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DETERMINATION OF EQUILIBRIUM CONSTANTS FOR A NUMBER OF METAL-PHOSPHATE COMPLEXES

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Many metal ions form soluble complexes with pyro- and tripolyphosphate. Complex formation entails a decrease in pH. By measuring the pH and in some cases the concentration of free metal ions, equilibrium constants for a number of metal-phosphate complexes were determined at 25° and at 40°. Activity corrections were applied. The tendency to form complexes increases in the following order:

$$\mathrm{Cs} \sim \mathrm{K} \sim \mathrm{Na} < \mathrm{Li} < \mathrm{Ba} < \mathrm{Sr} < \mathrm{Ca} < \mathrm{Mg} < \mathrm{Cd} \sim \mathrm{Zn}$$

Tripolyphosphate has somewhat stronger complexing properties than pyrophosphate. The influence of the temperature is in most cases small. Constants obtained are listed in Table V.

Introduction.

Pyrophosphate ($P_2O_7^{4-}$) and tripolyphosphate ($P_3O_{10}^{5-}$) are the lowest members of the group of the polyphosphates with the general formula:

$$(P_nO_{3n+1})^{(n+2)-} \qquad (n > 1)$$

In various ways it has been proved that the polyphosphates having n = 2, 3, and 4 respectively, actually exist as individual compounds. *Bonneman-Bémia*[1] established this for $Na_5P_3O_{10}$ by cryoscopic determination of the molecular weight, X-ray analysis, and recrystallization of a mixture of 3 $Na_4P_2O_7$ + $(NaPO_3)_3$, which has the same total composition as $Na_5P_3O_{10}$, but can be split into its components again. This is not feasible with tripolyphosphate.

Grunze[2], *Van Wazer*[3], and *Quimby*[4] review the chemistry of the

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[1] *P. Bonneman-Bémia*, Ann. chim. **16**, 395 (1941).

[2] Phosphat-Symposium, *J. A. Benckiser*, Ludwigshafen 1956, p. 7.

[3] *J. R. van Wazer, D. A. Campanella*, J. Am. Chem. Soc. **72**, 655 (1952).

[4] *O. T. Quimby*, Chem. Revs. **40**, 141 (1947).

polyphosphates, and notably *Mankowitz*[5] gives a survey of the various aspects of pyro- and tripolyphosphate research.

The sodium salts of pyro-, tripoly-, and hexametaphosphate find large-scale application in commercial detergents. It can safely be said that practically every heavy-duty synthetic detergent contains one or more of these phosphates in amounts varying from 10 to 50 %.

Polyphosphates are incorporated in detergents[6, 7, 8] mainly because:

(i) they prevent the deposition of calcium and magnesium salts, present in tap water, and bring about redissolution of old deposits on the fibre.

(ii) they increase the washing efficiency of the surface-active constituent.

The dissolution of calcium salts is based on the formation of soluble calcium-phosphate complexes. Other metal ions are also sequestered by phosphates. This is of importance with regard to the corrosion of metal washing utensils. It was therefore deemed worth while to investigate this complex formation more closely. We have limited our work to the alkaline region ($pH > 9$), where at most one hydrogen is bound to the phosphate ions. If a complex with a metal ion X is formed in this region, it withdraws completely dissociated phosphate ions from the equilibrium, thus shifting the equilibrium between phosphate and hydrogen-phosphate and causing a decrease of the pH. In the case of pyrophosphate and calcium the following two equilibria have to be satisfied simultaneously:

$$H_2O + P_2O_7^{4-} \leftrightarrows HP_2O_7^{3-} + OH^-$$
$$Ca^{2+} + P_2O_7^{4-} \leftrightarrows CaP_2O_7^{2-}$$

The complex constant can be found from the decrease of the pH on addition of the metal chloride. In this way equilibrium constants for a number of metal-phosphate complexes were determined at 25° and 40° C.

In this investigation liquid junction potentials were avoided and activity corrections kept as small as possible by carrying out measurements on cells with a hydrogen and a silver/silver chloride electrode in dilute solutions ($5 \cdot 10^{-4}$ and $15 \cdot 10^{-4}$ *M*) of sodium pyro- or tripolyphosphate in the presence of NaCl.

In the first place the acid dissociation constants (K_4 for pyrophos-

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[5] *M. M. Mankowitz,* J. Chem. Educ. **33**, 36 (1956).

[6] Symposium Synthetic Detergents, Ind. Eng. Chem. **46**, 1913 (1954).

[7] *O. Uhl,* Seifen - Oele - Fette - Wachse **21**, 613 (1957).

[8] *P. T. Vitale, J. Ross, A. M. Schwartz,* Soap and Chemical Specialities. **1956**, 41.

phate and K_5 for tripolyphosphate) have to be determined. The fact that these constants seemed to vary with the Na^+/phosphate ratio indicated the existence of sodium complexes. By the introduction of the complexes $NaP_2O_7^{3-}$ and $NaP_3O_{10}^{4-}$ constant values for K_4 and K_5 could be obtained. Complex constants for these alkali-metal complexes could also be derived.

In order to obtain thermodynamic dissociation constants, the values obtained have to be extrapolated to infinite dilution. This was done by explicit application of Debye-Hückel activity corrections (proportional to the square root of the ionic strength μ) and linear extrapolation with respect to μ.

As many of the ions in phosphate solutions carry high charges, the activity corrections are quite high, although concentrations were always kept below 0.01 molar (μ from 0.004 to 0.04).

It was found advisable to introduce non-extrapolated "experimental" dissociation constants "K_4", "K_5", etc., corrected for the square root effect expressed in eq. (1), but not for the linear and higher influences of μ.

When the values for "pK_{Na}", "pK_4", and "pK_5" are known for every ionic strength, it is possible to calculate the concentration of the various phosphate ions for any pH value. If other metal ions are added to the sodium phosphates, the amount of phosphate bound to such metal ions can be calculated from:

total phosphate — monosodium phosphate — monohydrogen phosphate — free phosphate = metal phosphate.

In this way, the equilibrium constants of the other alkaline metals (Li, K, and Cs) were calculated, on the assumption that solely 1 : 1 complexes of metal to phosphate occur.

In the case of the alkaline-earth metals it is more difficult to establish the complex constant, for these metals are so strongly complexed that only close to the equivalence point, where the metal/phosphate ratio is 1, does the free metal ion concentration reach a value high enough for calculation to become possible.

The equivalence point cannot, on the other hand, be exceeded to any great extent, since otherwise metal hydroxide or a metal phosphate, containing more metal than 1 : 1, will precipitate.

Moreover the pH will decrease, thus complicating the calculations owing to the occurrence of other phosphate ion species.

With all the metals investigated, the most important complex contains one metal ion and one phosphate. There are indications that basic complexes of the type $MgOHP_2O_7^{3-}$ are also present. The equilibrium constants of most of these complexes could be determined.

In the case of zinc a complex containing two pyrophosphate groups to one zinc ion was also found. Zinc and cadmium complexes are so strong that the concentration of free metal ions remains exceedingly low. It could, however, be determined by potentiometry with zinc and cadmium electrodes.

Finally, a number of semi-quantitative measurements with other metals were carried out.

Literature data

A great many publications have appeared on the determination of complexing constants. *Martell* and *Calvin*[9] give a survey of the various methods of determination.

After completion of the present paper an article in a recent review, by *Van Wazer* and *Callis*[9a], came to our attention.

As we are considering phosphate complexes at pH > 9, the first requirement is to know the dissociation constants of the acids

$$\text{pyrophosphate: } K_4 = \frac{H \times P_2O_7}{HP_2O_7} \text{ and } K_3 = \frac{H \times HP_2O_7}{H_2P_2O_7}$$

$$\text{tripolyphosphate: } K_5 = \frac{H \times P_3O_{10}}{HP_3O_{10}} \text{ and } K_4 = \frac{H \times HP_3O_{10}}{H_2P_3O_{10}}$$

In order to distinguish activities and concentrations, activities will be denoted by the chemical symbols, concentrations by the same symbols with index c. Indication of the electric charge will be omitted.

