

THE HYDROLYSIS OF THE CONDENSED PHOSPHATES¹

II (A). THE ROLE OF THE HYDROGEN ION IN THE HYDROLYSIS OF SODIUM PYROPHOSPHATE

II (B). THE DISSOCIATION CONSTANTS OF PYROPHOSPHORIC ACID

By J. D. MCGILVERY AND JOAN PEDLEY CROWTHER

ABSTRACT

The general rate equations for the hydrolysis of pyrophosphate anion proposed by Muus have been proved to be inapplicable over the pH range 2.0 to 11.0. A general rate equation is proposed which is based on the assumption that each anionic species of pyrophosphoric acid hydrolyzes at a rate which depends on its concentration, and that the only role of the hydrogen ion concentration is to determine the proportion of each species present in the solution. A mechanism for the hydrolysis of pyrophosphate anion is suggested.

The dissociation constants of pyrophosphoric acid have been determined at 65.5°C. for the concentration range 0.08 to 0.18 molar.

II (A). THE ROLE OF THE HYDROGEN ION IN THE HYDROLYSIS OF SODIUM PYROPHOSPHATE

INTRODUCTION

In the first paper (9) on this subject, it was established that the rate of hydrolysis of sodium pyrophosphate in solution depended on the hydrogen ion concentration but that this hydrolysis was a first order reaction when a constant hydrogen ion concentration was maintained. Fig. 1 is the curve obtained by

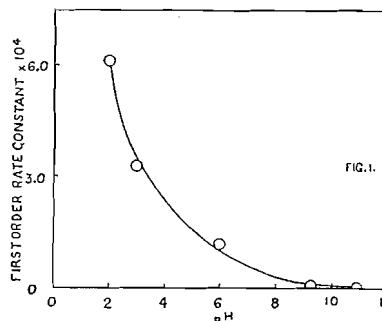


FIG. 1. Effect of pH on rate of hydrolysis of sodium pyrophosphate in solution.

plotting the first order rate constants against the pH of the pyrophosphate solutions.

Although there was no evidence of a base-catalyzed hydrolysis over the entire pH range investigated, Fig. 1 shows that hydrogen ion is an effective catalyst. It is also evident that the relationship between the rate of hydrolysis and the hydrogen ion concentration is not a simple one. If, for example, we assume a rate equation of the form:

$$[1] \quad \frac{dC}{dt} = -k[H^+]^n C$$

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where C is the concentration of pyrophosphate at time t (this includes all the various forms of pyrophosphate which may be present in the solution, as e.g. $\text{H}_4\text{P}_2\text{O}_7$, $\text{H}_3\text{P}_2\text{O}_7^-$, etc.), it is found that the data are best satisfied by a value of about $1/4$ for n .

It is difficult to conceive of a mechanism which would satisfactorily explain the fractional power of the hydrogen ion concentration. Furthermore, this rate equation implies that all the pyrophosphate forms in the solution are equivalent in so far as hydrolysis is concerned. Although this might be true, it seems likely that the reactivity of a pyrophosphate anion is influenced by its degree of ionization. Since pyrophosphoric acid is polybasic, pyrophosphate solutions contain a variety of partially dissociated anionic species, the relative amounts of which are determined by the pH of the solution and the dissociation constants. Thus, in a pyrophosphate solution, the following ions would be present: $\text{H}_3\text{P}_2\text{O}_7^{1-}$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$, $\text{HP}_2\text{O}_7^{3-}$, and $\text{P}_2\text{O}_7^{4-}$. In addition some undissociated acid $\text{H}_4\text{P}_2\text{O}_7$ would occur. For convenience in what follows, references to the anionic species present in pyrophosphate solutions will include the undissociated $\text{H}_4\text{P}_2\text{O}_7$.

