306. *Studies of Phosphates. Part IV. Pyrophosphates of Some Bivalent Metals and their Double Salts, and Solid Solutions with Sodium Pyrophosphate.*

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THE considerations which led Werner to his theory of co-ordination were largely based upon salt hydrates. It was chiefly those hydrates which contained 4 or 6 molecules of water per atom of metal which came under review. The co-ordination theory has given a very satisfactory explanation of these, but numerous salt hydrates exist for which no adequate structural ideas have been evolved. This is especially true of those containing relatively small amounts of water. Sidgwick's maximum covalency rule (1924) tells us the maximum co-ordination number which an element can have, but we have little guidance as to the lower values which are possible. Are any values below the maximum possible, or only certain values? There is considerable evidence that only even values of the co-ordination number and the zero value are possible, in normal circumstances, for hydrated salts and similar compounds. The term co-ordination is used in Werner's sense to mean a unit (held together by covalencies) which, if sufficiently stable, may persist as an ion in solution. It is not used in the crystallographic sense to indicate a purely spatial arrangement.

Evidence is accumulating which indicates that rearrangements and adjustments may occur in hydrates which contain small numbers of water molecules so that a part, if not the whole, of the kations may have a higher even co-ordination number than appears at first sight possible. Linkage of two or more metal ions by water molecules appears to be a very important factor in such adjustments (Bassett and Croucher, J., 1930, 1784; Bassett and Sanderson, J., 1932, 1855; Bassett *et al.*, J., 1933, 151; Bassett and Lemon, *ibid.*, p. 1423; Bassett and Sanderson, J., 1934, 1116).

The formation of solid solutions, often of an unexpected nature, has been very helpful in indicating the possible nature of several compounds (cf. the above references and also Bassett and Bedwell, J., 1933, 877).

An examination of the pyrophosphates of bivalent metals has now been made, and a marked tendency for the formation of solid solutions containing sodium has been found, although definite double salts also occur. The observed hydrates, double salts, and solid solutions fit in well with the views (*a*) that the water molecules are distributed so as to give

kations with even co-ordination numbers, and (*b*) that replacement of $[M(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$ or of $[M(H_2O)_2]^{..}$ by $2Na^{.}$ occurs owing to approximate equality of molecular volumes. Such replacement may go to completion, in which case definite double salts result, or it may be only partial. In one instance the whole range of solid solutions was obtained from the pure pyrophosphate to the pure double salt. Formation of definite double salts sometimes enables one to distinguish between two possible structures for the parent compound $M_2P_2O_7,xH_2O$.

Our theory gives a clue to the nature of these pyrophosphates, and of other compounds, which could scarcely be obtained from analysis alone. It enables one to foresee and understand double salts which might be considered ridiculous from their formulæ alone. We are not attempting to give a full account of the crystalline structure of these compounds: that may ultimately be done by the help of *X*-rays when sufficiently well-developed crystals can be obtained.

If equivalent amounts of MCl_2 and $Na_4P_2O_7$ solutions are mixed, the amorphous precipitate persists indefinitely without becoming crystalline. The precipitates are easily soluble in sulphurous acid, and crystalline hydrated pyrophosphates are deposited when the sulphur dioxide is removed (Schwarzenberg, *Annalen*, 1848, **65**, 133). Baer (*Pogg. Ann.*, 1848, **75**, 152) used acetic instead of sulphurous acid, but this method is restricted to the pyrophosphates of magnesium, cobalt, and nickel, since the others are insoluble in acetic acid. The use of acid, especially at temperatures above the ordinary, is, however, restricted by the danger of hydrolysis to orthophosphate. We find that, at the ordinary temperature, mixtures will keep for months or even years without any detectable orthophosphate formation in absence of acid. This is largely true also of acid mixtures at room temperature, but not for temperatures above about 50°.

The amorphous pyrophosphates (except those of manganese and cadmium) are, as a class, readily soluble in excess of alkali pyrophosphate, and a variety of crystalline products is obtainable from such solutions. The statement, sometimes made, that the amorphous pyrophosphates are soluble in excess of MCl_2 seems to be erroneous. It is for this reason that it is almost impossible to obtain crystalline products from mixtures containing excess of MCl_2. Magnesium and nickel were almost the only metals with which this could be done, and this is because their pyrophosphates have an appreciable solubility in pure water.

Almost all the early work on the simple and double bivalent metal pyrophosphates was done by Persoz (*Ann. Chim. Phys.*, 1847, **20**, 315; *Annalen*, 1848, **65**, 163), Schwarzenberg (*loc. cit.*), Baer (*loc. cit.*), or Fleitmann and Henneberg (*Annalen*, 1848, **65**, 387). As a rule, the products analysed by these workers had been dried at 100°, so that many of the hydrates they mention are doubtful.

Pahl (*Öfvers. K. Vet. Akad. Förh.*, 1873, **30**, 29; see also *Bull. Soc. chim.*, 1873, **19**, 115; *Ber.*, 1873, **6**, 1465; 1874, **7**, 478) prepared a number of pyrophosphates of bivalent metals, and double salts with sodium or potassium pyrophosphate. He gives more details about the method of preparation than do the earlier workers but, like them, says nothing about concentrations or proportions of reactants. It is therefore very difficult to repeat any of the older work. His analytical figures frequently differ considerably from those calculated for the formulæ assigned by him. We have failed to obtain some of the compounds given in the older work, in spite of repeated attempts. The only recent paper of importance on pyrophosphates is one by Rosenheim *et al.* (*Z. anorg. Chem.*, 1926, **153**, 126), who regard all the double pyrophosphates of bivalent metal and alkali metal as complex salts containing the whole of the bivalent metal in the anion. The fact that the mother-liquors, from which the salts have separated, do not always give positive reactions for the bivalent metal kations is an unsound argument for a similar complexity in the solid which separates. The double salts in most cases separate from solutions containing a far greater proportion of the alkali pyrophosphate. They are themselves too insoluble in water for direct tests to be applied. Pink cobalt compounds which, because of their colour, appear to be entirely kationic can separate from blue pyrophosphate solutions in which probably there are anionic cobalt complexes. Such behaviour we believe to be common. The *compound* $3Na_4P_2O_7,Cu_2P_2O_7,32H_2O$ is the only double pyrophosphate

obtained by us which appears certainly to be complex and to contain the copper in the anion. It forms dark blue prisms and is easily soluble in water without decomposition. All the other compounds now described are very insoluble. When they are coloured, the colours are those which we attribute to the bivalent metal in the kationic condition, and probably all are true double salts which exist only in the solid state and contain all the alkali and bivalent metal as kations.

In the tables which follow, the double salts and solid solutions have been referred to their " parent " hydrates. In calculating these, $[Na_2(H_2O)_2]^{··}$ is supposed to replace $[M(H_2O)_4]^{··}$ in the higher hydrates while $Na_2^{·}$ replaces $[M(H_2O)_2]^{··}$ in lower hydrates. Where solid solutions are partly acidic, $[H_2(H_2O)_2]^{··}$ is supposed to replace $[M(H_2O)_2]^{··}$.

In calculating the " parent " hydrates, small adjustments of the analytical figures have been made in a few cases. These are always shown in the tables, and have been made so that (a) the complete analysis may add up to 100%, and (b) total base may correspond to P_2O_5. The adjustment for correspondence of base and acid was made only in those cases where the slight disagreement was most probably due to analytical error. In other cases, large disagreements were certainly due to a real acidity of the preparations.

In some cases pure " parent " hydrates are obtainable, in other cases only pure double salts. In a few cases a wide range of solid solutions can be obtained, and in others a very restricted range. The chief determining factors are (a) the structure of the " parent " hydrate, and (b) the conditions under which it is obtainable. If the structure is such that replacement by sodium is possible, and if, in addition, the complex only separates in presence of a high concentration of sodium pyrophosphate, it naturally follows that replacement by sodium tends to go as far as the " parent's " structure permits.

Another very important point is that solid solutions will, in nearly all cases, be under a certain amount of strain due to the fact that the replacing ions or groups seldom have precisely the same dimensions. This tends to make them metastable towards either pure double salt or pure " parent hydrate " and, in such cases, the pure double salt will be crystallographically more different from pure parent hydrate than in cases where intermediate solid solutions can be obtained. It is not surprising, therefore, that intermediate solid solutions are not obtainable in all cases where the views outlined above would lead one to expect them. They are the exception rather than the rule, as they require so many conditions to be favourable.

Complete analyses were made in all but a few cases where it was not considered necessary or where material was scarce. Although great care was taken with the analyses, the assignment of formulæ (e.g., $M_2P_2O_7,2\cdot3H_2O$ rather than $M_2P_2O_7,2\cdot3H_2O$) depends partly upon general considerations such as the multiple required to give a whole number of water molecules. Fine distinctions of this sort cannot be made from the analyses alone. All preparations were carefully examined, so far as possible, with the petrological microscope.

The homogeneity of preparations could be established with considerable certainty even when they were so fine that little more than refractive indices could be determined. In cases where crystalline condition was better developed, the optical characters and crystallographic system were examined as fully as possible. All the compounds obtained appear to be either orthorhombic or monoclinic.

Few of the compounds are well crystallised. In many cases individual crystals are very small, and require the use of a $\frac{1}{6}''$ objective. This is the more surprising, at first sight, because they are frequently in equilibrium with solutions in which the gross solubility of the pyrophosphate in question is relatively large. This behaviour is quite consistent with our views which attribute relatively complex structures to many of the compounds, composed of several different ions some of which may be present in the solution in only very low concentrations. The compounds behave, in fact, from the point of view of their capacity to crystallise, as if they had extremely low solubility, and their behaviour towards pure water agrees with this.

Even when the glittering appearance and examination with a pocket lens suggest that a preparation is well crystallised, the microscope shows ill-developed intergrown crystals which are very difficult to study. It thus happens that analytical evidence is not always supported by optical evidence, since the latter is mainly negative. When preparations
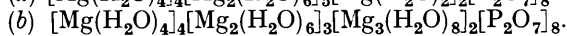
yielding similar analytical figures can be obtained by different methods, and when they remain unchanged for months in contact with the mother-liquor, we feel justified in regarding them as definite compounds even when unable to determine any very characteristic optical data. In other cases, a well-defined metastable hydrate slowly changes in contact with mother-liquor till a new limiting water content is reached, and the product may justifiably be regarded as a definite compound. In some cases a well-defined hydrate of one metal may give valuable support for similar but less well-defined hydrates of other metals.

Details of preparation, etc., of each compound are summarised in the tables. Most of the compounds are really metastable, and this renders the reproducibility of the preparations somewhat uncertain.

A brief discussion of each parent hydrate and its derived solid solutions and double salts is now given.

None of these crystalline hydrated pyrophosphates show any " glowing " phenomenon (see J., 1933, 854) on sudden strong ignition over a blowpipe, or, as a rule, any sintering when free from sodium. They generally melt when more than about 3% Na_2O is present.