Example:

P_2O_7 = activity of pyrophosphate ion

P_2O_{7c} = concentration of pyrophosphate ion.

a) Dissociation constants of the acids and the alkaline-metal complexes.

A compilation of the complexing constants is given in [10]. Below we only give the constants at 25° which have been extrapolated to $\mu \rightarrow 0$.

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[9] *A. E. Martell, M. Calvin,* Chemistry of the Metal Chelate Compounds. Prentice Hall, New York 1952.

[9a] *J. R. van Wazer, C. F. Callis,* Chem. Revs. 58, 1011 (1958).

[10] *J. Bjerrum, G. Schwarzenbach, L. G. Sillén,* Stability Constants, Part II. Inorganic Lingands. Metcalfe and Cooper Ltd., London 1957.

1. *Pyrophosphate*

pK_4	pK_3	pK_{Na}
9.62	6.57	2.35 [11]
9,29	6.63	— [12]
9.25	6.60	2.22 [13]
9.42	6.76	— [14]

2. *Tripolyphosphate*

The data relevant to this compound show much wider variations:

pK_5	pK_4	pK_{Na}
9.24	6.47	— [12]
9.24	6.50	— [14]
9.12	6.10	— [15]
8.90	6.26	— [16]
—	—	2.57 [11]

b) Complexes with other metals.

For the determination of the complexing constant for the metal ion X:

$$K_X = \frac{X \times \text{Phosphate}}{X\ \text{Phosphate}}$$

the concentration of free metal ions has to be known. For the alkaline-earth ions this concentration can be found from:

$$X_{\text{free}} = X_{\text{total}} - X_{\text{bound.}}$$

For the majority of the heavy metals, however, this is not possible on account of their strong complexing properties. Excess of metal over phosphate cannot be used in alkaline media, since metal hydroxides precipitate under these circumstances. In acid or neutral media, on the other hand, the multi-step dissociation of the phosphoric acids unduly complicates the analysis. For these reasons many authors have been satisfied with qualitative establishment of the type of complex

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[11] *C. B. Monk,* J. Chem. Soc. **1949**, 423; **1952**, 1317.

[12] *J. Beukenkamp, W. Rieman, S. Lindenbaum,* Anal. Chem. **26**, 505 (1954).

[13] *J. A. Davis,* Diss. Abstr. **15**, 2403 (1955).

[14] *S. H. Lambert, J. I. Watters,* J. Am. Chem. Soc. **79**, 4262 (1957).

[15] *E. D. Loughran,* Diss. Abstr. **16**, 446 (1956).

[16] *J. I. Watters, E. D. Loughran, S. M. Lambert,* J. Am. Chem. Soc. **78**, 4855 (1956).

formed from the shapes of titration curves, without deriving an equilibrium constant.

1. *Pyrophosphate*

All the literature data [10, 13, 17–24] indicate the existence of the 1 : 1 complex of a large number of metals, hence $XP_2O_7^{2-}$ in the case of a bivalent ion X.

With copper and zinc a 1 : 2 complex, $X(P_2O_7)_2^{6-}$, is generally found to exist [17, 18, 20–23]. In the majority of cases the concentrations employed far exceed those used in the work carried out here.

It is clear that at high concentrations the existence of the abovementioned complex $X(P_2O_7)_2^{6-}$ will be more readily apparent than at low concentrations.

Quantitative complexing constants, extrapolated to $\mu = 0$, however, are not available.

2. *Tripolyphosphate*

The presence of $XP_3O_{10}^{3-}$ ions was invariably established [15, 20, 24–28]. In two cases, with calcium and copper, $X(P_3O_{10})_2^{8-}$ is supposed to exist [15, 27]; but this is not very likely, because of the high negative charge of such a compound.

No thermodynamic complexing constants are known.

Theoretical Discussion

a) Dissociation constants of acids and complex binding of alkali metals.

From the work of other investigators it appears that the last two dissociation constants for pyro- and tripolyphosphate respectively are:

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[17] *J. I. Watters, A. Aaron,* J. Am. Chem. Soc. **75**, 611 (1953).

[18] *L. B. Rogers, C. A. Reynolds,* J. Am. Chem. Soc. **71**, 2081 (1949).

[19] *J. Ross, L. Shedlovsky, C. W. Jakob,* J. Am. Oil Chemists' Soc. **32**, 126 (1955).

[20] *M. Bobtelsky, S. Kertes,* J. Appl. Chem. (London) **4**, 419 (1954); **5**, 125, 675 (1955).

[21] *H. A. Laitinen, E. I. Onstott,* J. Am. Chem. Soc. **72**, 4729 (1950).

[22] *K. B. Yatsimirsky, V. P. Vasiyev,* Zhur. Anal. Khim. **11**, 536 (1956); J. Anal. Chem. (USSR) **11**, 573 (1956). (English translation).

[23] *J. Vaid, T. L. Rama Char,* Bull. India Sect. Electrochem. Soc. **7**, 5 (1958).

[24] *S. M. Lambert, J. I. Watters,* J. Am. Chem. Soc. **79**, 5606 (1957).

[25] *A. E. Martell, G. Schwarzenbach,* Helv. Chim. Acta **39**, 653 (1956).

[26] *K. R. Andress, K. Wüst,* Z. anorg. u. allgem. Chem. **237**, 113 (1938).

[27] *H. Rudy, H. Schloesser, R. Watzel,* Angew. Chem. **53**, 525 (1940).

[28] *O. T. Quimby,* J. Phys. Chem. **58**, 612 (1954).

pyrophosphate		*tripolyphosphate*	
pK_3	6.7	pK_4	6.4
pK_4	9.4	pK_5	9.2

These values imply that the concentrations of $H_2P_2O_7^{2-}$ and $H_2P_3O_{10}^{3-}$ can be neglected at a pH of 9, since the quantities of these ions are less than 1 % of the amount of $HP_2O_7^{3-}$ and $HP_3O_{10}^{4-}$ respectively.

In the following discussion pyrophosphate has been taken as an example. For tripolyphosphate the calculations proceed analogously, though the activity corrections are greater.

The experimental data are the composition of the solution and the E.M.F. of a cell without liquid junction, containing a hydrogen electrode and a silver/silver chloride electrode.

The solution is composed of distilled water, $Na_4P_2O_7.10\,H_2O$, NaCl, and HCl in varying quantities. The solution contains the following phosphate ions: $P_2O_7^{4-}$, $HP_2O_7^{3-}$, and $NaP_2O_7^{3-}$, while two equilibria are to be considered:

$$K_4 = \frac{H \times P_2O_7}{HP_2O_7} \text{ and } K_{Na} = \frac{Na \times P_2O_7}{NaP_2O_7}$$

If no acid or base is added, the only reactions in which OH^- and $HP_2O_7^{3-}$ are formed are:

$$H_2O + P_2O_7^{4-} \rightarrow OH^- + HP_2O_7^{3-}$$

$$H_2O + NaP_2O_7^{3-} \rightarrow Na^+ + OH^- + HP_2O_7^{3-}$$

The following equation is therefore applicable:

$$HP_2O_{7c} = OH_c \text{ (for } H^+ << OH^-)$$

If acid is added, we have:

$$HP_2O_{7c} = \text{added acid} + OH_c$$

The E.M.F. of the cell allows the calculation of pH_c and pOH_c with the following equations:

$$\frac{E.M.F. - E^\circ_{Ag/AgCl}}{2.303\ RT/F} = -\ pOH_c + pK_w + pCl_c$$

$$pH_c = pK_w - pOH_c - \sqrt{\mu}$$

Standard potentials of the silver/silver chloride electrode were determined separately for each electrode (about 222.5 and 212.0 mV at 25° and at 40° respectively). The values of the water exponent are $pK_w = 13.996$ (25°) and $pK_w = 13.535$ (40°) [29].

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[29] *R. A. Robinson, R. H. Stokes,* Electrolyte Solutions. Butterworths Scientific Publications, London 1955. p. 506.

Activity corrections were introduced with the aid of the simple Debye-Hückel equation, $-\log f_z = Az^2\sqrt{\mu}$, where μ is the ionic strength and A has been put equal to 0.5 both at 25° and at 40°.