Rate Equations for Hydrolysis of Sodium Pyrophosphate Solution

If the ease of hydrolysis of sodium pyrophosphate solutions depends on the anionic species, i.e. $\text{H}_3\text{P}_2\text{O}_7^{1-}$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$, $\text{HP}_2\text{O}_7^{3-}$, $\text{P}_2\text{O}_7^{4-}$, and $\text{H}_4\text{P}_2\text{O}_7$, it is doubtful whether any simple rate equation which takes the form of equation [1] will fit the observational data over a wide range of hydrogen ion concentrations.

A general rate equation for the acid-catalyzed hydrolysis of pyrophosphate solutions is:

$$[2] \quad -dC/dt = f_0[\text{H}^+][H_0] + f_1[\text{H}^+][H_1] + f_2[\text{H}^+][H_2] + f_3[\text{H}^+][H_3] + f_4[\text{H}^+][H_4],$$

where C is the concentration of pyrophosphate at time t ;

t is the reaction time;

$[\text{H}^+]$ is the hydrogen ion concentration;

$[H_0]$, $[H_1]$, $[H_2]$, $[H_3]$, and $[H_4]$ are the concentrations of $\text{P}_2\text{O}_7^{4-}$, $\text{HP}_2\text{O}_7^{3-}$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$, $\text{H}_3\text{P}_2\text{O}_7^{1-}$, and $\text{H}_4\text{P}_2\text{O}_7$, respectively;

$f_0[\text{H}^+]$, $f_1[\text{H}^+]$, $f_2[\text{H}^+]$, $f_3[\text{H}^+]$, and $f_4[\text{H}^+]$ are the hydrogen ion concentration functions associated with the rate of hydrolysis of H_0 , H_1 , H_2 , H_3 , and H_4 , respectively;

and $[H_0]$, $[H_1]$, $[H_2]$, $[H_3]$, and $[H_4]$ are interrelated in accordance with the dissociation constants of pyrophosphoric acid.

In order to find a rate equation for the hydrolysis of pyrophosphate solutions which fitted the experimental data, simple forms of equation [2] were investigated.

Muus (7) considered that the different anionic species of pyrophosphoric acid reverted at different rates, and the rate equation which he proposed assumed that:

$$f_i[\text{H}^+] = k_i[\text{H}^+]$$

where the k_i 's are the hydrolysis rate constants associated with the various anionic species and $i = 0, 1, 2, 3, 4$. Thus Muus' (7) rate equation took the form:

$$[3] \quad -dC/dt = [\text{H}^+]\{k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4]\},$$

where the symbols represent the same factors as above. Muus (7), however, only investigated the hydrolysis of pyrophosphate solutions over the pH range 0.91 to 1.4, and hence could not verify equation [3] outside this range. Within this pH range, Muus (7) believed that the anion $\text{H}_3\text{P}_2\text{O}_7^-$ (H_3) was the only species of pyrophosphate that played a significant rate determining role, and hence equation [3] reduced to the form:

$$[3a] \quad -dC/dt = k_3[H^+][H_3].$$

Another simple assumption from a kinetic point of view is that each anionic species hydrolyzes at its own specific rate which is quite independent of the hydrogen ion concentration. In such a picture, the only role of the hydrogen ion is to determine the proportion of each species present in the pyrophosphate solution, and thus

$$f_i[H^+] = k_i, \text{ where } i = 0, 1, 2, 3, 4.$$

The rate equation would then be:

$$[4] \quad -dC/dt = k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4],$$

where the symbols represent the same factors as above.

The above rate equations cannot be tested for applicability without a knowledge of the relationship between the proportions of each anionic species and the pH of the solution. To obtain such information the dissociation constants of a pyrophosphoric acid solution of suitable concentration were determined at 65.5°C. (II(B)) and the following values obtained:

$$[5] \quad K_1 = [H^+][H_3]/[H_4] = 0.107 \quad (\sigma = 0.009 \text{ where } n = 4),$$

$$[6] \quad K_2 = [H^+][H_2]/[H_3] = 7.58 \times 10^{-3} \quad (\sigma = 0.20 \times 10^{-3} \text{ where } n = 6),$$