The polynuclear kations postulated in various compounds have the following structures, all linkages being through the oxygen of water molecules.

$$[M_2(H_2O)_7]^{IV} = \begin{bmatrix} H_2O & & \overset{H_2}{O} & & OH_2 \\ H_2O{\rightarrow}M & & & M{\leftarrow}OH_2 \\ H_2O & & & & OH_2 \end{bmatrix}^{IV}$$

$$[M_2(H_2O)_6]^{IV} = \begin{bmatrix} H_2O & \overset{H_2}{O} & & OH_2 \\ & M & & M \\ H_2O & O & & OH_2 \\ & & H_2 & \end{bmatrix}^{IV}$$

M is 4 co-ordinate

$$[M_2(H_2O)_5]^{IV} = \begin{bmatrix} & \overset{H_2}{O} & \\ H_2O{\rightarrow}M & & M{\leftarrow}OH_2 \\ & OH_2 & \\ & O & \\ & H_2 & \end{bmatrix}^{IV}$$

$$[M_3(H_2O)_8]^{VI} = \begin{bmatrix} H_2O & \overset{H_2}{O} & \overset{H_2}{O} & OH_2 \\ & M & M & M \\ H_2O & O & O & OH_2 \\ & H_2 & H_2 & \end{bmatrix}^{VI}$$

M is 2 co-ordinate

$$[M_2(H_2O)_3]^{IV} = [H_2O{\rightarrow}M{\leftarrow}\overset{H_2}{O}{\rightarrow}M{\leftarrow}OH_2]^{IV}$$

$$[M_2(H_2O)_2]^{IV} = \begin{bmatrix} & \overset{H_2}{O} & \\ M & & M \\ & O & \\ & H_2 & \end{bmatrix}^{IV}$$

We regard $Co_3(PO_4)_2,8H_2O$ as typical of compounds containing the $[M_3(H_2O)_8]^{VI}$ ion. The complete absence of sodium from the crystals, even when they separate from solutions containing a high sodium-ion concentration (see Part II; J., 1933, 874), is important as it indicates the absence of either $[Co(H_2O)_4]^{\cdot\cdot}$ or $[Co(H_2O)_2]^{\cdot\cdot}$ kations and so excludes the structure $[Co(H_2O)_4][Co(H_2O)_2]_2[PO_4]_2$.

Octahydrates.—The octahydrate is the highest which could be obtained, and that only with cobalt, though there are strong indications of a nickel octahydrate, even more unstable

towards lower hydrates than the cobalt compound. The nickel *double salt* $Na_4P_2O_7,Ni_2P_2O_7,12H_2O$ was obtained, and can be derived from the parent hydrate $[Ni(H_2O)_4]_2P_2O_7$ by replacement of half the $[Ni(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$. The pure cobalt double salt was not prepared, as it is too unstable towards $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$, and only mixtures with this *compound* could be obtained. The cobalt octahydrate is too unstable to be obtained in other than a very finely divided, possibly amorphous, condition.

Heptahydrates.—A heptahydrate could be obtained only with magnesium, and even this is difficult to prepare owing to its instability towards lower hydrates. It is suggested that it has the structure $[(H_2O)_3MgH_2OMg(H_2O)_3]P_2O_7$ in which two 4-co-ordinate magnesium atoms are linked by one water molecule. The apparent absence of any double salt or solid solutions containing sodium derivable from a heptahydrate agrees with such a structure. The closeness with which the amorphous precipitate approximates to a hepta-hydrate is noteworthy : the alkali possibly present in this case was probably adsorbed ; some is nearly always present in amorphous pyrophosphate precipitates. The amorphous solid was returned to its mother-liquor, and in the course of 32 months gradually became well crystallised. Analysis of the crystals corresponded exactly to $Mg_2P_2O_7,7H_2O$, but microscopic comparison and other tests showed them to be the orthophosphate $MgHPO_4,3H_2O$. Hydrolysis to orthophosphate appeared to be connected with the growth of green algæ in the mother-liquor.

6·5-Hydrates.—There is some evidence that the 6·5-hydrate is a definite stage, but magnesium and nickel are the only metals yielding preparations in which no signs of inhomogeneity could be detected. The magnesium *compound* appears to be very unstable towards $Mg_2P_2O_7,6·25H_2O$.

6·25-Hydrates.—This stage of hydration was only obtained with the pyrophosphates of magnesium and nickel. The magnesium *compound* yields a wide range of solid solutions with $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$ as the limiting double salt. The grain size of the crystals is very small, but careful study with the petrological microscope showed no signs of inhomogeneity.

Pahl (*loc. cit.*) describes a similar copper salt, $Na_4P_2O_7,3Cu_2P_2O_7,21H_2O$, which we have failed to obtain. Two alternative structures for the parent hydrate, $Mg_2P_2O_7,6·25H_2O$, by complete replacement of $[Mg(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$ could give the double salt actually found ; they are (*a*) $[Mg(H_2O)_4]_4[Mg_2(H_2O)_6]_5[Mg(H_2O)_2]_2[P_2O_7]_8$ and
(*b*) $[Mg(H_2O)_4]_4[Mg_2(H_2O)_6]_3[Mg_3(H_2O)_8]_2[P_2O_7]_8$.
As a rule, sodium replacement does not go beyond that required for
$$Na_4P_2O_7,3Mg_2P_2O_7,21H_2O,$$
even when the double salt crystallises out alongside $Na_4P_2O_7,10H_2O$. It was found, however, that the sodium oxide content could be raised to 10·07%, as compared with 9·45% required by the double salt, if much sodium chloride was added to the mixture from which it separated. This supports structure (*a*) rather than (*b*), for after all $[Mg(H_2O)_4]^{..}$ had been replaced, further entry of sodium could occur by replacement of $[Mg(H_2O)_2]^{..}$ by $Na_2^{..}$. Structure (*a*) also agrees better with the marked tendency for acidic solid solutions to be formed from $Ni_2P_2O_7,6·25H_2O$ owing to replacement of $[Ni(H_2O)_2]^{..}$ by $[H_2(H_2O)_2]^{..}$.
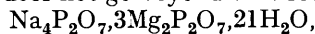
In structure (*a*) one-eighth of the metal is 2-co-ordinate, but in (*b*) it is all 4-co-ordinate. Alternative structures in which all the metal is 4-co-ordinate are possible, but they would not lead to $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$ as the limiting double salt.

One unusually well-crystallised magnesium preparation was obtained which may be regarded as the limiting double salt derived from a third form of $Mg_2P_2O_7,6·25H_2O$ with the structure $[Mg(H_2O)_4]_7[Mg_2(H_2O)_6]_8[Mg_3(H_2O)_8]_3[P_2O_7]_{16}$, in which all the metal is 4-co-ordinate. By replacement of all $[Mg(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$ this would give the double salt $7Na_4P_2O_7,25Mg_2P_2O_7,172H_2O$. The substance in question has almost exactly the composition required for such a double salt, and in view of the large proportion of sodium pyrophosphate compared to magnesium salt used in its preparation, it is highly probable that replacement by sodium had gone as far as possible (compare the case of $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$). The preparation consisted of single rectangular crystals which were certainly homogeneous and had a much higher birefringence than any other magnesium preparation, which is the chief reason for putting it in a separate class.

The $Ni_2P_2O_7,6\cdot25H_2O$ preparations are all poorly developed crystals. They consist of minute rhombohedra, usually assembled in layers to form a much larger aggregate, not easily crushed into its constituent rhombs. This makes it very difficult to examine the crystal properly.   The rhombs seem to give straight and oblique (possibly symmetrical) extinction ; α varied from 68° to 86°. Biaxial, either monoclinic or orthorhombic. Average n about 1·58 and birefringence about 0·02. The chief evidence for the entity of the compound is (*a*) the large number of samples obtained under different conditions, (*b*) their stability in the mother-liquor, (*c*) the fact that fine and coarse material of the same preparation, separated by decantation, have the same composition.

Hexahydrates.—Of the hexahydrates, that of cobalt is well crystallised, and the best-defined member of this group, whereas the *double salt* $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$ is one of the most striking of all the sodium double pyrophosphates. Magnesium pyrophosphate also forms a *hexahydrate*, but its development is poorer than that of the cobalt salt. It gives rise to solid solutions containing sodium, but none were obtained containing the full amount required by the limiting compound $Na_4P_2O_7,3Mg_2P_2O_7,20H_2O$. No intermediate solid solutions were obtained in the case of cobalt, but only the pure double salt, which is orthorhombic. The magnesium compound is probably orthorhombic too, but its development was not good enough to prove this. The double salts can be derived from a parent hydrate $M_2P_2O_7,6H_2O$, with structure either (*a*) $[M(H_2O)_4][M_2(H_2O)_6][M(H_2O)_2][P_2O_7]_2$ or (*b*) $[M(H_2O)_4][M_3(H_2O)_8][P_2O_7]_2$, by replacement of all $[M(H_2O)_4]^{\cdot\cdot}$ by $[Na_2(H_2O)_2]^{\cdot\cdot}$.

The pure cobalt pyrophosphate hexahydrate is monoclinic, and as it seems to be incapable of taking sodium into solid solution we suggest that it has the structure $[Co_2(H_2O)_6]P_2O_7$, with one binuclear kation in which both cobalt atoms are 4-co-ordinate.

Manganese and cadmium yield another type of double salt, $Na_4P_2O_7,M_2P_2O_7,8H_2O$, previously obtained by Pahl and by Rosenheim (*locc. cit.*), which can be derived from still a third form of the hexahydrate with the structure $[M(H_2O)_4]^{\cdot\cdot}[M(H_2O)_2]^{\cdot\cdot}P_2O_7''''$. The evidence for this lies in the fact that the composition of these double salts shows a small but significant range of composition. Solid solutions can be obtained which contain either more or less sodium than corresponds to the pure double salt. In the case of manganese it is difficult to get a larger proportion of sodium into the compound than corresponds to the pure double salt, for the latter appears to be the stable compound in equilibrium with both solid $Na_4P_2O_7,10H_2O$ and saturated solution at room temperature. In the case of cadmium, conditions are reversed, and it is easier to get solid solutions containing more sodium than corresponds to the pure double salt. One sample containing less sodium than the pure double salt was prepared at 100°, but at this temperature there is a general tendency to form lower hydrates, so the method could not be extended. All the manganese and cadmium preparations appear to be perfectly homogeneous. They are fairly well crystallised, and their forms are quite distinct from those of pure $Co_2P_2O_7,6H_2O$ or of the double salt $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$. The variations in composition of the solid solution which can be produced are small.   Several strongly acidic nickel preparations were obtained which appear to be derived from the same form of the hexahydrate as are the manganese and cadmium double salts.

Pentahydrates.—The pentahydrate is the lowest obtainable in the case of copper and zinc. The zinc *compound* is comparatively well crystallised and well defined. The results obtained with the other metals make it highly probable that they, too, yield similar compounds, but their crystalline development· is too poor for satisfactory microscopic examination. The situation is also rendered difficult because the pentahydrates result from decomposition of higher hydrates in some cases, whilst in others they tend to change into lower hydrates.

The freedom of the zinc pentahydrate from sodium indicates that the structure is probably $[(H_2O)Zn(H_2O)_3Zn(H_2O)]P_2O_7$. With other metals alternative structures, such as $[M_2(H_2O)_6][M(H_2O)_2]_2[P_2O_7]_2$, appear to occur, in which replacement of $[M(H_2O)_2]^{\cdot\cdot}$ by $Na_2^{\cdot\cdot}$ is possible and solid solutions are formed.

The results with zinc show that an apparently amorphous precipitate may have essentially the same composition as a well-crystallised preparation. The fact that the pentahydrates of magnesium, manganese, cobalt, and nickel appeared to consist of some

relatively well-crystallised and some very fine material does not show that they were really mixtures, since crystal growth with these very sparingly soluble substances is very slow. Pahl (*loc. cit.*) obtained the copper pentahydrate.

