210. *Studies of Phosphates. Part I. Ammonium Magnesium Phosphate and Related Compounds.*

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The work now described originated in an attempt to discover the causes of (1) the incandescence which is observed at a certain stage in the ignition of ammonium magnesium phosphate, and (2) the colour changes undergone by the solid when cobalt is precipitated as ammonium cobalt phosphate. Explanations of these phenomena have been obtained, but many erroneous statements in the literature had to be corrected and new material supplied. Although most of this deals with compounds regarded as well known, we consider it worth recording, especially as it has led to conclusions on the molecular structures and mutual relationships of some important phosphates. We have given enough detail to enable the work to be repeated and the value of our conclusions to be determined. This is necessary since the same reactants may yield different products according to the exact method of procedure followed.

The main conclusions are summarised as follows.

The " glowing " on ignition of ammonium magnesium phosphate occurs in the complete absence of organic matter.

Only the hexahydrate glows vigorously, the glow of the monohydrate being much fainter. These differences persist when magnesium is replaced by other bivalent metals, and are associated with colour differences in the case of metals like cobalt and nickel.

The colours indicate that in the hexahydrates the bivalent metal is kationic, whereas in the monohydrates it is partly kationic and partly anionic.

The complexity of the monohydrates is not due to ammine formation. They are true ammonium salts—since the corresponding *potassium* compounds can be obtained but no pyridine compounds.

The same differences of colour between hexa- and mono-hydrates are found in the potassium series as in the ammonium series, but none of the potassium salts glows on ignition.

All the monohydrates $M^{I}M^{II}PO_4,H_2O$ are considered to be quadrimolecular.

In the coloured anhydrous phosphates of the type $M^{I}M^{II}PO_4$ the colour is such as to indicate that the bivalent metal is entirely anionic. Two types of ammonium cobalt phosphate exist, an unstable " glowing " form, considered to be bimolecular, and another, non-glowing, obtainable in solid solution in ammonium zinc phosphate, probably quadrimolecular.

It is pyrophosphate formed by decomposition of the ammonium salts which glows in all the cases so far mentioned. A number of phosphates of the type $M^{II}HPO_4,xH_2O$ showed feeble glowing or none at all. Nearly all of these appear to be quadrimolecular.

An attempt has been made to develop structural formulæ for the compounds dealt with in this paper on the basis of the differences in behaviour mentioned above. These are set out in Table I.

The cause of the glowing on ignition of some of the phosphates is discussed on p. 859, *et seq.* Density and thermochemical measurements have shown that the unglowed pyrophosphate obtained from the hexahydrated compounds differs from the pyrophosphate obtained from the monohydrates. After the former has glowed, it becomes identical in properties with the latter. It is considered that the unglowed pyrophosphate is under strain and polymerises to $(M_2P_2O_7)_2$, with relief of strain and formation of a more closely packed molecule.

The complexity of some of the compounds dealt with is not due to the formation of polymerised phosphoric acids, but is determined by the strong co-ordinating tendency of the bivalent metals present. It is considered that the latter act with co-ordination numbers 0, 4, or 6, occasionally 2, but never 1, 3, or 5. Some of the observations made in the course of the work are of analytical interest for the precipitation of compounds of the type of ammonium magnesium phosphate.

The " Glowing " of Ammonium Magnesium Phosphate.—Although the incandescence which spreads through the mass on ignition of ammonium magnesium phosphate is very striking, it is hardly ever referred to in text-books of quantitative analysis.

Berzelius (" Lehrbuch der Chemie," Wöhler's translation, 1826, Vol. 2, p. 651) first noticed the glowing, and Rose ("Ausführliches Handbuch der analyt. Chemie," 1851, Vol. 2, p. 38) also recorded it. Popp (*Z. für Chem.*, 1870, ii, **6**, 305) stated that this phosphate always glowed if free from impurities, and more particularly from silica or calcium phosphate. He suggested that the glowing was due to a change from the crystalline pyrophosphate to an amorphous or glassy form, and showed that magnesium pyrophosphate prepared from sodium pyrophosphate by precipitation with excess of magnesium sulphate glowed similarly on ignition. His conclusions as to the influence of impurities were, however, found to be incorrect by Struve (*Z. anal. Chem.*, 1898, **37**, 485).

Ignited magnesium pyrophosphate is usually grey owing to the presence of traces of carbon, derived either from volatile organic bases in the ammonia used in the precipitation, or from filter-paper fibres, and enclosed in the pyrophosphate during sintering.

Karaoglanoff and Dimitroff (*Z. anal. Chem.*, 1918, **57**, 353) attributed the glowing entirely to the presence of organic matter, but their experimental results are unconvincing. The following experiment, in which the presence of organic matter was entirely avoided, completely disproved this view.

A solution of diammonium phosphate was prepared from synthetic ammonia solution * and A.R. phosphoric acid and used to precipitate a cold solution of A.R. magnesium chloride hexahydrate; the ammonium magnesium phosphate hexahydrate so obtained was filtered on asbestos, washed with dilute synthetic ammonia, and dried over sulphuric acid. The product glowed on ignition and gave a white pyrophosphate, showing that carbon had been successfully eliminated.

The Hexahydrates of the Ammonium Magnesium Phosphate Group.—The striking observation was soon made by us that the intense glow on ignition is only shown by ammonium magnesium phosphate hexahydrate, the monohydrate glowing so feebly that it can only be seen in the dark. The variable results of earlier workers were probably, in part, due to the fact that they were sometimes dealing with the hexahydrate, and sometimes with the monohydrate. We found that although the monohydrate, if precipitated, usually changes over into the hexahydrate when left in contact with the mother-liquor at room temperature for several hours, yet it does not always do so if large amounts are present.