$$[7] \quad K_3 = [H^+][H_1]/[H_2] = 1.45 \times 10^{-6} \quad (\sigma = 0.04 \times 10^{-6} \text{ where } n = 7),$$

$$[8] \quad K_4 = [H^+][H_0]/[H_1] = 9.81 \times 10^{-9} \quad (\sigma = 0.13 \times 10^{-9} \text{ where } n = 12),$$

where σ is the standard deviation (3) and equations 5, 6, 7, and 8 are simultaneous. The following equations relate the concentration of the various pyrophosphate anionic species to the dissociation constants, the hydrogen ion concentration, and the total pyrophosphate concentration:

$$[9] \quad [H_0] = K_1 K_2 K_3 K_4 C R,$$

$$[10] \quad [H_1] = K_1 K_2 K_3 [H^+] C R,$$

$$[11] \quad [H_2] = K_1 K_2 [H^+]^2 C R,$$

$$[12] \quad [H_3] = K_1 [H^+]^3 C R,$$

$$[13] \quad [H_4] = [H^+]^4 C R,$$

where $R = 1/(K_1 K_2 K_3 K_4 + K_1 K_2 K_3 [H^+] + K_1 K_2 [H^+]^2 + K_1 [H^+]^3 + [H^+]^4)$. Fig. 2, which shows the effect of the pH of the solution on the proportions of the various anionic species of pyrophosphate present, was constructed with the aid of equations [9] to [13], and the dissociation constants.

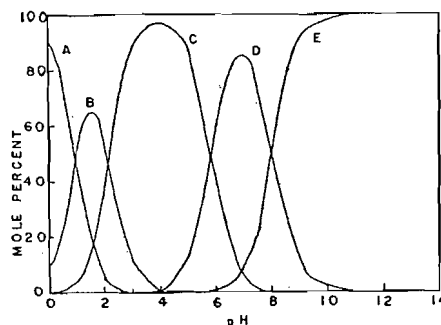


FIG. 2. Effect of pH on distribution of anionic species of pyrophosphate. A, $\text{H}_4\text{P}_2\text{O}_7$; B, $\text{H}_3\text{P}_2\text{O}_7^{1-}$; C, $\text{H}_2\text{P}_2\text{O}_7^{2-}$; D, $\text{HP}_2\text{O}_7^{3-}$; E, $\text{P}_2\text{O}_7^{4-}$.

The necessary data to solve equations [3] and [4] for the rate constants $k_0, k_1 \dots k_4$ have now been obtained, and are summarized in Table I. It will be noted that Abbott's (1) rate data have been included in Table I. Since our studies only covered the pH range 2.0–11.0, no rate data were obtained in the pH region where the concentration of $\text{H}_4\text{P}_2\text{O}_7$ was comparatively large. Therefore Abbott's (1) data, at pH 0.91 where 53% $\text{H}_4\text{P}_2\text{O}_7$ was present, were used to obtain a rough approximation of the rate constant, k_4 . It should be noted that values of k_4 , based on this data, are a very rough estimate since Abbott's (1) data were obtained for a 0.05 *M* pyrophosphate solution at 75°C. and our data were obtained for a 0.12 *M* solution at 65.5°C. Furthermore, Abbott (1) did not measure the rate at a constant hydrogen ion concentration.

Evaluation of k_i 's Assuming Muus' (7) Rate Equation

$$[3] \quad -dC/dt = [\text{H}^+]\{k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4]\}.$$

Since the hydrolysis of sodium pyrophosphate is a first order reaction at constant hydrogen ion concentration:

$$[14] \quad kC = [\text{H}^+]\{k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4]\},$$

where k is the over-all first order rate constant.

