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WITH HIGHER PHOSPHATES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Richard Ambrose Simonaitis, B.S., M.Sc.

The Ohio State University
1962

Approved by

James F. Warren
Adviser
Department of Chemistry
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## CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>METHOD</td>
<td>21</td>
</tr>
<tr>
<td>III</td>
<td>THE COMPLEXES OF MERCURY(I) WITH PYROPHOSPHATE</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Experimental Results and Discussion</td>
<td>33</td>
</tr>
<tr>
<td>IV</td>
<td>THE COMPLEXES OF MERCURY(I) WITH TRIPHOSPHATE</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>The Acidity Constants of Triphosphoric Acid in the Presence of 1 M Sodium and Potassium Ions</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>The Complexity Constants of Mercury(I) with Triphosphate</td>
<td>63</td>
</tr>
<tr>
<td>V</td>
<td>THE COMPLEXES OF MERCURY(I) WITH TETRAPHOSPHATE</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>Experimental Determination of Acidity Constants</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>Experimental Determination of Complexity Constants</td>
<td>90</td>
</tr>
<tr>
<td>VI</td>
<td>SUMMARY</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>AUTOBIOGRAPHY</td>
<td>124</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>
TABLES (contd.)

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>Contributions of Various Complex Species to $T_1$</td>
</tr>
<tr>
<td>16</td>
<td>Complexity Constants for Tetraphosphate-Mercury(I) System</td>
</tr>
<tr>
<td>17</td>
<td>Summary of Complexity Constants for Mercury(I) Polyphosphate System</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Survey Polarogram of the Mercury Pyrophosphate System</td>
</tr>
<tr>
<td>2</td>
<td>Potentiometric Potential Shifts as a Function of pH for the Mercury(I) Pyrophosphate System</td>
</tr>
<tr>
<td>3</td>
<td>Graphic Determination of $\beta_{011}$ and $\beta_{012}$ for the Mercury(I) Pyrophosphate System in the Presence of 1.0 M Sodium Ion</td>
</tr>
<tr>
<td>4</td>
<td>Graphical Determination of $\beta_{010}$ in the Presence of Potassium Ion</td>
</tr>
<tr>
<td>5</td>
<td>Percentage Distribution of Mercury(I) Pyrophosphate Complex Species as a Function of pH in the Presence of Sodium Ion</td>
</tr>
<tr>
<td>6</td>
<td>Percentage Distribution of Mercury(I) Pyrophosphate Complex Species as a Function of pH in the Presence of Potassium Ion</td>
</tr>
<tr>
<td>7</td>
<td>Potentiometric Potential Shifts as a Function of pH for the Mercury(I) Triphosphate System</td>
</tr>
<tr>
<td>8</td>
<td>Graphic Determination of $\beta_{011}$ and $\beta_{012}$ for the Triphosphate System in the Presence of Potassium Ion</td>
</tr>
<tr>
<td>9</td>
<td>Percentage Distribution of Mercury(I) Triphosphate Complex Species in the Presence of 1.0 M Sodium Ions</td>
</tr>
<tr>
<td>10</td>
<td>Percentage Distribution of Mercury(I) Triphosphate Complex Species in the Presence of 1.0 M Potassium Ions as a Function of pH</td>
</tr>
</tbody>
</table>
FIGURES (contd.)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Potentiometric Potential Shifts as a Function of pH for the Mercury(I) Tetraphosphate System</td>
<td>91</td>
</tr>
<tr>
<td>12</td>
<td>Graphic Determination of $\beta_{011}$ and $\beta_{012}$ for the Tetraphosphate System in the Presence of Sodium Ion</td>
<td>93</td>
</tr>
<tr>
<td>13</td>
<td>Graphic Determination of $\beta_{010}$ for the Tetraphosphate System in the Presence of Potassium Ion</td>
<td>98</td>
</tr>
<tr>
<td>14</td>
<td>Percentage Distribution of Mercury(I) Tetraphosphate Complex Species in the Presence of 1.0 M Sodium Ions as a Function of pH</td>
<td>111</td>
</tr>
<tr>
<td>15</td>
<td>Percentage Distribution of Mercury(I) Tetraphosphate Complex Species in the Presence of 1.0 M Potassium Ions as a Function of pH</td>
<td>113</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

Until recently, it was generally assumed that mercury(I) complexes were unstable with respect to disproportionation to form the more stable mercury(II) complex and free mercury. In contrast, the equilibrium constant for the formation of aquomercury(I) ion from elementary mercury and aquomercury(II) ion is 130 in 0.5 M NaClO₄.¹ The reaction is readily reversible.

¹S. Hietanen and L. G. Sillen, Arkiv Kemi, 10, 103 (1956).

On the basis of potentiometric evidence, Sillen and his co-workers¹,² have suggested weak complexes of mercury(I) ion formed by


nitrate, sulfate and perchlorate anions due to ion-pair association with formation constants of:

2.5 M⁻¹ (Hg₂(NO₃)₄), 0.5 M⁻² (Hg₂(NO₃)₂), 20 M⁻¹ (Hg₂SO₄),
250 M⁻² (Hg₂(SO₄)₂²⁻) and 0.9 M⁻¹ (Hg₂ClO₄²⁻).
However, during the nineteenth century, Stromeyer\(^3\) and then


Brand\(^4\) reported that a white precipitate forms and then redissolves in excess of reagent when sodium pyrophosphate solution is added to a mercury(I) solution which suggests the formation of a strong, stable complex.

Recently, Yamane and Davidson\(^5\) confirmed these observations and also reported stable mercury(I) complexes with tripolyphosphate, oxalate, \(\text{OC-Dimethylmalonate}\) and succinate anions. They employed a potentiometric method on a buffered solution in the present of 0.75 M \(\text{NaNO}_3\) at 27.4 °C and reported the principle complexes as

\[\text{Hg}_2\text{L}_2(\text{q-2})^-\text{ and Hg}_2\text{L(OH)}(\text{q-1})^-\text{, where L}^-\text{ is the anion. The overall complexity constant for Hg}_2(\text{P}_2\text{O}_7)\text{L}_2^-\text{ was found to be (2.4} \pm 0.6\) \(\times 10^{12}\) M\(^{-2}\); \(\text{Hg}_2(\text{OH})\text{P}_2\text{O}_7\text{L}^-\text{3 it was (4.4} \pm 0.6\) \(\times 10^{15}\) M\(^{-2}\) in a pH range of 7.45-9.55, for \(\text{Hg}_2(\text{P}_3\text{O}_{10})\text{L}^-\text{2 it was (1.7} \pm 0.3\) \(\times 10^{11}\) and for \(\text{Hg}_2(\text{OH})\text{P}_3\text{O}_{10}\text{L}^-\text{4 it was (1.0} \pm 0.2\) \(\times 10^{15}\) in the pH range 7.18 to 9.00. Expressions for these constants will be presented later.
Many investigators have studied the acidity constants of pyrophosphoric acid. Abbott and Bray,\(^6\) in a conductivity study of the hydrolysis, of ammonium salts of pyrophosphoric acid by a distribution method at 18\(^\circ\)C obtained the values \(K_1 = 1.14 \times 10^{-1}\); \(K_2 = 1.1 \times 10^{-2}\); \(K_3 = 2.9 \times 10^{-7}\); and \(K_4 = 3.6 \times 10^{-9}\) at zero ionic strength. Kolthoff and Bosch\(^7\) applied the Debye-Hückel relationship to data obtained from a hydrogen electrode at 18\(^\circ\)C extrapolated to infinite dilution and obtained the values, \(K_3 = 2.1 \times 10^{-7}\) and \(K_4 = 4.06 \times 10^{-10}\). Morton\(^8\)


\(^7\)I. M. Kolthoff and W. Bosch, Rec. trav. chim., \textbf{47}, 826 (1928).


obtained the values \(K_3 = 1.98 \times 10^{-7}\) and \(K_4 = 1.32 \times 10^{-10}\) at 30\(^\circ\)C and also noted complex formation with alkali metal and alkaline earth salts. In a hydrolysis study, McGilvery and Crowther,\(^9\) determined the acid dissociation constants at 65.5\(^\circ\)C. Substituting the data obtained by electrometric titrations into the basic stoichiometric equations by a series of approximations, they obtained the values, \(K_1 = 0.107\), \(K_2 = 7.58 \times 10^{-2}\), \(K_3 = 1.45 \times 10^{-6}\), and \(K_4 = 9.8 \times 10^{-9}\).
Monk\textsuperscript{10} studied pyrophosphoric acid by means of conductance measurements at 25\degree C and calculated the dissociation constant for the NaP\textsubscript{2}O\textsubscript{7}\textsuperscript{3-} complex. From pH measurements of solutions of the sodium salts and the acid he was able to calculate the acid dissociation constants of pyrophosphoric acid at \( u = 0 \) as \( K_{3} = 2.7 \times 10^{-7} \) and \( K_{4} = 2.4 \times 10^{-10} \) after taking the association between sodium ions and pyrophosphate ions into consideration. Lambert and Watters\textsuperscript{11} determined the acidity constants extrapolated to infinite dilution as \( pK_{1} = -\infty \), \( pK_{2} = 2.64 \), \( pK_{3} = 6.76 \), \( pK_{4} = 9.42 \). Huhn and Beck\textsuperscript{12} also calculated the dissociation constants of pyrophosphoric acid.

The tendency of pyrophosphate to form complexes with many metals through chelate ring formation has been the subject of many studies. In a polarographic study, Kolthoff and Watters\textsuperscript{13} determined the diffusion coefficients of the complex manganipyrophosphoric acid ion with the aid of the Ilkovic equation. From the relation between the


diffusion coefficient and the molecular weights compared to \( \text{Co(C} \text{O}_4 \text{)}_3 \). They calculated the approximate molecular weight and postulated the formula as \( \text{Mn(H}_2\text{P}_2\text{O}_7)_2^{3-} \). Rogers and Reynolds\(^{14}\) used potentiometric and conductometric measurements to study complexes of pyrophosphate. They found that the complex, \( \text{M(II)(P}_2\text{O}_7)^{2-} \) was formed by cadmium, cobalt, copper, lead, magnesium, nickel and zinc; \( \text{M(II)(P}_2\text{O}_7)_2^{6-} \) was formed by copper and zinc; and \( \text{M(II)(P}_2\text{O}_7)^{1-} \) and \( \text{M(III)(P}_2\text{O}_7)_2^{5-} \) was formed by aluminum and iron. Polarographic studies were made by Van Wazer and Campanella\(^{15}\) on aqueous solutions of barium or sodium with the tetramethylammonium salt of pyrophosphoric acid. These studies showed that the coordination number of barium is four and that of sodium is two in the complexes. They reported the dissociation constant of sodium as approximately \( 10^{-3} \) and of barium of about \( 10^{-9.5} \) based on the concentration of pairs of phosphorus atoms. In addition, they presented the effect of twenty metal ions on the pH titration curves of polyphosphoric acids and interpreted them in terms of complexion formation, which they divided into the following groups: (1) quaternary ammonium ions, which form no complexes, (2) alkali metal and similar cations forming weak complexes and (3) the other metals which form strong complexes. This complex formation was ascribed to


chelate ring structures formed along the polyphosphate chain. Souchay and Faucherre\textsuperscript{16} in a discussion of the relations that enable a calcul-

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lation of the coordination numbers and the equilibrium constants of complexes from the displacement of polarographic potentials found that the coordination number of cadmium pyrophosphate is two and that the equilibrium constant was $1.5 \times 10^4$. Watters and Kolthoff\textsuperscript{17} reported that both manganese(II) and manganese(III) coordinate three dihydrogen pyrophosphate ions at zero pH. In a polarographic study of sodium pyrophosphate-ferric chloride solutions, Eriksson\textsuperscript{18} found that there

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was a dipyro-ferric complex in weakly acid solutions and a dihydroxy-
monopyrophosphate-ferric complex in neutral and slightly alkaline solutions. He reported the complexity constant for CuF\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} in solutions of pH more alkaline than 11 to be $6 \times 10^{-14}$. Syrokomski and Avilov\textsuperscript{19} in their studies found the ferric ion also forms a 1:1 complex with pyrophosphate ion.