We have prepared a number of compounds analogous to ammonium magnesium phosphate and hexa- and mono-hydrates, as well as some related compounds, in the hope of being able to trace some connexion between the capacity for glowing and the degree of hydration and complexity of the compound as indicated, possibly, by differences in colour, since this property sometimes gives valuable information as to possible structure and complexity of salts (Bassett and Croucher, J., 1930, 1784). The fact that the several colours and colour changes observed with cobaltous phosphates appeared to be precisely similar to those found with cobaltous chloride was particularly helpful in this connexion.

The only other hexahydrates of the ammonium magnesium phosphate group which we have been able to prepare pure are the cobalt and nickel compounds, both of which were already known (Debray, *Compt. rend.*, 1864, **59**, 40; *Bull. Soc. chim.*, 1864, **2**, 11). Since other phosphates can be obtained from the same solutions according to the conditions, we give full details of our method (Expt. A).

Metals other than magnesium, cobalt, and nickel give mono- instead of hexa-hydrates, even at 0°; with zinc, one always obtains the anhydrous ammonium phosphate. Hexahydrates evidently have a great tendency to lose water.

Winkler ("Ausgewählte Untersuchungsverfahren für das chemische Laboratorium," 1931, pp. 115—116) states that when a manganese solution is precipitated hot with a solution of diammonium hydrogen phosphate and ammonium chloride, the amorphous precipitate is converted into needle-like crystals which slowly change into plate-like crystals. As the needles, if formed, might consist of the hexahydrate, we repeated these experiments under the prescribed conditions, but were unable to obtain needle-like crystals, the product always consisting of plate-like crystals of the monohydrate.

It is well known that salt hydrates which are unstable in the pure condition can often be obtained in solid solution in a stable isomorphous compound (Stortenbecker, *Z. physikal. Chem.*, 1895, **16**, 250). By precipitating suitable mixed solutions we obtained ammonium manganese, copper, zinc, and cadmium phosphate hexahydrates as solid solutions in the magnesium compounds. The excess of magnesium compound required to stabilise the other hexahydrates gives a rough indication of the order of the stabilities of the latter, which appears to be manganese, copper, cadmium, zinc (Expt. B).

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* Kindly supplied by Messrs. Synthetic Nitrates and Ammonia Ltd., Billingham-on-Tees.

All the hexahydrates glow on ignition, but whereas the incandescence of the magnesium compound is easily seen in daylight, the cobalt compound must be examined in the dark. For the nickel compound, stronger heating with a blowpipe is necessary. When the hexahydrates are heated in the dry condition in the steam-oven, they do not pass into the monohydrates in spite of statements to the contrary. Losses considerably greater than are required for the formation of monohydrates are suffered. Dehn and Heuse (*J. Amer. Chem. Soc.*, 1907, **29**, 1137) have shown that $NH_4MgPO_4,6H_2O$ loses both water and ammonia at temperatures well below 100° and we have confirmed this, finding a loss of about 86% of the total ammonia before constancy was reached after several days. The cobalt compound behaves similarly.

The Monohydrates of the Ammonium Magnesium Phosphate Group.—Compounds of the type NH_4MPO_4,H_2O were easily obtained with the metals magnesium, manganese, cobalt, nickel, copper, and cadmium, but not so easily with zinc. The *copper* compound had not previously been prepared (Expt. C). Above 80° (Debray, *loc. cit.*), the gelatinous precipitates first obtained by adding ammonium phosphate to solutions of metal salts gave pearly, crystalline plates of the compound NH_4MPO_4,H_2O ($M = Mg, Mn, Fe^{\cdot\cdot}, Co$, or Ni), whereas zinc gave the anhydrous salt.

Heintz (*Annalen*, 1867, **143**, 356) undoubtedly obtained NH_4ZnPO_4,H_2O by allowing it to crystallise at room temperature as the ammonia evaporated from a solution which was originally sufficiently ammoniacal to hold all the phosphate in solution.* This method is not at all trustworthy, however, for unless the monohydrate is caused to separate fairly rapidly, it is liable to lose its molecule of water. We found it better to precipitate it from ammoniacal solution by gradual addition of hydrochloric acid (Expt. D). Even at 20°, the monohydrate is fairly rapidly dehydrated when in contact with mother-liquor. It is much more stable in solid solution in NH_4CoPO_4,H_2O (Expt. E). Dick (*Z. anal. Chem.*, 1930, **82**, 401), describing estimations by the phosphate method, suggested that ammonium zinc phosphate is obtained as the monohydrate by hot precipitation. The figures given are obviously correct, and correspond to the anhydrous compound.

The properties of the monohydrates differ greatly from those of the hexahydrates. With the exception of the zinc compound, they all showed an incandescence visible in the dark if a thin layer of the finely ground compound was heated sufficiently rapidly. They all glow much less vigorously than the hexahydrates, the manganese compound showing best glowing. The two types of hydrate also differ markedly in respect to colour. Thus, the hexahydrates of cobalt and nickel have the red and green colours characteristic of the respective hydrated kations, whereas the corresponding monohydrates are purplish-red and greenish-yellow respectively, the copper analogue being greenish-blue.

Possible Structures of the Monohydrates and the Method of Distinguishing Between Them.—We conclude from these colour differences (cf. Bassett and Croucher, *loc. cit.*) (i) that the hexahydrates contain the whole of the bivalent metal as kation, and are to be formulated as $NH_4^{\cdot}[M(H_2O)_6]^{\cdot\cdot}PO_4'''$; (ii) that the monohydrates are complex, the bivalent metal being present partly as hydrated kation and partly as complex anion.