Using the data in Table I, equation [14] was solved and the following values obtained for the various rate constants:

$$\begin{aligned} k_0 &= 3.9 \times 10^5 \text{ min.}^{-1}, \\ k_1 &= -7.2 \times 10^6 \text{ min.}^{-1}, \\ k_2 &= 0.40 \text{ min.}^{-1}, \\ k_3 &= -0.21 \text{ min.}^{-1}, \\ k_4 &= 9.4 \times 10^{-2} \text{ min.}^{-1} \end{aligned}$$

Since k_1 and k_3 are negative values implying that orthophosphate anion was forming pyrophosphate anion (against which there is experimental evidence (4, 5)), equation [14] and hence equation [3] is inapplicable. If equation [3a] were applicable, the values for k_0, k_1, k_2 , and k_4 would have been insignificant or zero, and k_3 would have been positive. Since neither condition was satisfied on solving, equation [3a] is not applicable. Thus Muus' (7) rate equations are not applicable over the pH range 2.0–11.0.

TABLE I
CONCENTRATION OF INDIVIDUAL PYROPHOSPHATE ANIONS IN MOLES PYROPHOSPHATE PER LITER AT VARIOUS HYDROGEN ION CONCENTRATIONS

pH	Hydrogen ion concentration	First order rate constant (k in min.^{-1})	$\text{P}_2\text{O}_7^{4-}$ [H_0]	$\text{HP}_2\text{O}_7^{3-}$ [H_1]	$\text{H}_2\text{P}_2\text{O}_7^{2-}$ [H_2]	$\text{H}_3\text{P}_2\text{O}_7^{1-}$ [H_3]	$\text{H}_4\text{P}_2\text{O}_7$ [H_4]
10.9	1.26×10^{-11}	4.8×10^{-6}	1.22×10^{-1}	1.57×10^{-4}	—	—	—
9.3	5.01×10^{-10}	1.0×10^{-5}	1.17×10^{-1}	5.95×10^{-3}	2.06×10^{-6}	—	—
7.34	4.57×10^{-8}	$5.0 \times 10^{-5*}$	2.11×10^{-2}	9.83×10^{-2}	3.10×10^{-3}	—	—
6.0	1.0×10^{-6}	1.25×10^{-4}	7.07×10^{-4}	7.21×10^{-2}	4.97×10^{-2}	—	—
3.0	1.0×10^{-3}	3.31×10^{-4}	—	1.56×10^{-4}	1.08×10^{-1}	1.42×10^{-2}	1.33×10^{-4}
2.5	3.16×10^{-3}	$4.35 \times 10^{-4*}$	—	—	8.57×10^{-2}	3.57×10^{-2}	1.06×10^{-3}
2.0	1.0×10^{-2}	5.42×10^{-4}	—	—	5.01×10^{-2}	6.62×10^{-2}	6.18×10^{-3}
0.91	1.23×10^{-1}	$2.22 \times 10^{-3**}$	—	—	3.41×10^{-3}	5.54×10^{-2}	6.37×10^{-2}

*Rate constant source: Fig. 1.

**Rate constant source: Abbott (1).

Evaluation of k_i 's Assuming Alternate Rate Equation

$$[4] \quad -dC/dt = k_0[H_0] + k_1[H_1] + k_2[H_2] + k_3[H_3] + k_4[H_4],$$

where the symbols represent the same factors as above.

Using data from Table I, equation [4] was solved, and the following approximate values for the rate constants were obtained:

$$\begin{aligned} k_0 &= 4.7 \times 10^{-6} \text{ min.}^{-1}, \\ k_1 &= 5.25 \times 10^{-5} \text{ min.}^{-1}, \\ k_2 &= 2.8 \times 10^{-4} \text{ min.}^{-1}, \\ k_3 &= 7.3 \times 10^{-4} \text{ min.}^{-1}, \\ k_4 &= 3.9 \times 10^{-3} \text{ min.}^{-1}. \end{aligned}$$

These rate constants satisfy two necessary conditions for the applicability of equation [4] in that they are positive numbers and approximately satisfy all the data in Table I. However, the equation is not necessarily acceptable. This equation (developed by following the reasoning outlined earlier) contains sufficient constants that even if the reaction mechanism were not as pictured, a good fit might conceivably be obtained. However, since equation [4] permits a reasonable explanation of the role of the hydrogen ion and since our data approximately fit this equation, it is proposed as the general rate equation for the hydrolysis of pyrophosphate anion pending evidence to the contrary.