The ionic strength $\mu = \frac{1}{2}\Sigma c_i z_i^2$ depends of course on the actual ionic composition of the solution. Most of the calculations in this paper started from an estimate of the ionic strength, the value being improved in the course of the calculations, when the composition becomes known more accurately.

If the binding of sodium is neglected, pK_4 values can be calculated from equation (1).

$$pK_4 = pH_c + pP_2O_{7c} - pHP_2O_{7c} + 4\sqrt{\mu} \quad . \; . \; . \; . \; . \; . \quad (1)$$

The values so calculated depend strongly on μ and on the sodium/phosphate ratio (Fig. 2). They can be extrapolated, although not very accurately, to $\mu = 0$ and sodium/phosphate ratio $= 0$, to give the true thermodynamic dissociation constants.

The binding of sodium can be taken into account by choosing such a value of pK_{Na} that with three different sodium/phosphate ratios, at the same ionic strength, the same value for pK_4 is found. It then appears that the value of pK_{Na}

$$pK_{Na} = pNa_c + pP_2O_{7c} - pNaP_2O_{7c} + 4\sqrt{\mu} \quad . \; . \; . \; . \; . \quad (2)$$

is practically constant over the entire concentration range.

In this way a relationship between pK_4 and μ can be established (see Fig. 3). Extrapolation of these values to $\mu = 0$ again gives the thermodynamic dissociation constant. The actual values of pK_4 (only corrected for $\sqrt{\mu}$ effects) as a function of μ are used in all subsequent calculations, thus including higher-order activity corrections on this dissociation.

The complexing constants for the other alkali metals were determined in a completely analogous way. The pyro- and tripolyphosphates were prepared by double decomposition of silver pyro- or tripolyphosphate with alkali-metal chloride. For the measurement at a high metal/phosphate ratio, the conversion of the sodium phosphates *via* the silver salts could be omitted. Simple addition of alkali chloride (*e.g.* LiCl) to solutions of sodium phosphates allowed the calculation of the complexing constants for the alkali metal under consideration.

b) Complexes with bivalent metals.

If a metal chloride (XCl_2) is added to a solution of $Na_4P_2O_7$, the pH value will decrease when the metal complex is formed, for H^+ ions are released by the reaction:

$${}_{+2}X \qquad + HP_2O_7^{3-} \rightarrow XP_2O_7^{2-} + H^+$$

It is again possible to calculate H_c and HP_2O_{7c} ($= OH_c$) from the measured E.M.F. Using the relationship between μ and pK_4 as established above, it is now possible to calculate the concentration of free $P_2O_7^{4-}$ ions from the equation:

$$pP_2O_{7c} = pK_4 - pH_c + pHP_2O_{7c} - 4\sqrt{\mu}$$

and the amount of $NaP_2O_7^{3-}$ is found from:

$$pNaP_2O_{7c} = pNa_c + pP_2O_{7c} - pK_{Na} + 4\sqrt{\mu}$$

The phosphate not accounted for by the ions $P_2O_7^{4-}$, $HP_2O_7^{3-}$ and $NaP_2O_7^{3-}$ must be bound to the metal X. Indicating this amount of phosphate as $P_2O_7\,(X)_c$, we have:

$$P_2O_7\,(X)_c = \text{total phosphate} - P_2O_{7c} - HP_2O_{7c} - NaP_2O_{7c}$$

When these calculations are carried out, it appears that with the alkaline-earth metals and with zinc and cadmium, the term $P_2O_7(X)_c$ exceeds the total amount of metal added.

In principle this can be explained either by the presence of complexes of the type $X(P_2O_7)_2^{6-}$ or by hydroxyphosphate complexes, $XOHP_2O_7^{3-}$, which by binding OH^- ions destroy the equality of OH^- and $HP_2O_7^{3-}$, thus invalidating the calculations given above.

As the titration curves of phosphate with metal chloride do not give any specific indication of the existence of complexes like $X(P_2O_7)_2^{6-}$ (except in the case of zinc), we analysed our data while solely taking the complexes $XP_2O_7^{2-}$ and $XOHP_2O_7^{3-}$ into account. For zinc, in addition to these two, the complex $Zn(P_2O_7)_2^{6-}$ has also been reckoned with.

XOH^--ions can be left out of consideration; in the case of the alkaline-earth metals because their hydrolysis is negligible, in the case of zinc and cadmium because the complex binding is so strong that the concentration of free metal ions remains very small, and thus also the corresponding concentration of metalhydroxy ions (see *Kolthoff et al.* [30]).

1) *Complexes with alkaline-earth metals.*

After addition of large amounts of XCl_2, *i.e.* in the neighbourhood of the phosphate/metal ratio 1 : 1, the pH is rather low, the concentration of the complex $XOHP_2O_7^{3-}$ is negligible, and the concentration of free X^{2+} ions is high enough to be calculated by difference. In these circumstances the concentration $HP_2O_{7c} = OH_c$ can again

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[30] *I. M. Kolthoff, T. Kameda,* J. Am. Chem. Soc. **53**, 835 (1931).

be found directly from the pH, and P_2O_{7c} and NaP_2O_{7c} can be calculated from the equilibrium constants.

The amount of X bound as XP_2O_7 is equal to the phosphate not accounted for by the ions just mentioned:

$$XP_2O_{7c} = \text{total phosphate} - P_2O_{7c} - HP_2O_{7c} - NaP_2O_{7c}$$

$$X_c = \text{total X} - XP_2O_{7c}$$

By means of these data the complexing constant K_X can be calculated from:

$$pK_X = pX_c + pP_2O_{7c} - pXP_2O_{7c} + 8\sqrt{\mu} \quad . \; . \; . \; . \; . \quad (3)$$

When the X/phosphate ratio is small, the complexing is so strong that the free concentration of X cannot be determined in the above way. Moreover, the pH is higher; hence the complex $XOHP_2O_7{}^{3-}$ must also be considered. In these circumstances knowledge of the pH, pK_4, and pK_{Na} enables the determination of the ratios:

$$P_2O_{7c} : HP_2O_{7c} : NaP_2O_{7c}, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

but not of the individual amounts. As all X is present either as $XP_2O_7{}^{2-}$ or as $XOHP_2O_7{}^{3-}$, the following equation is valid:

$$\text{total phosphate} - \text{total X} = P_2O_{7c} + HP_2O_{7c} + NaP_2O_{7c} \quad (5)$$

From the sum (5) and the ratios (4) the individual concentrations can be calculated.

The ion $HP_2O_7{}^{3-}$ can be formed in two ways, *viz.*:

$$H_2O + P_2O_7{}^{4-} \rightarrow OH^- + HP_2O_7{}^{3-}$$

$$X^{2+} + H_2O + 2\,P_2O_7{}^{4-} \rightarrow XOHP_2O_7{}^{3-} + HP_2O_7{}^{3-}$$

Consequently the amount of $HP_2O_7{}^{3-}$ is equal to the sum of the OH^- ions and of the hydroxy complex, and thus the concentration of the hydroxy complex can be calculated from:

$$XOHP_2O_{7c} = HP_2O_{7c} - OH_c$$

The concentration of XP_2O_7 is then found from:

$$XP_2O_{7c} = \text{total X} - XOHP_2O_{7c}$$

As the complexing constant K_X is known from the data at high X/phosphate ratios, the concentrations of free X^{2+} ions can be calculated from eq. (3), and finally the complexing constant for the hydroxy complex is determined from:

$$pK_{XOH} = pX_c + pOH_c + pP_2O_{7c} - pXOHP_2O_{7c} + 6\sqrt{\mu} \quad (6)$$

2) *Complexes with zinc and cadmium.*

These metals are sequestered so strongly and their hydroxides are so insoluble that the concentration of free ions remains too small to be determined as described above for the alkaline-earth metals. Fortunately, in the presence of polyphosphates the zinc and cadmium electrodes are nicely reversible *, and thus the concentration of free ions can be determined from the potential of a zinc or cadmium electrode as measured against a calomel electrode with liquid junction or against a silver/silver chloride electrode. For high zinc/phosphate ratios, the complex $Zn(P_2O_7)_2{}^{6-}$ can be neglected and the calculations proceed along the same lines as those for high concentrations of alkaline-earth ions, the only difference being that instead of using K_X to calculate the concentration of the free metal ions, now the reverse is done, the concentration of Zn^{2+} (or Cd^{2+}) being known from the electrometric determination. For low zinc/pyrophosphate ratios, the complex $Zn(P_2O_7)_2{}^{6-}$ cannot be neglected. The other complexing constants being known, its concentration can be determined from:

$$Zn(P_2O_7)_{2c} = \text{total Zn} - ZnP_2O_{7c} - ZnOHP_2O_{7c}$$

and the equilibrium constant becomes

$$pK_{Zn_2} = pZn_c + 2\ pP_2O_{7c} - pZn(P_2O_7)_{2c}$$

c) Equilibrium constants of tripolyphosphate complexes.