There appeared to be two possible ways in which complexity of the monohydrates might arise: they might be ammines, and not true ammonium salts, or they might be polymerised, having a complex anion, $[M(H_2O)_4](NH_4)_4[(PO_4)_4M_3]$. Since experiment showed that practically the whole series of potassium compounds could be prepared (Expt. F), but no pyridine derivatives, it is clear that an ammine formula must be ruled out, and such compounds must be regarded as true ammonium salts. The failure to obtain pyridinium derivatives is, then, to be attributed mainly to the weakness of pyridine as a base. The structure shown in Table I is suggested, in which each M atom is 4-co-ordinate.

The Phosphates $KM^{II}PO_4,6H_2O$ *and* $KM^{II}PO_4,H_2O$.—No compounds of the type $KMPO_4,H_2O$ had previously been prepared. In crystalline form and colour they are identical with the corresponding ammonium salts. Of the hexahydrates, we were able to

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* This method is wrongly attributed by Mellor ("Comprehensive Treatise," 1923, IV, 661) to Bette (*Annalen*, 1835, **15**, 129).

obtain only the magnesium and the nickel compound (cf. Schröcker and Violet, *Annalen*, 1866, **140**, 229), but the latter had the same green colour as the ammonium compound (Expt. G). It must therefore be concluded that the structures of the hydrates of the potassium series are identical with those of the corresponding ammonium series. An important difference between the potassium and the ammonium compounds is that none of the former glows on ignition. Potassium compounds lose potassium oxide on ignition, and this loss seems to be more pronounced from the monohydrates than from the hexahydrates.

The Anhydrous Phosphates $NH_4M^{II}PO_4$.—Zinc ammonium phosphate is the only member of this group isolated easily in the pure state, and is the compound obtained in the well-known analytical method of precipitating zinc (cf. the corresponding method for cobalt).

Ammonium cobalt phosphate. When this salt is first formed, the pinkish or bluish flocculent precipitate passes, on its way to the final purple-red plates of the monohydrate, through an intermediate royal-blue phase. This is dense and crystalline, but under the microscope it is seen to consist of minute spherulites. There is little doubt that it consists of the anhydrous phosphate, although we have not obtained it pure (Expt. H). On several occasions, however, small amounts were obtained sufficiently pure to show as strong an incandescence on ignition as that of the ammonium magnesium hexahydrate. We believe that this has an important bearing on the nature of the anhydrous phosphates, and indicates that the dark blue, very unstable ammonium cobalt phosphate is probably $(NH_4CoPO_4)_2$, whereas the dark blue compound that can be easily obtained in solid solution in anhydrous ammonium zinc phosphate is probably the quadrimolecular salt (see p. 861). Dakin (*Z. anal. Chem.*, 1930, **39**, 789), recording the colour changes shown by the cobalt precipitate, refers to the initial amorphous precipitate as the tribasic cobalt salt.

Solid solutions of cobalt and zinc ammonium phosphates. Anhydrous ammonium cobalt phosphate is stabilised when in solid solution in the corresponding zinc compound, and, if mixed cobalt and zinc solutions are precipitated in the ordinary way with diammonium hydrogen phosphate, permanent, blue, crystalline precipitates are obtained of the mixed anhydrous phosphates (cf. Tamm, *Chem. News*, 1871, **24**, 148). Apart from their colour, these have all the characteristics of anhydrous ammonium zinc phosphate itself. The limiting solubility of the cobalt in the zinc compound occurs when about one part of cobalt is present to five of zinc (Expt. I). If solutions containing cobalt in greater proportion than this are precipitated, the excess cobalt is obtained as monohydrated ammonium cobalt phosphate, which no doubt contains the zinc analogue in solid solution (see Expt. E). We have obtained analogous solid solutions of the magnesium and the cadmium salt in ammonium zinc phosphate (Expt. I).

Ammonium cobalt phosphate monohydrate is stable up to about 110°, but decomposes above that temperature and becomes dark blue from loss of ammonia and water, so that it cannot be obtained anhydrous. At 180° the compound $(CoHPO_4)_4$ is formed—the polymeric formula being based on the formula which we assign to the monohydrate (see Table I) (Expt. J) (see p. 860).

The Anhydrous Phosphates $KM^{II}PO_4$.—The anhydrous potassium phosphates of cobalt and zinc are the only two members of this class obtained nearly pure from aqueous solutions (Expt. K). In appearance they resemble the ammonium compounds, but the cobalt compound does not glow on ignition. Neither of these compounds had previously been obtained by wet methods, but both of them, and the corresponding compounds of magnesium, manganese, nickel, copper, and cadmium, had been prepared by fusion methods (Grandeau, *Ann. Chim. Phys.*, 1886, **8**, 193; Ouvrard, *ibid.*, 1889, **16**, 289; *Compt. rend.*, 1888, **106**, 1729). The nickel compound forms yellow prisms, and the copper salt is greenish-blue. The colours of these anhydrous compounds are such as would be expected if the whole of the bivalent metal were contained in a complex anion.

The dark blue colour of the cobalt compound has been shown to be due to anionic cobalt by electrical experiments similar to those of Donnan and Bassett (J., 1902, **81**, 946). Similar experiments also showed that the yellow colour of the nickel compound and the blue of the copper could be attributed to complex anions containing those metals (Expt. L).

Metal Hydrogen Phosphates.—Since the glowing on ignition of the ammonium metal phosphates appeared to be due to pyrophosphate (Popp, *loc. cit.*), the behaviour on ignition of compounds of the type $MHPO_4,xH_2O$, which yield pyrophosphate, was of some interest. The compounds of this class prepared and examined by us are $MgHPO_4,7H_2O$; $MgHPO_4,3H_2O$; $MnHPO_4,3H_2O$; $CoHPO_4,2H_2O$; $CuHPO_4,H_2O$; $CaHPO_4,2H_2O$; $CaHPO_4$, most of which were obtained during the experiments with pyridine (p. 858) (Expt. M).