Order of Reaction

At constant hydrogen ion concentration equation [4] reduces to an equation for a first order reaction as demanded by the experimental data. Rewriting equation [4]:

$$[4a] \quad -\frac{dC}{dt} = C \text{ times the expression } \left\{ \frac{K_1 K_2 K_3 K_4 k_0 + K_1 K_2 K_3 [H^+] k_1 + K_1 K_2 [H^+]^2 k_2 + K_1 [H^+]^3 k_3 + [H^+]^4 k_4}{K_1 K_2 K_3 K_4 + K_1 K_2 K_3 [H^+] + K_1 K_2 [H^+]^2 + K_1 [H^+]^3 + [H^+]^4} \right\}$$

where C is the pyrophosphate concentration at time t .

The bracketed expression is a constant when the hydrogen ion concentration is constant, and equation [4a] becomes:

$$[15] \quad -dC/dt = kC,$$

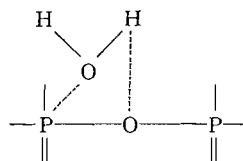
where k is the over-all first order rate constant.

Mechanism of Reaction

The magnitude of the rate constants evaluated for equation [4] indicate that the order of stability of the pyrophosphate anionic species is: $P_2O_7^{4-} > HP_2O_7^{3-} > H_2P_2O_7^{2-} > H_3P_2O_7^{1-} > H_4P_2O_7$. In addition the rate equation formulated implies that the hydrolysis is a simple reaction between water molecules and these various pyrophosphate anions. The question now arises as to why there should be such profound differences in the ease of hydrolysis of the various species.

A possible explanation might be based on the assumption that the primary steps in the hydrolysis are the formation of loose bonds between a phosphorus

atom and the oxygen atom of a water molecule, and between the oxygen atom of the P-O-P linkage and the hydrogen atom of the water molecule:



It follows that the orientation of a water molecule approaching a pyrophosphate anion will be of considerable importance. As is well known, water is a polar molecule—the fractional negative charge being located on the oxygen atom, and the fractional positive charge being located on the hydrogen atoms. It seems reasonable to suppose that, as the phosphorus atom becomes less negative, the possibility of a water molecule approaching in the required orientation for hydrolysis increases. Since the negativity of the phosphorus atoms in the various pyrophosphate anionic species decreases in the order: $\text{P}_2\text{O}_7^{4-}$, $\text{HP}_2\text{O}_7^{3-}$, $\text{H}_2\text{P}_2\text{O}_7^{2-}$, $\text{H}_3\text{P}_2\text{O}_7^{1-}$, $\text{H}_4\text{P}_2\text{O}_7$, it follows that the rate of hydrolysis of these various species will increase in the same order.

II (B). THE DISSOCIATION CONSTANTS OF PYROPHOSPHORIC ACID

INTRODUCTION

The dissociation constants of pyrophosphoric acid have been determined by Abbott and Bray (2) at 18°C. Muus (7) has also determined the second and third dissociation constants at 40°C., but he based his calculations on the assumption that the first dissociation constant was greater than two. As Abbott and Bray (2) found the value 0.14 for the first dissociation constant, Muus' (7) values seem unlikely. Since insufficient thermodynamic data were available to accurately extrapolate Abbott and Bray's (2) values, these dissociation constants were determined at 65.5°C.

EXPERIMENTAL

Procedure and Results

An electrometric titration method was employed for the determination of the dissociation constants. A mechanically stirred solution of sodium pyrophosphate, maintained at $65.5 \pm 0.1^\circ\text{C}$., was titrated with 3 *N* hydrochloric acid. The changes in the pH of the solution were plotted against the volume of acid added. The inflection points occurred at pH 10.0, 6.8, and 4.0. In the light of considerations which will be discussed shortly, regions between these inflection points were selected for further investigation.

