
IV.1.2. **Determination of the Capacity of Ion Exchange Resins**

(a) **Cationic Resins**

A weighed quantity (ca. 0.5 g.) of the hydrogen form of resin was placed in a glass column and eluted with \( \frac{N}{2} \) sodium hydroxide \( \text{sodium} \) (50 mls.). The effluent solution was analysed by titration with \( \frac{N}{2} \) hydrochloric acid using screened methyl orange as indicator. Duplicate determinations were carried out until agreement better than 0.2% was achieved.

(b) **Anionic Resins**

A weighed quantity (ca. 1 g.) of resin was placed in an ion exchange column. The resin was converted to the chloride form by eluting with the resin with IN hydrochloric acid. The resin was washed with deionised water until no trace of chloride ion could be detected in the effluent solution on testing with silver nitrate solution. The resin was eluted with IN nitric acid. The chloride content of the effluent solution was estimated using mercuric nitrate solution with sodium nitro-prusside solution as indicator \( (50) \). Duplicate determinations were carried out until agreement better than 0.2% was obtained.
IV.1.3. Batch Experiments

(a) Determination of the sign and size of charge of the complexes of iron(III) and orthophosphoric acid

(i) Cation-exchange Experiments

Cation exchanger, hydrogen form Zeo Kerb 225 was weighed out in exactly 0.5g. amounts, into 50ml. conical flasks. Solutions of iron(III) perchlorate in perchloric acid, orthophosphoric acid and water were added by pipette and burette to make up solutions of known pH and of 50ml. volume. The flasks were sealed, by wiring down a rubber bung and shaken on a mechanical shaker for at least four hours. Previous experiments had shown that this was adequate time to achieve equilibrium.

The resin was separated from solution in a sintered glass column; quickly washed with deionised water to remove any trace of solution adhering to it, eluted with 1N hydrochloric acid and the effluent made up to 250mls. with deionised water. The solution was analysed for orthophosphate using the ammonium molybdophosphato-vanadate method. As negligible amounts of orthophosphate were found on the resin, iron determinations were not carried out. The results obtained are shown in Table 1.
(ii) **Anion Exchange Experiments**

The anion exchanger, orthophosphate form De-Acidite FF (exactly 1.0g.) was weighed out into 50ml. conical flasks. Solutions of iron(III) orthophosphate, orthophosphoric acid and deionised water were added by pipette and burette to give solutions of known pH and of 50ml. volume. Blank solutions of the same pH volume, orthophosphate concentration and mass of resin containing no iron, were made up also in 50ml. conical flasks. The flasks were sealed and shaken for at least four hours on a mechanical shaker.

The resin was separated from the iron containing solution in a sintered glass column and washed with deionised water to remove any adhering solution. It was found that to achieve an effluent solution neutral to methyl orange, prolonged washing of the resin with water was necessary. However no iron was lost by the resin after the initial washings, as the effluent solution was iron free. When the effluent solution was neutral the resin was stripped with \( \frac{N}{2} \) nitric acid and the solution analysed colorimetrically for orthophosphate and for iron.
The resin that had been allowed to come to equilibrium with the iron-free orthophosphoric acid solution, was separated from the solution, washed with a similar amount of deionised water, eluted with N/2 nitric acid and the effluent analysed spectrophotometrically for orthophosphate. The capacity of the resin was determined on the actual samples used. The results obtained are shown in Table 2.

Another series of experiments was then carried out to ascertain the number of hydrogen atoms in the iron orthophosphate complex. The previous series enabled the determination of the iron: orthophosphate ratio to be carried out. The experiments were carried out as described above except that the resin samples from both the iron containing and iron free solutions were only washed with water (150mls.) so that in the case of the former the effluent solution was iron free. The results obtained are shown in Table 8.
(b) **Determination of the sign and size of charge of the complexes of titanium(III) and orthophosphoric acid**

The reaction vessel, Fig. 6, was weighed and clamped vertically on a retort stand such that tap \( G \) was at the base of the apparatus. The upper portion was removed and a small weighing bottle of resin, containing either cation exchanger (0.5g.), hydrogen form Zeo Xarb 225 or anion exchanger (1.0g.), orthophosphate form De-acidite FF was placed in the vessel. The required volumes of titanium(III) orthophosphate in orthophosphoric acid solution of known concentration, of both titanium(III) and orthophosphate, and water were pipetted into the vessel. The upper portion of the vessel was replaced and the vessel weighed quickly.

The vessel was replaced on the retort stand and socket joint 'a' was attached to ball joint 'b'. A lead to a vacuum pump, through a cold trap, was attached to end 'd' of the apparatus. Tap \( H \) was closed; the vacuum pump was turned on and tap \( F \) opened. Gas was allowed to bubble off from the solution. Tap \( F \) was closed. Taps \( E \) and \( H \) were opened and the vessel flooded with wet nitrogen.
The vessel was shaken to improve solution of nitrogen. Taps E and H were closed. Tap F was opened and the process repeated. The vessel was detached from the nitrogen line, weighed and placed on a mechanical shaker for five hours. Previous experiments showed that equilibrium was achieved within this time. The purpose of weighing the vessel at each stage was to check losses of solvent due to evaporation. It was found that insignificant losses occurred, using the technique outlined above.

Using a clean dry pipette, an aliquot (5 ml.) of solution was extracted from the vessel via port J. This was transferred to a one litre graduated glask where it was caught in 4N hydrochloric acid and the solution made up to the mark with 4N hydrochloric acid. This solution did not throw a precipitate of titanium dioxide for three to four hours. The orthophosphate concentration of the solution was estimated spectrophotometrically. The orthophosphate concentration of the resin was determined using the formula:

\[ C_R = \frac{(C_I - C_E) V}{W} \]

\[ \text{.................. l.} \]
where,

\( C_R \) = concentration of ion exchanged on exchanger.

\( C_I \) = concentration of ion in solution initially before exchanger added.

\( C_E \) = concentration of ion in solution at equilibrium.

\( d \) = fractional decrease in initial volume of solution on adding exchanger (\( d = 1 \))

\( V \) = initial volume of solutions.

\( W \) = Weight of ion exchanger.

The value of the factor 'd' was determined by equilibrating N/10 hydrochloric acid (25.0mL.) with anion exchanger (1.0g.) or cation exchanger (0.5g.) 'd' was always greater than 0.995 and so was taken to be unity throughout these experiments. The titanium concentration was determined by catching the remainder of the solution in ferric ammonium sulphate and titrating with potassium permanganate solution.

For the anion exchange experiments, blank solutions of the same orthophosphate concentration and pH as the titanium orthophosphate solution but containing no titanium was set up. They were shaken on a mechanical
shaker for at least five hours. The resin was separated from the solution in an ion exchange column; washed free of solution adhering to it with water and eluted with N/2 nitric acid. The effluent solution was analysed spectrophotometrically for orthophosphate. The cation exchange results obtained are listed in Table 4 and the anion exchange results are listed in Table 5.

(c) Determination of the sign and size of charge on the complexes of aluminium and orthophosphoric acid

(i) Cation Exchange

Cation exchange studies of aluminium orthophosphate solutions were carried out by a similar method to the iron(III) orthophosphate studies. Only a trace of orthophosphate ion was found on the exchanger and so it was assumed that cationic complexes were not formed in solution. Thus aluminium determinations were not carried out. The results obtained are shown in Table 6.

(ii) Anion Exchange

Similarly, the anion exchange studies of the aluminium orthophosphate solutions were carried out in a
like manner to those of the iron(III) orthophosphate studies. However, the aluminium concentration of the solution was determined gravimetrically before and after equilibrium was reached. The aluminium concentration on the resin was too small to be accurately analysed gravimetrically and was determined using equation 1 (Section IV.1.3(b)). The results obtained are shown in Table 7.
IV.1.4. RESULTS

Table 1. Cation Exchange Iron(III) Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Fe in solution mM</th>
<th>Amount PO₄²⁻ in solution mM</th>
<th>mMFe(III) absorbed per g. resin</th>
<th>mMPO₄²⁻ absorbed per g. resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>11.0</td>
<td>Not analysed</td>
<td>0.003</td>
</tr>
<tr>
<td>1.1</td>
<td>1.0</td>
<td>11.0</td>
<td>Not analysed</td>
<td>0.008</td>
</tr>
</tbody>
</table>

* Solution made up to required pH by addition of perchloric acid.