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19\textsuperscript{V}. S. Syrokomski and V. B. Avilov, Zavadakaya Labo, 16, 11 (1950).
\end{flushright}
From thermometric titration curves, transport experiments and pH titration of sodium pyrophosphate against a ferric chloride, Banerjee and Mitra\textsuperscript{20} formulated the complexes $\text{Fe}(P_2O_7)_2^{6-}$ and $\text{Fe}(P_2O_7)_2^{1-}$ and

\begin{equation}
\text{Fe}(P_2O_7)_2^{5-}
\end{equation}

\text{Banerjee and S. K. Mitra, Science and Culture, 16, 530 (1951).}

reported an instability constant of $2.8 \times 10^{-6}$ for the $\text{Fe}(P_2O_7)_2^{5-}$ complex from photometric measurements. Haldar\textsuperscript{21-24} studied pyrophosphate complexes with copper, nickel, cobalt, lead and zinc by thermometric, transport, conductometric, pH, magnetic and cryoscopic measurements in saturated $\text{Na}_2\text{SO}_4$ solutions. He found that the formulas for the complexes formed was $M(P_2O_7)_2^{6-}$ and $M(P_2O_7)_2^{2-}$, where $M$ indicates the metal ion. From polarographic data, Laitinen and Onstott\textsuperscript{25}

\text{B. C. Haldar, \textit{ibid.}, 14, 340 (1949).}

\text{B. C. Haldar, \textit{Nature}, 166, 744 (1950).}

\text{B. C. Haldar, \textit{Current Sci. (India)}, 19, 244 (1950).}

\text{B. C. Haldar, \textit{ibid.}, 19, 283 (1950).}

\text{H. A. Laitinen and E. I. Onstott, \textit{J. Am. Chem. Soc.}, 72, 4729 (1950).}

showed that copper(II) ion coordinated with two $P_2O_7^{3-}$ ions in solutions having more than one fold excess of the complexing ion, and that one $P_2O_7^{3-}$ ion was coordinated when less than one-fold excess of the complexing ion was present in the pH range of 3.6 to 5.3. They also gave evidence for the existence of $\text{Cu}(P_2O_7)(P_2O_7)^{5-}$ and/or $\text{Cu}(P_2O_7)_2^{6-}$
in the pH range of 7 to 10, and that \( \text{Cu(OH)(P}_2\text{O}_7)^{3-} \) existed in strongly alkaline solution. From polarographic data they calculated the dissociation constant of bismonohydrogenpyrophosphate-cuprate(II) as \( 1 \times 10^{-10} \), monohydrogenpyrophosphate-cuprate(II) as \( 4 \times 10^{-7} \) and hydroxopyrophosphate-cuprate(II) as \( 2 \times 10^{-16} \). Mayer and Schwartz\(^{26}\) measured the distribution of cerium(III) between ion-exchange resin Dowex 50 and solutions of pyrophosphoric acid and calculated the association constant for \( \text{CaP}_2\text{O}_7^{1-} \) to be \( 1.4 \times 10^{17} \). Lingane and Meites\(^{27}\) reported that they obtained data on the half-wave potentials and diffusion-current constants of the waves of vanadium(II), and vanadium(II) in pyrophosphate solutions but did not discuss the complex formulas. In a polarographic study of Thallium pyrophosphate complexes, Senise and Delahay\(^{28}\) found that the species \( \text{Tl(P}_2\text{O}_7)^{3-} \) was predominant in the neighborhood of pH 13 but that complexes of a higher order also existed. However, their formation constants could only be determined in a very approximate manner by the polarograph method. Watters and Aaron\(^{29}\) found that copper(II) and pyrophosphate ion give complexes

\(^{26}\) S. W. Mayer and D. Schwartz, \textit{ibid.}, 72, 5106 (1950).

\(^{27}\) J. J. Lingane and L. Meites, \textit{ibid.}, 73, 2165 (1951).

\(^{28}\) P. Senise and P. Delahay, \textit{ibid.}, 74, 6128 (1952).

\(^{29}\) J. I. Watters and A. Aaron, \textit{ibid.}, 75, 611 (1953).
having ratios of 1:2, 1:1, 2:1, and 4:1 in solutions containing the corresponding ratios of copper to pyrophosphate ion. The last two species were detected only in very dilute solutions. They found that the 1:2 ratio was predominant in solutions containing a moderate excess of pyrophosphate ion in the pH range of 10 to 7 and that the equilibrium shifted to form more of the 1:1 complex at lower concentrations of pyrophosphate ion or in weakly acidic solution. At an ionic strength of one, they reported the stepwise dissociation constants of the 1:2 complex as $2 \times 10^{-4}$ and $2 \times 10^{-1}$.

From equilibrium potential and conductivity measurements, Ukshe and Levin\textsuperscript{30} calculated the instability constants for Cu(P$_2$O$_7$)$_2^{6-}$ and Cu(P$_2$O$_7$)$_{2}^{2-}$ as $0.63 \times 10^{-6}$ and $0.5 \times 10^{-10}$, respectively. Bobtelsky and Kertes\textsuperscript{31,32} investigated pyrophosphate complexes of calcium, strontium, barium, magnesium, manganese, nickel, cobalt and copper by heterometric, potentiometric, pH and conductivity titration. They found that all the cations gave complexes of the type M(P$_2$O$_7$)$_2^{2-}$ and, in addition, copper and nickel gave the complexes Cu(P$_2$O$_7$)$_2^{6-}$, Cu(P$_2$O$_7$)$_3^{10-}$ and Ni$_3$(P$_2$O$_7$)$_2^{2-}$. 


\textsuperscript{32}M. Bobtelsky and S. Kertes, ibid., 5, 675 (1955).
Yatsimirskii and Vasilev\textsuperscript{33,34} in a solubility study of pyrophosphate salts reported complexes and their dissociation constants of 

\[
\begin{align*}
\text{CuP}_2\text{O}_7^{2-}, & \quad 2.0 \times 10^{-7}; \\
\text{Cu}(\text{P}_2\text{O}_7)_2^{6-}, & \quad 1 \times 10^{-9}; \\
\text{Ni}(\text{P}_2\text{O}_7)^{2-}, & \quad 1.5 \times 10^{-6}; \\
\text{Ni}(\text{P}_2\text{O}_7)_2^{6-}, & \quad 6.5 \times 10^{-8}.
\end{align*}
\]

They also found the complexes \(\text{Zn}(\text{P}_2\text{O}_7)^{6-}\) and \(\text{Pb}(\text{P}_2\text{O}_7)_2^{6-}\) but did not report any dissociation constants.

Vasilev\textsuperscript{35,36} determined by means of colorimetric pH measurements, the instability complexes of \(\text{M}(\text{P}_2\text{O}_7)^{2-}\), where \(\text{M}\) indicates magnesium, strontium, or barium to be \(5 \times 10^{-6}\), \(2.2 \times 10^{-5}\) and \(2.3 \times 10^{-5}\), respectively. Subrahmanya\textsuperscript{37-39} studied the polarographic behavior of complexes of pyrophosphate ion with iron, lead, cadmium, bismuth, titanium and niobium at various pH values. He determined the lead pyrophosphate complex formula as \(\text{Pb}(\text{P}_2\text{O}_7)^{2-}\) but was unable to ascertain the nature of the other complexes due to the irreversibility of their polarographic waves. By means of amperometric and visual titration,
and polarographic and solubility methods, Yakshova established the existence of Fe(HP₂O₇)₂⁻ in aqueous solutions containing pyrophosphate and iron(III) ions at pH of 6 to 9.6. He reported the dissociation constant of the ion to be 6.5 x 10⁻²³. Lambert and Watters calculated the stabilities of the complexes of pyrophosphate ion with magnesium(II) ion from pH lowering during titration with hydrogen ion at 25°, ionic strength of unity, to be Mg₂P₂O₇ = 10⁷⁻⁵, MgP₂O₇²⁻ = 10⁵⁻¹ and Mg(HP₂O₇)₁⁻ = 10³⁻⁰⁶. Vaid and Rama Char used potentiometric, conductometric and spectrophotometric methods to study complex formation between pyrophosphate ion and copper, zinc, tin, lead, nickel and cobalt ions. They found that a complex of the type (MP₂O₇)₂⁻, where M indicates the metal ion, was formed by all the ions and that the instability constants of the complexes were Sn, (2.2-2.5) x 10⁻¹⁴; Zn, (2.2-3.7) x 10⁻⁷; Cu (0.6 x 10⁻¹⁰); Pb, (6.8-8.7) x 10⁻¹¹; Ni, 2.4 x 10⁻¹³; and Co, 9.5 x 10⁻¹⁴. They also reported that complexes of the type M(P₂O₇)₂⁻ was formed by copper, nickel, cobalt and zinc but gave no instability constants. Copper and zinc pyrophosphates
were studied potentiometrically by Persiantseva and Titov.\textsuperscript{43} They also found complexes of the type $M(P_2O_7)_{6-}$ and $MP_2O_7^{2-}$ and reported the dissociation constants at $25^\circ$ to be $K_1 = 6.8 \times 10^{-9}$ and $K_2 = 1.02 \times 10^{-9}$ for the copper complex and $K_1 = 8.0 \times 10^{-7}$ and $K_2 = 8.06 \times 10^{-8}$ for the zinc complex. Tarayan and his coworkers\textsuperscript{44-46} used polarography and potentiometry to study pyrophosphate complexes with cerium and magnesium ion. They reported the complex $Mn(H_2P_2O_7)^{3-}$ to be the predominant species at a pH of 4.25 and that $Mn(HP_2O_7)^{2-}$ was the predominant species above that pH. In the case of the cerium complex they found that the complex had the form $Ce(H_2P_2O_7)^{3-}$ at a pH of 4.25 and that $Ce(HP_2O_7)^{2-}$ was the species at a pH of 7.5. Calcium complexes of pyrophosphate ion were studied at $25^\circ$ and unit ionic strength by Watters and Lambert\textsuperscript{47} using a pH titration procedure. The complexes they found and their respective complexity constants were $CaP_2O_7^{2-}$, $10^{4.95}$ and $Ca(HP_2O_7)^{1-}$, $10^{2.30}$. 


\textsuperscript{45}V. M. Tarayan and M. G. Ekimyan, ibid., 11, No. 1, 23 (1958).


Triphosphoric acid titration curves were first published by Rudy and Schloesser\textsuperscript{48} but, due to complex formation, no attempt was made to calculate the acidity constants. By application of the Debye-Hückel equation to data obtained in the titration of triphosphoric acid with potassium hydroxide, Beukenkamp, Riemann and Lindenbaum\textsuperscript{49} were able to report the values $pK_3 = 2.79$, $pK_4 = 6.47$ and $pK_5 = 9.24$. Watters, Loughran and Lambert\textsuperscript{50} reported $pK$'s for acidity constants at an ionic strength of unity and temperature $25^\circ$ as $pK_2 = 1.06$, $pK_3 = 2.11$, $pK_4 = 5.33$, and $pK_5 = 8.81$.

The tendency of triphosphate ion to form complexes with many metals has been studied by many investigators. Van Wazer and Campanella\textsuperscript{15} in polarographic studies on aqueous solutions of barium or sodium with tetramethylammonium salts of acids obtained from several condensed phosphates showed that the coordination number of barium is four and that of sodium is two in the polyphosphate complexes. They found that the sodium reduction was completely reversible and the dissociation constant was approximately $10^{-3}$ (based on concentration of pairs of phosphorus atoms) and that the barium reduction was
somewhat irreversible giving a calculated constant of approximately $10^{-9.5}$. The constants they calculated were independent of the polyphosphate molecular weight. In addition, they reported the effect of twenty metal ions on the pH titration curves of the polyphosphoric acids and interpreted them in terms of complex-ion formation, which was ascribed to chelate ring structures formed along the polyphosphate chain. Monk\textsuperscript{10} employed conductance to determine the sodium triphosphate complexity constant. Rudy and coworkers\textsuperscript{51-52} observed the possibility of a calcium complex by means of pH lowering during a study of lime soaps. Frankenthal\textsuperscript{53} observed that the addition of magnesium chloride to sodium triphosphate caused a depression of pH that depended on the concentration of the magnesium chloride, and that mixtures with a high magnesium chloride content had an even lower pH than magnesium chloride alone at the same concentration. The same results were observed in the presence of aluminum ion. Monnier, Bonnet and Brard\textsuperscript{54} briefly discussed the formation of calcium

\textsuperscript{51} H. Rudy, Angew. Chem., \textit{54}, 447 (1941).

\textsuperscript{52} H. Rudy, H. Schloesser and R. Watzel, Angew. Chem., \textit{53} (1940).


\textsuperscript{54} A. M. Monnier, V. Bonnet and R. Brard, Arch. Intern. Physiol., \textit{54}, 188 (1946).
complexes with triphosphate ion in body fluid. Bobtelsky and Kertes\textsuperscript{31,32} studied alkaline earth metals, manganese, cobalt, nickel, and copper complexes by heterometric, turbidity, pH, potentiometry, and conductivity measurements. In the presence of triphosphate ion they found that in all cases a soluble salt of the formula $\text{MP}_3\text{O}_{10}^{3-}$, where $M$ indicates metal ion, was formed, and in addition, soluble salts of the complex $\text{M}_2(\text{P}_3\text{O}_{10})_2^{3-}$ were obtained with nickel and cobalt and of $\text{M}_5(\text{P}_3\text{O}_{10})_3^{5-}$ with copper. By means of an acid titration method, Martell and Schwarzenbach\textsuperscript{55} also found that magnesium and calcium forms complexes with triphosphate ion of the formula $\text{MP}_3\text{O}_{10}^{3-}$. Kobayashi\textsuperscript{56,57} studied complexes of sodium triphosphate with nickel, lead and cadmium by means of amperometric titrations. He found that the predominant species for all three ions present was $\text{MP}_3\text{O}_{10}^{3-}$, where $M$ indicates the metal ion.

The stability of complexes of triphosphate ion with sodium, potassium and lithium from pH lowering during titrations of triphosphate ion with hydrogen ion were reported by Watters, Lambert and Loughran\textsuperscript{58}


\textsuperscript{57}M. Kobayashi, Nippon Kagaku Zasshi, \textbf{76}, 1023 (1955).

at 25° in 1 M methylammonium chloride. The formulas of the complexes and the values of their formation constants they found were:

- $\text{KPF}_3\text{O}_10^{-4}$, $10^{1.39}$;
- $\text{NaPF}_3\text{O}_10^{-4}$, $10^{1.64}$;
- $\text{LiPF}_3\text{O}_10^{-4}$, $10^{2.87}$;
- $\text{Na}(\text{HP}_3\text{O}_10)^{3-}$, $10^{0.77}$;
- $\text{Li}(\text{HP}_3\text{O}_10)^{3-}$, $10^{0.88}$.