4·2-Hydrate.—There is one somewhat doubtful representative of this group, formed by copper. It takes sodium into solid solution slightly beyond the amount required for complete replacement of $[Cu(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$ in

$$[Cu(H_2O)_4]_2[Cu(H_2O)_2]_2[Cu_2(H_2O)_3]_3[P_2O_7]_5$$

to give $Na_4P_2O_7,4Cu_2P_2O_7,17H_2O$. Small replacement of $[Cu(H_2O)_2]^{..}$ by $Na^{.}_2$ may occur as well.

Tetrahydrates.—These appear to represent a definite hydrate stage, separating from relatively dilute solutions at temperatures well above that of the room, although the copper *compound* may also be formed at room temperature. All the preparations are either too finely divided or too irregular for satisfactory microscopic examination. There seems to be a tendency for sodium to go into the compound. This suggests that the metal ions in the solid are now all 2-co-ordinate, with the structure $[M(H_2O)_2]_2[P_2O_7]$; $Na^{.}_2$ can replace $[M(H_2O)_2]^{..}$.

A few results are given for several metals, but it is difficult to get consistent results; the optical evidence is weak, and although the existence of tetrahydrates of these metals is probable, they are not as well established as could be wished. The copper salt, at least, seems definite, since decomposition of the pentahydrate stops at the tetrahydrate stage.

3⅔-Hydrate.—The only well-defined member of this group is the *double salt* $8Na_4P_2O_7,7Zn_2P_2O_7,23H_2O$, which is readily derived from $Zn_2P_2O_7,3\frac{2}{3}H_2O$ if this has the structure $[Zn(H_2O)_4][Zn(H_2O)_2]_{15}[Zn_2(H_2O)_3]_7[P_2O_7]_{15}$. Replacement of all $[Zn(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$ and all $[Zn(H_2O)_2]^{..}$ by $Na^{.}_2$ gives the double salt. There is also an ill-defined $Mg_2P_2O_7,3\frac{2}{3}H_2O$, and solid solutions which appear to be derived from $Cu_2P_2O_7,3\frac{2}{3}H_2O$. The zinc double salt appears to be metastable at 100° towards $2Na_4P_2O_7,2Zn_2P_2O_7,5H_2O$ derived from $Zn_2P_2O_7,3·25H_2O$.

3·6-Hydrates.—Manganese, zinc, and copper each form a hydrate which is probably of this type. The preparations are moderately well crystallised and somewhat similar in appearance. They do not seem to be the 3⅔-hydrate, although the analytical figures do not prove that conclusively. It is just possible that the copper compound is a 3½-hydrate.

3·25-Hydrates.—No parent hydrate of this type, free from sodium, has been obtained, but the well-defined *double salt* $2Na_4P_2O_7,2Zn_2P_2O_7,5H_2O$ would, by our method, be derived from such a hydrate by replacement of $[Zn(H_2O)_2]^{..}$ ions by $Na^{.}_2$. The great tendency to form the double salt suggests that such replacement is complete, and supports the view that both $[Zn_2(H_2O)_3]^{IV}$ and $[Zn_2(H_2O)_2]^{IV}$ ions are present, and that the structure of the parent hydrate is $[Zn(H_2O)_2]_4[Zn_2(H_2O)_3][Zn_2(H_2O)_2][P_2O_7]_4$. Pahl (*loc. cit.*) probably obtained this compound, but his statements are not clear on the matter.

Trihydrates.—Certain cadmium preparations correspond very closely to this stage of hydration, and copper gives a *double salt* and solid solutions derived from the trihydrate. The pure double salt can be crystallised out in very small amounts alongside the blue anionic complex salt. It is very pale blue, almost white, and very sparingly soluble, having, in fact, the characteristics of a double salt in which all the metal is kationic. It has the formula $8Na_4P_2O_7,7Cu_2P_2O_7,13H_2O$, which is derivable from a parent hydrate having the structure $[Cu(H_2O)_2]_{32}[Cu_2(H_2O)_2]_{13}Cu_2[P_2O_7]_{30}$ by replacement of all $[Cu(H_2O)_2]^{..}$ by $Na^{.}_2$. In our preparation all but $0·45CuO$ (see p. 1427) has been replaced by Na_2O, but under other conditions replacement by sodium proceeds only to a small extent.

2⅔-Hydrates.—This appears to be a definite type of hydrate, and cobalt yields a fairly well-defined *compound* $3Na_4P_2O_7,9Co_2P_2O_7,20H_2O$, which, according to our view, is derived from a parent $Co_2P_2O_7,2\frac{2}{3}H_2O$, with structure $[Co(H_2O)_2]_6[Co_2(H_2O)_3]_2[Co_2(H_2O)_2]_7[P_2O_7]_{12}$, by complete replacement of $[Co(H_2O)_2]^{..}$ by $Na^{.}_2$. All the cobalt in this parent hydrate is 2-co-ordinate. There was some indication of a similar magnesium double salt, and with cadmium the pure *hydrate* $Cd_2P_2O_7,2\frac{2}{3}H_2O$, free from sodium, was obtained. It is unstable in its mother-liquor at 100° towards $Cd_2P_2O_7,2\frac{1}{3}H_2O$.

$2\frac{1}{3}$-*Hydrates.*—This is the lowest hydrate we have obtained. It practically always contained some sodium, and in the case of zinc the amount was such as to indicate $3Na_4P_2O_7,9Zn_2P_2O_7,16H_2O$ as the limiting compound. Several of the preparations were notably acidic. Those of manganese and zinc were well crystallised, though individual crystals were small, and very close examination with the petrological microscope could detect no sign of heterogeneity. On the basis of $[Na_2]^{..}$ or $[H_2(H_2O)_2]^{..}$ replacing $[M(H_2O)_2]^{..}$, the parent hydrates agree very closely with $M_2P_2O_7,2\frac{1}{3}H_2O$ in all cases, especially if the small amount by which the total of the analytical results exceeds 100 is deducted from the percentage of water as given by the loss on ignition. With all preparations containing sodium, and with the zinc preparations in particular, the heating has to be done very carefully, first to a low temperature for some time, or high results for water are obtained owing to loss of sodium oxide.

The nature of the limiting double salt with zinc suggests that the structure of the parent hydrate is $[Zn(H_2O)_2]_3[Zn_2(H_2O)_2]_4Zn[P_2O_7]_6$ rather than $[Zn(H_2O)_2]_2[Zn_2(H_2O)_2]_5[P_2O_7]_6$, for the latter would lead to a limiting double salt $Na_4P_2O_7,5ZnP_2O_7,10H_2O$ containing only $6·3\%$ Na_2O. As the manganese and cadmium preparations appear to be microscopically similar to that of zinc, they probably all have similar structures. It is to be presumed that in this case the structure in which all the zinc is 2-co-ordinate does not pack so well as the alternative one.

Solid Solutions in Sodium Pyrophosphate Decahydrate.—Sodium pyrophosphate crystallises from solution at ordinary temperatures as a decahydrate in well-formed, clear crystals, but those crystals obtained from solutions containing cobalt or nickel were distinctly pink or green. Well-marked, absolutely clear crystals show these colours, which must be attributed to solid-solution formation. The extent of this has been examined in the case of all the metals dealt with in the present work, and the results are shown on p. 1428. The greatest tendency to solid-solution formation in $Na_4P_2O_7,10H_2O$ is found with cobalt and nickel, since solutions saturated with respect to the decahydrate can retain considerable amounts of the cobalt or nickel pyrophosphate in solution. Exactly the opposite applies to manganese and cadmium, and no evidence of solid solutions could be obtained with them. Magnesium and zinc pyrophosphates are about one-third as soluble in $Na_4P_2O_7,10H_2O$ as are the cobalt and nickel compounds. The case of copper is important, for its pyrophosphate is very soluble in sodium pyrophosphate solutions, but the stability of the anionic complexes is so great that in those solutions from which $Na_4P_2O_7,10H_2O$ can separate there can be few $[Cu(H_2O)_4]^{..}$ ions to go into solid solution. The value $0·007\%$ found for the content of CuO in the $Na_4P_2O_7,10H_2O$ may or may not represent a real solubility in those crystals, but it does show that the much higher results obtained with the other metals cannot be due to mechanical contamination of the deca-hydrate crystals with mother-liquor : if they were, just as high results should have been found for the copper content of the crystals.

Our theory of replacement at once enables an explanation of these solid solutions to be given, and at the same time gives a reasonable interpretation of the nature of $Na_4P_2O_7,10H_2O$. The evidence suggests that this compound is

$$[Na(H_2O)_4]_2[Na_2(H_2O)_2][P_2O_7].$$
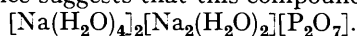
The solid solutions are due to replacement of some $[Na_2(H_2O)_2]^{..}$ by $[M(H_2O)_4]^{..}$, the reverse process of that hitherto considered. Naturally, this replacement can only occur to a small extent owing to the low concentration of $[M(H_2O)_4]^{..}$ ions in the solution and the great excess of sodium.

The Compound $Na_6Cu(P_2O_7)_2,16H_2O$ *or* $3Na_4P_2O_7,Cu_2P_2O_7,32H_2O$.—This *compound* is entirely different from any of the other double pyrophosphates. Its great solubility and deep blue colour indicate an anionic structure. Its behaviour towards potassium chromate and ferrocyanide also shows that the copper is present in a complex ion, though one of low stability. All the other copper sodium pyrophosphates are very pale blue, almost white, and insoluble.

No solid anionic complex salt could be obtained with any of the other metals. The marked solubility of the pyrophosphates of magnesium, cobalt, nickel, and zinc in concentrated sodium pyrophosphate solutions, and also the purple and yellowish-green colour

of the cobalt and nickel solutions, certainly point to complex-anion formation. The stability of the complex anions and solubility relationships never seem to be suitable for the formation of solid salts containing these complexes. Pahl (*loc. cit.*) says that, by spontaneous evaporation at summer heat, he obtained the compound

$$3Na_4P_2O_7,Zn_2P_2O_7,24H_2O$$
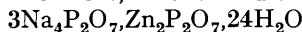
as long prismatic crystals. We have failed to find this in spite of many attempts, as also the copper salt with only $24H_2O$, which Pahl gives in addition to the usual compound with $32H_2O$, first prepared by him.

Manganese and, especially, cadmium pyrophosphates are practically insoluble in sodium pyrophosphate solutions, indicating little or no tendency to form complex anions. This is noteworthy, since cadmium is said to be very prone to form complex anions, although this is not our view (compare Bassett and Sanderson, J., 1934, 1116).

A reasonable structure for $Na_6Cu(P_2O_7)_2,16H_2O$ is $[Na(H_2O)_4]^{\cdot}_2[Na(H_2O)_2]^{\cdot}_4[Cu(P_2O_7)_2]^{vi\cdot}$.

EXPERIMENTAL.

Methods of Preparation of Pyrophosphates.—(a) Solutions of the chloride of the metal and of sodium pyrophosphate were mixed, the amorphous precipitate filtered off, washed, suspended in water, and dissolved by passing in sulphur dioxide. The gas was then removed either (i) by long standing exposed to the air, (ii) on the pump, (iii) by a stream of carbon dioxide, or (iv) by heating on the water-bath, according to circumstances. This method is favourable for preparing pure pyrophosphates free from sodium, but traces may be present, as the original amorphous precipitate may contain even several units %.