The two magnesium compounds had been prepared by Graham (*Phil. Trans.*, 1837, **127**, 47; *Annalen*, 1839, **29**, 24) and by Debray (*Compt. rend.*, 1861, **52**, 44; 1864, **59**, 40; *Bull. Soc. chim.*, 1864, **2**, 11; *Ann. Chim. Phys.*, 1861, **61**, 419). Debray's compound, $MgHPO_4,4{\cdot}5H_2O$, is probably a mixture of the hepta- and the tri-hydrate. The manganese compound was prepared by Heintz (*Pogg. Ann.*, 1848, **74**, 449), Bödeker (*Annalen*, 1849, **69**, 206), and Debray (*loc. cit.*, 1861), and the last also prepared $CoHPO_4,H_2O$. Neither $CoHPO_4,2H_2O$ nor $CuHPO_4,H_2O$ has been previously recorded.

Since it is difficult to get the desired phosphate, and details of preparation recorded in the literature are frequently insufficient, we have given particulars of the methods found to give good results in the case of all the hydrogen phosphates referred to above. It is to be noted that only the magnesium compounds glow on ignition, and that the colours of the cobalt and copper compounds, which are purple-pink and saxe-blue respectively, indicate that the metal is partly kationic and partly anionic (see Table I). Attempts to prepare suitable specimens of the monohydrogen phosphates of nickel, zinc, or cadmium failed. The two calcium salts were prepared by well-known methods and showed no signs of "glowing" on ignition. Graham (*loc. cit.*) described a zinc hydrogen phosphate monohydrate, but both we and Heintz (*Annalen*, 1867, **143**, 356) could only obtain $Zn_3(PO)_2,4H_2O$ by his method. This compound has the appearance (minute silvery plates) attributed by Graham to his compound, for which he determined only the loss on ignition (16·18%).

The Cause of the Incandescence Shown by Some of the Phosphates on Ignition.—The only recorded data upon the glowing of phosphates on ignition relate to ammonium magnesium phosphate and precipitated magnesium pyrophosphate. The heat evolution and the shrinkage observed are consistent with the view that the phenomenon of "glowing" is due to rearrangement and polymerisation of structurally unstable molecules. We have established the conditions under which $NH_4MgPO_4,6H_2O$ can be dehydrated without ceasing to glow on subsequent ignition (Expt. N), and we have also shown by density determinations on the glowed and the unglowed pyrophosphate that a considerable diminution of volume occurs during glowing (Expt. O). The results obtained explain certain discrepancies in the published densities of magnesium pyrophosphate (cf. Clarke, *Amer. J. Sci.*, 1877, **14**, 285, and Andersen, *J. Washington Acad. Sci.*, 1914, **4**, 318). Karaoglanoff and Dimitroff (*loc. cit.*) found that ammonium magnesium phosphate failed to glow if first of all heated gradually for about 4 hours at lower temperatures. We confirmed this by gradually heating the hexahydrate just above 600°. Difficulty was experienced, however, in expelling all the water below this temperature, and we therefore cannot confirm Miholić's statement (J., 1930, 200) that decomposition of the hexahydrate was complete at 480° (cf. Hoffman and Lundell, *U.S. Bur. Stand. J. Res.*, 1930, **5**, 279; Ellis and Fox, *Ann. Reports*, 1930, **27**, 218).

The densities of three different types of pyrophosphate have been determined: (*a*) "unglowed" pyrophosphate from $NH_4MgPO_4,6H_2O$; (*b*) "glowed" pyrophosphate from $NH_4MgPO_4,6H_2O$; and (*c*) pyrophosphate from NH_4MgPO_4,H_2O. The density of (*a*) was 15% less than that of (*b*) or (*c*), which only differed by 1%. The slightly lower density of (*c*) probably arises from the fact that, since it has suffered only a feeble glowing and no sintering, it is much more porous than the "glowed" pyrophosphate, thus preventing complete removal of air.

The identity of these two pyrophosphates was also shown by determinations of the heat of solution of the three kinds of pyrophosphate in hydrochloric acid (Expt. P). Similar measurements with similar results were made also with the cobalt and nickel compounds. The experiments, although not of extreme accuracy, sufficed to confirm the density determinations, and to show that the "unglowed" pyrophosphate from the hexahydrate is quite different from the glowed pyrophosphate from the hexahydrate or the pyrophosphate from the monohydrate, while the last two are identical. There is no change of colour when the pyrophosphates glow; both the unglowed and the glowed cobalt compound are pale blue, and both varieties of the nickel compound are pale brownish-yellow. In both cases the colours are similar to those of the anhydrous chlorides and are, we believe, those characteristic of non-ionic compounds (Bassett and Croucher, *loc. cit.*, pp. 1814—1816). Copper pyrophosphate, obtained from the monohydrated hydrogen or ammonium compound, is white, which indicates that it also is non-ionic.

We submit the following considerations to explain the glowing of pyrophosphates.

The fully ionic $NH_4^{\cdot}[M(H_2O)_6]^{\cdot\cdot}PO_4'''$ yields on gentle heating the non-ionic, unimolecular, pyrophosphate $M_2P_2O_7$, but on stronger heating this polymerises to $(M_2P_2O_7)_2$, identical with the compound formed directly from the complex monohydrate $[NH_4MPO_4,H_2O]_4$ (see Table I). The incandescence observed is due to the heat evolved in this polymerisation. This heat is considerable and can be regarded as indicating a severely strained condition in the $M_2P_2O_7$ molecule, due possibly to the initial formation of M atoms with co-ordination number 2. We believe that the 2-co-ordinated condition of bivalent metals is very unstable, and that polymerisation of the $M_2P_2O_7$ allows the formation of an unstrained ring structure in which all the M atoms are 4-co-ordinate. The results of the measurements of the heat of solution in hydrochloric acid of the pyrophosphates derived from the hexahydrated ammonium phosphates of cobalt and nickel and the corresponding monohydrates are very similar to those found for the magnesium compounds (Expt. P). This is important, for one would expect the heat evolution on passage from $M_2P_2O_7$ to $(M_2P_2O_7)_2$ to be of the same order in all cases. The heat evolved (in cals. per 2 g.-mols. of $M_2P_2O_7$) was 13,520, 20,990, and 36,330 for the magnesium, cobalt, and nickel compounds respectively.