Table 2. Anion Exchange Iron(III) Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Fe in solution mM</th>
<th>Amount PO₄²⁻ in solution mM</th>
<th>mMFe(III) absorbed per g. exchanger</th>
<th>mMPO₄²⁻ absorbed per g. exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>1.03</td>
<td>68.0</td>
<td>0.082</td>
<td>1.6</td>
</tr>
<tr>
<td>0.9</td>
<td>1.03</td>
<td>66.0</td>
<td>0.095</td>
<td>1.5</td>
</tr>
<tr>
<td>0.95</td>
<td>1.03</td>
<td>65.0</td>
<td>0.100</td>
<td>1.46</td>
</tr>
<tr>
<td>1.0</td>
<td>1.03</td>
<td>64.5</td>
<td>0.114</td>
<td>1.41</td>
</tr>
<tr>
<td>1.1</td>
<td>1.03</td>
<td>64.0</td>
<td>0.126</td>
<td>1.36</td>
</tr>
</tbody>
</table>
Table 3. Anion Exchange Iron(III) Orthophosphate System
Resin washed with water (150 x 4)

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Fe in solution mM</th>
<th>Amount PO₄³⁻ in solution mM</th>
<th>mMFe sorbed per g.exchanger</th>
<th>mMPO₄³⁻ sorbed per g.exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>1.0</td>
<td>64.6</td>
<td>0.095</td>
<td>1.83</td>
</tr>
<tr>
<td>1.1</td>
<td>1.0</td>
<td>63.8</td>
<td>0.119</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Table 4. Cation Exchange Titanium(III) Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Fe in solution mM</th>
<th>Amount PO₄³⁻ in solution mM</th>
<th>mMFe sorbed per g.exchanger</th>
<th>mMPO₄³⁻ sorbed per g.exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1.0</td>
<td>66.1</td>
<td>Not analysed</td>
<td>Nil</td>
</tr>
<tr>
<td>0.7</td>
<td>1.2</td>
<td>73.0</td>
<td>Not analysed</td>
<td>Trace</td>
</tr>
</tbody>
</table>
Table 5. Anion Exchange Titanium(III) Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Ti(III) in solution mM</th>
<th>Amount PO₄⁻ in solution mM</th>
<th>mM Ti(III) sorbed per g. exchanger</th>
<th>mM PO₄⁻ sorbed per g. exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.805</td>
<td>3.99</td>
<td>64.8</td>
<td>0.46</td>
<td>3.3</td>
</tr>
<tr>
<td>0.72</td>
<td>4.66</td>
<td>76.0</td>
<td>0.47</td>
<td>3.8</td>
</tr>
<tr>
<td>0.72</td>
<td>4.66</td>
<td>76.0</td>
<td>0.47</td>
<td>3.8</td>
</tr>
<tr>
<td>0.72</td>
<td>3.03</td>
<td>76.2</td>
<td>0.40</td>
<td>3.0*</td>
</tr>
</tbody>
</table>

* Different run, i.e. different value of 'z' or resin capacity.

Table 6. Cation Exchange Aluminium Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Al in solution mM</th>
<th>Amount PO₄⁻ in solution mM</th>
<th>mM Al sorbed per g. exchanger</th>
<th>mM PO₄⁻ sorbed per g. exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>1.0</td>
<td>10.0*</td>
<td>Not analysed</td>
<td>Nil</td>
</tr>
<tr>
<td>1.1</td>
<td>1.7</td>
<td>18.9*</td>
<td>Not analysed</td>
<td>Nil</td>
</tr>
</tbody>
</table>

* Solution made up to pH by addition of perchloric acid
Table 7. Anion Exchange Aluminium Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Amount Al in solution mM</th>
<th>Amount PO₄⁺ in solution mM</th>
<th>mM Al sorbed per g.exchanger</th>
<th>mMPO₄⁺ sorbed per g.exchanger</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28</td>
<td>1.1</td>
<td>26.9</td>
<td>0.070</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.071</td>
<td>2.37</td>
</tr>
<tr>
<td>1.1</td>
<td>1.83</td>
<td>44.9</td>
<td>0.086</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.087</td>
<td>2.44</td>
</tr>
</tbody>
</table>
If these results are inserted in equation (5), Section II.1.1.

\[ \frac{1}{1} = \frac{[a(x-z)-m-y]N_M + z}{z} \]

(A key to the symbols used in the above equation is to be found in Section II.1.)

e.g. the titanium(III) system at pH 0.86 \( \approx 0.72 \)

\[ N_M = \text{moles of titanium(III) sorbed on exchanger/eq. of exchanger} \]
\[ = \frac{0.47}{3.222} = 0.14617/\text{eq} \]

\[ N_L = \text{moles of phosphate sorbed on exchanger/eq. of exchanger} \]
\[ = \frac{3.8}{3.222} = 1.1814/\text{eq.} \]

\[ a = \text{number of molecules of phosphate/metal atom in complex} \]
\[ = 2 \text{ or } 3. \]

\[ x = \text{basicity of acid, orthophosphoric } = 3. \]

\[ m = \text{charge on metal } = 3 \]

\[ y = \text{number of hydrogen ions in complex (obtained from equation).} \]

\[ z = \text{average charge on phosphate ions in solution.} \]

\[ = \frac{\text{Capacity of ion-exchanger}}{\text{Moles of phosphate sorbed}} = \frac{3.222}{2.47} = 1.22 \]

Then the results shown overleaf are calculated.
Table 8. Anion Exchange Iron(III) Orthophosphate System

<table>
<thead>
<tr>
<th>pH</th>
<th>Capacity of exchanger meq/g.</th>
<th>Moles Fe(^{3+}) per eq ion exchanger (N_M)</th>
<th>Moles PO(_4^{3-}) per eq ion exchanger (N_L)</th>
<th>z</th>
<th>a</th>
<th>y</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.85</td>
<td>2.387</td>
<td>0.034</td>
<td>0.67</td>
<td>1.39</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>-1.8</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>2.387</td>
<td>0.040</td>
<td>0.63</td>
<td>1.51</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>-1.5</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>2.391</td>
<td>0.042</td>
<td>0.61</td>
<td>1.55</td>
<td>2</td>
</tr>
<tr>
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<td>3</td>
<td>-1.3</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>2.389</td>
<td>0.048</td>
<td>0.59</td>
<td>1.6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>3</td>
<td>-1.77</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.389</td>
<td>0.053</td>
<td>0.57</td>
<td>1.66</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>-1.34</td>
</tr>
<tr>
<td></td>
<td>(b)</td>
<td>0.95</td>
<td>2.379</td>
<td>0.040</td>
<td>0.77</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>3.5+</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>2.381</td>
<td>0.050</td>
<td>0.75</td>
<td>1.59</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>3.6+</td>
</tr>
</tbody>
</table>

*Resin samples washed with water (150mls.).

* Positive complex.
### Table 9. Anion Exchange Titanium(III) Orthophosphate System

<table>
<thead>
<tr>
<th>( \text{pH} )</th>
<th>Capacity of exchanger m. eq/g.</th>
<th>Moles Ti(III) per eq. ion exchanger ( N_M )</th>
<th>Moles PO(_4) per eq. ion exchanger ( N_L )</th>
<th>( z )</th>
<th>( a )</th>
<th>( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.805</td>
<td>3.221</td>
<td>0.143</td>
<td>1.02</td>
<td>1.3</td>
<td>2</td>
<td>2.7</td>
</tr>
<tr>
<td>0.72</td>
<td>3.222</td>
<td>0.146</td>
<td>1.18</td>
<td>1.22</td>
<td>2</td>
<td>3.6(^k)</td>
</tr>
<tr>
<td></td>
<td>3.223</td>
<td>0.146</td>
<td>1.18</td>
<td>2</td>
<td>3.6(^k)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.270</td>
<td>0.122</td>
<td>1.13</td>
<td>1.15</td>
<td>2</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>5.1</td>
<td></td>
</tr>
</tbody>
</table>

\( k \) Positive complex.

### Table 10. Anion Exchange Aluminium Orthophosphate System

<table>
<thead>
<tr>
<th>( \text{pH} )</th>
<th>Capacity of exchanger m. eq/g.</th>
<th>Moles Al per eq. ion exchanger ( N_M )</th>
<th>Moles PO(_4) per eq. ion exchanger ( N_L )</th>
<th>( z )</th>
<th>( a )</th>
<th>( y )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28</td>
<td>3.294</td>
<td>0.021</td>
<td>0.76</td>
<td>1.36</td>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>3.294</td>
<td>0.021</td>
<td>0.76</td>
<td>1.36</td>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>1.1</td>
<td>3.296</td>
<td>0.026</td>
<td>0.78</td>
<td>1.33</td>
<td>2</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>3.293</td>
<td>0.026</td>
<td>0.78</td>
<td>1.33</td>
<td>2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
IV.1.5. Discussion

Cation Exchange

Phosphate was either not absorbed or absorbed to a very slight extent by the cation exchanger in the cation exchange experiments with the aluminium, iron(III) and titanium(III) orthophosphate systems. This indicates that no cationic complexes were formed in solution, and these results agree with the findings of Jameson and Salmon (13) and confirm those of Genge and Salmon (18).

Anion Exchange

\[ K_1 \text{ for orthophosphoric acid is } 7.59 \times 10^{-3}; \ K_2 \text{ is } 7.99 \times 10^{-8} \text{ and } K_3 \text{ is } 5.01 \times 10^{-13} \text{ (27).} \]  

Over the pH range investigated in these experiments, \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) may be considered as the only orthophosphate ions present in solution. This is borne out by the value of 'z' (the average charge on the ions sorbed by the ion-exchanger in the control experiment). This varied from 1.16 to 1.36, i.e. a mixture of \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \) was sorbed.