(b) The amorphous precipitate obtained as in (a) is dissolved by passage of sulphur dioxide without being filtered off.

(c) The chloride solution was added to one of pyrophosphate containing acetic acid (or in a few cases hydrochloric acid); if a small precipitate formed rapidly this was usually filtered off. The mixtures slowly yielded crystalline deposits on standing.

(d) The two reagents, pyrophosphate usually being in excess, are mixed and left at a suitable temperature, with occasional shaking in a corked flask, until the original amorphous precipitate has become wholly crystalline.

(e) Sufficient pyrophosphate is used to dissolve the initial precipitate; the solution is then concentrated, either at room temperature or above, until crystalline deposits form.

Whichever method of preparation was used, the solid product was washed with cold water, then alcohol, and air-dried. Unless otherwise stated in the tables or implied in the method of preparation, the latter was carried out at room temperature.

Octahydrates, $M_2P_2O_7,8H_2O$.

Metal.	Method of prepn.	Proportions of reactants, etc.			Analysis, %.				Notes.
		$CoCl_2,6H_2O$, g.	$Na_4P_2O_7$, g.	Total vol., c.c.	H_2O.	CoO.	Na_2O.	P_2O_5.	
					33·03	34·40	—	32·57	1
Co	(b, ii) at 0°	20	7	120	32·85	34·68	—	32·50	2
					H_2O.	NiO.	Na_2O.	P_2O_5.	
Ni as $Na_4P_2O_7,Ni_2P_2O_7,12H_2O$.					27·93	19·32	16·03	36·72	3
	(d), 12 months	19 G. $Ni_2P_2O_7$ as freshly prepared washed solid added to 600 c.c. cold satd. $Na_4P_2O_7$ solution.			28·50	19·09	15·93	36·60	4
	(e)	Solutions satd. with respect to $Ni_2P_2O_7$ and $Na_4P_2O_7,10H_2O$ evaporated at room temp.; cryst. solid ground in mortar, and $Na_4P_2O_7,10H_2O$ extracted with cold water.			28·38	18·97	16·09	36·54	

The behaviour of the nickel compound over $18N\text{-}H_2SO_4$ in an evacuated desiccator showed that about 0·5% adsorbed water was present.

There appears to be a similar cobalt compound ($Na_4P_2O_7,Co_2P_2O_7,12H_2O$) formed in similar circumstances to the nickel compound as needles of straight extinction, but it yields $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$ on treatment with water and could not be got free from this.

¹ Calc. for $Co_2P_2O_7,8H_2O$.　　² Microcrystalline.　　³ Calc. for $Na_4P_2O_7,Ni_2P_2O_7,12H_2O$.
⁴ Plates, very low birefringence, almost isotropic.

Heptahydrate, $Mg_2P_2O_7,7H_2O$.

Method of prepn.	Proportions of reactants, etc.				Analysis, %.				Notes.
	$MgCl_2,6H_2O$, g.	$Na_4P_2O_7$, g.	HOAc, c.c.	Total vol., c.c.	H_2O.	MgO.	Na_2O.	P_2O_5.	
					36·13	23·15	—	40·72	1
(c), 2 hrs.	22	20	20	600	36·17	23·07	—	40·82	2
(b, ii), 4½ hrs.	17	7	—	127	35·77	23·16	—	41·17	3
	$MgSO_4,7H_2O$.								
(d), 3 days	13	6	—	400	36·23	22·90	0·54 ? (by diff.)	40·33	4

[1] Calc. for $Mg_2P_2O_7,7H_2O$. [2] Extremely minute crystals, n ca. 1·46.
[3] Microcrystalline. [4] Amorphous.

6·5-*Hydrates*, $M_2P_2O_7,6·5H_2O$.

Metal.	Method of prepn.	Proportions of reactants, etc.	Analysis, %.				Excess P_2O_5.	Parent hydrate.	Notes.
			H_2O.	MgO.	Na_2O.	P_2O_5.			
Mg			34·45	23·73	—	41·82			1
	(a, ii)	2 G. $Mg_2P_2O_7,4H_2O$ dissolved by SO_2 in 120 c.c. H_2O.	34·50	23·44	—	41·96	—	6·52H_2O	2

		$NiCl_2,6H_2O$, g.	$Na_4P_2O_7$, g.	Conc. HCl, c.c.	Total vol., c.c.	H_2O.	NiO.	Na_2O.	P_2O_5.			
Ni						28·65	36·58	—	34·77			3
	(d), 6 months	27	7·75	—	700	28·70	36·36	0·12	34·67	—	6·5H_2O }	4
	(d), 3 weeks	9	3	—	380	28·79	35·73	0·27	35·46	1·19	6·44H_4O * }	

[1] Calc. for $Mg_2P_2O_7,6·5H_2O$. [2] MgO taken as 23·66; P_2O_5 as 41·74% in calculating parent hydrate. [3] Calc. for $Ni_2P_2O_7,6·5H_2O$.
[4] Irregular masses of rhombic plates; after crushing, some fragments had n_D slightly greater than 1·584, others slightly less.

* P_2O_5 taken as 35·21% in calculating parent hydrate.

6·25-*Hydrate of* $Mg_2P_2O_7$, *and derived double salt* $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$.

Method of prepn.	Proportions of reactants, etc.				Analysis, %.				Parent hydrate calc. from analysis.	n.	Notes.
	$MgCl_2,6H_2O$, g.	$Na_4P_2O_7$, g.	HOAc, c.c.	Total vol., c.c.	H_2O.	MgO.	Na_2O.	P_2O_5.			
					33·58	24·04	—	42·38			1
(c)	26	20	210	750	33·37	23·85	0·50	42·51	6·23H_2O	{ n_{Da} 1·513 / $n_{D\gamma}$ 1·528 }	—
(c), 48 days	15	20	20	600	33·67	23·45	0·57	42·41	6·35H_2O		2
(c), 55 days	24	20	20	600	33·30	23·75	0·76	42·55	6·25H_2O	{ n_{Da} 1·515 / $n_{D\gamma}$ 1·530 }	—
{ (c), 52 days	20	20	20	600	33·03	23·46	1·01	42·55	6·24H_2O	{ n_{Da} 1·513 / $n_{D\gamma}$ 1·5275 }	—
{ (c), 52 days + 13 months	20	20	20	600	32·73	23·32	1·24	42·75	6·21H_2O		—
(c), 55 days	15	20	20	600	32·90	23·35	1·30	42·61	6·23H_2O	{ n_{Da} 1·513 / $n_{D\gamma}$ 1·527 }	—
(c), 62 days	24	20	20	600	32·55	23·21	1·43	42·84	6·16H_2O	{ n_{Da} 1·514 / $n_{D\gamma}$ 1·5265 }	3
(c), 70 days	15	20	40	600	32·48	22·70	2·12	42·87	6·25H_2O	{ n_{Da} 1·514 / $n_{D\gamma}$ 1·525 }	4
(b, iii), 4 days	3*	6	—	215	31·88	21·34 †	4·01	42·77	6·34H_2O	{ n_{Da} 1·515 / $n_{D\gamma}$ 1·522 }	5
(c), 46 days	15*	20	20	600	31·09	21·75	4·09	43·14	6·13H_2O	{ n_{Da} 1·514 / $n_{D\gamma}$ 1·523 }	6
(c), 55 days	15	20	20	600	31·82	21·38	4·41	42·52	6·38H_2O		—
(b, i), 1 month	2*	7	—	210	29·55	18·93	8·31	43·28	6·29H_2O		7
(d), 49 days	15	20	—	600	28·95	18·60	9·16	43·23		n_D (mean) 1·514	8
(d), 88 days	7	10	—	750	29·02	18·58	9·34	43·35			8
(c), 3 months	6	20	10	500	28·82	18·59	9·35	43·43		{ n_{Da} 1·506 / $n_{D\gamma}$ 1·515 }	8
(d), 1 year	23	20	—	600	28·82	18·49	9·44	43·40		{ n_{Da} 1·508 / $n_{D\gamma}$ 1·515 }	9
(d), 14 months	15	20	—	600	28·82	18·48	9·48	43·41		{ n_{Da} 1·506 / $n_{D\gamma}$ 1·515 }	
(d), 7 weeks	16·3	20	—	600	29·31	18·26	9·32 †	43·11			
(e), crystallised out from solution along with $Na_4P_2O_7,10H_2O$ which was washed out with cold water					29·36	18·27	9·16 †	43·21		{ n_{Da} 1·506 / $n_{D\gamma}$ 1·515 }	10
(d), ca. 1 year	8	10	80 g. NaCl	1000	29·05	18·12	10·07	43·25		{ n_{Da} 1·507 / $n_{D\gamma}$ 1·513 }	
					28·82	18·44	9·45	43·30			11

[1] Calc. for $Mg_2P_2O_7,6·25H_2O$. [2] MgO taken as 23·60; P_2O_5 as 42·26% in calculating parent hydrate. [3] MgO taken as 24·25; P_2O_5 as 42·76 in calculating parent hydrate. [4] MgO taken as 22·80; P_2O_5 as 42·70 in calculating parent hydrate. [5] MgO taken as 21·53 in calculating parent hydrate. [6] Elongated octagonal plates showing straight extinction. [7] MgO taken as 19·07 and P_2O_5 as 43·14 in calc. parent hydrate. [8] Nearly pure double salt. [9] Analysis gave practically identical figures after further 9 months in mother-liquor. [10] The crystal form is best shown by the pure double salt. Small rectangular plates and needles showing straight or symmetrical extinction. Positive elongation. [11] Calc. for $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$.

* $MgSO_4,7H_2O$. † By difference.

6·25-Hydrate of $Mg_2P_2O_7$, and derived double salt $7Na_4P_2O_7,25Mg_2P_2O_7,172H_2O$.

(b, i), 1 month	2*	7	—	210	29·55	18·93	8·31	43·28	6·29H₂O	n_{Da} 1·479	1
					29·43	19·15	8·25	43·19		$n_{Dγ}$ 1·517	2

¹ MgO taken as 19·07 and P₂O₇ as 43·14 in calc. parent hydrate.   ² Calc. for double salt.

* $MgSO_4,7H_2O$.

6·25-Hydrate of $Ni_2P_2O_7$.