In the same way as mentioned above for pyrophosphate, the following equations can be derived for tripolyphosphate:

$$pK_5 = pH_c + pP_3O_{10_c} - pHP_3O_{10_c} + 5\sqrt{\mu}\ . \quad . \quad . \quad . \quad . \quad (1')$$

$$pK_{Na} = pNa_c + pP_3O_{10c} - pNaP_3O_{10c} + 5\sqrt{\mu} \quad . \quad . \quad . \quad (2')$$

and for bivalent X:

$$pK_X = pX_c + pP_3O_{10c} - pXP_3O_{10c} + 10\sqrt{\mu}\ . \quad . \quad . \quad . \quad (3')$$

$$pK_{XOH} = pX_c + pP_3O_{10c} + pOH_c - pXOHP_3O_{10c} + 7\sqrt{\mu}\ (6')$$

Experimental Part.

a) Chemicals.

Two preparations of $Na_4P_2O_7.10H_2O$, of analytical grade, were used without further purification. Technical $Na_5P_3O_{10}.6H_2O$ was purified by recrystallization according to *Quimby* [31].

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* Metal electrodes often cause difficulties in alkaline solutions, which result in deviations from the thermodynamic value of the potential. This is mainly due to the formation of insoluble (hydr)oxide. The polyphosphates, however, are able to dissolve these insoluble products, deposited on the metal surface. The amount of metal that goes into solution in this way can be neglected, since the decrease in weight of zinc and cadmium, immersed in these solutions under hydrogen or nitrogen atmosphere, is extremely small.

[31] O. T. *Quimby*, Anal. Chem. **26**, 661 (1954).

The analyses*, using the gravimetric P_2O_5 determination (see *Vogel*[32]), after hydrolysis with acid gave the following results:

Table I

Gravimetric P_2O_5 determination (%)

	$Na_4P_2O_7.10H_2O$			$Na_5P_3O_{10}.6H_2O$	
	Amsterdamse Chinine fabriek	Analar	Theory	Recryst.	Theory
Loss on ignition (530° C)	40.46	40.48	40.36	22.88	22.69
P_2O_5	31.80	31.76	31.84	44.64	44.75
Reaction for orthophosphate[33]	neg.	neg.		neg.	
Do. for metaphosphate[33]	neg.	neg.		neg.	

The metal chlorides or metal sulphates employed (the latter being used when the pure chloride could not be obtained, as with Zn) are: "Merck analytical grade", or "Analar", with the exception of LiCl and CsCl.

LiCl was recrystallized in accordance with *Schoeller* and *Powell*'s method[34]; CsCl was used as such in a chemically pure state; the purities, calculated on the chlorine content, were:

$LiCl.1H_2O$: 99.3 %; CsCl :99.9 %.

These substances are free from bivalent metals. Distilled water was redistilled twice in a quartz apparatus and stored in polyethylene bottles, under hydrogen. The maximum conductivity was $2.10^{-6}\ \Omega^{-1}cm^{-1}$.

The phosphate solution was freshly prepared for every measurement. To this end, *ca.* 500 ml of water, under hydrogen, was introduced into a measuring flask (see Fig. 1), and solid phosphate and NaCl were added to it.

The metal salt was added from a burette as a roughly 0.1 molar solution, in the cases where hydrolysis was slight or absent. The strength of this solution was determined by means of chloride or metal analysis.

The hydrolysing salts were added in the solid form. At the end of the experiment, the exact volume, and hence the concentration of the added substances, was calculated by weighing the solution. The hydrogen was freed from oxygen by passing it through the following wash bottles:

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* The analyses were carried out by the analytical department of the Unilever Research Laboratory, Vlaardingen.

[32] *A. I. Vogel,* A Textbook of Quantitative Inorganic Analysis. 2nd ed. Longmans, Green and Co., London 1951, p. 499.

[33] *A. I. Vogel,* A Textbook of Qualitative Chemical Analysis. Longmans, Green and Co., London 1951, p. 297, 298.

[34] *W. R. Schoeller, A. R. Powell,* The Analysis of Minerals and Ores of the Rarer Elements. C. Griffin and Co., London 1955, p. 44.

0.2 *N* $KMnO_4$, 4 × anthraquinone solution *, water, 0.1 *N* H_2SO_4, and water. The hydrogen passed through polyvinyl chloride tubes, so as to avoid any sulphur uptake from rubber.

b) **Measuring apparatus** (see *Fig. 1*).

Distilled water is transferred by hydrogen pressure from the supply bottle A to the measuring flask C, *via* the calibrated tube B. Flask C has previously been

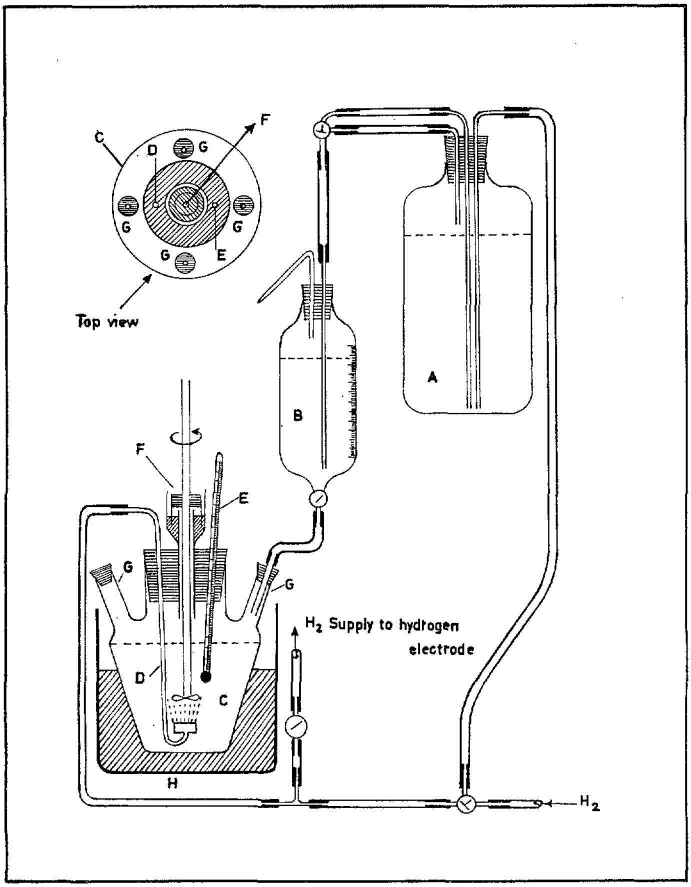

Fig. 1

Measuring apparatus

A: water supply bottle
B: calibrated tube
C: measuring flask
D: *gas distributor*
E: thermometer
F: stirrer with mercury gas lock
G: four openings, containing the electrodes, the water inlet, the *burette*
H: water bath

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* This solution consisted of: 20 g of the sodium salt of 9-10-anthraquinone-2-sulphonic acid, 200 g of KOH, 150 g of $Na_2S_2O_4$, water to 1000 ml.

filled with hydrogen by means of the gas distributor D. The four outlets G are used for the insertion of the hydrogen electrode, the silver/silver chloride electrode (and possibly other types of electrodes), and also for a burette for the addition of acid or metal chloride. Solid substances, in weighing glasses, are also introduced into the flask through G. The solution is stirred by means of a stirrer F, which passes through a mercury gas lock. E is a thermometer and H a water bath. The E.M.F. measurements were carried out with a Tinsley potentiometer, type 4025. The readings (accuracy 0.1 mV) were not taken until the E.M.F. was constant, which may take up to 45 min after the addition of metal salt.

c) **Electrodes.**

The hydrogen electrodes were daily platinized anew, in accordance with the procedure by *Potter*[35]. The preparation of silver/silver chloride electrodes has been described by *Jones et al.*[36]; it was found that these electrodes could be used several times. All the metal electrodes were prepared from pure metal (Zn and Fe: Merck, analytical grade; Cd and Sn: 99.9 % purity, from N.V. Kopermetaal, Delft, the Netherlands).