Only anionic complexes are being dealt with, thus the value of 'a' cannot equal one, as with a trivalent metal this can only give a neutral or positive complex.
Aluminium, iron and titanium were sorbed by the anion exchanger, thus all these metal ions formed anionic orthophosphate complexes.

IV.1.5.1. Aluminium Orthophosphate System

From the results displayed in Table 7 the following complexes may be present in solution at pH 1.28:

\[ \text{Al}H_{1.7}(\text{PO}_4)_{2.3}^- \quad \text{or} \quad \text{Al}H_{3.3}(\text{PO}_4)_{2.7}^- \]

and at pH 1.1

\[ \text{Al}H_{1.8}(\text{PO}_4)_{2.2}^- \quad \text{or} \quad \text{Al}H_{3.5}(\text{PO}_4)_{2.5}^- \]

The 3:1 complexes are more likely to be present in solution since

(a) the aluminium concentration on the resin is small indicating that complexes with a high charge are most likely, since the resin capacity, that is, the available exchange sites, are then fully occupied with minimum metal. The 3:1 complexes have higher charge than the 2:1 complexes.

(b) the 2:1 complexes would involve the \( \text{PO}_4^{3-} \) ion in the complex and, as discussed earlier, the only ions likely to be present under these conditions are \( \text{H}_2\text{PO}_4^- \) and \( \text{HPO}_4^{2-} \).
(c) both the iron(III) and titanium(III) complexes are of the form ML₃.

Thus, though both the 2:1 and the 3:1 complex ions give a similar value for the percentage capacity of the exchanger occupied 100%, the complexes present in solution are a mixture of Al(HPO₄)₃⁻ and Al(H₂PO₄)(HPO₄)₂⁻ at pH 1.1 and pH 1.28.

IV.1.5.2. Titanium(III) Orthophosphate System

The results, Table 9, suggest that the complexes formed at pH 0.805 are either

\[ \text{TiH}_{2.7}(\text{PO}_4)_{2}^{3-} \] or \[ \text{TiH}_{4.4}(\text{PO}_4)_{1.6}^{-} \]

and the complex formed at pH 0.72 is

\[ \text{TiH}_{5.3}(\text{PO}_4)_{0.7}^{-} \]

Since only a 3:1 complex is formed at the lower pH the complex present in solution is the one shown. At the higher pH the 3:1 complex is probably present as

(a) the charge on the 2:1 complex is smaller than on the 3:1 species at pH 0.72 and if the 2:1 complex was formed, more titanium(III) would be sorbed at the higher pH than at the lower. This is not so.
(b) the 3:1 complex at the lower pH has a higher charge than the 2:1 complex at the higher pH. It is unlikely the negative charge of an ion would increase as the hydrogen ion concentration of the solution increased. The 3:1 complex at the higher pH has a larger negative charge than the complex present at the lower pH.

Thus the complexes formed are:

at pH 0.305, \[ TiH_{4.4}(PO_4)^{1.6-} \], a mixture of

\[ [Ti(H_2PO_4^-)(HPO_4^{2-})_2^-] \text{ and } [Ti(H_2PO_4^-)_2(HPO_4^{2-})] \]

and at pH 0.72, \[ TiH_{5.3}(PO_4)^{0.7-} \], a mixture of

\[ [Ti(H_2PO_4^-)_2(HPO_4^{2-})]^- \text{ and } [Ti(H_2PO_4^-)(HPO_4^{3-})_2]^- \]

IV.1.5.3. Iron(III) Orthophosphate System

The results shown in Table 8 suggest that over a wide range of pH the complex formed is \[ Fe(PO_4)_3^{6-} \]. However, the concentration of PO_4^{3-} ion in orthophosphoric acid solution at this pH is very small, it is thus unlikely that this complex is sorbed from solution. In order to free the resin washings of orthophosphoric acid, it was necessary to wash with a large volume of water.
This would suggest that breakdown of the complex occurred on the resin from FeH$_x$(PO$_4$)$_3$$_{(6-x)}^-$ to Fe(PO$_4$)$_3^-$. 

\[ R(6-x)[FeH_x(PO_4)_3] + RH_2PO_4 \rightarrow R_0Fe(PO_4)_3 + 2H_3PO_4 \]

Whilst similar extended washing of the ion exchanger in the control experiment would give:

\[ 2R H_2PO_4 \xrightarrow{H_2O} R_0HPO_4 + H_3PO_4 \]

Where R represents an exchange site on the anion exchanger.

This partial breakdown of the complex is verified by there being no trend discernable in the complex sorbed with change in hydrogen ion concentration of the solution. Thus the complex sorbed on the resin is likely to be a 3:1 complex, i.e. Fe H$_x$(PO$_4$)$_3$$_{(6-x)}^-$. 

The results shown in Table 3(b), where the resin was only washed with a small amount of water, suggest that the complex predominating in solution at pH 0.95 and 1.1, is [Fe H$_2$(PO$_4$)$_3$]$. The 2:1 complexes at these pH's would have to be cationic to satisfy the results and so only the 3:1 complex is formed. The complex formed is [Fe(H$_2$PO$_4$)$_2$(HPO$_4$)$^2-$].
IV.2. DETERMINATION OF THE STABILITY CONSTANTS
OF THE COMPLEX SPECIES

The complexing of iron, titanium and aluminium with orthophosphoric acid has been shown to occur forming anionic species by anion exchange experiments (Section IV.1.). The measurement of the stability constants of iron and titanium orthophosphate complexes is described in this section. Attempts were made to measure the stability constant of the aluminium orthophosphate complexes, but these failed due to the difficulties in obtaining accurate analysis of trace quantities of aluminium in solution in the presence of a large excess of orthophosphate. The eriochrome cyanine R colorimetric method (51) is completely ruined, by large excess of orthophosphate ion and consistent results could not be obtained. No suitable radio isotope is available (52). Further attempts to measure the aluminium concentration on the resin directly failed because on washing the resin with water, a varying proportion of the tracer concentration of aluminium bound to the exchanger was removed leading to inconsistent results.
IV.2.1. Determination of the Stability Constants of Iron(III) Orthophosphate System

(a) Batch Experiments
(b) Results and Calculations

(a) Batch Experiments

A solution of orthophosphoric acid in dilute perchloric acid of known ionic strength, pH and concentration of orthophosphoric acid, was prepared. Also a blank solution of the same ionic strength and pH but containing no orthophosphoric acid was made up. The batch sample of cation exchanger, hydrogen form Zeo Karb 225, was conditioned and generated as described in Section III.2.1. It was stirred with an excess of blank solution to ensure constant ionic strength was maintained throughout the batch experiment. The resin was separated from the solution; washed and air dried. Various aliquots of the orthophosphate solution were added, by burette, to a clean and dry 50ml. conical flask containing hydrogen form Zeo Karb 225 resin (0.5g.). Ferric perchlorate solution (1ml.), prepared as described in Section IV.1(b).(ii), containing
a known amount of iron, was added by pipette. Sufficient blank solution was added from a burette to give a final volume of 50ml. In this way a series of solutions of constant ionic strength and pH but varying in orthophosphate concentration was prepared. The flasks were stoppered with wired-down rubber bungs and were shaken on a mechanical shaker for at least four hours. Previous experiments had shown that equilibrium was reached in this time. The equilibrated solution was drawn off with a pipette and analysed spectrophotometrically for iron using bathophenanthroline. The pH was checked, but no change was found.

The value of the swelling factor 'd' (Section II.1.2.) was determined by equilibrating N/10 hydrochloric acid (25ml.) with the cation exchange resin (0.5g.) and measuring the final pH of the solution. It was found that 'd' was always greater than 0.995 and hence its value was taken to be unity in all calculations.

In order to vary the ionic strength of the solutions, sodium perchlorate was added to the orthophosphate and blank solutions. The sodium perchlorate was twice recrystallised: B.D.H. "low in chloride" sodium perchlorate
(160g.) was dissolved in hot water (40ml.) and filtered hot. The solution was allowed to cool to ca. 30°C and seeded with sodium perchlorate monohydrate. Sodium perchlorate crystallised out and was filtered off. These crystals were dissolved in hot water (20ml.), boiled and filtered hot. The filtered solution was carefully evaporated until crystallisation just started; cooled to room temperature; the crystals filtered off and washed with a little cold water. The yield was poor (ca 30g.). A sample was dissolved in water and checked with a pH meter for the presence of alkali. The crystals were stored in a desiccator and were dried for twelve hours at 110°C before use to ensure a salt of constant composition. All experiments were carried out at room temperature 21° ± 2°.