It will be realised that the polymerisation of the pyro- and ortho-phosphates dealt with in this paper and in Part II, as also the formation of the various complex types of phosphate, is in no way a special function of phosphoric acid. It is determined essentially by the co-ordinating tendency of the various bivalent metals concerned. Anhydrous sodium pyrophosphate is probably an electrovalent compound $Na^{\cdot}_4P_2O_7''''$, and there is no reason why it should polymerise on heating; it is not at all surprising, therefore, to find that, even after strong ignition, it gives rise to "unglowed" magnesium pyrophosphate when dissolved in water and used as precipitating agent for a magnesium salt. The heat of solution of the dehydrated magnesium pyrophosphate thus obtained was intermediate between that of the "glowed" and the "unglowed" form of $Mg_2P_2O_7$ (Expt. Q), but nearer to that of the latter.

Stages passed through in the Conversion of $(NH_4MPO_4,H_2O)_4$ *into* $(M_2P_2O_7)_2$.—Expt. J indicates that two intermediate stages are passed through when the monohydrates are ignited, and that the immediate precursor of $(M_2P_2O_7)_2$ is $MHPO_4$. The latter must be regarded as quadrimolecular, $(MHPO_4)_4$, if the original ammonium salt is considered to have this complexity.

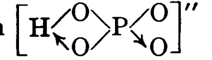
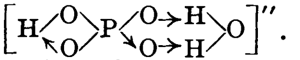
The faint glowing characteristic of the monohydrates occurs during the decomposition of the $(MHPO_4)_4$ stage, for it was found that the $(CoHPO_4)_4$ obtained in Expt. J still glowed faintly to about the same extent as the $(NH_4CoPO_4,H_2O)_4$ from which it had been obtained. We suggest that it is due to the process of ring formation from the chain structure of the orthophosphate.

With cobalt, the two intermediate stages have a rather dark blue colour, which, after glowing, changes to pale blue. Somewhat similar colour differences are found with nickel. It is possible that the intermediate stages correspond to conditions in which the original $Co(H_2O)_4^{\cdot\cdot}$ kation has become anhydrous, so that they contain a cobaltous ion in association with complex chain anions. During the final complete removal of water, this ion is drawn into the complex when ring closure occurs. Something similar happens with the hexahydrates, for when $NH_4CoPO_4,6H_2O$ is ignited it does not go directly to $Co_2P_2O_7$; instead, an intermediate fairly dark blue stage is seen which we suggest is $Co^{\cdot\cdot}[HPO_4CoPO_4H]''$.

We attribute the rather dark blue colour of the intermediate stages containing unco-ordinated cobalt kations to the dark blue colour of the complex anions completely swamping the colour of the red cobalt ions, which is probably much paler than that of $[Co(H_2O)_4]^{\cdot\cdot}$ or $[Co(H_2O)_6]^{\cdot\cdot}$. A similar explanation would hold for nickel compounds.

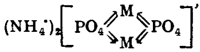
Structures of NH_4MPO_4 *and* $KMPO_4$.—The great instability of monohydrated ammonium zinc phosphate with respect to the dehydrated salt shows that, if we are correct in assigning the polymeric formula $(NH_4ZnPO_4,H_2O)_4$ to the former, the anhydrous compound must also be not less complex than $(NH_4ZnPO_4)_4$. There is no reason to suppose that it is any more complex, but it would be very unreasonable to suppose that, just in the case of zinc, a compound $(NH_4ZnPO_4,H_2O)_4$, obtainable only at ordinary temperatures, would tend to form, at higher temperatures, a less complex form such as $(NH_4ZnPO_4)_2$, in spite of the fact that with all the other ammonium metal phosphates examined the tendency is for molecular complexity to increase at higher temperatures—the unimolecular hexahydrates giving the quadrimolecular monohydrates. It follows from this that $(NH_4ZnPO_4)_4$ already has what is really the structure of the " glowed " phosphates, and it is thus natural that it shows no " glowing " on ignition.

The instability of the dark blue anhydrous ammonium cobalt phosphate, and the ease with which it passes into the monohydrate at ordinary or higher temperatures (just the converse of what happens with the zinc compounds), together with the significant fact that it glows intensely on ignition, are sufficient, we think, to show that the cobalt compound which appears as an intermediate stage in the formation of $(NH_4CoPO_4,H_2O)_4$ is really $(NH_4CoPO_4)_2$, the anion of which has a structure very similar to that of the un-ionised pyrophosphate. It is also under just as much strain, which accounts for the difficulty in keeping the compound from passing into the monohydrate having an unstrained structure. It corresponds to the $(CoHPO_4)_2$ formed as an intermediate stage during the conversion of $NH_4CoPO_4,6H_2O$ into pyrophosphate. The dark blue anhydrous ammonium cobalt phosphate, which forms solid solutions with the anhydrous zinc compound, is evidently not the same as the above, and must be the quadrimolecular form, and, in agreement with this, none of these solid solutions, even those richest in cobalt, shows any glow on ignition. The anhydrous potassium metal phosphates are crystallographically similar to anhydrous ammonium zinc phosphate, so the quadrimolecular formula follows for them also.