The maximum spread in the E.M.F. of the H_2-Ag/AgCl cell is 1 to 2 mV. The standard deviation corresponds to *ca.* 0.01 pH unit.

Results.

The results are represented in Figs. 2–8.

Figures 2, 1–IV

These figures give the values of pK_4 (pyrophosphate) and pK_5 (tripolyphosphate), calculated with eq. (1) and (1′), *i.e.* neglecting the formation of sodium complexes. Simultaneous extrapolation to $\mu \rightarrow 0$ and Na/phosphate ratio $\rightarrow 0$ leads to rather uncertain values of pK_4 and pK_5.

Figures 3, I–IV

The same data are now recalculated, taking sodium complexes into account. With the values 2.3 for $pK_{NaP_2O_7}$, at 25° and at 40°, and 2.8 for $pK_{NaP_3O_{10}}$, also at both temperatures, the values of pK_4 and pK_5 become independent of the Na/phosphate ratio, although they still change with μ. Extrapolation to $\mu = 0$ is more certain than in Fig. 2.

	T = 25°	T = 40°
pK_4 of pyrophosphate		
direct extrapolation (Fig. 2)	9.54	9.56
calculation with $pK_{Na} = 2.3$ (Fig. 3)	9.53	9.57
pK_5 of tripolyphosphate		
direct extrapolation (Fig. 2)	9.55	9.61
calculation with $pK_{Na} = 2.8$ (Fig. 3)	9.52	9.62

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[35] *E. C. Potter,* Electrochemistry. Cleaver-Hume Press, London 1956, p. 102.

[36] *G. Jones, M. L. Hartmann,* J. Am. Chem. Soc. **37**, 752 (1915).

Figures 4, I–IV

From pH measurements (hydrogen – Ag/AgCl cell) of mixtures of $Na_4P_2O_7$ and $Na_5P_3O_{10}$ with LiCl, using the values of pK_4, pK_5, and pK_{Na} as determined previously, pK_{Li} has been calculated.

Fig. 2 I, II, III, IV

pK_4 and pK_5 of polyphosphates, calculated without considering sodium complexes. Measurement with hydrogen and Ag/AgCl electrodes in solutions containing polyphosphate and NaCl, in some cases titrated with HCl.

– – – extrapolation to $\mu \rightarrow 0$ and $\frac{\text{Na}}{\text{phosph.}} \rightarrow 0$.

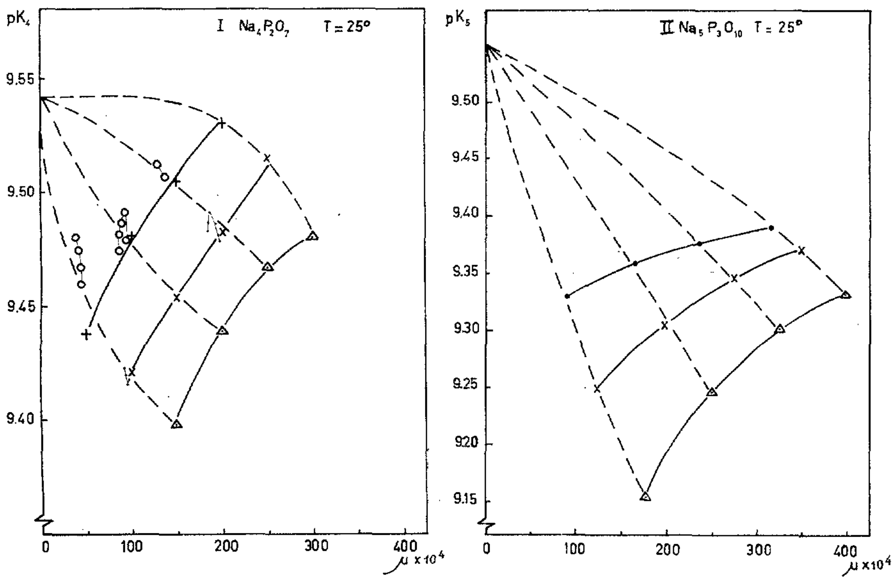

Fig. 2, I

Fig. 2, II

+ 5 } 10⁻⁴ M NaCl with 5, 10,
× 50 } 15, and 20.10^{-4} M $Na_4P_2O_7$
100 }
• 50.10^{-4} M NaCl with 5 and 15.10^{-4} M $Na_4P_2O_7$ with added HCl
o 5, 10, and 15.10^{-4} M $Na_4P_2O_7$ with added HCl

• 17 } 10^{-4} M NaCl with 5, 10,
× 50 } 15 and 20.10^{-4} M $Na_5P_3O_{10}$
△ 100 }

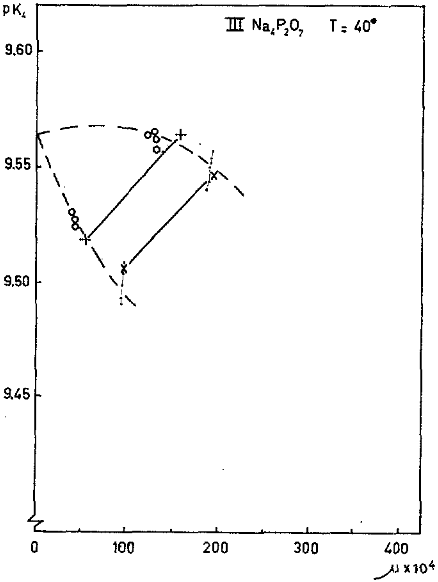

Fig. 2, III

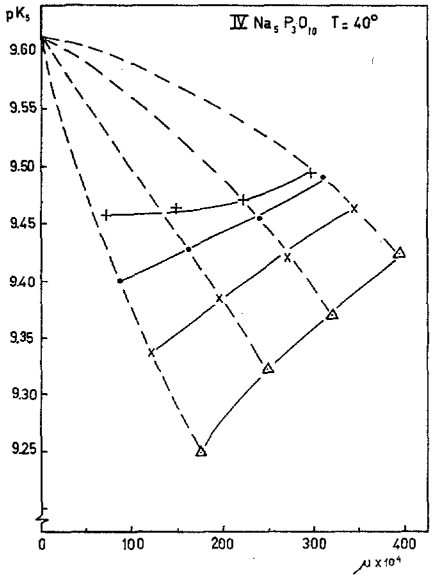

Fig. 2, IV

+ 10 } 10^{-4} M NaCl with 5 and
× 50 } 15.10^{-4} M $Na_4P_2O_7$

• 50.10^{-4} M NaCl with 5 and 15.10^{-4} M $Na_4P_2O_7$ with added HCl

o 5 and 15.10^{-4} M $Na_4P_2O_7$ with added HCl

+ 5 }
• 17 } 10^{-4} M NaCl with 5, 10,
× 50 } 15 and 20.10^{-4} M $Na_5P_3O_{10}$
△ 100 }