Having thus delineated the critical pH regions, accurate measurements of the acid increments and the resulting pH values were made. Fifty milliliter portions of a 0.179 molar sodium pyrophosphate solution were titrated with 1 *N* hydrochloric acid. The experimental conditions were as described above, but particular care was taken to minimize the time required in obtaining the measurements. None of the samples were subjected to acid conditions for more than five minutes. This procedure was followed on three separate portions of the sodium pyro-

phosphate solution, and the averages of the results are recorded in Table II. For the same volume of acid added, the pH readings checked within ± 0.02 units. In the present experiments, the accuracy of the pH measurements is the limiting factor in calculating the dissociation constants.

TABLE II

Volume <i>N</i> HCl added (ml.)	Average pH*	Average hydrogen ion concentration (gew/l.)
0	9.52	3.020×10^{-10}
2.00	8.48	3.311×10^{-9}
3.00	8.26	5.495×10^{-9}
4.00	8.05	8.913×10^{-9}
6.00	7.66	2.188×10^{-8}
12.00	6.06	8.710×10^{-7}
12.50	5.95	1.122×10^{-6}
13.00	5.87	1.349×10^{-6}
14.00	5.65	2.239×10^{-6}
19.00	2.88	1.318×10^{-3}
19.50	2.72	1.905×10^{-3}
20.00	2.57	2.692×10^{-3}
24.00	1.90	1.259×10^{-2}
25.00	1.78	1.660×10^{-2}

*These figures are the averages of three separate determinations.

Theory of the Method

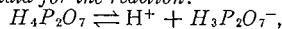
It is possible to estimate the dissociation constants of a polybasic acid such as pyrophosphoric by a method of successive approximations utilizing the data obtained from an electrometric titration of the material. Although theoretically all of the anionic species will be present at a given pH, the concentrations of one or more of the species will always be small enough at that pH to be neglected in making approximate calculations of the dissociation constants (6). These values of the dissociation constants may then be used to estimate the concentrations of the components which were neglected in the first approximation. The appropriate corrections may then be made, and the dissociation constants estimated for a second time. This process may, of course, be continued indefinitely, but it was found that the second approximation was satisfactory in every case.

As stated earlier the inflection points in the electrometric titration curve of sodium pyrophosphate at 65.5°C. occur at the pH values: 10.0, 6.8, and 4.0, and at these points the concentration of $\text{P}_2\text{O}_7^{4-}$, $\text{HP}_2\text{O}_7^{3-}$, and $\text{H}_2\text{P}_2\text{O}_7^{2-}$ respectively, predominate. At intermediate points two of the species predominate, and it is in these regions that the most accurate estimations of the dissociation constants may be obtained. The method of calculation also permits the inclusion of one minor component in obtaining the first approximation of K_1 , K_2 , and K_3 . The pH regions chosen and the anionic species assumed to be present in calculating the first approximations to the various dissociation constants are shown in Table III. The predominating species in each pH range are underlined.

TABLE III

Dissociation constant	Anionic species assumed present	pH Range
K_1	$\underline{H_4P_2O_7}, \underline{H_3P_2O_7^{1-}}, \underline{H_2P_2O_7^{2-}}$	< 2
K_2^*	$\underline{H_3P_2O_7^{1-}}, \underline{H_2P_2O_7^{2-}}, \underline{HP_2O_7^{3-}}$	2.5-3.0
K_3	$\underline{H_2P_2O_7^{2-}}, \underline{HP_2O_7^{3-}}, \underline{P_2O_7^{4-}}$	5.6-6.2
K_4	$\underline{HP_2O_7^{3-}}, \underline{P_2O_7^{4-}}$	8.0-9.5

*In the pH region below pH 4, $H_4P_2O_7$, $H_3P_2O_7^{1-}$, and $H_2P_2O_7^{2-}$ predominate, but little $H_4P_2O_7$ would be present in the region 2.5-3.0. At 18°C., Abbott and Bray's (2) dissociation constants indicate that approximately three per cent $H_4P_2O_7$ is present at pH 3. Furthermore, Thomsen's (8) heat of ionization data for the reaction:



show that increasing the temperature will shift the equilibrium to the right. Thus the first approximation to the second dissociation constant was calculated assuming that no $H_4P_2O_7$ was present in the pH range 2.5-3.0.