Compounds $MHPO_4,xH_2O$, as a class, on ignition either did not glow at all or only very faintly. The magnesium hepta- and tri-hydrates were the only two, of those which we were able to prepare and examine, which showed any certain " glowing," and even this was not comparable with that of hexahydrated ammonium magnesium phosphate, but only with that of the monohydrate. Since the magnesium heptahydrate passed easily into the trihydrate on heating to constant weight in a steam-oven, the absence of intense glowing has to be considered only with reference to the possible structure of the latter compound. It appears reasonable to suppose that the low order of glowing of this trihydrate is due to its being a polymerised compound, and in fact quadrimolecular, just as is NH_4MgPO_4,H_2O. Results reported in Part III of this series have led us to the conclusion that the most likely structure for the trihydrate is that shown in Table I, one link of the chain anion being formed by two atoms of hydrogen. The heptahydrate, which easily passes into the above polymeride, has, in all probability, a simple structure (Table I). There is little evidence that the phosphate ion tends to hydrate in the same way that the sulphate ion does, but it is not unlikely that, under favourable conditions, the less symmetrical HPO_4'' ion  would tend to form . The mixed colours of $CoHPO_4,2H_2O$ and $CuHPO_4,H_2O$ are strong evidence for their complexity, and the apparent absence of glowing on ignition is best explained on the basis of the quadrimolecular formulæ indicated in Table I. Similar formulæ are adequate to explain the non-glowing of $CaHPO_4,2H_2O$ and $CaHPO_4$. In the latter compound the two calcium kations would have zero co-ordination.

In Table I are summarised our observations on the orthophosphates which are considered in the present paper. Italics in column 3 indicate that the compound in question is now described for the first time.

TABLE I.

Type of phosphate.	Structural formulæ assigned by us.	Metals yielding this type of compound.	Colour.	Behaviour on ignition.
$NH_4MPO_4,6H_2O$	$NH_4^{\cdot}[M(H_2O)_6]^{\cdot\cdot}PO_4'''$	Magnesium	—	* Glow visible with ease in daylight.
		Cobalt	Pink	Glow visible in dark over Bunsen burner.
		Nickel	Green	Glow visible in dark over a blow-pipe.
$KMPO_4,6H_2O$	$K^{\cdot}[M(H_2O)_6]^{\cdot\cdot}PO_4'''$	Magnesium *Nickel*	 Green	Non-glowing.
NH_4MPO_4,H_2O	$(NH_4^{\cdot})_4[M(H_2O)_4]^{\cdot\cdot}[PO_4\ M\ PO_4\ M\ PO_4\ M\ PO_4]^{VI}$	Magnesium	—	† Glow visible only in the dark using finely ground material in thin layers. They all glow much less vigorously than the members of the hexahydrate class. The vigour of glowing varies somewhat in the group, the Mn compound showing it best, and Cd with most difficulty. Sudden vigorous heating is required in all cases.
		Manganese	Pale pink	
		Cobalt	Purple-pink	
		Nickel	Greenish-yellow	
		Copper	Greenish-blue	
		Cadmium	—	
		Zinc	—	No glowing occurs. Sudden vigorous heating causes fusion before any glowing can be seen.
$KMPO_4,H_2O$	$K_4^{\cdot}[M(H_2O)_4]^{\cdot\cdot}[PO_4\ M\ PO_4\ M\ PO_4\ M\ PO_4]^{VI}$	*Magnesium*	—	The members of this class are all non-glowing.
		Manganese	Cream	
		Cobalt	Purple-pink	
		Nickel	Greenish-yellow	
		Copper	Turquoise-blue	
		Cadmium	—	
$MHPO_4,7H_2O$	$[M(H_2O)_6]^{\cdot\cdot}[HPO_4,H_2O)]''$	Magnesium	—	Glow just visible in the dark over blow-pipe.
$MHPO_4,3H_2O$	$[M(H_2O)_4]_2^{\cdot\cdot}\left[HPO_4\ M\ PO_4 \substack{H\\H} PO_4\ M\ PO_4\ H\right]^{IV}$	Magnesium	—	,, ,, ,,
		Manganese	Pale pink	Slight "glowing" may possibly occur in these two cases and in that of Cu when heated in dark.
$MHPO_4,2H_2O$	$[M(H_2O)_4]_2^{\cdot\cdot}\left[HPO_4\ M\ PO_4 \substack{H\\H} PO_4\ M\ PO_4\ H\right]^{IV}$	*Cobalt*	Purple-red	
		Calcium	—	Non-glowing.
$MHPO_4,H_2O$	$[M(H_2O)_4]^{\cdot\cdot}M^{\cdot\cdot}\left[HPO_4\ M\ PO_4 \substack{H\\H} PO_4\ M\ PO_4\ H\right]^{IV}$	*Copper*	Saxe-blue	(See Mn and Co, above.)
$MHPO_4$	$M_2^{\cdot\cdot}\left[HPO_4\ M\ PO_4 \substack{H\\H} PO_4\ M\ PO_4\ H\right]^{IV}$	Calcium	—	Non-glowing.
NH_4MPO_4	 $(NH_4^{\cdot})_2\left[PO_4 \substack{M\\M} PO_4\right]''$	*Cobalt*	Dark blue	Glow visible in daylight.
NH_4MPO_4	$(NH_4^{\cdot})_4\left[PO_4 \substack{M\ PO_4\ M\\M\ PO_4\ M} PO_4\right]^{IV}$	Zinc	—	Probably non-glowing, but melts.
$KMPO_4$	$K_4^{\cdot}\left[PO_4 \substack{M\ PO_4\ M\\M\ PO_4\ M} PO_4\right]^{IV}$	Cobalt	Dark blue	Non-glowing.
		Zinc	—	,, ,,

*These differences, we think, are mainly due to the unpolymerised nickel compounds being much the most stable and having to be heated to a higher temperature for polymerisation to occur.