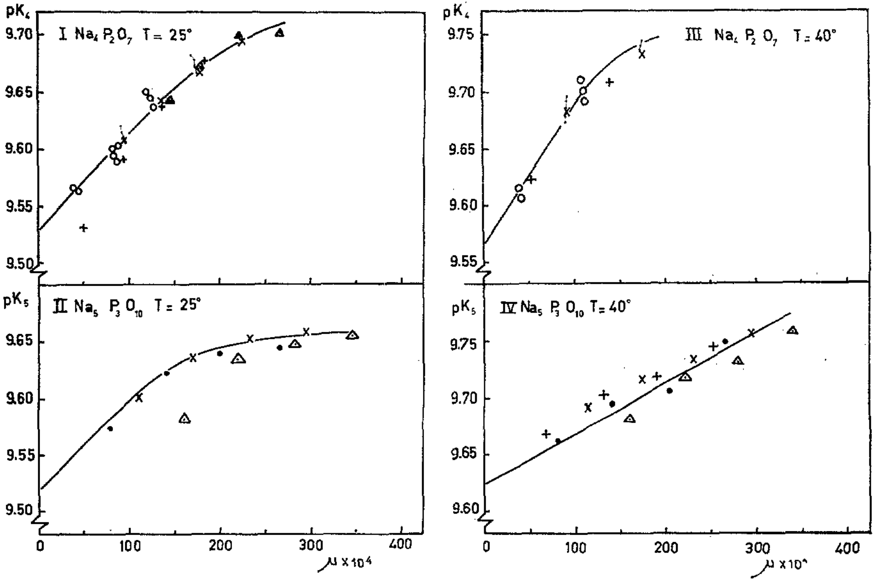

Fig. 3 I, II, III, IV
pK_4 and pK_5 of polyphosphates. Calculation with $pK_{Na} =$ 2.30 (pyrophosphate) and 2.80 (tripolyphosphate). Same data and symbols as used in fig. 2.

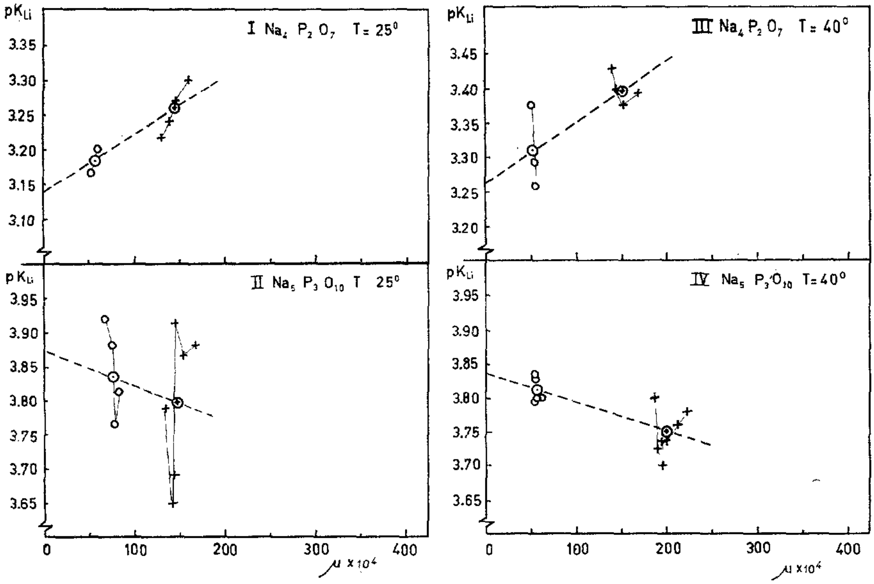

Fig. 4 I, II, III, IV

pK$_{Li}$ from sodium polyphosphates + LiCl.

○ = 5.10^{-4} M polyphosphate with added LiCl

(⊙ = mean)

+ = 15.10^{-4} M polyphosphate with added LiCl

(⊕ = mean)

Similar measurements with KCl or CsCl showed so little difference from the measurements with NaCl that it must be concluded that the values of pK$_K$ and pK$_{Cs}$ are identical with those of pK$_{Na}$ within the experimental error. When sodium ions were not present, *e.g.* owing to the preparation of $KCl - K_4P_2O_7$ solutions *via* silver phosphates, the same values were also obtained as with the corresponding $NaCl$-$Na_4P_2O_7$ solutions.

Figures 5, I and II

These figures represent the pH$_c$'s of solutions of sodium polyphosphate on addition of the chlorides of Mg, Ca, Sr, and Ba. The addition was continued beyond the X/phosphate ratio = 1. In the more concentrated phosphate solutions ($15 \cdot 10^{-4}$-molar) a precipitation of Ca- and Sr-pyrophosphate and Ba-tripolyphosphate occurs. Solubility products were estimated from the point where the turbidity starts, assuming the precipitates to be $Ca_2P_2O_7$, $Sr_2P_2O_7$, and $NaBa_2P_3O_{10}$. These are listed in Table IV. Ba-pyrophosphate is so in-

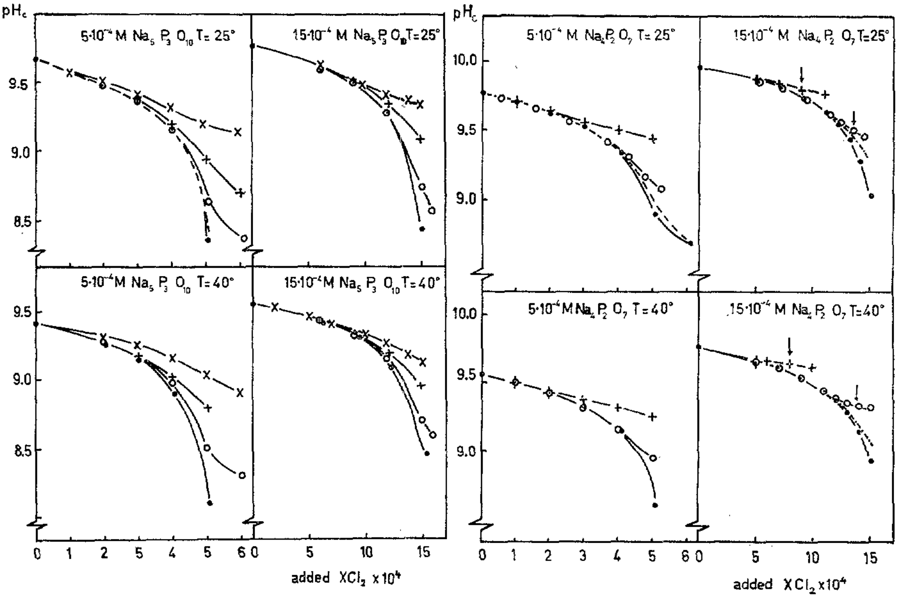

Fig. 5 I, II

Trend of pH_c on addition of alkaline earth-metal chlorides (XCl_2) to 5 and 15.10^{-4} M sodium polyphosphate + 50.10^{-4} M NaCl.

At the point indicated by an arrow (↓), the solution becomes turbid.

• = Mg
○ = Ca
+ = Sr
× = Ba
- - - - pH_c calculated for Mg with the equilibrium constants of table 5
– . – . – pH_c calculated for Ca with the equilibrium constants of table 5

soluble that it is already precipitated from the most dilute solutions used. Complex formation could not therefore be observed.

Complexing constants were calculated in the way described in the section "Theoretical Discussion". They are listed in Table IV. The accuracy of the constants is not very high. They can be considered to be independent of the ionic strength (except for the $\sqrt{\mu}$ correction which has been explicitly applied) within the error of the method.

The dotted lines in Fig. 5 have been calculated for magnesium and for calcium (when insoluble calcium salts are formed) with the constants given in Table IV (pK_4 and pK_5 as read from Fig. 3 at the corresponding value of μ).

Figures 6, I and II

The distribution of magnesium over the different ions in which it occurs is shown. The very low concentration of free Mg^{++} ions, except close to the equivalence point, and the maximum in the concentration of MgOH-phosphate are striking and justify the previously indicated method of calculation. By way of example the numerical values of two of the titrations are given in the following table II.