Watters and Lambert also studied complexes of triphosphate ion with calcium and magnesium ions by a pH titration method. The complexes and the complexity constants they found at 25° in one molar tetramethylammonium chloride were:

- $\text{Mg}_2\text{PF}_3\text{O}_10^{-1-}$, $10^{7.96}$;
- $\text{MgPF}_3\text{O}_10^{-3-}$, $10^{5.83}$;
- $\text{Mg}(\text{HP}_3\text{O}_10)^{2-}$, $10^{3.34}$;
- $\text{CaPF}_3\text{O}_10^{-3-}$, $10^{5.44}$; and
- $\text{Ca}(\text{HP}_3\text{O}_10)^{2-}$, $10^{3.01}$.

Pamfilov, Lopreshanskaya and Gusel reported that the triphosphate complexes of lead and cadmium were of the type $M_3(\text{P}_3\text{O}_{10})^{4-}$, the coordination number of the metals were four. They obtained the dissociation constants as $3 \times 10^{-5}$ and $9 \times 10^{-10}$ for the lead and cadmium complexes, respectively. Subbaraman and his coworkers used polarography to study uranyl and also lead, bismuth, titanium and niobium complexes. They reported that all of the polarographic waves except those for lead at pH 5 were irreversible but gave no discussion of any complexity formulas. Ion-exchange experiments were made on solutions of sodium and copper triphosphate.
complexes by Heitner-Wirguin, Salmon and Mayer.\(^{62}\) They found no evidence of complexes containing more than two triphosphate ligands.

In the presence of chloride ion a 1:1 complex was found that was more strongly sorbed in competition with other ions than complexes formed in the absence of chloride ion which they ascribed to the formation of a mixed chlorophosphate complex. Wolhoff and Overbeek\(^{63}\) studied complex formation by means of a pH lowering method. They found that both pyro- and triphosphoric acids had the same acid dissociation constants, namely, \(10^{-9.52}\) at \(25^\circ\). They also found that triphosphate had somewhat stronger complexing properties than pyrophosphate and listed the formation constants for lithium, sodium, potassium, cesium, magnesium, calcium, strontium, barium, zinc, and cadmium ions.

Fleitmann and Henneberg\(^{64}\) first claimed the preparation of sodium tetraphosphate by a fusion of sodium metaphosphate with sodium pyrophosphate in a 2:1 ratio. Schwarz\(^{65}\) claimed to prepare Fleitmann and

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\(^{64}\) Fleitmann and W. Henneberg, Liebig's Ann. Chem., 65, 324 (1848).

Henneberg's acid tetraphosphate, NaH$_2$P$_4$O$_7$ from the salt, Na$_2$H$_2$P$_2$O$_7$ by the removal of the water of crystallization. Strange stated that


he was able to confirm this. Later, however, three sets of workers


contradicted the existence of the compound by means of x-ray studies. In 1949, Thilo and Ratz prepared sodium tetraphosphate by mild


alkaline hydrolysis of sodium metaphosphate at 40°. They obtained a colorless, viscous oil which they were unable to crystallize although they were able to obtain insoluble calcium, silver and zinc tetraphosphates which were amorphous to x-rays. The existence of the tetraphosphate ion was confirmed by the use of chromatography by Westman and Scott and also by Ebel, but they also failed to succeed in

isolating a crystalline tetraphosphate. Quimby, in a study on


soluble crystalline polyphosphates succeeded in crystallizing the
hexaguanidine tetraphosphate from a formamide rich solution which was
purified to 95-99 per cent and confirmed by means of x-ray diffraction.

By heating appropriate mixtures of Pb(H₂PO₄)₂ and PbHPO₄ to
constant weight at 550°C, Osterheld and Langguth, were able to form

(1955).

lead tetraphosphate which they confirmed by means of x-ray diffraction.
Schulz also prepared lead tetraphosphate and also bismuth tetraphos-


phate which he analyzed by x-ray diffraction and paper chromatography,
showing the former to be the same salt as prepared by Osterheld and
Langguth. Schulz was unable to prepare anhydrous tetraphosphates of
zinc, cadmium or lithium and reached the conclusion the anhydrous
crystalline tetraphosphates exist only for elements with relatively
high atomic number and large ionic radius.

Tetraphosphate complexes with cadmium, lead and zinc were studied
by Pamfilov, Lopushanskaya and Mandel'ev77 using polarography. They

77A. V. Pamfilov, A. I. Lopushanskaya and A. M. Mandel'ev,
found that the tetraphosphate complexes gave irreversible waves and that the specific velocity of reduction of zinc, cadmium and lead tetraphosphates did not depend on the pH or the temperature.
CHAPTER II

METHOD

Leden's method was used for the evaluation of the equilibrium constants. He showed how the several complex species which exist simultaneously in solution can be considered in potentiometric studies.

The general expression for the equilibria of the aquo metal ion with several ligands, assuming only mononuclear complexes are formed and the overall formation constant for the reaction is

$$M + iA + jB + kC \rightleftharpoons MA_iB_jC_k; \quad \beta_{ijk} = \frac{(MA_iB_jC_k)}{(N)(A)^i(B)^j(C)^k} \quad (1)$$

where i, j, and k may vary from zero to N, the maximum number of coordinated groups but their sum cannot exceed N. Rearranging equation (1) and summing the equations for all species of M, yields

$$\sum_{i=0}^{N} \sum_{j=0}^{N'} \sum_{k=0}^{N''} \beta_{ijk}(A)^i(B)^j(C)^k \quad (2)$$

$$\sum_{i=0}^{N} \sum_{j=0}^{N'} \sum_{k=0}^{N''} (MA_iB_jC_k)$$
The Nernst equation for the simple aquo metal ion is

\[ E_{eq} = E_f + S \log (M)_T \quad (3) \]

where \( S \) is \( 2.303 \text{ RT}/nF \), \( E \) is the measured electrode potential versus the standard hydrogen electrode and \( E_f \) is the formal potential for the electrode reaction of the aquo metal ion.

The Nernst equation for the complex ion is given by

\[
E_C = E_f + S \log \left( \sum_{i=0}^{N} \sum_{j=0}^{N'} \sum_{k=0}^{N''} (MA_{i}B_{j}C_{k}) \right) \quad (4)
\]

The equation for conservation of the metal ion is expressed as

\[
(M)_T = \sum_{i=0}^{N} \sum_{j=0}^{N'} \sum_{k=0}^{N''} (MA_{i}B_{j}C_{k}) \quad (5)
\]

If the concentration of the metal ion is kept constant, and a constant large excess of supporting electrolyte is present, substituting equation (5) into equation (4) and subtracting from equation (3), yields

\[
E_{eq} - E_C = S \log \left( \sum_{i=0}^{N} \sum_{j=0}^{N'} \sum_{k=0}^{N''} \beta_{ijk}(A)^i(B)^j(C)^k \right) \quad (6)
\]

Rearranging equation (6) and by definition of the function \( F_0 \),

\[
F_0 = \text{antilog} \left( \frac{E_{eq} - E_C}{S} \right) = \sum_{i=0}^{N} \sum_{j=0}^{N'} \sum_{k=0}^{N''} \beta_{ijk}(A)^i(B)^j(C)^k \quad \frac{1}{S} \quad (7)
\]
When only one type of ligand is complexed, equation (7) expands to
\[ F_0 = 1 + \beta_1(A) + \beta_2(A)^2 + \ldots + \beta_n(A)^n \] (8)
which can be rearranged to
\[ F_1 = \frac{F_0 - 1}{(A)} = \beta_1 + \beta_2(A) + \ldots + \beta_n(A)^{n-1} \] (9)
If the successive \( \beta \)'s are sufficiently separated, the constants can be determined by a graphical plot of \( F_1 \) versus \( A \). A straight line will be obtained with an intercept equal to \( \beta_1 \) and a slope equal to \( \beta_2 \). After the first constant has been determined, higher \( F \) functions can be used to obtain the higher constants.
\[ F_2 = \frac{F_1 - \beta_1}{(A)} = \beta_2 + \beta_3(A) + \ldots + \beta_n(A)^{n-2} \] (10)
In general,
\[ F_x = \frac{F_{x-1} - \beta_{x-1}}{(A)} = \beta_x + \ldots + \beta_n(A)^{n-x} \] (11)
If only a single complex exists over a large range of \( (A) \) values, the \( F \) function will remain constant and can be determined directly. The \( F \) function will also remain constant if all the other complex species present in the particular range of \( (A) \) values are known and the appropriate values can be subtracted from the function.

In complicated situations such as those in which many complex species are formed with one type of ligand throughout the entire concentration range of study so that at no time is one species the predominant one or if complexes can form with more than one ligand or if complexes can form with two variable ligands at the same time, it is
necessary to solve for the constants by use of simultaneous equations. The use of determinants for the calculations of stability constants has been discussed by Hindman and Sullivan.\textsuperscript{79} Procedures for mixed complexes and those associating with hydrogen ions have been developed in this laboratory.\textsuperscript{80} For the case of a metal ion complexing with two ligands, the equations take the form of

\begin{equation}
F_1 = \beta_{10} \text{f} \beta_{20}(A) \text{f} \beta_{01}(B) \text{f} \beta_{02}(B)^2 \text{f} \beta_{11}(B)
\end{equation}

Complexes containing hydrogen ions can be treated in this way if one considers the hydrogen ion and the ligand bound to the metal ion rather than the hydrogen ion bound to the ligand as is normally considered. Thus, the equilibrium would be written as

\begin{equation}
M \text{f} iA \text{f} jB \text{f} kC \rightleftharpoons MA_iB_jC_k
\end{equation}

and the complexity constant would be expressed as

\begin{equation}
\beta_{ijk} = \frac{(MA_iB_jC_k)}{(N)(A)^i(B)^j(C)^k}
\end{equation}

where \(iA, jB,\) and \(kC\) in equation (13) indicates the number of hydrogen ions, polyphosphate ions and hydroxyl ion in the complex, rather than as normally expressed

\begin{equation}
M \text{f} iAB \text{f} kC \rightleftharpoons M(AB)_iC_k
\end{equation}
and its complexity constant,
\[ \beta_{ik} = \frac{(M(AB)_i)^k}{(M)(AB)^{i+k}} \]  
(16)

One can convert \( ijk \) to the more generally accepted \( ik \) form from

the acid dissociation equation
\[ A_1B_j \rightleftharpoons iA \neq jB \]  
(17)

and the dissociation constant
\[ K_a = \frac{(A)^i(B)^j}{(A_1B_j)} \]  
(18)

Multiplying equation (14) by equation (18) one obtains equation (16).

Thus,
\[ \frac{(MA_1B_1C_k)}{(M)(A)^i(B)^j(C)^k} \times \frac{(A)^i(B)^j}{(A_1B_j)} = \frac{(MA_1B_1C_k)}{(M)(A_1B_j)(C)^k} \]  
(19)

The true concentration of hydrogen and hydroxyl ions are actually not known, but rather their activities, since a pH meter standardized against buffers of known hydrogen ion activity, is used in studies of this type. However, by use of hybrid acidity constants determined at the same ionic strength one can convert the hybrid complexity constants to the true complexity constant.

After the complexity constants have been determined, either by use of determinants or by means of graphical interpretation, the appropriate substitution of these values and the ligand concentrations into equations of the type of equation (12) allows the calculation of a theoretical \( F_1 \) at the various experimental values based on potential shift. A much smaller value of the experimentally determined \( F_1 \) than the theoretical \( F_1 \) would indicate the existence of a complex species.
which was not taken into consideration, while agreement between the
two values is a good indication of the accuracy of the calculated
complexity constants as well as an indication that the proper species
were assumed to be present.

The hybrid acidity constants of the polyphosphoric acids were
calculated from a titration of the acid. Using pyrophosphoric acid,
as an example, the stepwise dissociations and corresponding hybrid
constants are

\[
\begin{align*}
H_4Py & \rightleftharpoons H^+ + H_3Py^{1-} & k_1 &= \frac{[H^+][H_3Py^{1-}]}{[H_4Py]} \quad (20) \\
H_3Py^{1-} & \rightleftharpoons H^+ + H_2Py^{2-} & k_2 &= \frac{[H^+][H_2Py^{2-}]}{[H_3Py^{1-}]} \quad (21) \\
H_2Py^{2-} & \rightleftharpoons H^+ + HPy^{3-} & k_3 &= \frac{[H^+][HPy^{3-}]}{[H_2Py^{2-}]} \quad (22) \\
HPy^{3-} & \rightleftharpoons H^+ + Py^{4-} & k_4 &= \frac{[H^+][Py^{4-}]}{[HPy^{3-}]} \quad (23)
\end{align*}
\]

where Py indicates the pyrophosphate ion, brackets indicate activities,
and parentheses indicate concentrations.