Method of prepn.	Proportions of reactants, etc.				Analysis, %.				Parent hydrate calc. from analysis.	Notes.
	NiCl₂,6H₂O. g.	Na₄P₂O₇. g.	HOAc. c.c.	Total vol. c.c.	H₂O.	NiO.	Na₂O.	P₂O₅.		
					27·85	36·99	—	35·16		1
(c), 16 months	20	20	110	600	27·61	36·36	0·44	35·39	6·21H₂O	2
(b, i), 5 months	15	7	—	180	28·13	36·17	0·38	35·40	6·30H₂O	3
(c), 9 months	20	20	30	610	27·66	36·34	0·50	35·26	6·26H₂O	4
(b, iii) and (b, i), 6 months	20	7	—	180	28·37	35·88	0·29	35·27	6·29H₂O	5
Mother-liquor from last prepn.evap. to dryness at room temp. Soluble salts removed with cold water.					27·99	36·37	0·31	35·27	6·27H₂O	6
(c), 8 months	20	20	30	670	27·68	36·14	0·53	35·53 †	6·24H₂O	7
(c), 8 months	8	20	30	600	27·71	36·25	0·53	35·52 †	6·24H₂O	—
(b, i), 4 months	25	20	—	600	27·76	36·41	0·34	35·26	6·25H₂O	8
	Ni₂P₂O₇.		Conc. HCl,							
(c), 4 weeks	5	50 c.c. cold satd. soltn.	4 c.c.	225	27·80 ‡	36·35	0·16	35·43 ‡	6·23H₂O	9

¹ Calc. for Ni₂P₂O₇,6·25H₂O.   ² P₂O₅ calc. for base = 35·06. NiO taken as 36·56% for calcn. of parent hydrate. This makes analysis add up to 100%.   ³ P₂O₄ calc. for base = 34·82; P₂O₅ taken as 35·20, and excess balanced by [H₂(H₂O)₂] in calculating parent hydrate.   ⁴ If NiO is taken as 36·48, base and P₂O₅ would balance, and analysis add up to 99·9%. NiO taken as 36·48 to calc. parent hydrate.   ⁵ P₂O₅ taken as 35·46 to make analysis add up to 100%; total base requires P₂O₅, 34·44. Excess P₂O₅ taken as balanced by H₂(H₂O)₂ in calculating parent hydrate.   ⁶ P₂O₅ taken as 35·33 to make analysis add up to 100%; P₂O₅ is then 0·40 too high for total base. This is assumed to be balanced by [H₂(H₂O)₂].   ⁷ If NiO is taken as 36·27% to make total 100%, P₂O₅ is then 0·44% too high for total base. Excess P₂O₅ balanced by [H₂(H₂O)₂].   ⁸ If NiO is taken as 36·64% to make total 100%, it is seen that the parent hydrate is almost exactly Ni₂P₂O₇,6·25H₂O.   ⁹ NiO taken as 36·61 to make total 100%; there is then 0·45% excess P₂O₅.

† These two solids were each separated into coarse and fine : the composition of both parts was practically identical.
‡ The results were unaltered after the substance had stood for a further 2 months in the mother-liquor.

Hexahydrate of $Mg_2P_2O_7$ and the derived double salt $Na_4P_2O_7,3Mg_2P_2O_7,20H_2O$.

Method of prepn.	Proportions of reactants, etc.				Analysis, %.				Parent hydrate calc. from analysis.	n.	Notes.
	MgCl₂,6H₂O. g.	Na₄P₂O₇. g.	HOAc. c.c.	Total vol. c.c.	H₂O.	MgO.	Na₂O.	P₂O₅.			
					32·66	24·40	—	42·94			1
(c), 2 hrs.	18	7	14	185	32·44	24·60	—	43·10			—
(a, i), 28 days	11	7	—	200	32·96	24·25	—	42·94			—
(c), 10 days	12	3	1 (conc. HCl)	380	32·59	24·40	—	43·08		n_{Da} 1·512, $n_{Dγ}$ 1·533	2
(c), 19 days	12	2	10 (1·8N-HCl)	210	32·79	24·68	—	†		n_{Da} 1·512, $n_{Dγ}$ 1·533	—
(c), 2 months	24	20	210	680	32·51	23·88	0·89	42·66	6·04H₂O		—
(c), 15½ months	15	20	20	600	32·80	23·23	1·20	42·75	6·12H₂O	n_{Da} 1·508, $n_{Dγ}$ 1·528	3
(c), 17 months	24	20	20	600	32·31	23·59	1·30	42·98	6·05H₂O	n_{Da} 1·508, $n_{Dγ}$ 1·528	4
(c), after another year in mother-liquor	24	20	20	600	32·57	23·57	†	†	6·05H₂O		—
(c), 15 months	15	20	20	600	32·33	22·68	2·37	42·67	5·97H₂O		5
(c), 14 months	24	20	20	590	30·75	22·45	3·69	43·39	5·98H₂O		6
(c), 16 months	15	20	20	570	28·70	19·42	7·96	43·77	6·02H₂O		7
					27·82	18·68	9·55	43·88			8

¹ Calc. for Mg₂P₂O₇,6H₂O.   ² Small rectangular plates and rhombs showing straight or symmetrical extinction.   ³ From Mg₂P₂O₇,6·25H₂O (with 0·57Na₂O) after 13 months in mother-liquor.   ⁴ From Mg₂P₂O₇,6·25H₂O (with 0·76Na₂O) after 15 months in mother-liquor.   ⁵ From Mg₂P₂O₇,6·25H₂O (with 1·30Na₂O) after 13 months in mother-liquor.   ⁶ MgO taken as 22·25 in calc. parent hydrate.   ⁷ MgO taken as 19·63 and P₂O₅ as 43·71 in calc. parent hydrate.   ⁸ Calc. for double salt.

† Not determined.

Analysis.—The methods employed were the same as those indicated in Parts I and III of this series (J., 1933, 862, 879), except that nickel was determined as metal after electrolytic deposition from ammoniacal solution.

Cadmium was weighed as sulphate after separation as sulphide. Pyrophosphate was converted into orthophosphate by digestion with nitric acid (20 c.c., d 1·42) for at least 2 hours. With manganese preparations, hydrochloric acid was used instead of nitric to avoid formation of insoluble products (Bassett and Sanderson, this vol., p. 208). Excess acid was removed by evaporation before the analyses.

Owing to the solubility of sodium zinc uranyl acetate and the relative freedom from sodium of the reagents, it was found advisable to ensure positive blanks of about 0·04 g. in the sodium estimations by addition of a standard amount of very dilute sodium chloride solution.

Hexahydrate of $Co_2P_2O_7$ and the derived double salt $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$.

Method of prepn.	CoCl₂,6H₂O g.	Na₄P₂O₇ g.	HOAc c.c.	Total vol., c.c.	H₂O	CoO	Na₂O	P₂O₅	n.	Notes.
					27·00	37·50	—	35·50		1
(d), 6 months	8	4·5	—	400	27·06	37·61	—	35·58	{$n_{Dα}$ 1·583, $n_{Dγ}$ 1·590}	2
(filtered off about half ppt. and then added 5 g. more of CoCl₂,6H₂O in 30 c.c. H₂O)										
(b, i), 1 month	13	7	—	170	27·06	37·37	—	35·33		
(d), 5½ months	12	20	200	620	27·00	37·50	—	35·62		
					23·97	29·96	8·25	37·81		3
(d), 4 months	12	20	30	580	23·97	30·01	8·11	37·95	{$n_{Dα}$ 1·555, $n_{Dβ}$ 1·563, $n_{Dγ}$ >1·563}	4
(d), 11 months	12	20	30	580	23·97	30·00	Not determined			
(d), 2 years	11	20	—	?	23·97	30·00	Not determined			

¹ Calc. for $Co_2P_2O_7,6H_2O$. ² Crystals large and well developed in rectangular plates with the corners truncated so that all internal angles are very close to 135°. Pleochroic, pale rose along slow, and rose along fast direction. Slow direction is optic axial plane. Optic sign could not be determined, as brush remained very straight on rotation and nearly disappeared in 45° position; 2V is therefore large. The square plates show straight extinction. When the crystals are tilted on one edge extinction is also straight, but when on the edge at right angles it is oblique at 29° ± 1°. Monoclinic, but quite different from the double salts derived from Mn and Cd analogues. ³ Calc. for double salt. ⁴ Usually crystallises in six-sided plates, but from acid solution in rectangular plates with bevelled edges. Extinction straight, with two edges of six-sided forms or with all sides of rectangular forms. Pleochroic, yellowish-pink along α, heliotrope-pink along β. The indices presented by the six-sided plates showing internal angles of 86° and 137° lying flat are 1·563 along length and 1·555 across length. Small rectangular tablets show 1·563 along length and a slightly higher index across length. These represent an edgewise view of the six-sided plates. The system is orthorhombic and is quite different from that of $Co_2P_2O_7,6H_2O$.

Hexahydrate of $Ni_2P_2O_7$.

Method of prepn.	NiCl₂,6H₂O g.	Na₄P₂O₇ g.	HOAc c.c.	Total vol., c.c.	H₂O	NiO	Na₂O	P₂O₅	Parent hydrate calc. from analysis	Excess P₂O₅	Notes.
					27·04	37·41	—	35·55			1
(d), 6½ months	30	20	200	720	27·45	36·44	0·17	35·93	5·99H₂O	1·10	
(d), 8 months	13	20	110	210	27·60	36·11	0·32	35·92	6·03H₂O	1·22	2
	Amorphous Ni₂P₂O₇.		Conc. HCl.								
(b), 3 weeks	5	5	1	100	27·91	36·52	—	35·57	6·14H₂O	0·85	—

¹ Calc. for $Ni_2P_2O_7,6H_2O$. ² Aggregates consisting of layers of tiny rhombs, some showing unsymmetrical extinction, and rectangular tablets showing straight extinction; possibly monoclinic. n between 1·579 and 1·589.

Hexahydrate of $Mn_2P_2O_7$ as the double salt $Na_4P_2O_7,Mn_2P_2O_7,8H_2O$.

Method of prepn.	MnCl₂,4H₂O g.	Na₄P₂O₇, g.	Total vol., c.c.	H₂O	MnO	Na₂O	P₂O₅	Notes.
				20·75	20·46	17·87	40·92	1
(d), 9 days	5	20	600	21·21	21·10	17·29	40·79	
(d), 9 days	5	20	650	21·27	20·55	17·78	40·96	
(d), 7 months	5	20	650	21·21	20·49	17·85	40·86	
(d), 9 days	10	20	650	21·19	21·14	†	40·84	
(d), 9 days	10	20	650	21·19	20·88	17·72	40·90	
(d), 7 months	10	20	650	21·21	20·65	17·85	40·93	
(d), 12 days	15	20	650	21·23	20·82	17·77	40·82	2
(d), 4½ weeks	15	20	650	21·05	20·74	†	40·95	
(d), 7 months	15	20	650	21·10	20·51	17·62	40·84	
(d), 9 days	4	20	600	21·26	20·40	†	40·89	
(d), 2 days	3	20+20NaCl	660	21·06	20·45	†	40·96	
(d), 6 days	2	7+40NaCl	600	21·28	20·46	†	40·84	
Crystallised out by evapn. of satd. soln. with Na₄P₂O₇,10H₂O, which was washed out of the powdered solid with cold water				20·87	20·42	17·87	†	
Conc. Na₄P₂O₇ solution satd. with amorphous Mn₂P₂O₇ at 60°, separated in the cold at room temp.				21·20	20·84	17·38	40·82	—
				21·33	20·70	17·47	40·87	—
(d), on boiling water-bath (15 mins.)	2	6	200	20·73	20·60	17·64	40·87	—
" " "	2	4	200	20·98	20·92	17·38	40·61	—
Amorphous Mn₂P₂O₇ from 5 g. MnCl₂,4H₂O and 3·5 g. Na₄P₂O₇ in 600 c.c. satd. Na₄P₂O₇ for 2¼ months				21·18	20·24	18·05	41·04	—
Amorphous ppt. from 20 g. MnCl₂,4H₂O and 14 g. Na₄P₂O₇ in 600 c.c. satd. Na₄P₂O₇ for 7 weeks				21·25	20·24	18·07	41·04	—

¹ Calc. for double salt. ² n (mean of all specimens) = 1·532. They consisted of clusters of needles of extinction varying from straight to symmetrical oblique at about 45°. Birefringence very low. All needles having straight or nearly straight extinction had positive elongation; monoclinic and similar to the corresponding cadmium compound.