† In this case the problem is not so much to heat the compound to a high enough temperature to cause it to glow, as to heat it suddenly enough to a temperature sufficiently high for glowing to be possible. The reaction causing the "glowing" occurs so readily that it tends to take place gradually and at such a low temperature that the rise of temperature produced is insufficient to cause visible "glowing."

It will be seen from Table I that there are wide differences in the ease with which the glowing occurs, and also in its visibility. These both depend essentially upon the rate of liberation of heat during the rearrangement of the unstable molecules, *i.e.*, upon the rate at which the rearrangement occurs. This will depend partly upon the individual compound concerned, but very largely upon the temperature to which the compound is heated, and the suddenness with which this temperature is reached. Fairly rapid heating is necessary in nearly all cases, but it needs to be extremely sudden in some. It was very difficult to estimate the relative intensities of the glowing, but it was obvious that that shown by ammonium magnesium phosphate hexahydrate was much brighter than that shown by the monohydrate or the hydrated magnesium hydrogen salt.

EXPERIMENTAL.

Analytical Methods.—(1) *Determination of magnesium, manganese, cobalt, and zinc.* (*a*) In absence of potassium, these metals were precipitated with diammonium hydrogen phosphate by standard methods, and weighed as pyrophosphate after ignition. A trace of cobalt remained in solution; consequently this filtrate was saturated with hydrogen sulphide and the resulting liquid concentrated until the brown solution cleared. The cobalt sulphide so precipitated was filtered off, well washed, and weighed as Co_3O_4 after strong ignition.

(*b*) In the presence of potassium, magnesium was separated with 8-hydroxyquinoline, the precipitate dissolved in acid, reprecipitated, and weighed as the dihydrate after drying to constant weight at 100—105°; the other three metals were precipitated as sulphide. Manganese and zinc were weighed in this form, but the cobalt sulphide was dried, ignited, dissolved in concentrated hydrochloric acid, and the cobalt precipitated from this solution with ammonium phosphate, the filtrate being treated as in (*a*).

(*c*) Cobalt in the presence of zinc was precipitated with α-nitroso-β-naphthol and weighed as Co_3O_4; the two metals were also precipitated together with ammonium phosphate and weighed as mixed pyrophosphate. Zinc and magnesium were separated by precipitation with diammonium hydrogen phosphate from solution, subsequently made strongly ammoniacal; the liquid was kept hot and well stirred for some time and then kept cold over-night. The zinc separated from the filtrate after the excess of ammonia had been removed by evaporation. Reprecipitation of the magnesium was necessary, the second filtrate being subsequently added to the first. Manganese and magnesium were separated, after removal of phosphoric acid with tin and nitric acid, by precipitating the manganese as sulphide and estimating magnesium in the filtrate in the usual way.

(2) *Determination of nickel, copper, and cadmium.* (*a*) Nickel was precipitated from ammoniacal solution with dimethylglyoxime, the mixture being kept hot for about an hour, and then standing over-night. Copper was precipitated with sodium thiosulphate and weighed as cuprous sulphide. In order to determine cadmium, its slightly acid solution was heated to incipient boiling, and hydrogen sulphide passed through until the liquid was quite cold (1½—2 hours); the precipitate was collected on a Gooch crucible, thoroughly washed with water saturated with hydrogen sulphide, dried at 105°, and weighed as cadmium sulphide.

(*b*) Cadmium or copper was separated from magnesium as sulphide, the magnesium being subsequently precipitated as ammonium magnesium phosphate. Cadmium was also separated from zinc by means of hydrogen sulphide. Double precipitation of the cadmium sulphide was necessary from solutions containing about 10 c.c. of 2*N*-hydrochloric acid per 100 c.c. The zinc was subsequently precipitated as ammonium zinc phosphate.

(3) *Other determinations.* Potassium was usually weighed as perchlorate, but in some cases as chloride, after removal of heavy metals, by hydrogen sulphide under appropriate conditions, and of phosphoric acid, either by the ferric chloride method or by means of tin and nitric acid; the latter was the more satisfactory. Magnesium, if present, was removed with 8-hydroxyquinoline, excess of the latter and ammonium salts being removed by ignition.

Water was estimated together with other volatile constituents by ignition, and ammonia by distillation into standard acid. Phosphoric acid was weighed as magnesium pyrophosphate after separation by the molybdate method.

Preparation of the Compounds described in the Present Paper.

A solution of diammonium or dipotassium hydrogen phosphate was slowly added to a solution of magnesium or heavy-metal chloride with stirring. The mixture of precipitate and mother-liquor was then kept at room temperature or digested in the water-bath until the precipitate became crystalline. (The time required varied within very wide limits.) The precipitate was then collected at the pump, and washed with water, followed by absolute alcohol and absolute ether. Details of concentration, etc., varied, and are given below for each compound.

Expt. A (*Theory, p.* 856). *The Ammonium Metal Phosphate Hexahydrates,* $NH_4MPO_4,6H_2O$.—(1) *Magnesium.* This was prepared in the usual way.

(2) *Cobalt.* A solution of 3 g. of $CoCl_2,6H_2O$ in 50 c.c. of water was used. (*a*) This was added to one of 15 g. of diammonium hydrogen phosphate in 450 c.c.; after 12 hours at room temperature, large pink square-ended prisms had formed (Found: CoO, 27·13; P_2O_5, 25·67; loss on ignition, 47·70. Calc.: CoO, 26·78; P_2O_5, 25·36; loss, 47·85%).

(*b*) The cobalt solution was added to one of 3 g. of ammonium phosphate and 30 g. of ammonium chloride in 450 c.c. The precipitate was entirely crystalline as above after 12 hours at room temperature (Found: CoO, 26·77; loss, 48·48%).