(b) Results and Calculations

Equation 20. (Section II.1.2(a)) becomes

\[ \Delta = \Delta_0 \left\{ 1 + \beta \left( \frac{C}{x} \right)^2 \left( \frac{k_2}{[H^+]} \right) \right\} \]

i.e.

\[ \Delta = \Delta_0 \left\{ 1 + \beta \frac{k_2}{\alpha^3 f_2 [H^+]^3} \right\} \]
By comparison with equation 21 (Section II.1.2(a))

\[ A = \frac{k_{2} \beta_{1}}{\alpha f_{2}[H^+]^{2}} = \gamma \beta_{1} \]

\[ \beta_{1} \text{ is the stability constant for the reaction,} \]

\[ \text{Fe}^{3+} + 2[H_{2}PO_{4}^{-}] + [HPO_{4}^{2-}] \rightleftharpoons [\text{Fe}(H_{2}PO_{4})_{2}(HPO_{4}^{2-})]^{-} \]

\[ \alpha \text{ may be calculated by means of equation 9a (Section II.1.2(a))}. \]

\[ \alpha = \left\{ \frac{[H^{+}]f_{2}^{2}}{k_{1}} + 1 + \frac{k_{2}}{[H^{+}]f_{2}} \right\} \]

\[ f_{2} \text{ may be calculated by the Davies Equation.} \]

The technique of least squares is applied to the results obtained and the value of A may be evaluated and hence, \( \beta_{1} \). C in equation 20 (Section II.1.2(a) refers to the concentration of free orthophosphate. Since the concentration of the metal, in solution, was small the total concentration of orthophosphate was taken as the concentration of free orthophosphate. The results are given in Tables 10 to 14.
Table 11.

<table>
<thead>
<tr>
<th>$\Delta \times 10^{-3}$</th>
<th>$C \times 10^{-2} M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.29</td>
<td>1.25</td>
</tr>
<tr>
<td>5.38</td>
<td>2.50</td>
</tr>
<tr>
<td>6.13</td>
<td>3.75</td>
</tr>
<tr>
<td>7.68</td>
<td>5.00</td>
</tr>
<tr>
<td>10.05</td>
<td>6.125</td>
</tr>
</tbody>
</table>

$pH = 1.0$, $I = 0.132$ Initial iron concentration $= 1.254 \times 10^{-4} M$

Volume of solution $= 50ml$. Mass of exchanger $= 0.5g$.

$\Delta o = 5.0 \times 10^{-3}$, $(\Delta - \Delta o)C^3 = 1.56 \times 10^{-8}$, $\Delta o \ C^6 = 3.57 \times 10^{-12}$,

$k_1 = 0.755 \quad k_2 = 0.57 \quad k_1 = 7.85 \times 10^{-3}$

$k_2 = 7.99 \times 10^{-8} [H^+] = 0.132$,

Hence $A = 4.37 \times 10^3$ \Rightarrow $\log \beta_1 = 12.66$.

The values of $\Delta$ obtained, using this value of $A$, plotted against corresponding values of $C$ are shown, along with the experimental points obtained, over the page.
Table 12.

<table>
<thead>
<tr>
<th>$\Delta \times 10^{-3}$</th>
<th>$C \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.92</td>
<td>1.25</td>
</tr>
<tr>
<td>5.55</td>
<td>2.50</td>
</tr>
<tr>
<td>7.55</td>
<td>3.75</td>
</tr>
<tr>
<td>9.6</td>
<td>5.00</td>
</tr>
<tr>
<td>10.6</td>
<td>6.125</td>
</tr>
</tbody>
</table>

$pH = 1.0$, $I = 0.14$, Initial iron concentration = $1.254 \times 10^{-4}$ M.
Volume of solution = 50ml. Mass of exchanger = 0.5g.

$\Delta_0 = 4.9 \times 10^{-3}$, $(\Delta - \Delta_0)C^3 = 2.048 \times 10^{-8}$, $\Delta_0 C^6 = 3.43 \times 10^{-12}$.

$f_1 = 0.751$, $f_2 = 0.564$, $k_1 = 7.35 \times 10^{-3}$.

$k_2 = 7.99 \times 10^{-8}$, $[H^+] = 0.132$, $Y = 9.79 \times 10^{-10}$

Hence $A = 5.972 \times 10^3$ \(\Delta\) Log $\beta_1 = 12.79$.

The values of $\Delta$, obtained by using this value of $A$ plotted against corresponding values of $C$, are shown in Fig. (8) overleaf, with the experimental points.
pH = 1.0, I = 0.15, Initial iron concentration = 1.25 x 10^{-4} M
Volume of solution = 50 ml, Mass of exchanger = 0.5 g.
Δo = 4.0 x 10^{-3}, (Δ-Δo)C^3 = 1.379 x 10^{-8}, Δo C^6 = 2.787 x 10^{-12}.
f_1 = 0.73, f_2 = 0.532, k_1 = 7.83 x 10^{-3}
k_2 = 7.99 x 10^{-8}, [H^+] = 0.132, Y = 1.152 x 10^{-9}.

Hence A = 4.948 x 10^3 . . . Log β_1 = 12.63

The values of Δ, obtained by using this value of A plotted against corresponding values of C, are shown in Fig. (9) overleaf, with the experimental points.
Table 14.

<table>
<thead>
<tr>
<th>$\Delta$</th>
<th>$C \times 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.64</td>
<td>1.25</td>
</tr>
<tr>
<td>6.36</td>
<td>2.50</td>
</tr>
<tr>
<td>6.92</td>
<td>3.75</td>
</tr>
<tr>
<td>8.0</td>
<td>5.00</td>
</tr>
<tr>
<td>10.83</td>
<td>6.125</td>
</tr>
</tbody>
</table>

$\text{pH} = 1.1$, $I = 1.1$, Initial ion concentration = $1.25 \times 10^{-4} \text{M}$.

Volume of solution = 50.0 ml., Mass of exchanger = 0.5 g.

$\Delta_0 = 5.0 \times 10^{-3}$, $(\Delta - \Delta_0)C^3 = 1.838 \times 10^{-8}$, $\Delta_0 C^6 = 3.573 \times 10^{-12}$

$f_1 = 0.766$, $f_2 = 0.588$, $\kappa_1 = 7.85 \times 10^{-8}$

$k_2 = 7.99 \times 10^{-8}$, $[\text{H}^+] = 0.103$, $Y = 2 \times 10^{-9}$.

Hence $A = 5.145 \times 10^3$, $\therefore \log \beta_1 = 12.41$.

The experimental values of $\Delta$ plotted against $C$ are shown overleaf in Fig. (10). The line represents the plot of calculated value of $\Delta$ using the value of $A$ above against $C$. 
IV.2.2. Determination of the Stability Constants of the Titanium(III) Orthophosphate System

(a) Batch Experiments

(b) Results and Calculations

(a) Batch Experiments

A series of solutions of known orthophosphate concentration and pH such that when an aliquot (45ml.) was mixed with a stock solution of titanium(III) orthophosphate (5ml.), the resulting solution had a pH of 0.805. The titanium(III) and orthophosphate concentrations of the stock solution were known. All pH measurements were made on a Pye Dyna-Cap pH Meter. The batch sample of hydrogen form cation exchanger, Zeo Kerb 225, was conditioned and generated as described in Section III.2.1. The resin was air dried. Then an aliquot (45ml.) of orthophosphate solution was run into the vessel shown in Fig. 6. Hydrogen form cation exchanger (2g.) was added to the solution through the part J. The vessel was weighed. The solution was deoxygenated as described in Section IV.1.3. then reweighed. The part J was opened
and nitrogen allowed to flow through the vessel, over the solution and out of port J. An aliquot (5ml.) of the stock titanium(III) orthophosphate solution, which was stored under nitrogen, was pipetted into the vessel. Port J was closed; the vessel weighed, deoxygenated and reweighed. All the titanium(III) solutions were similarly made up. The vessels were shaken on a mechanical shaker for four hours, this being greater the time taken for equilibrium to be reached, as shown by previous experiments. The experiments were carried out at room temperature = 21° ± 2°C. The port J was opened. An aliquot of solution was removed by pipette and analysed for titanium using the hydrogen peroxide method, spectrophotometrically. The final pH of the solution was checked, but no change was noted. As in the case of iron(III) the value of 'd' was always greater than 0.995 and so was assumed to be unity throughout the calculations.