Calculation of the Fourth Dissociation Constant (K_4)

The initial solution of sodium pyrophosphate is in the pH range where $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ are the only anionic species present in significant amounts. Therefore to a first approximation:

$$[1] \quad H_0 + H_1 = P_T,$$

where H_0 and H_1 are the amounts of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ respectively, and P_T is the total amount of pyrophosphate present.

A quantity of acid is now added which lowers the pH of the solution but does not take it out of the range where $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ are the only major components. However, the acid does convert an equivalent amount of $P_2O_7^{4-}$ to $HP_2O_7^{3-}$ as indicated by the equation:



The amounts of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ present become $(H_0 - H_a^+)$ and $(H_1 + H_a^+)$ respectively, when H_a^+ is the equivalent amount of acid added.

The dissociation constant K_4 is defined by the expression:

$$[3] \quad K_4 = [H^+] [P_2O_7^{4-}] / [HP_2O_7^{3-}].$$

Since a ratio of anionic species is involved, it is immaterial which units are employed to express the amounts of $P_2O_7^{4-}$ and $HP_2O_7^{3-}$ so long as they are identical for both species. Therefore, before adding acid:

$$[4] \quad K_4 = [H^+]_i H_0 / H_1.$$

After adding acid:

$$[5] \quad K_4 = [H^+]_f (H_0 - H_a^+) / (H_1 + H_a^+),$$

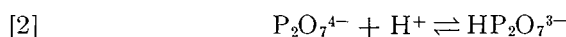
where $[H^+]_i$ and $[H^+]_f$ are the initial and final hydrogen ion concentrations. Equating [4] and [5] and substituting $(P_T - H_1)$ for H_0 , a quadratic in H_1 is obtained which may be solved. Although two positive solutions are obtained,

only one solution gives reasonable results in the calculation of K_4 . The latter calculation is made by simply substituting values for H_1 , H_0 (which is $P_T - H_1$), and $[H^+]_i$ in equation [4].

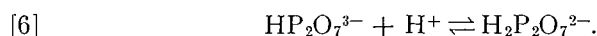
Calculation of the Third Dissociation Constant (K_3)

Having now obtained a value for K_4 it is possible to determine K_3 using much the same procedure as in estimating K_4 .

A quantity of acid is added to the initial solution of sodium pyrophosphate such that the resulting pH of the solution lies in the range 5.6–6.2 where $HP_2O_7^{3-}$ and $H_2P_2O_7^{2-}$ are the major components and $P_2O_7^{4-}$ is the largest minor component. The acid added is consumed in two reactions:



and



If the total amount of acid added is H_b^+ and an amount B is consumed in reaction [2], then $(H_b^+ - B)$ is consumed in reaction [6]. Consequently the amounts of the various species after the addition of the acid are as follows:

$$\begin{aligned} P_2O_7^{4-} &= H_0 - B &= P_T - H_1 - B, \\ HP_2O_7^{3-} &= H_1 + B - (H_b^+ - B) &= H_1 - H_b^+ + 2B, \\ H_2P_2O_7^{2-} &= &= H_b^+ - B. \end{aligned}$$

If the hydrogen ion concentration at this point is designated by $[H^+]_f$, then by substituting in equation [3], the following equation is obtained:

$$[7] \quad K_4 = [H^+]_f (P_T - H_1 - B) / (H_1 + H_b^+ + 2B).$$

Since B is the only unknown it may be evaluated.