† Not determined.

Bassett, Bedwell, and Hutchinson :

Hexahydrate of $Cd_2P_2O_7$ as the double salt $Na_4P_2O_7,Cd_2P_2O_7,8H_2O$.

| | Proportions of reactants, etc. | | | Analysis, %. | | | | |
Method of prepn.	$CdCl_2$, g.	$Na_4P_2O_7$, g.	Total vol., c.c.	H_2O.	CdO.	Na_2O.	P_2O_5.	Notes.
				17·81	31·75	15·33	35·12	1
(d), 2½ days	10	20	600	18·38	31·10	15·69	35·35	
(d), 6½ months	10	20	600	18·20	31·24	15·48	35·31	
(d), 4½ days	15	20	600	18·33	31·20	15·52	35·32	
(d), 6½ months	15	20	600	18·17	31·56	15·30	35·22	
(d), 2½ days	3	7+40NaCl	600	18·34	31·45	15·41	35·16	
Amorphous $Cd_2P_2O_7$ from 2 g. $CdCl_2$ + 1·5 g. $Na_4P_2O_7$ in 600 c.c. satd. $Na_4P_2O_7$ for 8 days				18·40	31·11	15·64	35·32	
Ditto, but stood for 13 days				18·01	30·78	15·96	35·44	
Amorphous $Cd_2P_2O_7$ from 4 g. $CdCl_2$ + 3 g. $Na_4P_2O_7$ in 600 c.c. satd. $Na_4P_2O_7$ for 10 days				18·35	30·78	16·01	35·45	2
Amorphous $Cd_2P_2O_7$ from 4 g. $CdCl_2$ + 3 g. $Na_4P_2O_7$ in 150 c.c. satd. $Na_4P_2O_7$ diluted to 600 c.c., for 33 days				18·03	31·62	15·43	35·18	
Amorphous $Cd_2P_2O_7$ from 20 g. $CdCl_2$ and 15 g. $Na_4P_2O_7$ in 600 c.c. satd. $Na_4P_2O_7$ for 26 days				18·36	30·71	15·96	35·42	
Conc. $Na_4P_2O_7$ satd. with amorphous $Cd_2P_2O_7$ at 60° filtered and kept for a few days				18·20	31·06	15·77	35·27	
				18·40	31·03	15·78	35·21	
(d), 2 hrs. at 100°	2	4	100	17·86	31·98	15·08	35·22	

[1] Calc. for double salt. [2] The solid solution with most sodium had n_D 1·533, that with least sodium $n_{D\alpha}$ 1·537, $n_{D\gamma}$ 1·541. All specimens consisted of small elongated needles with extinction varying from straight to oblique of 45°. All needles having straight or nearly straight extinctions had positive elongation; monoclinic and similar to corresponding manganese compound. The presence of solid $Na_4P_2O_7,10H_2O$ in the Cd or Mn preparations would not explain sodium contents above that for pure double salt, for the P_2O_5 content in $Na_4P_2O_7,10H_2O$ is considerably less than that in pure double salt. The P_2O_5 contents go up with increase in sodium.

Pentahydrates.

Metal.	Method of prepn.	$MCl_2,6H_2O$, g.	$Na_4P_2O_7$, g.	Total vol., c.c.	H_2O.	MO.	Na_2O.	P_2O_5.	Parent hydrate.	Notes.
Mg					28·77	25·80	—	45·40		1
	(c), 15 hrs.	15	20	600 §	28·67	25·11	0·56 (by diff.)	45·66		2
	(c), a few days	11	10	350 §	28·96	Not detd.		45·44		—
	(b, iii), 8 hrs. at 68°	3 ‡	6	220	26·19	22·16	5·80	45·94	5·07H₂O	3
Mn †					24·06	37·97	—	37·97		4
	(b, ii), after 4 months in mother-liquor	11	7	170	23·96	38·03	—	37·92		5
	A similar prepn. after 2 hrs. was microcrystalline				22·86	35·39	2·96	38·78	5·00H₂O	
	Same prepn. after standing over-night in mother-liquor had reverted to pure $Mn_2P_2O_7,5H_2O$				23·82	38·13	—	38·08		
Co					23·56	39·27	—	37·17		6
	(b, iv), 8 hrs. on boiling water-bath	8	4·5	400	23·76	39·12	—	37·14	} 7	
	" " "	8	4·5	400	24·11	38·95	—	36·97		
Ni					23·60	39·16	—	37·24		8
	(b, iv), 12 hrs. on water-bath	8	4·5	500	24·04	39·04	—	36·95		
	(b, iii and iv), 8 hrs. on water-bath	3	6·3	165	22·68	35·07	4·15	38·04	5·2H₂O	} 9
	(b, iii and iv), 10 hrs. on water-bath	3	6	215	22·79	36·95	2·37	37·87	5·04H₂O	
Cu					23·01	40·68	—	36·31		10
	(b, i), 8 hrs.	15 **	8	400	22·99	40·75	—	36·37	} 11	
	(b, iv), 10 days	15 **	8	200	22·75	40·56	—	36·49		
Zn					22·80	41·23	—	35·97		12
	(b, i), 15 days	15 ††	7	180	22·78	41·36	—	36·07		13
	(d), 3½ days	5·5 ‡‡	5·32	500	22·91	41·17	—	35·76		14
Cd	Indications were obtained that $Cd_2P_2O_7,5H_2O$ exists, but even at 0° it is so unstable towards lower hydrates that no pure preparation has been isolated.									

[1] Calc. for $Mg_2P_2O_7,5H_2O$. [2] Aggregates of minute plates, n_D ca. 1·52; birefringence about 0·01, straight extinction, negative elongation, also a few spherulites. [3] H_2O taken as 26·10, MgO as 22·25, and P_2O_5 as 45·85% for calcn. of parent hydrate. [4] Calc. for $Mn_2P_2O_7,5H_2O$. [5] Mainly minute needles, birefringence about 0·02, with a few larger plates of n_D ca. 1·57. Needles too small to determine n. [6] Calc. for $Co_2P_2O_7,5H_2O$. [7] Bulk of material too fine to determine n (crystallinity doubtful). A few small rectangular tablets ($\times$ 556) showing straight extinction; n somewhat greater than 1·56. [8] Calc. for $Ni_2P_2O_7,5H_2O$. [9] Very fine, possibly minutely spherulitic, solid; n ca. 1·56—1·58; birefringence 0·01—0·02. [10] Calc. for $Cu_2P_2O_7,5H_2O$. [11] After remaining in mother-liquor for 8 months had changed to tetrahydrate. Very finely divided. Pale green, almost white. Distinctly crystalline. [12] Calc. for $Zn_2P_2O_7,5H_2O$. [13] Nicely crystalline. Probably orthorhombic, possibly monoclinic. Facetted plates; $n_{D\alpha}$ 1·55; $n_{D\gamma}$ 1·56. [14] Amorphous; separated before it had crystallised. Expts. by method (b) with excess $Na_4P_2O_7$ indicate that $Zn_2P_2O_7,5H_2O$ is formed first and gradually changes into a solid solution with sodium derived from a lower hydrate—probably $Zn_2P_2O_7,3⅓H_2O$.

† $MnCl_2,4H_2O$ used. ‡ $MgSO_4,7H_2O$ used. § Including 20 c.c. of HOAc.
** $CuSO_4,5H_2O$ used. †† $ZnSO_4,7H_2O$ used. ‡‡ $ZnCl_2$ used.

$4\cdot2$-Hydrate of $Cu_2P_2O_7$ and derived double salt $Na_4P_2O_7,4Cu_2P_2O_7,17H_2O$.

Method of prepn.	Proportions of reactants, etc.				Analysis, %.				Parent hydrate.	Notes.
	$CuCl_2,2H_2O$. g.	$Na_4P_2O_7$. g.	Conc. HCl, c.c.	Total vol., c.c.	H_2O.	CuO.	Na_2O.	P_2O_5.		
					20·06	42·25	—	37·69		1
(c), 120 days	12	1·6	2	350	19·66	42·49	—	37·93		—
Compound separated after a few minutes when 1 g. $CuSO_4,5H_2O$ in 5 c.c. was added to 170 c.c. of solution, from a previous preparation, which contained about 3 g. $Na_4P_2O_7$ and 1 g. $CuSO_4,5H_2O$					18·01	37·49	5·10 *	39·40	$4\cdot2H_2O$	2
(b, iii), 24 hrs.	2	6	—	210	17·06	36·62	6·40	40·34	$4\cdot1H_2O$	3
(b, iii), 1½ hrs.	1 †	6	—	210	17·61	35·38	7·21	39·95	$4\cdot29H_2O$	—
					17·22	35·84	6·98	39·96		4

¹ Calc. for $Cu_2P_2O_7,4\cdot2H_2O$.   ² This was the best crystallised prepn.; needles and spherulites. Straight extinction, n_D 1·556 and 1·574.   ³ Bases require P_2O_5, 40·00%, which has been used to calc. parent hydrate.   ⁴ Calc. for $Na_4P_2O_7,4Cu_2P_2O_7,17H_2O$.

* By difference.   † $CuSO_4,5H_2O$ used.

Tetrahydrates.

Metal.	Method of prepn.	Proportions of reactants, etc.			Analysis, %.				Parent hydrate.	Notes.
		$MCl_2,6H_2O$. g.	$Na_4P_2O_7$. g.	Total vol., c.c.	H_2O.	MO.	Na_2O.	P_2O_5.		
Mg					24·43	27·34	—	48·20		1
	(b, iv), 23 hrs., evap. to 500 c.c.	12	7	600	24·30	27·04	(0·33) (by diff.)	48·33		2
	(b, iv), 9½ hrs.	2 †	6	210	23·51	26·40	1·76	48·78	$3\cdot99H_2O$	—
Co					19·78	41·21	—	39·01		3
	(b, iv), 18 hrs.	8	1	350	19·57	41·47	—	39·12		4
Ni	(b, iv), 41 hrs.	3·5	10	250	15·38	32·49	(9·90) calc.	41·97	$3\cdot95H_2O$	5
Cu					19·29	42·65	—	38·08		6
	Formed from $Cu_2P_2O_7,5H_2O$ after 7 months in mother-liquor				19·23	42·58	—	38·11		7
	(b, iv), 4 hrs.	6·8 ‡	5·32	500	19·43	42·52	—	38·04		—
	(b, i), 14 months	14 §	20	600	19·00	42·43	0·26	38·33	$3\cdot95H_2O$	—

¹ Calc. for $Mg_2P_2O_7,4H_2O$.   ² Aggregates of needles and small plates—probably rhombs; n_D ca. 1·506, 1·514, and 1·525.   ³ Calc. for $Co_2P_2O_7,4H_2O$.   ⁴ Extremely fine but probably crystalline.   ⁵ Microcrystalline; P_2O_5 taken as 42·23% to balance with bases in calc. parent hydrate and make total 100%.   ⁶ Calc. for $Cu_2P_2O_7,4H_2O$.   ⁷ Very fine; n ca. 1·590—1·620.

† $MgSO_4,7H_2O$ used.   ‡ $CuCl_2,2H_2O$ used.   § $CuSO_4,5H_2O$ used.

$3\tfrac{2}{3}$-Hydrates.