(b) Results and Calculations

In this case, equation 35 (Section II.1.2(b)) becomes:

$$\Delta = \Delta_0 (1 + \beta_2 k_1^2 a + \beta_j k_1 a^2)$$
Thus by comparison with equation 37 (Section II.1.2(b))

\[ D = k_1^2 \beta_2, \quad E = k_1 \beta_3. \]

\( \beta_2 \) is the stability constant for the reaction:

\[ \text{Ti}^{3+} + 2(\text{HPO}_4^{2-}) + (\text{H}_2\text{PO}_4^-)\rightleftharpoons [\text{Ti}^{3+}(\text{H}_2\text{PO}_4^-)(\text{HPO}_4^{2-})]^{2-} \]

\( \beta_3 \) is the stability constant for the reaction:

\[ \text{Ti}^{3+} + 2(\text{H}_2\text{PO}_4^-) + (\text{HPO}_4^-)\rightleftharpoons [\text{Ti}^{3+}(\text{H}_2\text{PO}_4^-)_2(\text{HPO}_4^{2-})]^{-} \]

As outlined, in Section II.2.1(b), the method of least squares is applied to the results obtained and values for \( D \) and \( E \) calculated. The large concentration of orthophosphoric acid acts a buffer solution and so keeps the activities of the singly and doubly charged ions constant. The effect of the small quantities of titanium(III) on the final activity of dihydrogen and monohydrogen orthophosphate ions was negligible. Thus the activity of the ions in solution was taken to be the activity from calculations based on the value of the total orthophosphate concentration. The results obtained and the calculation of \( D \) and \( E \) are shown in Table 15.
It was found that $\Delta_0 = 0.111$ gave the best fit to experimental points. $p_H = 0.805$, volume of solution = 50ml. Mass of exchanger = 2.0g. Initial titanium(III) concentration = $3.82 \times 10^{-3}$ molar.

The experiment was carried out at room temperature ($21^\circ + 2^\circ C$).

$\Delta_0 \sum \alpha^2 = 0.01919$, $\Delta_0 \sum \alpha^3 = 0.003635$, $\Delta_0 \sum \alpha^4 = 0.000697$,

$\sum \alpha (\Delta - \Delta_0) = 0.575389$, $\sum \alpha^2 (\Delta - \Delta_0) = 0.110233$.

Hence Equations 43, 44 (Section 11.1.2(b)) become

$0.575389 = 0.01919D + 0.003635E$

$0.110233 = 0.003635D + 0.000697E$

Hence $D = 1.38$ $\therefore \log_{10} \beta = 14.3$

$E = 150.98$ $\therefore \log_{10} \beta = 9.3$
Fig. (11) shows the experimental points and the curve obtained using a series of values of $\Delta$ calculated from equation 37 (section II.1.2b) using $D$ and $E$. 
IV.3. SPECTROPHOTOMETRIC EXPERIMENTS

IV.3.1. Experimental

IV.3.2. Results

IV.3.3. Discussion

IV.3.1.(i) Iron(III) Orthophosphate System

A solution of known concentrations of orthophosphate and iron at a known pH was made up by mixing iron(III) perchlorate solution with orthophosphoric acid. The optical density of this solution and also of separate iron perchlorate solution and orthophosphoric acid were measured on a Unicam SP800 spectrophotometer over both the visible and ultra violet ranges in a 1 cm. silica cell against a blank of pure water. The system was not studied in detail since the spectra of the iron(III) ion is very sensitive to small changes in pH. The results obtained are shown in Table 16 and Fig.(13).

IV.3.1.(ii) Titanium(III) Orthophosphate System

The simple method above, used for iron(III), could not be used in this case as it was not possible to prepare
Table 16.

pH solution = 1.0, iron(III) concentration = 1.0x10^{-5} M, orthophosphate concentration = 0.1

<table>
<thead>
<tr>
<th>Wavelength ( \lambda )</th>
<th>Optical density iron(III) perchlorate solution</th>
<th>Optical density iron(III) orthophosphate solution</th>
<th>&quot;Theoretical&quot; iron(III) orthophosphate solution optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>315</td>
<td>0.021</td>
<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>310</td>
<td>0.028</td>
<td>0</td>
<td>0.014</td>
</tr>
<tr>
<td>305</td>
<td>0.042</td>
<td>0</td>
<td>0.021</td>
</tr>
<tr>
<td>300</td>
<td>0.060</td>
<td>0</td>
<td>0.030</td>
</tr>
<tr>
<td>295</td>
<td>0.085</td>
<td>0.022</td>
<td>0.042</td>
</tr>
<tr>
<td>290</td>
<td>0.110</td>
<td>0.051</td>
<td>0.055</td>
</tr>
<tr>
<td>285</td>
<td>0.142</td>
<td>0.092</td>
<td>0.071</td>
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<tr>
<td>280</td>
<td>0.180</td>
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<td>0.090</td>
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<tr>
<td>275</td>
<td>0.223</td>
<td>0.260</td>
<td>0.112</td>
</tr>
<tr>
<td>270</td>
<td>0.259</td>
<td>0.379</td>
<td>0.130</td>
</tr>
<tr>
<td>265</td>
<td>0.299</td>
<td>0.505</td>
<td>0.150</td>
</tr>
<tr>
<td>260</td>
<td>0.341</td>
<td>0.650</td>
<td>0.170</td>
</tr>
<tr>
<td>255</td>
<td>0.382</td>
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</tr>
<tr>
<td>250</td>
<td>0.442</td>
<td>0.870</td>
<td>0.220</td>
</tr>
<tr>
<td>245</td>
<td>0.475</td>
<td>0.920</td>
<td>0.238</td>
</tr>
<tr>
<td>240</td>
<td>0.540</td>
<td>0.940</td>
<td>0.270</td>
</tr>
<tr>
<td>235</td>
<td>0.580</td>
<td>0.950</td>
<td>0.290</td>
</tr>
<tr>
<td>230</td>
<td>0.620</td>
<td>0.850</td>
<td>0.310</td>
</tr>
<tr>
<td>225</td>
<td>0.680</td>
<td>0.785</td>
<td>0.340</td>
</tr>
<tr>
<td>220</td>
<td>0.710</td>
<td>0.740</td>
<td>0.350</td>
</tr>
<tr>
<td>215</td>
<td>0.740</td>
<td>0.720</td>
<td>0.370</td>
</tr>
<tr>
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<td>0.760</td>
<td>0.740</td>
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<tr>
<td>205</td>
<td>0.740</td>
<td>0.770</td>
<td>0.370</td>
</tr>
<tr>
<td>200</td>
<td>0.700</td>
<td>0.790</td>
<td>0.350</td>
</tr>
</tbody>
</table>

* Theoretical iron orthophosphate curve plotted by calculating mean of sum of optical density of iron perchlorate and orthophosphoric acid. Fig. 13. Curve 1 shows iron(III) orthophosphate plot; Curve 2 shows iron(III) perchlorate plot; Curve 3 shows theoretical iron(III) orthophosphate plot.
a stable titanium(III) perchlorate solution (Section III.1.3.).

In order to compare the effect of orthophosphate complexing on the spectra of the hexaquo titanium ion, a blank run was carried out on titanium(III) chloride solution. A series of solutions of titanium(III) orthophosphate (at the same concentration as the titanium(III) chloride solution), and orthophosphoric acid at a known pH were made up and their optical densities measured, over both visible and ultra violet ranges, in 1cm. silica cells. The entire procedure had to be carried out under nitrogen using the apparatus shown in Fig. 12: Taps F, G, I, J were opened and the system evacuated. Tap F was closed and tap E opened. The vessel was flooded with pure nitrogen. Tap E was closed; tap F opened and the process repeated. Tap I was closed. Known volumes of titanium(III) orthophosphate (stored under nitrogen), deoxygenated orthophosphoric acid and water, to give a solution of known pH, titanium and orthophosphate concentration, were introduced by pipette through port I while pure nitrogen was flowing through the apparatus. Tap G was closed. The vessel was quickly detached and weighed; shaken to mix the solutions
and deoxygenated by alternate evacuation and passage of nitrogen. The vessel was weighed again to ensure that no significant change in the volume of solution and hence pH and concentration occurred. Tap I was opened and the vessel shaken to transfer solution into the cell. When the cell was full, taps I and J were closed and the apparatus opened at joint 2. The optical density of the solution could then be determined using the Unicam SP500 spectrophotometer.

The results obtained are shown in Tables 17 and 18 and Figs. 14 and 15.

IV.3.3. Discussion

If Fig. 13 is considered: Curve 2 shows the ultra violet absorption spectrum of iron(III) perchlorate at pH 1.0; curve 1 shows the ultra violet absorption spectrum of a mixture of iron(III) perchlorate and orthophosphoric acid. Curve 3 is the plot of the theoretical absorption spectrum of a 1:1 mixture calculated from the mean of the curves for iron(III) perchlorate and orthophosphoric acid. The absorption of orthophosphoric
Table 17.
Titanium concentration = 0.04M, pH = 0.8,
Orthophosphoric acid concentration = 1.7M.