The third dissociation constant K_3 is defined by the expression:

$$[8] \quad K_3 = [H^+] [HP_2O_7^{3-}] / [H_2P_2O_7^{2-}].$$

Therefore:

$$[9] \quad K_3 = [H^+]_f (H_1 - H_b^+ + 2B) / (H_b^+ - B).$$

Since all the factors on the right-hand side of equation [9] are known, K_3 may be evaluated.

Calculation of the Second (K_2) and First (K_1) Dissociation Constants

The second and first dissociation constants are determined in a similar manner making the appropriate assumptions with regard to the anionic species present.

Table IV illustrates the distribution of the various anionic species in each pH range used in the calculation of dissociation constants.

H_c^+ and H_d^+ are the amounts of acid added to the pyrophosphate solution to change from the initial pH to pH values in the ranges 2.5–3.0 and <2.0 respectively.

C is the amount of acid consumed in the reaction:

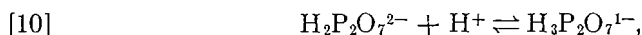


when H_c^+ is the amount of acid added.

TABLE IV
 DISTRIBUTION OF ANIONIC SPECIES ASSUMED IN CALCULATION OF DISSOCIATION CONSTANTS

Amounts ionic species assumed present	Dissociation constant			
	K_1	K_2	K_3	K_4
	pH range			
	8.0-9.5	5.6-6.2	2.5-3.0	< 2.0
H_0	$P_T - H_1 - H_a^+$	$P_T - B$	—	—
H_1	$H_1 + H_a^+$	$H_1^+ + 2B - H_b^+$	$P_T - C$	—
H_2	—	$H_b^+ - B$	$P_T + 2C - H_c^+ - H_1$	$P_T - D$
H_3	—	—	$H_c^+ - C - P_T + H_1$	$2P_T + 2D - H_d^+ - H_1$
H_4	—	—	—	$H_d^+ - D - 2P_T + H_1$

Similarly D is the amount of acid consumed in the reaction:



when H_d^+ is the amount of acid added.

On substituting the data in Table II into the approximate equations developed in this manner, the following average values for the dissociation constants of pyrophosphoric acid were obtained:

$$\begin{aligned} K_1 &= 0.122 & (\sigma = 0.014 \text{ where } n = 4), \\ K_2 &= 7.29 \times 10^{-3} & (\sigma = 0.37 \times 10^{-3} \text{ where } n = 6), \\ K_3 &= 1.45 \times 10^{-6} & (\sigma = 0.04 \times 10^{-6} \text{ where } n = 7), \\ K_4 &= 9.72 \times 10^{-9} & (\sigma = 0.12 \times 10^{-9} \text{ where } n = 12), \end{aligned}$$

where σ is the standard deviation (3).

Using the above dissociation constants and the method of calculation outlined, the following set of values were obtained as a second approximation to the dissociation constants. Further approximations did not alter the values appreciably.

$$\begin{aligned} K_1 &= 0.107 & (\sigma = 0.009 \text{ where } n = 4), \\ K_2 &= 7.58 \times 10^{-3} & (\sigma = 0.20 \times 10^{-3} \text{ where } n = 6), \\ K_3 &= 1.45 \times 10^{-6} & (\sigma = 0.04 \times 10^{-6} \text{ where } n = 7), \\ K_4 &= 9.81 \times 10^{-9} & (\sigma = 0.13 \times 10^{-9} \text{ where } n = 12), \end{aligned}$$

where σ is the standard deviation (3).

The standard deviations indicate the precision of the experiment but not the accuracy.

Since no attempt was made to distinguish between the concentration and the activity of these anionic species, the concentration range in which the dissociation constants are applicable must be specified. Abbott and Bray (2) found that the values of the dissociation constants changed very little with the molarity of the pyrophosphate solution if that concentration were higher than 0.08 molar. Thus the dissociation constants, determined above, are considered to be applicable at least over the concentration range 0.08 to 0.18 molar.

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