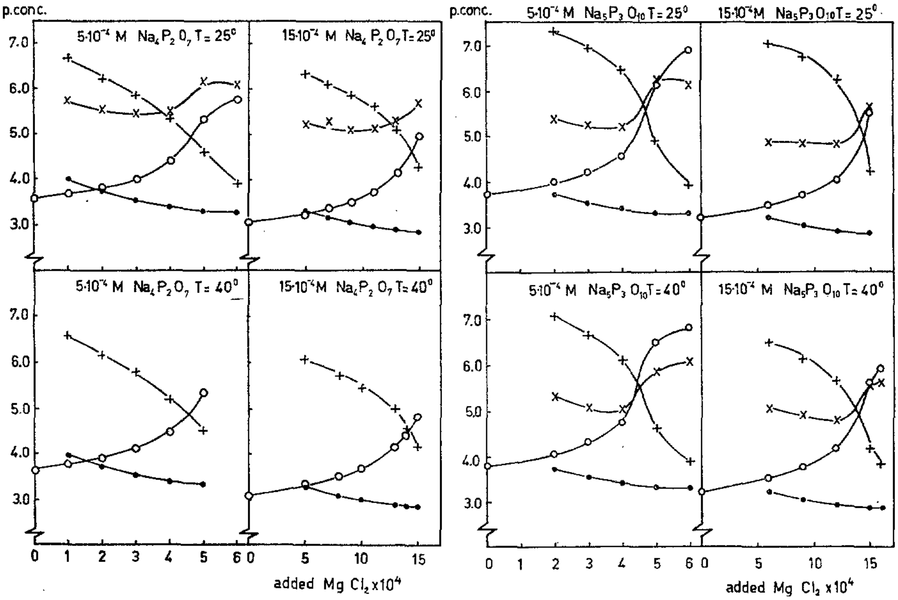

Fig. 6 I, II

Concentrations (logarithmic scale) of polyphosphate ion and of ions containing magnesium when $MgCl_2$ is added. Same measurements as in fig. 5. H-phosphate and Na-phosphate are not shown.

○ = $pP_2O_{7_c}$ or $pP_3O_{10_c}$

• = $pMgP_2O_{7_c}$ or $pMgP_3O_{10_c}$

× = $pMgOHP_2O_{7_c}$ or $pMgOHP_3O_{10_c}$

\+ = pMg_c

Figures 7, I and II

As mentioned in the theoretical part, the sequestration of zinc and cadmium is so strong that the concentration of free metal ions remains exceedingly small in the presence of phosphates. Hence, it is not sufficient to determine the pH of these solutions; the pX has also been measured electrometrically.

Table II

Concentration of phosphate and magnesium ions, present in the solution of $5 \,.\, 10^{-4}$ M of sodium polyphosphate + $50 \,.\, 10^{-4}$ M of NaCl + $MgCl_2$ added, as expressed by their negative logarithm. Temperature = 25°.

Pyrophosphate

Added $MgCl_2 \times 10^4$:	0	1	2	3	4	5	6
Ions:							
H	9.77	9.72	9.64	9.54	9.34	8.88	8.67
P_2O_7	3.57	3.68	3.82	4.03	4.40	5.35	5.77
HP_2O_7	4.12	4.17	4.24	4.33	4.51	5.00	5.22
NaP_2O_7	3.81	3.91	4.05	4.25	4.62	5.56	5.98
MgP_2O_7	—	4.00	3.70	3.52	3.39	3.32	3.31
$MgOHP_2O_7$	—	5.70	5.52	5.46	5.52	$(6.18)^x$	$(6.12)^x$
Mg	—	$(6.66)^x$	$(6.22)^x$	$(5.85)^x$	$(5.35)^x$	4.61	3.93
pK_{Mg}	—	$(7.1)^\circ$	$(7.1)^\circ$	$(7.1)^\circ$	$(7.1)^\circ$	7.37	7.11
pK_{MgOH}	—	9.35	9.34	9.34	9.34	$(9.34)^+$	$(9.34)^+$

Tripolyphosphate

Added $MgCl_2 \times 10^4$:	0	2	3	4	5	6
Ions:						
H	9.62	9.48	9.36	9.16	8.35	8.04
P_3O_{10}	3.73	3.99	4.20	4.55	6.15	6.90
HP_3O_{10}	4.27	4.38	4.46	4.61	5.40	5.83
NaP_3O_{10}	3.59	3.82	4.01	4.35	5.95	6.70
MgP_3O_{10}	—	3.70	3.53	3.40	3.31	3.31
$MgOHP_3O_{10}$	—	5.40	5.25	5.22	$(6.2)^x$	$(6.1)^x$
Mg	—	$(7.30)^x$	$(6.93)^x$	$(6.47)^x$	4.90	3.96
pK_{Mg}	—	$(8.6)^\circ$	$(8.6)^\circ$	$(8.6)^\circ$	8.70	8.50
pK_{MgOH}	—	11.02	11.10	11.22	$(11.1)^+$	$(11.1)^+$

x These ion concentrations have been neglected in the calculations.

o These complexing constants have been adopted from the values found with larger magnesium contents and have been used to calculate Mg_c.

\+ These constants have been adopted from the values with small magnesium contents and have been used to calculate $MgOHP_2O_{7_c}$ and $MgOHP_3O_{10_c}$ with a high magnesium content.

Figures 7 give the results of the pH_c measurements. pX_c is plotted in Figures 8.

Figures 8, I and II

These figures illustrate the distribution of zinc over the different ions. The concentration of free Zn ions (pZn_c) was derived directly from the electrometrical determination. From the pH_c and pZn_c values, pK's were calculated.

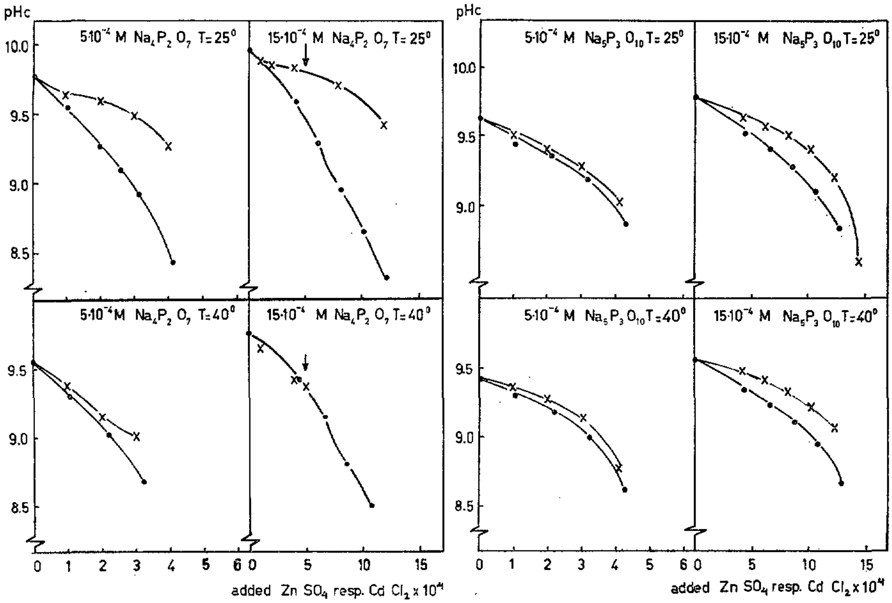

Fig. 7 I, II

Trend of pH_c on addition of $ZnSO_4$ or $CdCl_2$ to 5 and 15.10^{-4} M sodium polyphosphate + 50.10^{-4} M NaCl. At the point indicated by an arrow (↓) the Cd-solution becomes turbid.

• = Zn
× = Cd

Table III

Determination of pK_{Zn_2} in pyrophosphate solutions at 25°, pK_{Zn} = 8.7. Concentrations in mol. × 10^4/l.