<table>
<thead>
<tr>
<th>Wavelength $\lambda$ ($\mu$m)</th>
<th>Optical density</th>
<th>Optical density</th>
<th>Wavelength $\lambda$ ($\mu$m)</th>
<th>Optical density</th>
<th>Optical density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>titanium(III)</td>
<td>orthophosphate</td>
<td></td>
<td>titanium(III)</td>
<td>chlorides</td>
</tr>
<tr>
<td>400</td>
<td>0.485</td>
<td>0.025</td>
<td>630</td>
<td>0.317</td>
<td>0.058</td>
</tr>
<tr>
<td>410</td>
<td>0.511</td>
<td>0.036</td>
<td>640</td>
<td>0.280</td>
<td>0.042</td>
</tr>
<tr>
<td>420</td>
<td>0.594</td>
<td>0.051</td>
<td>650</td>
<td>0.254</td>
<td>0.040</td>
</tr>
<tr>
<td>430</td>
<td>0.580</td>
<td>0.060</td>
<td>660</td>
<td>0.221</td>
<td>0.033</td>
</tr>
<tr>
<td>440</td>
<td>0.640</td>
<td>0.072</td>
<td>670</td>
<td>0.203</td>
<td>0.019</td>
</tr>
<tr>
<td>450</td>
<td>0.685</td>
<td>0.091</td>
<td>680</td>
<td>0.182</td>
<td>0.010</td>
</tr>
<tr>
<td>460</td>
<td>0.705</td>
<td>0.110</td>
<td>690</td>
<td>0.161</td>
<td>0.00</td>
</tr>
<tr>
<td>470</td>
<td>0.708</td>
<td>0.131</td>
<td>700</td>
<td>0.134</td>
<td>-</td>
</tr>
<tr>
<td>480</td>
<td>0.703</td>
<td>0.142</td>
<td>710</td>
<td>0.120</td>
<td>-</td>
</tr>
<tr>
<td>490</td>
<td>0.700</td>
<td>0.159</td>
<td>720</td>
<td>0.105</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td>0.683</td>
<td>0.161</td>
<td>730</td>
<td>0.097</td>
<td>-</td>
</tr>
<tr>
<td>510</td>
<td>0.680</td>
<td>0.159</td>
<td>740</td>
<td>0.082</td>
<td>-</td>
</tr>
<tr>
<td>520</td>
<td>0.660</td>
<td>0.158</td>
<td>750</td>
<td>0.080</td>
<td>-</td>
</tr>
<tr>
<td>530</td>
<td>0.642</td>
<td>0.149</td>
<td>760</td>
<td>0.071</td>
<td>-</td>
</tr>
<tr>
<td>540</td>
<td>0.621</td>
<td>0.142</td>
<td>770</td>
<td>0.060</td>
<td>-</td>
</tr>
<tr>
<td>550</td>
<td>0.589</td>
<td>0.139</td>
<td>780</td>
<td>0.042</td>
<td>-</td>
</tr>
<tr>
<td>560</td>
<td>0.560</td>
<td>0.132</td>
<td>790</td>
<td>0.038</td>
<td>-</td>
</tr>
<tr>
<td>570</td>
<td>0.545</td>
<td>0.124</td>
<td>800</td>
<td>0.020</td>
<td>-</td>
</tr>
<tr>
<td>580</td>
<td>0.490</td>
<td>0.118</td>
<td>810</td>
<td>0.015</td>
<td>-</td>
</tr>
<tr>
<td>590</td>
<td>0.454</td>
<td>0.104</td>
<td>820</td>
<td>0.008</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>0.419</td>
<td>0.090</td>
<td>830</td>
<td>0.000</td>
<td>-</td>
</tr>
<tr>
<td>610</td>
<td>0.380</td>
<td>0.083</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>620</td>
<td>0.351</td>
<td>0.065</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 14: Curve 1 shows the titanium(III) chloride plot
Curve 2 shows the titanium(III) orthophosphate plot.
Titanium concentration = $1.1 \times 10^{-3}$ M, pH = 0.8
Orthophosphoric acid concentration = 1.3 M.

<table>
<thead>
<tr>
<th>Wavelength $\lambda$ (nm)</th>
<th>Optical density titanium(III) orthophosphate</th>
<th>Optical density titanium (III) chloride</th>
<th>Optical density orthophosphoric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.98</td>
<td>0.715</td>
<td>0.442</td>
</tr>
<tr>
<td>205</td>
<td>1.03</td>
<td>0.450</td>
<td>0.410</td>
</tr>
<tr>
<td>210</td>
<td>1.07</td>
<td>0.312</td>
<td>0.372</td>
</tr>
<tr>
<td>215</td>
<td>1.09</td>
<td>0.209</td>
<td>0.330</td>
</tr>
<tr>
<td>220</td>
<td>1.085</td>
<td>0.140</td>
<td>0.300</td>
</tr>
<tr>
<td>225</td>
<td>1.06</td>
<td>0.100</td>
<td>0.278</td>
</tr>
<tr>
<td>230</td>
<td>0.99</td>
<td>0.063</td>
<td>0.260</td>
</tr>
<tr>
<td>235</td>
<td>0.91</td>
<td>0.038</td>
<td>0.254</td>
</tr>
<tr>
<td>240</td>
<td>0.805</td>
<td>0.018</td>
<td>0.250</td>
</tr>
<tr>
<td>245</td>
<td>0.707</td>
<td>0.0</td>
<td>0.250</td>
</tr>
<tr>
<td>250</td>
<td>0.630</td>
<td>-</td>
<td>0.250</td>
</tr>
<tr>
<td>255</td>
<td>0.560</td>
<td>-</td>
<td>0.248</td>
</tr>
<tr>
<td>260</td>
<td>0.502</td>
<td>-</td>
<td>0.240</td>
</tr>
<tr>
<td>265</td>
<td>0.453</td>
<td>-</td>
<td>0.226</td>
</tr>
<tr>
<td>270</td>
<td>0.402</td>
<td>-</td>
<td>0.210</td>
</tr>
<tr>
<td>275</td>
<td>0.356</td>
<td>-</td>
<td>0.181</td>
</tr>
<tr>
<td>280</td>
<td>0.310</td>
<td>-</td>
<td>0.172</td>
</tr>
<tr>
<td>285</td>
<td>0.260</td>
<td>-</td>
<td>0.139</td>
</tr>
<tr>
<td>290</td>
<td>0.204</td>
<td>-</td>
<td>0.119</td>
</tr>
<tr>
<td>295</td>
<td>0.160</td>
<td>-</td>
<td>0.099</td>
</tr>
<tr>
<td>300</td>
<td>0.112</td>
<td>-</td>
<td>0.020</td>
</tr>
<tr>
<td>305</td>
<td>0.083</td>
<td>-</td>
<td>0.060</td>
</tr>
<tr>
<td>310</td>
<td>0.063</td>
<td>-</td>
<td>0.042</td>
</tr>
<tr>
<td>315</td>
<td>0.050</td>
<td>-</td>
<td>0.038</td>
</tr>
<tr>
<td>320</td>
<td>0.045</td>
<td>-</td>
<td>0.012</td>
</tr>
<tr>
<td>325</td>
<td>0.030</td>
<td>-</td>
<td>0.010</td>
</tr>
<tr>
<td>330</td>
<td>0.020</td>
<td>-</td>
<td>0.008</td>
</tr>
<tr>
<td>335</td>
<td>0.010</td>
<td>-</td>
<td>0.0</td>
</tr>
<tr>
<td>340</td>
<td>0.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 15. Curve 1 shows the titanium(III) orthophosphate plot.
Curve 2 shows the orthophosphoric acid plot.
Curve 3 shows the titanium(III) chloride plot.
acid was negligible and was assumed to be zero. The theoretical curve lies below curve 2. The actual curve lies above the iron(III) perchlorate spectrum, i.e. it has a higher optical density over most of the range covered and has a broad peak at 242m\(\mu\), whereas the peak in the iron(III) perchlorate spectrum is at 210m\(\mu\). This may be taken as evidence for the complexing of iron(III) by orthophosphoric acid at pH 1.0.

If the titanium(III) ion is considered, the single d electron will occupy a \(t_{2g}\) orbital. On irradiation with light of frequency \(\nu\), where

\[
\nu = \frac{\Delta}{h}, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 1.
\]

\(\Delta\) is the energy difference between \(t_{2g}\) and \(e_g\) levels.

\(h\) is Planck's Constant.

It is possible that the ion can absorb a quantum of radiant energy and convert it into energy of excitation of the electron from the \(t_{2g}\) and \(e_g\) orbitals. In the case of the hexaquotitanium(III) ion, the absorption band due to this process is in the visible spectrum and is the cause of the
violet colour of titanium(III) chloride solutions. This absorption peak is shown at 500μ in Fig. 14. The spectrum of titanium(III) orthophosphate solution shows a much larger absorption of energy and the maximum of the spectrum is at 495μ in a broader peak. The colour of titanium(III) orthophosphate solutions is purple-brown. Again these results would suggest that complexing was occurring and water molecules were being replaced as ligands by orthophosphate ions.

For [Ti(H₂O)₆]³⁺ ions

Let \( \nu_1 = \frac{\Delta_1}{h} \)

For titanium(III)-orthophosphate complex

Let \( \nu_2 = \frac{\Delta_2}{h} \)

\( \nu \propto \frac{1}{\lambda} \)

\( \lambda \) is the wavelength associated with light frequency

\( \therefore \) since, by observation, \( \lambda_1 < \lambda_2 \)

\( \nu_1 > \nu_2 \)
i.e. the splitting energy of titanium(III) orthophosphate complexes is greater than that of the hexaquotitanium(III) ion. This is to be expected on a purely electrostatic model as the charged orthophosphate ions will have a greater electron repulsion effect than the uncharged water molecules, causing a greater splitting between the $t_{2g}$ and $e_g$ levels.