Let \( b \) equal the number of millimoles of hydroxide added per
millimole of pyrophosphoric acid originally present and \( C_p \) equal the
molarity of pyrophosphoric acid present in any solution. Then, for
the conservation of pyrophosphate in all forms, \( C_p = (H_4Py) \neq (H_3Py^{1-}) \neq (H_2Py^{2-}) \neq (HPy^{3-}) \neq (Py^{4-}) \quad (24) \)

and for the conservation of sodium ions,

\( bC_p = (Na^+) \quad (25) \)
The equation for conservation of neutrality is

\[
\left( \text{Na}^+ \right) + (\text{H}^+) = (\text{H}_3\text{Py}^{1-}) + 2(\text{H}_2\text{Py}^{2-}) + 3(\text{HPy}^{3-}) + 4(\text{Py}^{1-}) + (\text{OH}^-) \tag{26}
\]

When \( b \) is appreciably less than 1, the only forms of the pyrophosphate which need to be considered are \( \text{H}_4\text{Py} \) and \( \text{H}_3\text{Py}^{1-} \). The others can be neglected since there is a negligible secondary ionization or hydrolysis of an acid or base for which the ionization constants differ by 100 fold. Thus, equations (24) and (25) reduce to

\[
C_p = (\text{H}_4\text{Py}) \neq (\text{H}_3\text{Py}^{1-}) \tag{27}
\]

and,

\[
bC_p \neq (\text{H}^+ ) = (\text{H}_3\text{Py}^{1-}) \neq (\text{OH}^-) \tag{28}
\]

Subtracting equation (27) from equation (28), yields

\[
(\text{H}_4\text{Py}) = (1-a)C_p - (\text{H}^+) \neq (\text{OH}^-) \tag{29}
\]

Solving equation (27) for the \( (\text{H}_3\text{Py}^{1-}) \) species, yields,

\[
(\text{H}_3\text{Py}^{1-}) = aC_p \neq (\text{H}^+) - (\text{OH}^-) \tag{30}
\]

Substituting equations (29) and (30) into (20) yields,

\[
k_1 = \frac{[\text{H}^+ \left[ \frac{bC_p \neq (\text{H}^+) \neq (\text{OH}^-)}{(1-b)C_p \neq (\text{H}^+) \neq (\text{OH}^-)} \right]}}{(1-b)C_p \neq (\text{H}^+) \neq (\text{OH}^-)} \tag{31}
\]

By definition of hydrogen ion activity,

\[
[\text{H}^+] = f(\text{H}^+) \tag{32}
\]

and, from the ionization of water,

\[
(\text{OH}^-) = \frac{K_w}{[\text{H}^+]} = \frac{K_w}{[\text{H}^+] / f} \tag{33}
\]

Solving equation (31) in terms of hydrogen ion activity,

\[
k_1 = \frac{[\text{H}^+ \left[ \frac{bC_p \neq ([\text{H}^+] / f - \frac{K_w}{[\text{H}^+] / f})}{(1-b)C_p \neq ([\text{H}^+] / f - \frac{K_w}{[\text{H}^+] / f})} \right]}}{(1-b)C_p \neq ([\text{H}^+] / f - \frac{K_w}{[\text{H}^+] / f})} \tag{34}
\]
When the value of \( b \) is between 1 and 2, the species of pyro-phosphoric acid which need to be considered are \((\text{H}_3\text{Py}^{-1})\) and \((\text{H}_2\text{Py}^{2-})\).

In this case, equations (24) and (25) reduce to

\[
\text{C}_p = (\text{H}_3\text{Py}^{-1}) \neq (\text{H}_2\text{Py}^{2-}) \tag{35}
\]

and

\[
\text{bC}_p \neq (\text{H}^f) = (\text{H}_3\text{Py}^{-1}) \neq 2(\text{H}_2\text{Py}^{2-}) \neq (\text{CH}^-) \tag{36}
\]

Subtracting the above two equations yields,

\[
(\text{H}_2\text{Py}^{2-}) = (b-1)\text{C}_p \neq (\text{H}^f) \neq (\text{CH}^-) \tag{37}
\]

Solving for \((\text{H}_3\text{Py}^{-1})\) yields,

\[
(\text{H}_3\text{Py}^{-1}) = (2-b)\text{C}_p - (\text{H}^f) \neq (\text{CH}^-) \tag{38}
\]

Substituting equations (37), (38), (39) and (33) into (21) yields

\[
k_2 = \frac{\left[ \text{H}^f \right] \left[ (b-1)\text{C}_p \neq \frac{\text{H}_f}{f} - \frac{\text{K}_w}{[\text{H}_f]/f} \right]}{(2-b)\text{C}_p - \frac{[\text{H}_f]}{f} - \frac{\text{K}_w}{[\text{H}_f]/f}} \tag{39}
\]

To solve for \(k_3\) the value for \(b\) between the values 2 and 3 where the species \(\text{H}_2\text{Py}^{2-}\) and \(\text{HPy}^{3-}\) predominant needs to be considered. In this situation equation (24) is written as

\[
\text{C}_p = (\text{H}_2\text{Py}^{2-}) \neq (\text{HPy}^{3-}) \tag{40}
\]

and equation (25) is written as

\[
\text{bC}_p \neq (\text{H}^f) = 2(\text{H}_2\text{Py}^{2-}) \neq 3(\text{HPy}^{3-}) \neq (\text{CH}^-) \tag{41}
\]

Solving equations (40) and (41) for \((\text{HPy}^{3-})\) yields

\[
(\text{HPy}^{3-}) = (b-2)\text{C}_p \neq (\text{H}^f) \neq (\text{CH}^-) \tag{42}
\]

Solving for \((\text{H}_2\text{Py}^{2-})\) yields

\[
(\text{H}_2\text{Py}^{2-}) = (3-b)\text{C}_p - (\text{H}^f) \neq (\text{CH}^-) \tag{43}
\]
Substituting (32), (33), (42), and (43) into (22) yields

\[
k_3 = \frac{[H^+] \left[ (b-2)C_p \left( \frac{[H^+]}{f} - \frac{K_w}{[H^+] / f} \right) \right]}{(3-b)C_p - \frac{[H^+]}{f} + \frac{K_w}{[H^+] / f}}
\]

(44)

Similarly, \(k_1\) is solved in the region where \(b\) lies between the values 3 and 4. In this region, the species which need to be considered are \((HPy^3\text{~})\) and \((Py^{4-})\). Therefore, equation (24) reduces to

\[C_p = (HPy^3\text{~}) \neq (Py^{4-})\]

(45)

and equation (25) reduces to

\[bC_p \neq (H^+) = 3(HPy^3\text{~}) \neq 4(Py^{4-}) \neq (OH^-)\]

(46)

Solving the above two equations for \((Py^{4-})\) yields

\[(Py^{4-}) = (b-3)C_p \neq (H^+) - (OH^-)\]

(47)

and, \((HPy^3\text{~})\) is given by the equation

\[(HPy^3\text{~}) = (4-b)C_p - (H^+) \neq (OH^-)\]

(48)

Substituting equations (32), (33), (47), and (48) into (23) yields

\[
k_4 = \frac{[H^+] \left[ (b-3)C_p \left( \frac{[H^+]}{f} \right) - \frac{K_w}{[H^+] / f} \right]}{(4-b)C_p - \frac{[H^+]}{f} + \frac{K_w}{[H^+] / f}}
\]

(49)

Similar derivations were made for triphosphoric and tetraphosphoric acids. In general, the dissociation constants of the acid are given by the equation

\[
k_n = \frac{[H^+] \left[ (b-n+1)C_p \left( \frac{[H^+]}{f} - \frac{K_w}{[H^+] / f} \right) \right]}{(n-b)C_p - \frac{[H^+]}{f} + \frac{K_w}{[H^+] / f}}
\]

(50)
If the acid is not too dilute and the constants are between $10^{-5}$ and $10^{-9}$ constants are given by the equation

$$k_n = \left[ H^n^+ \right] \text{ at } b = n^{-\frac{1}{2}}$$

(51)

To solve for the free concentration of the alkaline polyphosphate ion the following derivation was made using pyrophosphate ion as an example.

The stepwise dissociation of pyrophosphoric acid was given by equations (20) through (23). Solving these equations in terms of $(Py^{4-})$ and substituting into equation (24) yields

$$C_p = \left[ \frac{[H]^4}{k_1 k_2 k_3 k_4} + \frac{[H]^3}{k_2 k_3 k_4} + \frac{[H]^2}{k_3 k_4} + \frac{[H]}{k_4} + 1 \right] \times (Py^{4-})$$

(52)

converting to a common denominator and solving for $(Py^{4-})$ yields,

$$(Py^{4-}) = \frac{k_1 k_2 k_3 k_4 C_p}{k_1 k_2 k_3 [H]^4 + k_1 k_2 [H]^2 + k_1 [H]^3 + [H]^4}$$

(53)

Since $[H^+]$ can be measured by a pH meter and the acid dissociation constants were previously determined, the concentration of free polyphosphate ion is readily calculated.

The amount of complexed ligand can be neglected if the concentration of free alkaline polyphosphate is much greater than that of the metal ion. At lower ligand concentrations, a correction must be applied for the amount of ligand present in the complex.
CHAPTER III
THE COMPLEXES OF MERCURY(I) WITH PYROPHOSPHATE

Experimental

Following the procedure of Pugh,\textsuperscript{81} a stock solution of mercury(I) nitrate was prepared by shaking red mercury(II) oxide, mercury and nitric acid until after the addition of sodium chloride, a filtered aliquot gave no test for mercury(II) ion upon testing with $\text{H}_2\text{S}$. It was then standardized by titration versus a standard sodium chloride solution using 0.04 per cent bromophenol blue as the indicator.

Mercury(II) nitrate was prepared by dissolving metallic mercury with freshly boiled concentrated nitric acid and diluting. The mercury(II) nitrate solution was standardized against standard thiocyanate using ferric alum indicator following the method of Kolthoff and Sandell.\textsuperscript{82}

\textsuperscript{81} W. Pugh, J. Chem. Soc., 1824 (1937).

Throughout this thesis, $C_{Hg^2}$ will indicate the molar concentration of $Hg^2^{2+}$ ions which is equal to $\frac{1}{2}$ the molar concentration of mercury(I) atoms.

The sodium pyrophosphate (Baker analyzed reagent grade) was titrated with nitric acid to ascertain its purity and concentration.

Potassium pyrophosphate was prepared following the method of Kolthoff and Watters$^{13}$ by heating dibasic potassium phosphate (Baker analyzed reagent grade) for 3 hours at 500-700°C. After dissolving the salt in distilled water, an aliquot was titrated with standard nitric acid using a Beckman Model G pH meter to determine the concentration and the apparent acidity constants in the presence of 1 molar potassium ion.

The potential of the aquo solution of mercury(I) mercury was measured at pH 1.90 in the presence of sodium ions and 3.07 in the presence of potassium ion. These pH's were used because the potential and the pH of the solutions varied with time and were very slow to reach an equilibrium potential.

Potentials were measured with a Rubicon Model 2780 potentiometer. Most of the polarograms were made with a manual polarogram designed by Watters.$^{83}$ However, some survey work was done using a Sargent-

with a "general purpose" glass electrode was used for all pH measurements.

All experiments were performed in a constant temperature water bath maintained at 25\(\pm0.1\) degrees centigrade. In all experiments the alkaline pyrophosphate solution was used for the highest pH values and the lower pH values were obtained by making stock solutions containing varying amounts of nitric acid. In the studies made in the presence of alkali metals the saturated calomel half-cell and the dropping electrode half-cell were connected by means of two 3 per cent agar-agar bridges of 11 mm inner diameter containing 1 M KNO₃, dipping into an intermediate beaker containing 1 M KNO₃.

Experimental Results and Discussion

Preliminary polarograms of pyrophosphate complexes with both mercury(1) and mercury(II) obtained by means of a Sargent-Heyrovsky Model XII Polarograph are shown in Figure 1. Both mercury(I) and mercury(II) solutions yielded the same spontaneous potential but the mercury(II) aquo ion has a diffusion current which is somewhat lower. However, it was noted that in the presence of pyrophosphate ion the polarographic waves of both mercury(II) and mercury(I) exactly coincided. The addition of chloride ion indicated the presence of mercury(I) ion in the mercury(II) pyrophosphate solution, while the mercury(I) pyrophosphate solution showed no evidence of mercury(II) ion after precipitation of mercury(I) chloride, filtration and the addition of hydrogen sulfide to the filtrate. These results indicate
Figure 1. Survey Polarogram of the Mercury Pyrophosphate System

Curve 1: \[1.22 \times 10^{-3} \text{M } \text{Hg}_{2}(\text{NO}_{3})_{2}\]
\[5 \times 10^{-2} \text{M } \text{Na}_{4}\text{Py}\]
\[0.0005\% \text{ Methyl Red}\]

\[1.23 \times 10^{-3} \text{M } \text{Hg}(\text{NO}_{3})_{2}\]
\[5 \times 10^{-2} \text{M } \text{Na}_{4}\text{Py}\]
\[0.0005\% \text{ Methyl Red}\]

Curve 2: \[1.22 \times 10^{-3} \text{M } \text{Hg}_{2}(\text{NO}_{3})_{2}\]
\[1 \text{M } \text{NaNO}_{3}\]
\[0.0005\% \text{ Methyl Red}\]

Curve 3: \[1.23 \times 10^{-3} \text{M } \text{Hg}(\text{NO}_{3})_{2}\]
\[1 \text{M } \text{NaNO}_{3}\]
\[0.0005\% \text{ Methyl Red}\]

Curve 4: \[5 \times 10^{-2} \text{M } \text{Na}_{4}\text{Py}\]
\[0.0005\% \text{ Methyl Red}\]
that a stable mercury(I) pyrophosphate complex is formed. Furthermore, after mixing a solution of mercury(II) pyrophosphate with elementary mercury for one hour, exactly two moles of mercury(I) were precipitated for each mole of mercury(II) originally present. These observations were also made by Yamone and Davidson.5

A polarographic study of millimolar mercury(I) pyrophosphate was begun using the manual polarograph. However, it was soon noted that a very limited range of pH was available due to precipitation of the mercury(I) pyrophosphate. The concentration of mercury(I) ion was then reduced to $10^{-5}$ M and it was noted that the polarographic waves practically coincided with the residual current wave. The spontaneous potential was determined primarily by the residual or charging current of the dropping mercury electrode. Therefore, it was decided to use a quiet mercury pool similar to that used by Mason in his studies of the complexes of mercury(II) with ethylenediamine tetraacetate.