$Na_4P_2O_7$	$ZnSO_4$	NaCl	pH_c	pZn_c	pP_2O_{7c}	$pZnP_2O_{7c}$	$pZnOHP_2O_{7c}$	$pZn(P_2O_7)_{2c}$	pK_{ZnOH}	pK_{Zn_2}
10	1	50	9.79	8.92	3.32	4.46	4.41	4.55	12.6	11.0
15	1	50	9.89	9.14	3.11	4.59	4.46	4.38	12.6	11.0
15	4.1	50	9.58	8.53	3.28	4.12	3.83	3.72	13.0	11.3
15	6.2	50	9.29	8.01	3.44	3.74	3.61	3.82	13.2	11.0
20	1	50	9.94	9.23	2.97	4.66	4.51	4.31	12.5	10.8
25	1	50	9.97	9.28	2.87	4.70	4.42	4.35	12.6	10.7
25	2	50	9.93	9.16	2.90	4.60	4.29	3.82	12.6	11.1

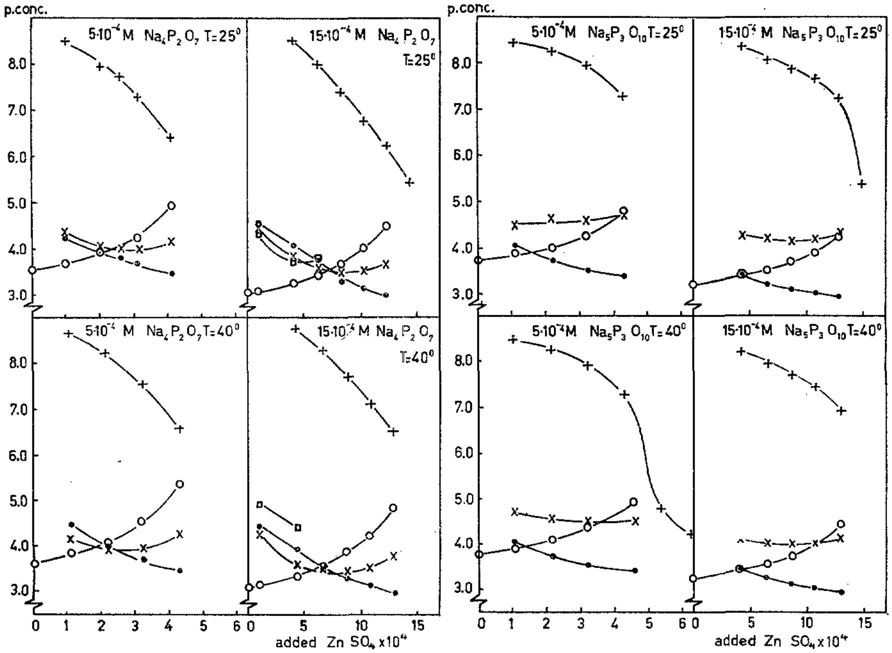

Fig. 8 I, II

Concentration (logarithmic scale) of polyphosphate ion and of ions containing zinc when $ZnSO_4$ is added. Same measurements as in fig. 7. H-phosphate and Na-phosphate are omitted.

○ = $pP_2O_{7_C}$ or $pP_3O_{10_C}$
• = $pZnP_2O_{7_C}$ or $pZnP_3O_{10_C}$
× = $pZnOHP_2O_{7_C}$ or $pZnOHP_3O_{10_C}$
+ = pZn_C
□ = $pZn(P_2O_7)_{2_C}$

The comparatively large proportion of the complex $ZnOHP_2O_7$ (as compared with the alkaline-earth metals) and the importance of the complex $Zn(P_2O_7)_2$ are obvious.

Apart from the points given in Figs. 7 and 8, a number of mixtures were measured separately, to make surer of the existence of the complex $Zn(P_2O_7)_2$. The results obtained are listed in Table III.

Qualitative tests with other metals.

Finally, some exploratory experiments were carried out with aluminium, chromium (III), tin (II), lead (II), nickel (II), cobalt (II), and iron (II).

Table IV

Dissociation constants, complex constants, and solubility products.

Constants	Pyrophosphate			Tripolyphosphate	
	25°	40°		25°	40°
pK_4	9.53 ± 0.05	9.57 ± 0.05	pK_5	9.52 ± 0.05	9.62 ± 0.05
pK_{Li}	3.1 ± 0.2	3.3 ± 0.2		3.9 ± 0.2	3.8 ± 0.2
pK_{Na}					
pK_K	2.3 ± 0.1	2.3 ± 0.1		2.8 ± 0.1	2.8 ± 0.1
pK_{Cs}					
pK_{Mg}	7.2 ± 0.3	7.1 ± 0.3		8.6 ± 0.3	8.3 ± 0.3
pK_{MgOH}	9.3 ± 0.5	—		11.0 ± 0.5	10.4 ± 0.5
pK_{Ca}	6.8 ± 0.3	6.5 ± 0.3		8.1 ± 0.3	7.8 ± 0.3
pK_{CaOH}	8.9 ± 0.5	—		10.4 ± 0.5	9.8 ± 0.5
pK_{Sr}	5.4 ± 0.5	5.3 ± 0.5		7.2 ± 0.5	7.0 ± 0.5
pK_{SrOH}	7.7 ± 0.5	—		9.3 ± 0.5	8.4 ± 0.5
pK_{Ba}	—	—		6.3 ± 0.3	6.1 ± 0.3
pK_{BaOH}	—	—		—	—
pK_{Zn}	8.7 ± 0.5	9.2 ± 0.5		9.7 ± 0.5	9.7 ± 0.5
pK_{ZnOH}	13.1 ± 0.5	13.3 ± 0.5		13.0 ± 0.5	12.8 ± 0.5
pK_{Zn_2}	11.0 ± 0.5	10.8 ± 0.5		—	—
pK_{Cd}	8.7 ± 0.5	8.6 ± 0.5		9.8 ± 0.5	10.1 ± 0.5
pK_{CdOH}	11.8 ± 0.7	12.4 ± 0.7		12.6 ± 0.5	12.5 ± 0.5
pS_{Ca} *	7.9	7.9		—	—
pS_{Sr} *	7.5	7.5		—	—
pS_{Ba} **	—	—		9.8	9.7

* $pS = pX_c + pXP_2O_{7_c} + 4\sqrt{\mu}$

** $pS_{Ba} = pBa_c + pNa_c + pBaP_3O_{10_c} + 7\sqrt{\mu}$

In the case of zinc and cadmium, complex formation is so strong that the precipitation of the hydroxide is prevented. Some metals, however, cannot be sequestered in alkaline solution by the phosphates and form hydroxides. In this case the addition of XCl_2 has the same effect as the addition of 2 HCl: $XCl_2 + 2\,H_2O \rightarrow X(OH)_2 + 2\,HCl$.

The E.M.F. of the hydrogen-calomel cell (with saturated KCl salt bridge) in a solution of $50 \cdot 10^{-4}$ *M* of sodium pyrophosphate + $50 \cdot 10^{-4}$ *M* of NaCl at 25° was determined before and after the addition of $4 \cdot 10^{-4}$ *M* of XCl_2. In the case of aluminium and chromium $2/3 \times 4 \cdot 10^{-4}$ *M* of metal salt is used.

Table V

Difference in mV of E.M.F. of hydrogen-calomel cell after addition of $4 . 10^{-4}$ *M* of metal salt to $15 . 10^{-4}$ *M* of $Na_4P_2O_7$ + $50 . 10^{-4}$ *M* of NaCl at 25°.

Metal salt	E.M.F.
$Al_2(SO_4)_3$	60 *
$CrCl_3$	52 *
$SnCl_2$	50
$ZnSO_4$	23
$CdCl_2$	14
$Pb(NO_3)_2$	11.8
$NiCl_2$	8.5
$CoCl_2$	7.5
$FeCl_2$	6.3
$MgSO_4$	4.4
$8 \cdot 10^{-4}$ M of HCl	60

* Solution is turbid.

In the case of tin, the solution is opalescent.

This proves that aluminium and chromium are precipitated as hydroxides, and that tin is dissolved either as colloidal $Sn(OH)_2$ or as a basic phosphate complex, in accordance with the work of *Davis* [13].

The other metals, the E.M.F. drop of which is smaller than that of zinc and greater than that of magnesium, will probably all form a basic complex to some extent.

Remark:

Some authors [37-39] deny the existence of well-defined complexes between polyphosphates and metal ions. They consider the polyphosphates to be dissolved ion exchangers. One of the main reasons for this hypothesis is the dependence of the sequestering power on the NaCl concentration. We believe we have shown that this argument is not sound, at least not for pyro- and tripolyphosphate, since this phenomenon can be explained by the formation of sodium complexes.

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(Received, May 12th 1959).

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