In Fig. 15 it will be seen that the "theoretical" spectrum for titanium(III) orthophosphate calculated from the curves of the hexaquotitanium(III) ion (curve 3) and orthophosphoric acid (curve 2) would lie beneath curve 2 for most of its range and slightly above it for the range $210 \mu \text{m} \rightarrow 200 \mu \text{m}$. The actual spectrum (curve 3) has a peak at $225 \mu \text{m}$ and a higher absorbance over all the range. This is evidence for the complexing of titanium(III) ions by orthophosphoric acid.
IV.4. DISCUSSION

The results obtained for the tervalent iron, tervalent titanium and aluminium orthophosphate systems are given below.

Iron(III) orthophosphate

In solutions containing only tervalent iron and orthophosphoric acid at pH values of approximately 1, the following equilibrium was shown to exist

$$\text{Fe}^{3+} + 2\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} \rightleftharpoons [\text{Fe(H}_2\text{PO}_4)_2\text{HPO}_4^-]^-$$

and the following values were obtained for $\beta_1$, the stability constant of the complex.

<table>
<thead>
<tr>
<th>pH</th>
<th>Ionic Strength</th>
<th>$\log \beta_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.132</td>
<td>12.66</td>
</tr>
<tr>
<td>1.0</td>
<td>0.14</td>
<td>12.79</td>
</tr>
<tr>
<td>1.0</td>
<td>0.15</td>
<td>12.63</td>
</tr>
<tr>
<td>1.1</td>
<td>0.103</td>
<td>12.41</td>
</tr>
</tbody>
</table>
Titanium(III) orthophosphate

In solutions containing only tervalent titanium and orthophosphoric acid at pH values of approximately 0.3, the following equilibria were shown to exist,

\[
\begin{align*}
\text{Ti}^{3+} + 2\text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^- & \rightleftharpoons [\text{Ti(H}_2\text{PO}_4\text{)}(\text{HPO}_4\text{)}_2]^{2-} \\
\text{Ti}^{3+} + 2\text{H}_2\text{PO}_4^- + \text{HPO}_4^{2-} & \rightleftharpoons [\text{Ti(H}_2\text{PO}_4\text{)}_2(\text{HPO}_4\text{)}]^{-}
\end{align*}
\]

and the following values were obtained for \(\beta_2\) and \(\beta_3\), the stability constants of the doubly and singly charged species respectively.

<table>
<thead>
<tr>
<th>pH</th>
<th>Log (\beta_2)</th>
<th>Log (\beta_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.805</td>
<td>14.3</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Aluminium orthophosphate

In solutions containing only aluminium and orthophosphoric acid at pH 1.28, the following two equilibria were shown to exist.

\[
\begin{align*}
\text{Al}^{3+} + 3\text{HPO}_4^{2-} & \rightleftharpoons [\text{Al(HPO}_4\text{)}_3]^{2-} \\
\text{Al}^{3+} + 2\text{HPO}_4^{2-} + \text{H}_2\text{PO}_4^- & \rightleftharpoons [\text{Al(H}_2\text{PO}_4\text{)}(\text{HPO}_4\text{)}_2]^{2-}
\end{align*}
\]
The same two complex species were shown to be present in solutions at pH 1.1 but with a higher proportion of the doubly charged anion.

Unfortunately it was not possible to carry out all of the experiments under the same conditions of pH and ionic strength but, despite this, there is good agreement between the results. To assess the accuracy of the figures it is necessary to consider carefully the various assumptions which have been made.

For the ion exchange experiments to determine the nature of the complexes present in solution it was assumed that only $\text{HPO}_4^{2-}$ and $\text{H}_2\text{PO}_4^-$ ions existed and that the amount of $\text{PO}_4^{3-}$ present was negligible. For orthophosphoric acid

\[
\begin{align*}
\kappa_1 &= 7.85 \times 10^{-3} \\
\kappa_2 &= 7.99 \times 10^{-8} \\
\kappa_3 &= 4.2 \times 10^{-13}
\end{align*}
\]

and hence this does seem a reasonable assumption.

It is further assumed that the maximum value for the orthophosphate : metal ratio is 3:1, that is, no more than three orthophosphate ligands can combine with a metal atom. No comparable soluble species with more than this have ever
been reported and, if it is assumed that the orthophosphate is acting as a bidentate ligand, only three such ligands could attach to the metal with maximum coordination number of six.

For the determination of the stability constants, the Fronaeus approach was modified and the equations simplified by assuming that only mononuclear anionic complex species were present in solution.

At the metal concentrations used, the presence of polynuclear species is very unlikely. If formed they would almost certainly be insoluble and appear as a precipitate.

In the ion exchange experiments to determine the nature of the ions, it was shown that no cationic complexes were present but these experiments could not be used to show the absence or otherwise of neutral species. However,
all attempts to take up metal phosphate complexes in less polar solvents such as acetone and chloroform or in non-polar solvents such as carbon tetrachloride were unsuccessful.

For a tervalent metal with $H_2PO_4^-$ and $HPO_4^{2-}$ ions, the possible neutral complexes are

$$[M(H_2PO_4)_3]^0$$

$$[M(H_2PO_4)(HPO_4)]^0$$

Although there is no evidence to show that this is a source of inaccuracy in this work, it is useful to appreciate the error which would be obtained in the calculated stability constants if a further complex species were present in the solution.

Assuming the presence of such a complex, for example,

$$[M(H_2PO_4)_3]^0$$

Equation 20 - Section II.1.2(a) becomes,

$$\Delta = \Delta_0 + k_2 \frac{c^3}{\alpha} + \frac{\beta_n(c)^3}{\alpha}$$

where $\beta_n$ represents the stability constant for the reaction:

$$Fe^{3+} + 3(H_2PO_4^-) \rightleftharpoons [Fe(H_2PO_4)_3]^c$$
Equation 1. may be represented as

\[ \Delta = \Delta_0[1 + (a + b)c^3] = F(c) \]  \hspace{1cm} 2.

where \( a = \frac{k_2 \beta_1}{[H^+]^2 \alpha^3} \) and \( b = -\frac{\beta_2}{\alpha^3} \).

Applying the method of least squares, as in Section II.1.2.(a),

\[ S = \sum [(\Delta - F(c))^2] \]

\[ \frac{S}{2} = -2 \sum [(\Delta - F(c)) \frac{\partial F}{\partial a}] \]

\[ \frac{S}{b} = -2 \sum [(\Delta - F(c)) \frac{\partial F}{\partial b}] \]

\[ \frac{\partial F}{\partial a} = \frac{\partial F}{\partial b} = \Delta_0 c^3 \]

Hence only one expression, relating \( \Delta, \Delta_0 \) and \( c \) can be derived from the above equations:

\[ \sum [(\Delta - \Delta_0 - \Delta_0 ac^3 - \Delta_0 bc^3)c^3] = 0. \]

Without further information it is impossible to evaluate the two unknowns, \( a \) and \( b \), in this equation. Hence it is not possible to use the method of least squares to evaluate \( \beta_1 \) and \( \beta_n \).

One answer to this problem which has the virtues of simplicity and ease of calculation, is to assume that the
stabilities of both anionic and neutral complex species are similar and examine the effect of the presence of neutral species on the stability constant of the anionic complexes, as derived by Equation 2.

Let $\beta_1 = \beta_n = \beta_1'$

Let $A^1 = (a + b)$

\[
A' = \left( \frac{k_2}{[H^+]f_2} + \frac{1}{\alpha^3} \right) \beta_1'
\]

\[
A' = \frac{k_2 + [H^+]f_2}{[H^+]f_2} \frac{[H^+]f_2}{\alpha^3} \beta_1'
\]

As $[H^+]f_2 \approx k_2$

\[
A' = \frac{\beta_1'}{\alpha^3}
\]

Solving Equation 2, for all sets of experimental results

<table>
<thead>
<tr>
<th>$\log \beta_1$</th>
<th>$\log \beta_1'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.66</td>
<td>6.72</td>
</tr>
<tr>
<td>12.79</td>
<td>6.84</td>
</tr>
<tr>
<td>12.63</td>
<td>6.69</td>
</tr>
<tr>
<td>12.41</td>
<td>6.53</td>
</tr>
</tbody>
</table>
The values of $\log \beta'$ may be taken to represent the maximum error in the determination of the stability constants if a neutral complex of equal stability were present in the solution. The values of $\log \beta$ represent the stability constant of the charged iron orthophosphate complex if no such neutral species exists.

Similar arguments may be raised in the case of the titanium orthophosphate complexes. The main assumptions in this work were,

(a) that the experimentally measured $pH$ was equal to $-\log a_{H^+}$. If it is assumed that the liquid junction potentials of the pH meter system equal zero, this is true and with the use of saturated potassium chloride bridges, this assumption is reasonable.