The hybrid acidity constants for pyrophosphoric acid were obtained using equation (50) on data obtained by titrating the salt in the presence of one molar alkali metal with standard nitric acid. In the presence of one molar sodium ion, the constants obtained were $pK_4 = 7.48$ and $pK_3 = 5.40$ while in the presence of one molar potassium ion the values obtained were 7.89 and 5.66, respectively. It was found that the first and second hydrogen ion, corresponding to $K_1$ and

---

$K_2$ were not associated sufficiently to have effect on the calculation of the free pyrophosphate ion. Thus, equation (53) reduces to

$$\frac{(Py)}{K_2K_4(Fy)} = \frac{K_3K_4}{K_3[BF_3] + [BF_3]^2}$$

(54)

For the mercury(1) pyrophosphate system in the presence of one molar sodium ion it was found that the data were consistent with the assumption that $Hg_2Py$, $Hg_2Py$, $Hg_2PyOH$, and $Hg_2Py(OH)_2$. Thus equation (7) can be written as

$$F_0 = \text{antilog} \left( \frac{\varepsilon_{\text{aq}} - \varepsilon_c}{s} \right) = \beta_0010(Py) + \beta_0020(Py)^2 + \beta_0011(Py)(OH^-) + \beta_0012(Py)(OH^-)^2$$

(55)

where $Py$ indicates the pyrophosphate ion and the charges on the ions are omitted for convenience.

It then follows that

$$F_1 = \frac{F_0 - 1}{(Py)} = \beta_0010 + \beta_0020(Py) + \beta_0011(OH^-) + \beta_0012(OH^-)^2$$

(56)

A series of $F_1$ terms were calculated from the shift of electrode potential by varying the pH of a stock solution containing mercury(1) ion and pyrophosphate ion in the presence of one molar sodium ion. These potential shifts as a function of pH are shown in Figure 2. It was found that $F_1$ had a constant value of $10^{10.83}$ in the pH range of 5.29-4.56. This value corresponds to $\beta_010$.

$$Hg_2^{2+} + P_2O_7^{4-} \rightleftharpoons Hg_2(P_2O_7)^{2-}; \quad \beta_{010} = \frac{(Hg_2(P_2O_7)^{2-})}{(Hg_2^{2+})(P_2O_7^{4-})} = 10^{10.83}$$

(57)

(in the presence of 1.0 M Na$^+$.)
Figure 2. Potentiometric Potential Shifts as a Function of pH for the Mercury(1) Pyrophosphate System.

\[ C_{\text{Hg}_2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{\text{Py}} = 3.88 \times 10^{-2} \text{ M} \]

Curve 1: In the presence of 1.0 M Sodium Ion.
Curve 2: In the presence of 1.0 M Potassium Ion.
Pyrophosphate
To solve for $\beta_{020}$, a higher $F$ function was obtained.

$$F_2 = \frac{F_1 - \beta_{010}}{(Py)} = \beta_{020} + \beta_{011} \frac{(OH^-)}{(Py)} + \beta_{012} \frac{(OH^-)^2}{(Py)}$$

(58)

Again a pH region was found where $F_2$ was constant. This range was from a pH of 8.32 to 5.73. Thus

$$\text{He}_{2}^{2+} + 2\text{P2O}_7^{4-} \rightleftharpoons \text{He}_{2}(\text{P2O}_7)^{6-}; \beta_{020} = \frac{(\text{He}_{2}(\text{P2O}_7)^{6-})}{(\text{He}_{2}^{2+})(\text{P2O}_7)^{4-})^2} = 10^{11.72}$$

(in the presence of 1.0 M Na$^+$).

To solve for the complex species containing hydroxyl ion a new function was written as

$$F_{2a} = \frac{F_1 - \beta_{010} - \beta_{020}(Py)}{(OH^-)} = \beta_{011} + \beta_{012}(OH^-)$$

(60)

The above equation was solved graphically in Figure 3. A plot of $F_{2a}$ versus hydroxyl ion concentration yielded a slope equal to $\beta_{012}$

$$\text{He}_{2}^{2+} + \text{P2O}_7^{4-} + 2\text{OH}^- \rightleftharpoons \text{He}_{2}(\text{P2O}_7)(\text{OH})^{1-}; \beta_{012} = \frac{(\text{He}_{2}(\text{P2O}_7)(\text{OH})^{1-})}{(\text{He}_{2}^{2+})(\text{P2O}_7)^{4-})(\text{OH}^-)}$$

$$= 10^{20.41}$$

(in the presence of 1.0 M Na$^+$).

and an intercept equal to $\beta_{011}$

$$\text{He}_{2}^{2+} + \text{P2O}_7^{4-} + \text{OH}^- \rightleftharpoons \text{He}_{2}(\text{P2O}_7)(\text{OH})^{3-}; \beta_{011} = \frac{(\text{He}_{2}(\text{P2O}_7)(\text{OH})^{3-})}{(\text{He}_{2}^{2+})(\text{P2O}_7)^{4-})(\text{OH}^-)}$$

$$= 10^{15.07}$$

(in the presence of 1.0 M Na$^+$).

The value obtained for $\beta_{012}$ was further checked by the equation

$$F_{3a} = \frac{F_{2a} - \beta_{011}}{(OH^-)} = \beta_{012}$$

(63)
Figure 3. Graphic Determination of $\beta_{011}$ and $\beta_{012}$ for the Mercury(I) Pyrophosphate System in the Presence of 1.0 M Sodium Ion

$C_{Hg^2} = 1.22 \times 10^{-5} \text{ M}$

$C_{Py} = 0.05 \text{ M}$

$C_{Na} = 1.0 \text{ M}$
Mercurous Pyrophosphate in 1.0 M Na⁺.
and a constant value for $F_{38}$ was obtained of $10^{20.14}$ which agrees very well with that obtained graphically.

The potentiometric potential shifts as a function of pH for the mercury(I) pyrophosphate system in the presence of one molar potassium ion is also shown in Figure 2. In solving equation (56) for $F_1$ it was found that $F_1$ never assumed a constant value but decreased with decreasing pH and then increased as pH continued to decrease. It was then postulated that a $(\text{Hg}_2\text{Py})$ complex existed at low pH values and equation (56) was rewritten as

$$F_1 = \frac{F_{C-1}}{(F_{Py})} = \beta_{110} \left(\frac{\text{HPy}}{(F_{Py})}\right) + \beta_{010} + \beta_{020} + \beta_{011} \left(\text{ OH}^-\right) + \beta_{012} \left(\text{ OH}^-\right)^2$$

(64)

Consequently, $\beta_{010}$ was determined by plotting the free pyrophosphate ion concentration versus the $F_1$ term in the pH range were $F_1$ decreased with decreasing pH in Figure 4. The intercept was taken for the $\beta_{010}$ value

$$\text{Hg}_2^{2+} + 2\text{P}_2\text{O}_7^{\text{4-}} \rightleftharpoons \text{Hg}_2(\text{P}_2\text{O}_7)^{2-}$$

$$\beta_{010} = \frac{(\text{Hg}_2(\text{P}_2\text{O}_7)^{2-})}{(\text{Hg}_2^{2+})(\text{P}_2\text{O}_7^{4-})} = 10^{9.25}$$

(in the presence of 1.0 M K$^+$).

and the slope was $\beta_{020}$

$$\text{Hg}_2^{2+} + 2\text{P}_2\text{O}_7^{\text{4-}} \rightleftharpoons \text{Hg}_2(\text{P}_2\text{O}_7)^{6-}$$

$$\beta_{020} = \frac{(\text{Hg}_2(\text{P}_2\text{O}_7)^{6-})}{(\text{Hg}_2^{2+})(\text{P}_2\text{O}_7^{4-})^2} = 10^{12.25}$$

(in the presence of 1.0 M K$^+$)

To solve for $\beta_{110}$ equation (19) was used

$$\beta_{110} = \frac{F_{C-1} - \beta_{010}}{[\text{H}^+]^2} \times K_4$$

(19)
Figure 4. Graphical Determination of $\rho_{010}$ in the Presence of Potassium Ion.

\[ C_{He2} = 1.22 \times 10^{-5} \text{ M}; \]
\[ C_{Py} = 3.88 \times 10^{-2} \text{ M}; \]
\[ C_K = 1.0 \text{ M} \]
The three logarithm values of \((F_1 - \beta_{010}) / [H^+]\) were found to be 13.83, 13.78 and 13.88 at pH's 4.99, 4.84 and 4.63 respectively. Thus, 
\[
\beta_{110} = \frac{(\text{Hg}_2\text{HP}_2\text{O}_7^-)}{(\text{Hg}_2^{2+})(\text{HP}_2\text{O}_7^-)^3} = 10^{13.83} \times 10^{-7.89} = 105.94
\]  
(67)

The complex species \(\text{Hg}_2\text{HPy}\) was found to be negligible in the acidity range where the species \(\text{Hg}_2\text{Py}_2, \text{Hg}_2\text{PyCH}\) and \(\text{Hg}_2\text{Py(OH)}_2\) existed.

Therefore, the graphical determination of \(\beta_{010}\) and \(\beta_{020}\) was valid and equations (58), (60) and (63) used in the presence of sodium ion could also be used when potassium ion was present. The values obtained were

\[
\text{Hg}_2^{2+} + 2\text{P}_2\text{O}_7^- \rightleftharpoons \text{Hg}_2(\text{P}_2\text{O}_7^-)_2; \beta_{020} = \frac{(\text{Hg}_2(\text{P}_2\text{O}_7^-)_2^-)}{(\text{Hg}_2^{2+})(\text{P}_2\text{O}_7^-)^2} = 10^{12.27}
\]  
(in the presence of 1.0 M Kf)

\[
\text{Hg}_2^{2+} + \text{P}_2\text{O}_7^- + \text{OH}^- \rightleftharpoons \text{Hg}_2(\text{P}_2\text{O}_7^-)(\text{OH})^-; \beta_{011} = \frac{(\text{Hg}_2(\text{P}_2\text{O}_7^-)(\text{OH})^-)}{(\text{Hg}_2^{2+})(\text{P}_2\text{O}_7^-)(\text{OH}^-)} = 10^{15.85}
\]  
(in the presence of 1.0 M Kf)

\[
\text{Hg}_2^{2+} + \text{P}_2\text{O}_7^- + 2\text{OH}^- \rightleftharpoons \text{Hg}_2(\text{P}_2\text{O}_7^-)(\text{OH})_2^-; \beta_{012} = \frac{(\text{Hg}_2(\text{P}_2\text{O}_7^-)(\text{OH})_2^-)}{(\text{Hg}_2^{2+})(\text{P}_2\text{O}_7^-)(\text{OH}^-)^2} = 10^{20.05}
\]  
(in the presence of 1.0 M Kf)

In Tables 1 and 3 are listed the potential data for the mercury(I) pyrophosphate system in the presence of one molar sodium and potassium ions, respectively, along with the logarithm terms for the concentration of free alkaline pyrophosphate ion and the various F functions.
The logarithm contributions of the various complex species to $F_1$ are listed in Tables 2 and 4 for the system in the presence of one molar sodium and potassium ions, respectively. From these tables the percentage distribution of the complex species as a function of pH shown in Figures 5 and 6 was calculated.

The summary of the complexity constants found is given in Table 5.
Table 1
Potential Data of Pyrophosphate-Mercury(I) System in the Presence of 1 M Sodium Ion

\( C_{Hg^2} = 1.22 \times 10^{-5} \text{ M; } C_{By} = 0.05 \text{ M; } C_{Na} = 1.0 \text{ M; } E_{aq} = 0.3852 \text{ v. vs. S.C.E.} \)

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Table 2

Contributions of Various Complex Species to $F_1$

$C_{\text{Hg}_2} = 1.22 \times 10^{-5} \text{ M}; C_{\text{Py}} = 0.05 \text{ M}; C_{\text{Na}} = 1.0 \text{ M}; E_{eq} = 0.3852 \text{ v. vs. S.C.E.}$

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Table 3
Potential Data of Pyrophosphate-Mercury(I) System in the Presence of 1 M Potassium Ion

\[ C_{Hg2} = 1.22 \times 10^{-5} \text{ M; } C_{Py} = 3.88 \times 10^{-2} \text{ M; } C_K = 1.0 \text{ M; } E_{aq} = 0.3753 \]

v. vs. S.C.E.