Metal.	Method of prepn.	Proportions of reactants, etc.			Analysis, %.						Notes.
		$MgCl_2,6H_2O$. g.	$Na_4P_2O_7$. g.	Total vol., c.c.	H_2O.	MgO.	P_2O_5.				
Mg					22·87	27·94	49·19				1
					22·55	28·04	49·41				2
	(b, iv), 16 hrs. at ca. 70°	6	4	300	22·87	27·88	49·37				
	(b, iv), 4 hrs. at 70°	6	4	300	23·51	27·82	48·92				3
	(b, iv), 23 hrs. at 70°. Vol. reduced to 150 c.c. during heating	12	7	600	23·38	27·92	49·00				

					H_2O.	CuO.	Na_2O.	P_2O_5.	Excess P_2O_5.	Parent hydrate.	
Cu	SO_2 passed in till green-ish-white ppt. formed	2	6	110	17·45	35·92	5·20	41·39	3·39	$3\cdot74H_2O$	
	,, ,, ,,	2	6	110	16·54	38·38	4·56	41·01	1·53	$3\cdot70H_2O$	4
	,, ,, ,,	2	6	110	16·59	37·53	5·22	40·61	1·13	$3\cdot76H_2O$	
	SO_2 blown out from filtrate of last expt. Filtered after 6 days				14·80	35·89	8·19	41·35	—	$3\cdot73H_2O$	

¹ Calc. for $Mg_2P_2O_7,3\tfrac{2}{3}H_2O$.   ² Calc. for $Mg_2P_2O_7,3\cdot6H_2O$.   ³ Very small rectangular plates and prisms, often matted together, and spherulites; negative elongation, straight extinction; $n_{D\alpha}$ ca. 1·515; $n_{D\gamma}$ ca. 1·495.   ⁴ Groups of needles and spherulites; n_D 1·560, 1·590.

$3\cdot25$-Hydrate of $Zn_2P_2O_7$ as the double salt $2Na_4P_2O_7,2Zn_2P_2O_7,5H_2O$.

Method of prepn.	Proportions of reactants, etc.			Analysis, %.				Notes.
	$ZnCl_2$, g.	$Na_4P_2O_7$, g.	Total vol., c.c.	H_2O.	ZnO.	Na_2O.	P_2O_5.	
				7·31	26·43	20·14	46·12	1
(d), 5 months	6·7	20	560	7·37	26·64	20·06	46·19	
(d), 18 weeks	5·2	20	590	7·35	26·48	20·24	46·27	2
(d), 15 months	9·0	20	650	7·29	26·54	20·05	46·23	
(d), 3 hrs. on boiling water-bath	2·3	6	225	7·59	26·57	19·90	45·97	

¹ Calc. for double salt.   ² Plates showing a variety of faces and angles; biaxial, probably mono-clinic. First two prepns. in table consisted almost entirely of hemimorphic plates showing straight extinction with one square end and one pointed (74°). These plates showed n_D 1·49 and 1·502.

$3\frac{2}{3}$-*Hydrate of* $Zn_2P_2O_7$ *as the double salt* $8Na_4P_2O_7,7Zn_2P_2O_7,23H_2O$.

Method of prepn.	Analysis, %.				Parent hydrate.	Notes.
	H₂O.	ZnO.	Na₂O.	P₂O₅.		
	8·87	24·36	21·22	45·55		1
The proportions of Na₄P₂O₇ and Zn₂P₂O₇ used in different preparations varied somewhat						
Satd. Na₄P₂O₇,10H₂O solutions were satd. with pptd. Zn₂P₂O₇, filtered, and evapd. nearly to dryness at 50°; solid which crystallised out was extracted with water at 50°. Crystalline residue analysed	9·10 (9·02)	25·37	20·27	45·38 (45·34)	3·62H₂O	
Very similar to above	9·15 (8·78)	24·62	21·03	(45·57) calc.	3·68H₂O	
Very similar. Compound crystallised from hot filtrate	9·81 (9·27)	24·28	21·10	(45·35) calc.	3·74H₂O	2
In a similar prepn. the Na₄P₂O₇,10H₂O which separated in the early stages of the evapn. was washed with hot water and left crystals of the given composition	9·05 (9·27)	25·50	20·03	(45·20) calc.	3·65H₂O	
The filtrate from the above Na₄P₂O₇,10H₂O was evapd. over CaCl₂ at room temp. The crystals separating were washed with cold water to remove Na₄P₂O₇,10H₂O and the crystalline residue analysed	10·00 (9·70)	26·25	19·18	44·93 (44·87)	3·66H₂O	

¹ Calc. for double salt. ² The yield was very small, often not enough for complete analysis. In these cases P₂O₅ was calculated from the total base. In two cases where a figure in parentheses is shown below the experimental value for P₂O₅ it is the value equivalent to total base and has been used to calculate the " parent " hydrate. The H₂O values in parentheses have been used for the same purpose. They are the values which give analyses adding up to 100%. Preparations are well crystallised though crystals are small, but quite homogeneous. Straight extinction; n_D *ca.* 1·516; birefringence *ca.* 0·02. Possibly orthorhombic. In hot liquors this compound tends to yield $2Na_4P_2O_7,2Zn_2P_2O_7,5H_2O$.

3·6-*Hydrates*.

Metal.	Method of prepn.	Proportions of reactants, etc.			Analysis, %.				Notes.
		Na₄P₂O₇, g.		Total vol., c.c.	H₂O.	MO.	Na₂O.	P₂O₅.	
Mn					18·58	40·68	—	40·73	1
					18·85	40·55	—	40·60	2
	(b, iv), 12 hrs.	7·92 g. MnCl₂,4H₂O	5·32	500	18·90	40·77	—	40·74	3
Zn					17·53	44·04	—	38·43	4
					17·80	43·90	—	38·32	5
	(b, iv), 12 hrs.	5·5 g. ZnCl₂	5·32	500	17·42	44·14	—	38·37	6
Cu					17·30	43·71	—	38·99	7
					17·70	43·50	—	38·80	8
	(b, iv), 35 mins. at 100°	2 g. CuSO₄,5H₂O	7	210	17·58	43·55	0·16	38·83	9
	(b, iv), 4¼ hrs. at 80°	2 g. CuSO₄,5H₂O	6	210	17·55	43·58	0·11	(38·76) (by diff.)	

¹ Calc. for Mn₂P₂O₇,3·6H₂O. ² Calc. for Mn₂P₂O₇,3⅔H₂O. ³ Rhombic plates and bundles of needles. Former showed angles of 81° and 99° and an extinction angle of 40°. Distinction between max. and min. *n* difficult. Mean n_D 1·553. Needles showed straight extinction. ⁴ Calc. for Zn₂P₂O₇,3·6H₂O. ⁵ Calc. for Zn₂P₂O₇,3⅔H₂O. ⁶ Very small, elongated, diamond-shaped plates showing angles of 40° and 140°. Symmetrical extinction. Differentiation of two indices difficult; mean n_D 1·586. ⁷ Calc. for Cu₂P₂O₇,3·5H₂O. Calc. for Cu₂P₂O₇,3·6H₂O. ⁹ Well-developed rhombic plates showing angles of 85° and 95°, the latter bisected by the fast direction. Symmetrical extinction; n_D 1·585 and 1·620. The third index appears to be 1·560.

Solid Solutions in $Na_4P_2O_7,10H_2O$.—The general method of preparation is to make a hot concentrated solution of Na₄P₂O₇, in it dissolve amorphous M₂P₂O₇, filter, and allow it to cool and crystallise. The solid solutions will have their maximum content of M₂P₂O₇ when the Na₄P₂O₇,10H₂O crystallises out in conjunction with the double Na,M pyrophosphate having the largest proportion of Na₄P₂O₇. Conditions must be so adjusted that Na₄P₂O₇,10H₂O separates

in large isolated crystals so that one can be sure that none of the double salt is present. In practice, therefore, one must work a little on the $Na_4P_2O_7$ side of the point at which the two solid phases can coexist in equilibrium with solution. The values given on p. 1428 (middle) for the solid-solution concentrations are thus not maximum values, although probably not

Trihydrate of $Cu_2P_2O_7$ *as the double salt* $8Na_4P_2O_7,7Cu_2P_2O_7,13H_2O$.

Method of prepn.	Proportions of reactants, etc. CuSO₄,5H₂O, g.	Na₄P₂O₇, g.	Total vol., c.c.	Analysis, %. H₂O.	CuO.	Na₂O.	P₂O₅.	Parent hydrate.	Notes.
				5·23	24·92	22·19	47·66		1
60 G. Na₄P₂O₇ in 400 c.c. satd. with Cu₂P₂O₇; filtered and evapd. to 70 c.c. at 40°; 120 c.c. H₂O added to dissolve the blue anionic compound; the very small amount of insoluble compound was collected and analysed				5·23	25·37	21·80 (calc.)	47·44	2·96H₂O	2
(b, iv), 5 hrs.	2	6	160	11·24	36·84	9·07	42·99	3·03H₂O	3
(b, iv), 2 hrs.	1	6	205	11·47	36·98	8·87	43·05	3·00H₂O	4

¹ Calc. for double salt.   ² Amount too small for complete analysis. If P₂O₅ is taken as 47·60 instead of 47·44 then Na₂O (by diff.) is 21·80%, and total base and P₂O₅ agree. These values used to calculate "parent" hydrate. Small six-sided plates, biaxial, straight extinction, negative elongation; n_D rather less than 1·56; birefringence *ca.* 0·02.   ³ CuO taken as 36·63 and P₂O₅ as 43·06% to calculate "parent" hydrate.   ⁴ H₂O taken as 11·21 and CuO as 36·87% to calculate "parent" hydrate. Optical characters of last two prepns. as above, but n_D *ca.* 1·60.

Trihydrate of $Cd_2P_2O_7$.

Method of prepn.	Proportions of reactants, etc. CdCl₂, g.	Na₄P₂O₇, g.	Conc. HCl, c.c.	Total vol., c.c.	Analysis, %. H₂O.	CdO.	P₂O₅.	Note.
					11·93	56·71	31·36	1
(b, i)	7·3	5·3	—	500	11·97	56·76	31·37 (by diff.)	2
(d), 24 days	12	2	1	390	11·92	56·55	31·40	

¹ Calc. for $Cd_2P_2O_7,3H_2O$.   ² Minute spherulites. n_D *ca.* 1·62.

$2\frac{2}{3}$-*Hydrate of* $Co_2P_2O_7$ *as double salt* $3Na_4P_2O_7,9Co_2P_2O_7,20H_2O$.