(b) It is also assumed that the activities of singly charged ions are the same. There is no way of calculating accurately the activities of ions in concentrated solutions as used in these experiments and this assumption is unlikely to introduce a large error into the calculations.
As in the case of iron orthophosphates, the initial ion exchange experiments showed the absence of any positively charged cationic complexes but the absence of neutral complexes has to be assumed although, as in the other experiments attempts to extract into organic solvents such as chloroform were unsuccessful.

Regarding possible structures of these complexes it is assumed that the orthophosphate ion can act as a monodentate or as a bidentate ligand.

**Monodentate:** $\text{H}_2\text{PO}_4^-$

![Monodentate structure](image)

**Bidentate:** $\text{HPO}_4^{2-}$

![Bidentate structure](image)
In the case of the bidentate ligand, a four membered chelate ring is formed. Orthophosphate ion complexes in such a manner in substituted cobaltamines\(^{(53)}\), and similar 5 and 6 membered rings have been suggested for hypophosphoric acid\(^{(23)}\) and pyrophosphoric acid\(^{(24)}\).

Thus the structure of \([M(H_2PO_4^-)(HPO_4^{2-})_2]^{2-}\) is likely to be

![Diagram of the structure of \([M(H_2PO_4^-)(HPO_4^{2-})_2]^{2-}\)](attachment)

The \([M(H_2PO_4^-)(HPO_4^{2-})_2]^-\) complex ions would have a similar structure:

![Diagram of the structure of \([M(H_2PO_4^-)(HPO_4^{2-})_2]^-\)](attachment)
However, it is possible that the complexes could be formed from bidentate groups with the extra protons held by hydrogen bonds. Notwithstanding the extra stability conferred by chelation, the possibility of linear complexes being formed from a pair of $\text{H}_2\text{PO}_4^-$ ions is unlikely.

Once the process started there is no reason why it should not continue to produce a giant linear molecule which would precipitate. This happens in the case of the aluminium and iron(III) orthophosphate systems when the pH of the solution is raised and precipitation of the metal orthophosphate occurs. It is likely that this happens in the case of the titanium(III) system, but since titanium(III) oxide is a good absorbent of anions either by surface effects or acting as an ion exchanger, it is impossible to say whether titanium(III) orthophosphate, or orthophosphoric acid sorbed on titanium(III) oxide, or precipitated, or a mixture of both.

It is interesting to compare the stability constants obtained for the ferric orthophosphate complexes with those
obtained by Carpenter for the ferric hypophosphate complexes. In the case of the singly charged species, the figures obtained were approximately 12.7 for the orthophosphate and 11 for the hypophosphate. Unfortunately few deductions are permissible from the comparison as the experiments were carried out at significantly different pH conditions - 0.9 for the hypophosphate and 1.0 for the orthophosphate.

Whilst it is not possible to predict quantitatively the stability constants for complexes of this sort it is possible to test the accuracy of the experimental results to some extent by comparing the figures obtained for the different species. In general the stability of any complex can be related to the electronegativity of the central metal atom and the electron donor power of the ligand, together with certain other factors such as the formation of a chelate ring.

If one considers a series of metal-anionic ligand complexes with different metals but the same ligand, as the electronegativity of the metal ion concerned increases, the complex formed will have an increased stability. The
Electronegativities for iron(III) and titanium(III) are given below. These values were taken from the work of Little and Jones (5k).

Electronegativities:

Fe = 1.64
Ti = 1.32

Thus, all other factors being equal iron(III) complexes should be more stable than titanium(III) complexes.

Genge (39) calculated the optimum ionic radius for a metal ion so that the least strained ring would be achieved with a bidentate orthophosphate ion. This was 0.75Å.

Both iron(III) and titanium(III) have approximately this ionic radius.

ionic radius of iron(III) = 0.79Å
ionic radius of titanium(III) = 0.72Å

Thus the orthophosphate ion can form slightly strained bidentate rings with both metals.

If we compare the stabilities of the two singly charged complexes [Fe(HPO₄)(H₂PO₄)₂]⁻ and Ti(HPO₄)(H₂PO₄)₂]⁻. It is found that the iron complex is more stable than the corresponding titanium(III) complex. The electronegativity of iron(III) is higher than that of titanium(III) and so the
ligand in the iron complex will act as a more efficient electron donor. If it is considered that a proportion of $H_2PO_4^-$ ions act as bidentate ligands the higher electronegativities of iron(III) will still be an important factor.

If the stabilities of the singly charged species $[Fe(H_2PO_4)_2(HPO_4)]^-$ and the doubly charged $[Ti(H_2PO_4)(HPO_4)]^{2-}$ are compared, the higher stability of the titanium complex is probably due to the increased electron donating power of the higher charged smaller $HPO_4^{2-}$ groups, of which the titanium complex has a higher proportion and to the extra stability gained by chelation. The titanium complex contains a higher proportion of bidentate groups. Thus a more stable complex would be formed.

The results of Carpenter (23) for iron(III) hypophosphate complexes containing both bidentate and monodentate ligand ions, in a 3:1, ligand to metal ratio, at pH 0.9 give an average value of $\log \beta = 13.8$. The electron donating power of an orthophosphate ion is higher than a similarly charged hypophosphate ion, as the latter is a larger ion and so has a lower electron density. However the ability to donate electrons is probably greater in the case of $H_2P_2O_6^{2-}$.
than \((\text{H}_2\text{PO}_4^-)\) and the hypophosphate complex has a larger proportion of doubly charged groups. Also \((\text{H}_2\text{P}_2\text{O}_7^{2-})\) ion when it forms a bidentate band will form a five membered chelate ring:

\[
\begin{align*}
\text{H} & \text{--O--P--O--P--O--P--O--P--O--}\text{H} \\
& \text{M}
\end{align*}
\]

Barring resonance effects the five membered chelate ring is the most stable. Thus the higher stability of the hypophosphate complex is due to its higher proportion of doubly charged groups. Both, because of the extra stabilisation by chelation since it has two bidentate groups and because of the higher average charge on its ligands.

However, in the comparison of the stabilities of \([\text{Ti(HP}_4\text{)}_2(\text{H}_2\text{PO}_4)^2-]\) ions and \([\text{Fe(H}_2\text{P}_2\text{O}_6)_2(\text{H}_3\text{P}_2\text{O}_6)^2-]\), it is found that the values of \(\log \beta\) of both complexes are approximately equal, bearing in mind the probable experimental error and the difference in pH. For \([\text{Ti(H}_2\text{PO}_4)(\text{HP}_4\text{)}_2]\) \(\log \beta = 14.2 \pm 0.3\) for \([\text{Fe(H}_2\text{P}_2\text{O}_6)^2-][\text{H}_3\text{P}_2\text{O}_6^-]\) \(\log \beta = 13.3\). In this comparison there are three main
factors affecting the strength of the co-ordinate bond between the ligand and the metal ion. The higher electronegativity of iron(III) will follow the formation of a stronger band than in the case of titanium(III). \((H_2P_2O_6^{2-})\) will form the more stable five membered bidentate rings with iron but \((H_2PO_4^-)\) will only form four membered rings with titanium(III). The four membered ring will be more strained than the five and so this will reduce the strength of the orthophosphate ion-titanium bond compared to the hypophosphate iron band. The charge density of \((H_2PO_4^{2-})\) is higher than \((H_2P_2O_6^{2-})\). Both ions have the same charge, but \((H_2P_2O_6^{2-})\) has a larger volume and the tendency for electron donation to occur and hence for stronger bonds to be formed is greater in the case of orthophosphoric acid. Thus, although stronger bonds are formed with orthophosphoric acid than hypophosphoric acid, the stabilisation of chelation compensates for this and so the stabilities of these two complex ions are approximately the same.

From all these arguments and comparisons it would seem that the stabilities obtained for the orthophosphate complexes are as would be expected from the values obtained
previously with hypophosphate complexes and that the stabilities of the various iron(III) and titanium(III) species are in the correct order.
PART V

REFERENCES
(2) A. Weller, Berliner Ber., 1882, 15, 25, 92.
(3) C. Reinhardt, Stahl u. Eisen, 1884, 4, 709,
(4) R.F. Weinland and F. Ensgraber, Z. Anorg. Chem. 1914,
    84, 340.
    1931, 2, 85.
(7) L. Dede, Z. Anorg. u. allgem. chem. 1923, 125, 28.
(8) E. Ricca and P. Meduri, Gazzetta, 1934, 64, 235.
    1946, 56, 130.
(13) J.E. Salmon, J. Chem. Soc. 1952, 2316,
    J. Chem. Soc. 1953, 2644,
(14) U. Belluco, L. Busullini and R. Barbieri, La Ricerca
    Scientifica, 1959, 22, 2329.
    1963, 25, 567.


(21) See Reference (19).


(24) O. Samuelson, IVA, 1946, 17, 9.


    (b) S. Fronaeus, Svensk Kem. Tidskr., 1953, 65, 1.
    (c) S. Fronaeus, Svensk Kem. Tidskr., 1953, 65, 19.


(b) L.I. Katzin and E. Gebert, J. Am. Chem. Soc., 1950, 72, 5455.