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Table 4

Contributions of Various Complex Species to $F_1$

$C_{Hg^2} = 1.22 \times 10^{-5} \text{ M}; C_{Py} = 3.88 \times 10^{-2} \text{ M}; C_R = 1.0 \text{ M}; E_{aq} = 0.3753$

v. vs. S.C.E.

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Table 4 (contd.)

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Figure 5. Percentage Distribution of Mercury(I) Pyrophosphate Complex Species as a Function of pH in the Presence of Sodium Ion.

\[ C_{\text{Hg}^2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{\text{Py}} = 0.05 \text{ M} \]
\[ C_{Na} = 1.0 \text{ M} \]

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<td>( \text{Hg}_2\text{PyOH} )</td>
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<td>Curve 4</td>
<td>( \text{Hg}_2\text{Py(OH)}_2 )</td>
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Percentage Distribution of Complex Species

Complexes of Mercurous Pyrophosphate in the Presence of 1.0 M Sodium Ions.
Figure 6. Percentage Distribution of Mercury(I) Pyrophosphate Complex Species as a Function of pH in the Presence of Potassium Ion.

\[ C_{Hg_2} = 1.22 \text{ M} \]
\[ C_{Py} = 0.04 \text{ M} \]
\[ C_K = 1.0 \text{ M} \]

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Complexes of Mercurous Pyrophosphate in the Presence of 1.0 M Potassium Ion.
Table 5

Complexity Constants for Pyrophosphate-Mercury(I) System

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CHAPTER IV
THE COMPLEXES OF MERCURY(I) WITH TRIPHOSPHATE

Experimental

The experimental procedures and equipment were the same as for the pyrophosphate study. The sodium triphosphate was purified before use by the procedure described by Watters, Loughran and Lambert. For brevity the triphosphate ion will sometimes be indicated by the symbol, Tp.

Potassium triphosphate was prepared by means of ion-exchange chromatography. A 100 cm. by 4 cm. Pyrex column filled to a height of 60 cm. with Dowex 50-x12 cation exchange resin, 100-200 mesh, low porosity, supported on a Pyrex glass wool plug was used. This column was fitted with a Pyrex water jacket through which ice water could be circulated to decrease the extent of hydrolysis. The column was initially charged by means of a 15 per cent solution of hydrochloric acid. A 10 per cent solution of potassium chloride containing just enough potassium hydroxide to make the solution slightly basic was then passed through the column. The inclusion of base insured the complete replacement of hydrogen ion. Next a 15 per cent solution of potassium chloride was passed through the column, after which it was rinsed overnight with distilled water. Then, a solution of sodium triphosphate of approximately twice the desired concentration was...
passed through. The first 5 per cent of effluent, which yielded a flame test for potassium, was collected and discarded, after which, 85 per cent of effluent was collected and used immediately. Continual flame tests for sodium were negative throughout the period of collection. The solutions used on the column were transferred to a separatory funnel which was then tightly stoppered. The stem was inserted into the column at the desired liquid level and, once set, this feed mechanism automatically maintained the desired level of liquid above the resin.

The Acidity Constants of Triphosphoric Acid in the Presence of 1 M Sodium and Potassium Ions

From the results of a titration of 0.05 molar sodium triphosphate adjusted to 1.0 molar sodium ion with sodium nitrate versus 0.96 molar nitric acid containing 1.0 molar sodium nitrate the acidity constants for triphosphoric acid, in the presence of 1.0 molar sodium ion, were determined to be, $pK_5 = 7.00$ and $pK_4 = 4.83$ by use of equation (50).

To determine the constants in the presence of potassium ions, a preliminary titration of the effluent from the ion-exchange column was performed to determine the correct amount of potassium ion to be added to bring the total concentration of potassium ion up to 1.0 molar. After a similar titration as in the case in the presence of sodium ion the acidity constants for triphosphoric acid in the presence of 1.0 molar potassium ion were determined to be $pK_5 = 7.36$ and $pK_4 = 4.96$. 
The calculation of the concentration of free triphosphate ion was made by use of equations similar to equation (53). As in the situation of pyrophosphate, only the last two acidity constants were required to make this calculation.

The Complexity Constants of Mercury(I) with Triphosphate

The experimentally determined potentiometric potential shifts as a function of pH are shown in Figure 7. It was possible to measure the potential shift in the presence of sodium ion down to a pH of 4. However, in the presence of potassium ion, the difference in potential remained constant as the pH was decreased below a pH of 6.75.

The complexity constants for the mercury(I) triphosphate system in the presence of 1.0 molar sodium ion were obtained from equation (56) by use of determinants and the complexity constants were

\[
Hg_2^{2+} + H_3P_3O_10^4- \rightleftharpoons Hg_2(H_3P_3O_10)^2-; \beta_{110} = \frac{(Hg_2(H_3P_3O_10)^2-)}{(Hg_2^2)(H_3P_3O_10^4-)} = 10^{4.34} \tag{71}
\]

\[
Hg_2^{2+} + 2H_3P_3O_10^5- \rightleftharpoons Hg_2(H_3P_3O_10)^3-; \beta_{010} = \frac{(Hg_2(H_3P_3O_10)^3-)}{(Hg_2^2)(H_3P_3O_10^5-)} = 10^{7.16} \tag{72}
\]

\[
Hg_2^{2+} + 2H_3P_3O_10^5- \rightleftharpoons Hg_2(H_3P_3O_10)^2-; \beta_{020} = \frac{(Hg_2(H_3P_3O_10)^2-)}{(Hg_2^2)(H_3P_3O_10^5-)^2} = 10^{8.90} \tag{73}
\]
Figure 7. Potentiometric Potential Shifts as a Function of pH for
the Mercury(I) Triphosphate System.

Curve 1: \[ C_{Hg^2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{IP} = 3.58 \times 10^{-2} \text{ M} \]
\[ C_K = 1.0 \text{ M} \]

Curve 2: \[ C_{Hg^2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{TP} = 5.0 \times 10^{-2} \text{ M} \]
\[ C_{Na} = 1.0 \text{ M} \]
These results are summarized in Table II.

A slightly different procedure was used to calculate the complexity constants for the mercury(I) triphosphate system in the presence of 1.0 molar potassium ion. In this case, the problem was solved starting from the higher pH values. Equation (56) was modified to

$$\frac{F_1}{(OH^-)} = \beta_{011} + \beta_{012}(\text{OH}^-)$$

The graph of the above equation shown in Figure S, gave a nearly straight line for the more basic solutions with an intercept of $\beta_{011} = 10^{14.31}$ and a slope of $\beta_{012} = 10^{20.35}$. The use of determinants confirmed that the predominant complexes present in this range of acidity were $\text{Hg}_2\text{TpOH}$ and $\text{Hg}_2\text{Tp(OH)}_2$, and the values for $\beta_{011}$ and $\beta_{012}$ obtained were

$$\text{Hg}_2^{2+} + \text{P}_3\text{O}_{10}^- + \text{OH}^- \rightleftharpoons \text{Hg}_2\text{(P}_3\text{O}_{10})\text{(OH)}_4^-; \beta_{011} = \frac{(\text{Hg}_2\text{(P}_3\text{O}_{10})\text{(OH)}_4^-)}{(\text{Hg}_2^{2+})(\text{P}_3\text{O}_{10}^-)(\text{OH}^-)} = 10^{14.22}$$

(in the presence of 1 M $\text{K}^+$)
Figure 8. Graphic Determination of $\beta_{011}$ and $\beta_{012}$ for the Triphosphate System in the Presence of Potassium Ion.
Graphic Determination of $\beta_{11}$ and $\beta_{12}$ for Triphosphate in Potassium System.
\[
\begin{align*}
\text{After } \beta_{011} \text{ and } \beta_{012} \text{ were determined, equation (56) was rewritten as} \\
F_1 - \beta_{011}(\mathrm{CH}^-) - \beta_{012}(\mathrm{OH}^-)^2 &= \beta_{010} + \beta_{020}(\text{Tp}) \\
\text{Equation (79) was solved by means of determinants and the values obtained in the presence of 1 M K}^+ \text{ were} \\
\beta_{010} &= \frac{\langle \text{Hg}_2^2'(\text{P}_3^{10}^-) \rangle}{\langle \text{Hg}_2^2'(\text{P}_3^{10}^-) \rangle} = 10^{7.84} \\
\beta_{020} &= \frac{\langle \text{Hg}_2^2'(\text{P}_3^{10}^-)^2 \rangle}{\langle \text{Hg}_2^2'(\text{P}_3^{10}^-)^2 \rangle} = 10^{9.47}
\end{align*}
\]

These complexity constants are summarized in Table 11.

The potential data for the mercury(I) triphosphate system along with the logarithm term for the concentration of free alkaline triphosphate ion and the various F functions in the presence of one molar sodium ion are listed in Tables 6, 7, and 8, while the data in the presence of one molar potassium ion are listed in Tables 9 and 10.
Table 6
Potential Data of Triphosphate-Mercury(I) System in the Presence of 1 M Sodium Ion at High pH Range

\[ C_{\text{Hg2}} = 1.22 \times 10^{-5} \text{ M}; \ C_{\text{Tp}} = 0.05 \times 10^{-2} \text{ M}; \ C_{\text{Na}} = 1.0 \text{ M}; \ E_{\text{aq}} = 0.3852 \text{ vs. S.C.E.} \]

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Table 7
Potential Data of Triphosphate-Mercury(I) System in the Presence of 1 M Sodium Ion at Low pH Range

\( \text{C}_{\text{Hg}_2} = 1.22 \times 10^{-5} \text{M}; \text{C}_{\text{Tp}} = 5 \times 10^{-2} \text{ M}; \text{C}_{\text{Na}} = 1.0 \text{ M}; \text{E}_{\text{aq}} = 0.3852 \text{ v. vs. S.C.E.} \)

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Table 8

Contributions of Various Complex Species to $F_1$

$C_{Hg^2} = 1.22 \times 10^{-5} \ M; \ C_{T_p} = 5 \times 10^{-2} \ M; \ C_{Na} = 1.0 \ M; \ E_{aq} = 0.3852 \ v. \ vs. \ S.C.E.$

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Table 9

Potential Data of Triphosphate-Mercury(I) System in the Presence of 1.0 M Potassium Ion

\[ C_{Hg_2} = 1.22 \times 10^{-5} \text{ M}; \quad C_{Tp} = 3.58 \times 10^{-2} \text{ M}; \quad C_K = 1.0 \text{ M} \]

\[ E_{aq} = 0.3753 \text{ v. vs. S.C.E.} \]

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Table 10

Contributions of Various Complex Species to $F_1$

$C_{Hg_2} = 1.22 \times 10^{-5} \text{ M}$; $C_{Tp} = 3.58 \times 10^{-2} \text{ M}$; $C_K = 1.0 \text{ M}$; $E_{eq} = 0.3753$ v. vs. S.C.E.

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Table 10 (contd.)

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Figure 9. Percentage Distribution of Mercury(I) Triphosphate Complex Species in the Presence of 1.0 M Sodium Ions.

\[ C_{Hg^2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{Tp} = 4.35 \times 10^{-2} \text{ M} \]
\[ C_{Na} = 1.0 \text{ M} \]

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<td>Hg₂Tp₂</td>
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<td>Hg₂TpOH</td>
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<td>Hg₂Tp(CH)₂</td>
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Percentage Distribution of Complex Species

Complexes of Mercurous Triphosphate in the Presence of 10 M Sodium Ion.
Figure 10. Percentage Distribution of Mercury(I) Triphosphate Complex Species in the Presence of 1.0 M Potassium Ions as a Function of pH.

\[ C_{Hg^2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{Tp} = 3.58 \times 10^{-2} \text{ M} \]
\[ C_{K} = 1.0 \text{ M} \]

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<td>Hg(_2)Tp(CH(_2))_2</td>
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Complexes of Mercurous Triphosphate in the Presence of 1.0 M Potassium ion.
From Tables 3 and 10 the percentage distribution of the complex species as a function of pH was calculated and is shown in Figures 9 and 10 in the presence of one molar sodium ion and potassium ion, respectively.

The logarithms of the complexity constants for the Mercury(I) triphosphate in the presence of 1 molar concentrations of these two alkali metals that were determined are listed in Table 11.
Table 11

Complexity Constants for Triphosphate-Mercury(I) System

<table>
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<tr>
<th>Alkali metal concentration</th>
<th>$\log_{10} C_{10}$</th>
<th>$\log_{10} C_{010}$</th>
<th>$\log_{10} C_{020}$</th>
<th>$\log_{10} C_{011}$</th>
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<td>1.0 M Potassium</td>
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<td>7.84</td>
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CHAPTER V

THE COMPLEXES OF MERCURY(I) WITH TETRAPHOSPHATE

Experimental

The experimental procedures and equipment were the same as for the pyrophosphate and triphosphate studies. Tetraphosphate ion was prepared, according to a slight modification of a procedure by Quimby and his coworkers85 by opening the cyclic 4 member ring in tetramer-

—


...phosphate by hydrolysis in alkaline solution. Hexaguanidine tetraphosphate was crystallized from the solution to separate tetraphosphate from other hydrolysis products. Subsequent studies indicated that guanidine forms a complex with tetraphosphate. Consequently, the acidity constants and the complexity constants obtained were in the presence of 0.15 molar guanidine. The source of the tetrametaphosphate was a commercial product "Cyclophos" manufactured by the Victor Chemical Co., 155 N. Wacker Dr., Chicago 6, Illinois.