Method of prepn.	Proportions of reactants, etc. CoCl₂,6H₂O, g.	Na₄P₂O₇, g.	Total vol., c.c.	Analysis, %. H₂O.	CoO.	Na₂O.	P₂O₅.	Parent hydrate.	Notes.
				9·51	35·66	9·82	45·00		1
40 G. Na₄P₂O₇ in 400 c.c. H₂O satd. with pptd. Co₂P₂O₇ on boiling water-bath; Na₄P₂O₇,10H₂O which separated on cooling was filtered off, the soltn. concentrated to 200 c.c. and more Na₄P₂O₇,10H₂O filtered off. Filtrate evapd. to dryness at 40—50° and extracted with hot water. Residue filtered and analysed				10·53	35·50	9·76	44·82	2·74H₂O	2
(d), 18 hrs. on water-bath	2	6	350	10·06	35·96	9·43 †	44·84	2·68H₂O	3
(b, iv), warmed at 70° for 12 hrs. with reflux. First lot of solid filtered off. It was definitely a mixture (with 3·8% Na₂O) of Co₂P₂O₇,5H₂O (microscopic identification) and the sodium compound derived from 2⅔-hydrate. Filtrate now heated to 80° for 12 hrs., but gave no reactions for orthophosphate	2	7	210	10·28	36·20	9·15	44·74 (calc. from base)	2·68H₂O	4
(b, iv). Similar to last, the same mixture coming out during 8 hrs. at 80°. The whole mixture was then heated to 100° for 3¼ hrs. and was then free from plates of Co₂P₂O₇,5H₂O				10·44	36·37	8·94	44·63	2·69H₂O	5

¹ Calc. for double salt.   ² Very finely divided (amorphous?) solid; H₂O taken as 9·92 (which makes analysis total 100%) in calculating parent hydrate.   ³ Microcrystalline; H₂O taken as 9·77% in calculating parent hydrate.   ⁴ Homogeneous spherulites, positive elongation, straight extinction. $n_{Dα}$ 1·594, $n_{Dγ}$ 1·578. Birefringence *ca.* 0·03. H₂O taken as 9·91% in calculating parent hydrate.   ⁵ Minute needles.

† Calculated from P₂O₅.

$2\frac{2}{3}$-*Hydrates of* $Cd_2P_2O_7$ *(and* $Mg_2P_2O_7$*)*.

Method of prepn.	Proportions of reactants, etc. CdCl₂, g.	Na₄P₂O₇, g.	Total vol., c.c.	Analysis, %. H₂O.	CdO.	P₂O₅.	Notes.
				10·72	57·48	31·78	1
(b, iv), 1 hr.	7·3	5·3	500	11·16	57·16	31·61	2
Cd₂P₂O₇ from 2·6 g. Na₄P₂O₇ and 3 g. CdCl₂ in 500 c.c. filtered off and dissolved by SO₂ in 200 c.c.; mixture heated on water-bath with reflux for 2¼ hrs.				10·88	57·30	31·61	3

There were indications that magnesium forms a sodium compound, similar to that of cobalt, derived from $Mg_2P_2O_7,2\frac{2}{3}H_2O$.

¹ Calc. for $Cd_2P_2O_7,2\frac{2}{3}H_2O$.   ² Needles of spherulitic origin; negative elongation, straight extinction; n_D *ca.* 1·63.   ³ Minute spherulites; n_D *ca.* 1·63. This compound very slowly changes to $Cd_2P_2O_7,2\frac{1}{4}H_2O$ in the hot liquor.

2⅓-*Hydrates of* $Mn_2P_2O_7$ *and* $Cd_2P_2O_7$, *and double salt* $3Na_4P_2O_7,9Zn_2P_2O_7,16H_2O$.

Metal.	Method of prepn.	Na₄P₂O₇, g.	Total vol., c.c.	H₂O.	MO.	Na₂O.	P₂O₅.	Parent hydrate.	n.	Notes.
		Proportions of reactants, etc.		Analysis, %.						
Mn				12·89	43·51	—	43·60			1
	(b, iv), 4½ hrs. at 80°	2 g.	7	300	12·25	41·41	2·33	44·03	2·43H₂O	—	—
	MnSO₄,4H₂O										
	Ppt. dissolved by SO₂	24 g.	20	600	12·79	41·73	1·09	44·40		$n_{Dα}$ 1·60	2
	and reprecipitated by MnCl₂,4H₂O				12·83	41·70	1·03	44·47	2·32H₂O		
	passing CO₂ for 2 hrs.				—	41·60	1·08	42·98†		$n_{Dγ}$ 1·62	
	Much SO₂ still present. Stood 13 months.										
	ZnSO₄,7H₂O, g.										
Zn					7·5	38·3	9·7	44·5			3
	(b, iv), 8 hrs. at 60° then 4 hrs. at 75°	2	7	210	8·67	38·94	8·75	43·87‡	2·4H₂O		
	(b, iv), 12 hrs. at 75°	3	7	215	8·35	38·70	8·90	44·39§	2·3H₂O	n_D ca. 1·58	4
	(b, iv), 12½ hrs. at 75°	2	5	210	9·00	38·50	8·50	44·31**	2·37H₂O		
	(b, iv), 9½ hrs. at 75°	3	7·5	115	8·74	38·85	8·94	44·40††	2·30H₂O		
	CdCl₂, g.										
Cd					9·53	58·25	—	32·21			5
	(b, iv), filtered after 1 hr. on water-bath. Filtrate then heated 12 hrs. on water-bath	7·3	5·3	500	9·64	58·30	—	32·06 (by diff.)		$n_{Dα}$ ca. 1·64; $n_{Dγ}$ ca. 1·65	6
	(b, i), 4 days	2	7	210	9·93	55·98	0·94	33·28‡‡	2·34H₂O	n_D ca. 1·63	7

¹ Calc. for $Mn_2P_2O_7,2\frac{1}{3}H_2O$. ² Different analyses of the same prepn. Well-crystallised specimen. Rhombic plates, many facetted, probably monoclinic. No sign of heterogeneity after very close examination. ³ Calc. for double salt. ⁴ Nicely crystallised in needles and some tablets showing multiple twinning. Most needles have positive elongation: some have straight and some oblique extinction. Probably monoclinic. Slowly formed from $Zn_2P_2O_7,3\cdot6H_2O$: change can be followed under microscope. ⁵ Calc. for $Cd_2P_2O_7,2\frac{1}{3}H_2O$. ⁶ Elongated rhombs; monoclinic?; nicely crystalline. ⁷ Bundles of fine needles, mostly spherulitic.

† Calc. from total base.   ‡ Total base requires P_2O_5, 44·00%.   § Excess $P_2O_5 = 0\cdot42\%$.
** Excess $P_2O_5 = 0\cdot98\%$.   †† Excess $P_2O_5 = 0\cdot27\%$.   ‡‡ Excess $P_2O_5 = 1\cdot25\%$.

far from them. The crystals of $Na_4P_2O_7,10H_2O$ are well washed with a nearly saturated solution of this salt, which is very effective in removing original mother-liquor.

Metal.	MO, %, in Na₄P₂O₇,10H₂O.	
Mg	0·067 ⎫	Probably 0·1% is the limit attainable. Some higher results were open to
Mg	0·093 ⎭	doubt owing to possible presence of $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$.
Mn	—	Position unfavourable. No evidence for solid-solution formation.
Co	0·3	
Ni	0·3	
Ni	0·47	This result may be too high owing to possible presence of a trace of $Na_4P_2O_7,Ni_2P_2O_7,12H_2O$.
Cu	0·007	This may or may not represent a real solubility in the solid $Na_4P_2O_7,10_2HO$.
Zn	0·09	
Zn	0·09	
Cd	—	Position unfavourable. No evidence for solid-solution formation.

The Compound $Na_6Cu(P_2O_7)_2,16H_2O$ (*or* $3Na_4P_2O_7,Cu_2P_2O_7,32H_2O$).—This *compound* is very soluble in water, and very large dark blue prismatic crystals can be obtained. It yields a congruent solution from which it can be crystallised unchanged. 100 G. of the solution saturated at 25° contain 37 g. of the anhydrous salt. These data allow suitable details of preparation to be calculated; *e.g.*, 10 g. of anhydrous $Na_4P_2O_7$, dissolved in water, are added to a solution containing a small excess of copper chloride. The precipitated $Cu_2P_2O_7$ is filtered off, washed at the pump, and added to a hot solution of 30 g. of anhydrous $Na_4P_2O_7$ in 30 c.c. water. When all $Cu_2P_2O_7$ has dissolved the filtered solution is left to cool and crystallise [Found : H_2O, 34·76; CuO, 9·47; Na_2O, 22·13; P_2O_5, 33·70. $Na_6Cu(P_2O_7)_2,16H_2O$ requires H_2O, 34·39; CuO, 9·48; Na_2O, 22·21; P_2O_5, 33·92%].

SUMMARY.

1. The pyrophosphates of magnesium, manganese, cobalt, nickel, copper, zinc, and cadmium have been examined.

2. Evidence has been obtained for hydrates $M_2P_2O_7,xH_2O$ where x may have the values 8, 7, 6·5, 6·25, 6, 5, 4·2, 4, 3⅔, 3·6, 3·25, 3, 2⅔, or 2⅓. The whole series is not obtainable with any one metal.

3. The following double salts have been prepared :
$Na_4P_2O_7,Ni_2P_2O_7,12H_2O$; $Na_4P_2O_7,3Mg_2P_2O_7,21H_2O$; $7Na_4P_2O_7,25Mg_2P_2O_7,172H_2O$; $Na_4P_2O_7,3Co_2P_2O_7,20H_2O$; $Na_4P_2O_7,Mn_2P_2O_7,8H_2O$; $Na_4P_2O_7,Cd_2P_2O_7,8H_2O$;
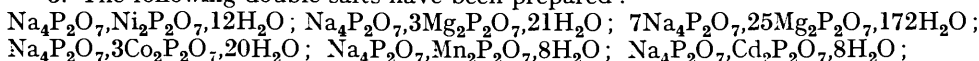
$Na_4P_2O_7,4Cu_2P_2O_7,17H_2O$; $8Na_4P_2O_7,7Zn_2P_2O_7,23H_2O$; $2Na_4P_2O_7,2Zn_2P_2O_7,5H_2O$; $8Na_4P_2O_7,7Cu_2P_2O_7,13H_2O$; $3Na_4P_2O_7,9Co_2P_2O_7,20H_2O$; $3Na_4P_2O_7,9Zn_2P_2O_7,16H_2O$. These double salts represent in some cases the limit in a series of solid solutions.

4. A theory of replacement is developed according to which the above double salts and solid solutions are derived from " parent " hydrates, containing no sodium, by replacement of $[M(H_2O)_4]^{..}$ by $[Na_2(H_2O)_2]^{..}$, or, in the case of less hydrated salts, by replacement of $[M(H_2O)_2]^{..}$ by $Na^._2$. The order in which the double salts are placed in the above list is that of decreasing hydration of the " parent " hydrates.

5. In some cases replacement of $[M(H_2O)_2]^{..}$ by $[H_2(H_2O)_2]^{..}$ may occur, and acidic preparations result.

6. On the basis of this theory, structures are developed for all the above double salts and their " parent " hydrates. They are all considered to be true double salts, with the whole of the metal in the kationic condition.

7. One true complex salt was also obtained, *viz.*, $Na_6[Cu(P_2O_7)_2],16H_2O$ (or $3Na_4P_2O_7,Cu_2P_2O_7,32H_2O$). This is very soluble to a congruent solution and is well crystallised.

8. Most of the double salts are only very sparingly soluble in water, and few of them crystallise well even from acid or sodium pyrophosphate solutions in which the gross solubility may be considerable. This is attributed to the low concentration in the mother-liquor of some or all of the constituent ions which go to build up the crystals.

9. The $Na_4P_2O_7,10H_2O$ which separates in large transparent crystals from solutions containing magnesium, cobalt, nickel, or zinc pyrophosphate contains a small amount of these in solid solution. This is explicable on the basis of the above theory, and indicates $[Na(H_2O)_4]_2^.[Na_2(H_2O)_2]^{..}[P_2O_7]''''$ as a probable structure for $Na_4P_2O_7,10H_2O$.