In this procedure, 300 grams of crude Na₄P₄O₁₂·H₂O was dissolved in 2 liters of water at room temperature and filtered. Ethanol was added in a steady small stream until precipitation began, after which, the rate was reduced so that the remainder of one liter of ethanol was
added over a period of at least one hour, the solution being stirred vigorously throughout the addition. The solution was filtered and washed twice, first with 300 ml. of 50 per cent ethanol, then with 300 ml. of 35 per cent ethanol. The crystals were redissolved and re-precipitated as before with a total of 1 ml. of ethanol for each 2 ml. of water used.

A 10-15 per cent solution of Na₄P₄O₁₂ was prepared and, after cooling, mixed with sufficient cold concentrated NaOH to yield a 8.5-10 per cent solution of Na₄P₄O₁₂ and three moles NaOH per mole of Na₄P₄O₁₂, without allowing the temperature to exceed 40°C. This solution was stored at a constant temperature of 32°C until two moles of NaOH had been consumed, as shown by periodic titrations of the excess NaOH to a pH of about 10. The time required was three weeks.

A more concentrated solution was prepared by mixing an equal volume of ethanol with the above solution of Na₄P₄O₁₂ and allowing it to stand until clear liquid layers formed. The lower layer, which was a syrupy liquid containing about 44 per cent Na₄P₄O₁₂, was separated by means of a separatory funnel. Further purification was effected by adding three volumes of water to one volume of the 44 per cent solution, mixing well, then adding four volumes of ethanol and separating as before.

To 100 grams of the syrupy liquid (ca. 44 g. or 0.094 moles Na₄P₄O₁₂) 121 grams of guanidinium chloride (hereafter indicated as (GuH)Cl) (Eastman Organic Chemicals) in 121 ml. water was added. To the aqueous solution at 25-28°C, formamide was gradually added with
vigorous stirring until the solution became faintly turbid and further small additions were periodically made until the turbidity persisted. This required about 700 ml. of formamide. Upon the addition of 5 ml. of water, crystallization began. Stirring was continued for one hour after which the crystals were filtered off on a sintered glass filter and washed three times with 50 ml. portions of anhydrous ethanol. The crystals were air-dried to constant weight at 25-28°C and a relative humidity of 50 per cent. The yield of air-dried product was about 75 per cent.

For higher purity, the crystals were recrystallized by dissolving 45 grams of (GuH)6P4O17H2O and 5 grams of (GuH)Cl in 75 ml. of water and diluted gradually with sufficient formamide (about 70 ml.) to produce a permanent turbidity. The crystals were filtered off and washed as above. About 85 per cent of the hexaguanidinium tetraphosphate was recovered.

Experimental Determination of Acidity Constants

Since a titration of 0.25 molar hexaguanidinium tetraphosphate in the presence of 10 molar alkali metal ion with 0.200 molar hydrochloric acid containing 1.0 molar alkali metal ion gave only a very slight inflection at the point where one equivalent of acid had been added per equivalent of the salt titrated, Bjerrum's method was applied in a manner applied by Watters, Loughran and Lembert in their studies of the acidity constants of triphosphoric acid. It was
necessary to use this method as the constants have values which do not differ greatly. The constants are expressed as stepwise complexity constants, thus

$$\beta^n = \frac{(H_n P_4 C_{13}^{(6-n)})}{([H^+]^n)(P_4 C_{13}^{6-})}$$

(82)

where parentheses again indicate concentrations and brackets indicate activities. The symbol $P$ will be used to indicate the tetraphosphate ion.

Bjerrum's formation function is written in the form

$$\bar{n} = (1-n) \beta_1 [H^+] + (2-n) \beta_2 [H^+]^2 + (3-n) \beta_3 [H^+]^3 + (4-n) \beta_4 [H^+]^4 + (5-n) \beta_5 [H^+]^5 + (6-n) \beta_6 [H^+]^6$$

(83)

It was found that in the range of interest only the first two terms on the right side of equation (83) were required to calculate the first two acidity constants. To calculate $\bar{n}$, the average number of bound hydrogen ions per tetraphosphate ion, the total number of moles of hydrogen and tetraphosphate ion were obtained from the titration data, the concentrations of free hydrogen ions are assumed to be equal to the known concentration of hydrochloric acid having the same pH in the presence of the same concentration of indifferent electrolyte. These $P_CH$ values were found to be $0.10 \pm 0.02$ units smaller than the measured pH values giving a corresponding activity coefficient of 0.80 which is consistent with the results of Harned and Ehlers$^{86}$ and with

The simultaneous solution of equations (83) by use of determinants yielded the results for the stepwise acidity constants as $pK_6 = 6.53$; $pK_5 = 4.97$; in the presence of 1 M sodium ion; 0.15 M guanidinium ion and $pK_6 = 6.92$ and $pK_5 = 5.22$ in the presence of 1 M potassium ion and 0.15 M guanidinium ion.

Experimental Determination of Complexity Constants

Solutions containing $1.22 \times 10^{-5}$ M Hg$_2$(NO$_3$)$_2$, $2.5 \times 10^{-2}$ M (Gua)$_6$P$_3$O$_{13}$, 1.0 M NaNO$_3$ and varying amounts of HNO$_3$ were prepared. One of the solutions was then added to a half-cell of the potentiometric apparatus, mercury was introduced and electrical connection made by means of a platinum wire which was totally immersed in the mercury layer. After the potential versus the saturated calomel electrode was read, the pH was taken by means of a Beckman Model G pH meter. Acid variations were made by the addition of solutions of different acidity than the first.

In the presence of one molar potassium ion the above procedure was repeated with the exception that 1.0 M KNO$_3$ replaced the 1.0 M NaNO$_3$.

The experimentally determined potential shifts as a function of pH are shown in Figure 11. As was the case for mercury(I) triphosphate in the presence of 1.0 molar potassium ion, the difference in potentials remained constant below a pH of about 6.

Equation (76), the graph of which is shown in Figure 12 was used to calculate $\beta_{011}$ and $\beta_{012}$ for the mercury(I) tetraphosphate system.
Figure 11. Potentiometric Potential Shifts as a Function of pH for the Mercury(I) Tetraphosphate System.

\[ C_{He2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{Pq} = 2.50 \times 10^{-2} \text{ M} \]

Curve 1: In the presence of 1.0 M Sodium Ion.
Curve 2: In the presence of 1.0 M Potassium Ion.
Figure 12. Graphic Determination of $\beta_{011}$ and $\beta_{012}$ for the Tetraphosphate System in the Presence of Sodium Ion.
Graphic Determination of $\beta_{11}$ and $\beta_{12}$ in the Tetraphosphate Sodium System.
in the presence of 1.0 molar sodium ion. A straight line was obtained in the more alkaline region. The results obtained were

\[
\text{Hg}_2^{2+} + P_{4}O_{13}^{6-} + \text{OH}^- \rightleftharpoons \text{Hg}_2(P_{4}O_{13})(\text{OH})^5^-; \beta_{011} = \frac{(\text{Hg}_2)(P_{4}O_{13})(\text{OH})^5^-}{(\text{Hg}_2^{2+})(P_{4}O_{13})^2(\text{OH}^-)} = 10^{15.91}
\]

(in the presence of 1.0 M Na\(^+\) and 0.15 M guanidinium ion) \(\text{(84)}\)

and,

\[
\text{Hg}_2^{2+} + P_{4}O_{13}^{6-} + 2\text{OH}^- \rightleftharpoons \text{Hg}_2(P_{4}O_{13})_2(\text{OH})^6^-; \beta_{012} = \frac{(\text{Hg}_2)(P_{4}O_{13})(\text{OH})^6^-}{(\text{Hg}_2^{2+})(P_{4}O_{13})^2(\text{OH}^-)^2} = 10^{22.64}
\]

(in the presence of 1.0 M Na\(^+\) and 0.15 M guanidinium ion) \(\text{(85)}\)

After the above results were found equation (79) was solved by means of determinants to find \(\beta_{010}\) and \(\beta_{020}\) and the results obtained were

\[
\text{Hg}_2^{2+} + P_{4}O_{13}^{6-} \rightleftharpoons \text{Hg}_2(P_{4}O_{13})^{4^+}; \beta_{010} = \frac{(\text{Hg}_2)(P_{4}O_{13})^{4^+}}{(\text{Hg}_2^{2+})(P_{4}O_{13})^2} = 10^{6.98}
\]

(in the presence of 1.0 M Na\(^+\) and 0.15 M guanidinium ion) \(\text{(86)}\)

and,

\[
\text{Hg}_2^{2+} + 2P_{4}O_{13}^{6-} \rightleftharpoons \text{Hg}_2(P_{4}O_{13})^{10^+}; \beta_{020} = \frac{(\text{Hg}_2)(P_{4}O_{13})^{10^+}}{(\text{Hg}_2^{2+})(P_{4}O_{13})^2} = 10^{9.42}
\]

(in the presence of 1.0 M Na\(^+\) and 0.15 M guanidinium ion) \(\text{(87)}\)

These results are summarized in Table 16.

The use of determinants on equations of the type of equation (76) gave the values of
\[ \begin{align*}
&\text{in the presence of 1.0 M } K^+ \text{ and 0.15 M guanidinium ion) (88)}\
&\text{and,}\
&\text{in the presence of one molar potassium ion. Then, equation (79) was used to solve for } \beta_{010} \text{ and } \beta_{020} \text{ graphically as is shown in Figure 13. The results obtained were}\
&\text{in the presence of 1.0 M } K^+ \text{ and 0.15 M guanidinium ion) (90)}\
&\text{and,}\
&\text{in the presence of 1.0 M } K^+ \text{ and 0.15 M guanidinium ion) (91)}
\end{align*} \]

These results are also summarized in Table 16.

The potential data for the mercury(II) tetraphosphate system in the presence of one molar sodium or potassium ions along with the logarithm terms for the concentration of free alkaline tetraphosphate ion and the various F functions are listed in Tables 12 and 14, respectively. Tables 13 and 15 list the logarithm contributions of
the various complex species found and also the calculated log F value. The data from Tables 13 and 15 were then used to calculate the percentage distribution of the various complex species as a function of pH which is shown in Figures 14 and 15.
Figure 13. Graphic Determination of $\beta_{010}$ for the Tetraphosphate System in the Presence of Potassium Ion.
Graphic Determination of $\beta_4$ in the Tetraphosphate Potassium System.
Table 12
Potential Data of Tetraphosphate-Mercury(I) System in the Presence of 1.0 M Sodium Ion

\[ \text{C}_{\text{Hg}2} = 1.22 \times 10^{-5} \text{ M}; \text{C}_{\text{Pq}} = 2.491 \times 10^{-2} \text{ M}; \text{C}_{\text{Na}} = 1.0 \text{ M}; E_{\text{aq}} = 9.3852 \text{ v. vs. S.C.E.} \]

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Table 13
Contributions of Various Complex Species to $F_1$

\[ C_{\text{Hg}_2} = 1.22 \times 10^{-5} \text{ M}; \ C_{\text{Pq}} = 2.49 \times 10^{-2} \text{ M}; \ C_{\text{Na}} = 1.0 \text{ M}; \ E_{\text{eq}} = 0.3852 \text{ v. vs. S.C.E.} \]

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Table 14
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\[ c_{e2} = 1.22 \times 10^{-5} \text{ M}; \ c_{pq} = 2.484 \times 10^{-2} \text{ M}; \ c_k = 1.0 \text{ M}; \ E_{eq} = 0.3753 \]

v. vs. S.C.E.

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</table>
Table 15
Contributions of Various Complex Species to $F_1$

$C_{Hg^2} = 1.22 \times 10^{-5} \text{ M; } C_{Pq} = 2.484 \times 10^{-2} \text{ M; } C_K = 1.0 \text{ M; } E_{eq} = 0.3753$


ds. vs. S.C.E.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\log F_1$</th>
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Table 15 (contd.)

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<th>Calcd. log $F_1$</th>
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</table>
Table 16

Complexity Constants for Tetraphosphate-Mercury(I) System

<table>
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<tr>
<th>Alkali metal concentration</th>
<th>Logarithm of Complexity Constants</th>
<th>$\beta_{010}$</th>
<th>$\beta_{020}$</th>
<th>$\beta_{011}$</th>
<th>$\beta_{012}$</th>
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<tbody>
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<td>15.91</td>
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<td>1.0 M Potassium</td>
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<td>7.32</td>
<td>9.88</td>
<td>15.26</td>
<td>22.45</td>
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</table>
Figure 14. Percentage Distribution of Mercury(I) Tetraphosphate Complex Species in the Presence of 1.0 M Sodium Ions as a Function of pH.

\[
\begin{align*}
C_{\text{Hg}_2} &= 1.22 \times 10^{-5} \text{ M} \\
C_{\text{Pq}} &= 2.491 \times 10^{-2} \text{ M} \\
C_{\text{Na}} &= 1.0 \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Curve</th>
<th>Complex Species</th>
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<tbody>
<tr>
<td>1</td>
<td>$\text{Hg}_2\text{PqOH}$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{Hg}_2\text{Pq(CH)}_2$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Hg}_2\text{Pq}_2$</td>
</tr>
<tr>
<td>4</td>
<td>$\text{Hg}_2\text{Pq}$</td>
</tr>
</tbody>
</table>
Figure 15. Percentage Distribution of Mercury(I) Tetraphosphate Complex Species in the Presence of 1.0 M Potassium Ions as a Function of pH.

\[ \text{Curve} \quad \begin{array}{c|c} \text{Complex Species} \\ \hline 1 & \text{Hg}_2\text{Pq(OH)}_2 \\ 2 & \text{Hg}_2\text{PqOH} \\ 3 & \text{Hg}_2\text{Pq}_2 \\ 4 & \text{Hg}_2\text{Pq} \\ \end{array} \]

\[ C_{\text{Hg}_2} = 1.22 \times 10^{-5} \text{ M} \]
\[ C_{\text{Pq}} = 2.484 \times 10^{-2} \text{ M} \]
\[ C_K = 1.0 \text{ M} \]
Complexes of Mercurous Tetraphosphate in the Presence of 1.0 M Potassium Ion.

Percentage Distribution of Complex Species.
The experimentally determined complexity constants can be used to determine the stepwise formation constants of the various species, thus

\[
\text{Hg}_2^2 + L \rightleftharpoons \text{Hg}_2L \\
\beta_{010} = K_{010}^{000} = \frac{(\text{Hg}_2 L)}{(\text{Hg}_2^2)(L)}
\]

(92)

\[
\text{Hg}_2L + L \rightleftharpoons \text{Hg}_2L_2
\]

(93)

\[
K_{010} = \frac{(\text{Hg}_2L_2)}{(\text{Hg}_2)(L)} = \frac{\beta_{020}}{\beta_{010}}
\]

\[
\text{Hg}_2LOH + OH^- \rightleftharpoons \text{Hg}_2L(OH)_2
\]

(94)

\[
K_{011} = \frac{(\text{Hg}_2L)(OH)_2}{(\text{Hg}_2LOH)(OH^-)} = \frac{\beta_{011}}{\beta_{010}}
\]

(95)

\[
\text{Hg}_2L + OH^- \rightleftharpoons \text{Hg}_2LOH
\]

(96)

\[
K_{012} = \frac{(\text{Hg}_2L)(OH)_2}{(\text{Hg}_2LOH)(OH^-)} = \frac{\beta_{012}}{\beta_{011}}
\]

(97)

Similar equations can be derived for the displacement constant

\[
\text{Hg}_2L_2 + OH^- \rightleftharpoons \text{Hg}_2LOH + L
\]
The values of the above constants along with those of Yamane and Davidson\textsuperscript{5} are summarized in Table 17.

Also included are the last two hybrid acidity constants of the polyphosphoric acids. The logarithms of these acidity constants are 0.1 to 0.4 smaller in the presence of sodium ion which forms a more stable complex with polyphosphates than does potassium ion. This difference persists in the stepwise constants for the addition of the polysphosphate, \( K_{010}^{000} \) and \( K_{010}^{010} \), but not in those for the addition of hydroxyl. Sturrock has already shown that the presence of alkali metal ions can actually enhance the stability of copper polysphosphate complexes proving that these ions may also be present in the complex. It is reasonable that a similar situation exists in the mercury(1) polyphosphate complexes. This study indicates that the complexes are slightly more stable in the presence of potassium ion. The magnitudes of the stepwise constants obtained in this study for the mercury(1) pyrophosphate and triphosphate complexes are surprisingly similar to those obtained by Sturrock for the corresponding copper(II) complexes. The largest discrepancy between the results in this study and that of Yamane and Davidson occurs in \( \beta_{020} \) of the triphosphate. This leads to a value of 4.07 for \( \log K_{020}^{010} \) which is relatively large for the second stepwise constant of an ionic ligand. In general, the differences between their results and those of this study are due to the fact that they found fewer complexes to be present. No other studies of tetraphosphate systems are available for comparison.
Table 17

Summary of Complexity Constants for Mercury(I) Polyphosphate System
Expressed as Logarithms

<table>
<thead>
<tr>
<th>Medium</th>
<th>pK_N</th>
<th>pK_{N-1}</th>
<th>β_{010}</th>
<th>β_{020}</th>
<th>β_{011}</th>
<th>β_{012}</th>
<th>K_{000}</th>
<th>K_{010}</th>
<th>K_{011}</th>
<th>K_{012}</th>
<th>K_{020}</th>
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<tr>
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<td>7.89</td>
<td>5.66</td>
<td>9.75</td>
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<td>11.71</td>
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<td>8.83</td>
<td>2.88</td>
<td>5.34</td>
<td>4.34</td>
<td>3.77</td>
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<tr>
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<td>12.38*</td>
<td>15.64*</td>
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</table>

B Triphosphate

<table>
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<th>pK_{N-1}</th>
<th>β_{010}</th>
<th>β_{020}</th>
<th>β_{011}</th>
<th>β_{012}</th>
<th>K_{000}</th>
<th>K_{010}</th>
<th>K_{011}</th>
<th>K_{012}</th>
<th>K_{020}</th>
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<td>6.38</td>
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<td>15.00*</td>
<td>7.16*</td>
<td>4.07*</td>
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C Tetraphosphate

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*Results by Yamane and Davidson.
As one might predict from the relative magnitudes of the tri-
phosphate and tetraphosphate acidity constants, the first stepwise
constant of the tetraphosphate complex is slightly smaller than that
of the triphosphate. It was not anticipated that the second stepwise
constant of the tetraphosphate complex would be larger than that of
the triphosphate. However this may be due to the fact that the re-
pulsive forces between the two ligands are smaller in the tetraphos-
phate since the negative charge is distributed over more phosphate
tetrahedra, some of which may not be found to Hg\(^{2+}\).

In a review, Bjerrum\(^{37}\) discussed statistical corrections to be


applied to formation constants in order to evaluate other contribu-
tions. On purely statistical grounds, the first ligands to be
taken up would be bound more strongly than the subsequent ones. Since
two polyphosphates can be added to Hg\(^{2+}\), there are at least two ways
of adding the first polyphosphate but only one way this polyphosphate
can ionize once added. There is one way a second polyphosphate ion
can be added to Hg\(_2\)Py\(^{-}\) and either of two polyphosphate ions can
ionize. Hence, a statistical effect of 0.3 logarithm units subtracted
from the first stepwise formation constant and added to the second
will give the statistically free formation constants. On a purely
statistical basis, the difference of logarithm of the first and the
second stepwise formation constants should be 0.60. However the dif-
ference between the stepwise constants is much larger. This is to be
anticipated when the bound ligand is charged.
The accuracy of the constants determined are dependant on the relative percentage distribution. In the mercury(I) pyrophosphate system in the presence of sodium ion, the species, \( \text{Hg}_2\text{PyOH} \), was never the dominant species. Consequently, the value of its constant is least accurate in this system. In the presence of potassium ion the greatest accuracy is to be expected for the species, \( \text{Hg}_2\text{Py} \) and \( \text{Hg}_2\text{Py}_2 \) while the others are somewhat less accurate. For the mercury(I) triphosphate system in the presence of sodium ion the most accurately determined complexity constants are those for \( \text{Hg}_2\text{Tp} \) and \( \text{Hg}_2\text{TpOH} \) while the least accurate is the constant for \( \text{Hg}_2\text{Tp}_2 \). In the presence of potassium ion, the constant for \( \text{Hg}_2\text{Tp}(\text{OH})_2 \) is the most accurate while the others are about equally accurate because these species reach nearly equal distribution at the proper pHs. For the mercury(I) tetraphosphate system in the presence of sodium ion the species \( \text{Hg}_2\text{Pq}_2 \) and \( \text{Hg}_2\text{Pq} \) were present to the extent of not more than 5 percent so that their constants are not very accurate. In the presence of potassium ion only the species \( \text{Hg}_2\text{Pq}(\text{OH})_2 \) was ever the dominant one, the others consequently, could be determined only with much less accuracy.

Many investigators in their studies of higher phosphates found more acid complexes than in this study, especially Schupp, Sturrock and Watters who were able to investigate copper complexes at a much higher acidity and found complexes of \( \text{CuHPy}^{-} \), \( \text{CuH}_2\text{Py}^{0} \), \( \text{CuHPy}_2^{-} \), \( \text{CuH}_2\text{Py}_2^{1-} \), \( \text{CuH}_3\text{Py}_2^{2-} \), and \( \text{CuH}_4\text{Py}_2^{2-} \).
In the present study the potentials decreased and then increased with decreasing pH, so that potentials could not be determined at the acidities where more acid complexes could exist. The pH limits were 4.56 for pyrophosphate in the presence of sodium ion, 4.63 for pyrophosphate in the presence of sodium, 6.60 for triphosphate in the presence of potassium ion, 5.98 for tetraphosphate in the presence of sodium ion, and 6.15 for tetraphosphate in the presence of potassium ion. This lower limit of pH may be due to the oxidation of the mercury pool. The formation of acidic complexes is probable and the magnitude of the constants found in this study are reasonable. However, the fact that the complexes could not be detected in all of the systems makes these constants less reliable than the others.

Although the results of this study do not lead directly to the structure of the complexes or to the reason why certain ligands are able to form stable complexes with mercury(I), some deductions are possible.

Whether mercury is in the uni- or divalent state, all of its inner d orbitals are filled. On the basis of the atomic orbital approach, this leaves the possibility of forming linear sp, trigonal sp², or tetrahedral sp³ bonds around each mercury(II) or mercury(I) ion. Since mercury(I) exists as the dimer ion, Hg₂⁺, in which one bond is shared between the mercury(I) ions, this leaves a possibility of forming two additional linear sp bonds, four additional sp² bonds, or six additional sp³ bonds. Consequently, the classical configurations, linear, tetrahedral, and octahedral, remain as possible structures in either mercury(I) or (II).
The linear structure occurs in mercury(I) halides. In an x-ray study of the Hg-Hg bond length of the mercury(I) ion, Grdenic and Djordjevic\textsuperscript{88,89} found that in mercury(I) nitrate dihydrate each mercury atom was surrounded by four atoms, namely the next mercury atom, two oxygen atoms of the same nitrate ion and one oxygen atom belonging to a water molecule. A very short bond distance between the mercury atom and the water molecule suggested a polarization effect of the mercury(I) ion on the water molecule and that the oxonium ion exists in the crystal structure as well as in aqueous solution. The values for the distance from mercury to the nitrate-oxygen atoms are less than the sum of corresponding van der Waal radii so that they also suggest a tetrahedral configuration around each mercury(I) ion.

If the free energy of bond formation of the mercury(II) complex is greater than twice that of all the bonds in the Hg\textsuperscript{2+} complex including the mercury to mercury bond, the mercury(I) complex may be expected to disproportionate to form free mercury and the mercury(II) complex. This situation occurs whenever the ligand contains nitrogen as the electron pair donor. However, it is a curious fact that when oxygen is the electron pair donor, the complex bond strength decreases rapidly from cadmium(II) to zinc(II) to mercury(II), which are the


\textsuperscript{89} D. Grdenic and C. Djordjevic, ibid., 1956, 1316.
terminal members of the di-transition series.\textsuperscript{90} In this case the


ligand bond strength of mercury(II) does not seem to be sufficient to
cause disproportionation. This is consistent with the fact that the
only stable complexes of mercury(I) which have been observed are those
with ligands containing oxygen as the electron pair donor, namely,
water, oxalate, malonate, and polyphosphates.\textsuperscript{5}

Since there is a negative charge of 1- or 2- on every PO\textsubscript{4}
tetrahedron and a 1+ charge on each mercury(I), it seems reasonable
that each polyphosphate ion is bound to both mercury(I) ions. This
is supported by the fact that the second polyphosphate ligand is bound
much more weakly than the first.

Polyphosphates could be bound by six-membered or larger rings in
a variety of structures without strain. However, studies of the acid
properties of the copper(II) complexes indicate that six-membered
rings are probable. The fact that one pyrophosphate ion can be re­
placed by one hydroxyl, does not eliminate the possibility of chelate
ring structures since one water molecule may be complexed along with
the hydroxyl ion. Furthermore, the sp\textsuperscript{2} or sp\textsuperscript{3} structure could be re­
placed by the linear sp structure. Nuclear magnetic resonance studies
may show which phosphate tetrahedra are complexed. If the complex
species can be found in crystal structures, x-ray studies may also
yield information concerning the structure.
The study of mercury(I) complexes is a new and exciting field for research which may yield rewards in theoretical and applied chemistry.
I, Richard A. Simonaitis, was born in Chicago, Illinois, on December 7, 1930. I received my primary and secondary education in the schools of Chicago, Illinois. I received my B.S. in Chemistry from the University of Illinois in June 1952 and entered the Graduate School of The Ohio State University in October 1952. From October 1952 to December 1954, I was employed by the Department of Chemistry as a teaching assistant. From January 1955 to October 1956, I served in the Army of the United States. I returned to The Ohio State University in October 1956 and received my M.S. degree in August 1957. Since my return I have served as a teaching assistant in the Chemistry Department.