(*c*) As in (*b*), except that triammonium phosphate was used (Found: loss on ignition, 48·15%).

Method (*a*) tends to give a product contaminated with NH_4CoPO_4,H_2O. This can be avoided by using method (*b*) or (*c*).

(3) *Nickel.* Preparation as in (*a*) above. The compound formed large green prisms (Found: NiO, 26·74; P_2O_5, 25·57; NH_3, 6·23; loss on ignition, 48·05. Calc.: NiO, 26·73; P_2O_5, 25·37; NH_3, 6·08; loss, 47·90%).

Attempted Preparation of Ammonium Manganese, Copper, Zinc, or Cadmium Phosphate Hexahydrates.—Many attempts were made to prepare these compounds at room temperature or at 0°, using widely different concentrations, and with varying amounts of ammonia or ammonium chloride added to the ammonium phosphate solution used for precipitation, but the product obtained was always the ammonium metal phosphate monohydrate, except with zinc, of which the anhydrous compound was produced.

Expt. B (Theory, p. 856). *Preparation of Ammonium Manganese, Copper, Zinc, or Cadmium Phosphate Hexahydrates as Solid Solutions in Excess of Ammonium Magnesium Phosphate Hexahydrate.*—For each experiment 20 g. of diammonium hydrogen phosphate were dissolved in about 150 c.c. of water and added to a solution which always contained 3 g. of magnesium chloride hexahydrate together with an amount of the other metal chloride required for the ratio given in the first column of Table II. The total volume, after mixing, was about 400 c.c.

Table II summarises the results obtained; the calculated figures under (A) and (B) are based on the assumption that the metals other than magnesium are present as hexahydrate and monohydrate respectively (or as the anhydrous compound in the case of zinc).

TABLE II.

Mol. ratio MgO/MO in the solid analysed.	Time allowed for crystn. (mins.).		Composition, %.		
			Found.	Calc. (A).	Calc. (B).
Manganese.					
1 : 1	30	Loss	49·20 *	51·43	41·30
1 : 1	(Over-night)	Loss	44·31	51·43	41·30
3·92 : 1	30	Loss	53·35	53·26	49·58
		P_2O_5	28·40	28·33	30·43
		MgO	12·48	12·76	—
		MnO	5·73	5·75	—
Copper.					
6·57 : 1	30	Loss	53·51	53·50	51·23
		P_2O_5	28·40	28·33	29·74
		MgO	14·03	13·96	—
		CuO	4·08	4·20	—
Zinc.					
1 : 1	30	Loss	41·62	50·48	37·73
1 : 1	(Over-night)	Loss	40·70	50·48	37·73
6·5 : 1	30	Loss	52·61	53·45	51·11
13·11 : 1	,,	Loss	54·13	54·00	52·50
		P_2O_5	28·63	28·60	29·50
		MgO	14·90	15·08	—
		ZnO	2·29	2·32	—
Cadmium.					
1 : 1	30	Loss	41·25 *	46·31	36·43
4 : 1	,,	Loss	50·32	50·96	47·34
8·62 : 1	,,	Loss	52·65	52·66	50·85
		P_2O_5	28·11	27·91	29·20
		MgO	14·08	14·19	—
		CdO	5·20	5·25	—

* Preparation losing weight at room temperature.

The results demonstrate that these metals can form ammonium phosphate hexahydrates of a similar type to magnesium; the preparations in which both metals were present as hexahydrate were identical microscopically with ammonium magnesium phosphate hexahydrate.

Expt. C (Theory, p. 857). *The Ammonium Metal Phosphate Monohydrates,* NH_4MPO_4,H_2O.—Magnesium, manganese, cobalt, nickel, and cadmium compounds were obtained in the usual way by mixing hot solutions of diammonium hydrogen phosphate and the chloride of the metal, and then keeping the mixtures hot until crystallisation was complete (about 1 hour) All the monohydrates form thin rectangular plates of a fair size.

Copper. This *compound* could not be obtained by hot precipitation, but was prepared by the following method at room temperature.

(*a*) A solution of 3 g. $CuCl_2,2H_2O$ in 50 c.c. water added to one of 20 g. diammonium hydrogen phosphate in 500 c.c. The precipitate had become transformed into large greenish-blue crystals after standing at room temperature for 3 months (Found : CuO, 40·67; P_2O_5, 36·67; NH_3, 8·86; loss on ignition, 22·96. NH_4CuPO_4,H_2O requires CuO, 40·84; P_2O_5, 36·54; NH_3, 8·74; loss, 22·63%).

(*b*) A solution of 2 g. $CuCl_2,2H_2O$ in 50 c.c. water added to one of 60 g. of diammonium hydrogen phosphate in 500 c.c. The resulting blue solution had deposited small greenish-blue crystals after standing at room temperature for 24 hours (Found : loss on ignition, 23·66%).

Expt. D (*Theory, p.* 857). *Zinc, by Heintz's method.* (*a*) 3·4 G. of zinc chloride in 100 c.c. of water were added to a solution of 15 g. of diammonium hydrogen phosphate and 30 c.c. of ammonia (*d* 0·88) in 300 c.c. After standing at room temperature in an open vessel for 3 weeks, the microcrystalline deposit which had separated was analysed (Found : ZnO, 43·88; P_2O_5, 37·94; loss on ignition, 18·11. Calc. for 54·77% NH_4ZnPO_4 + 45·23% NH_4ZnPO_4,H_2O : ZnO, 43·74; P_2O_5, 38·14; loss 18·11%).

(*b*) As above, except that the mixture stood for 3 months to allow of complete volatilisation of the ammonia (Found : ZnO, 45·96; loss on ignition, 14·74. Calc. for NH_4ZnPO_4 : ZnO, 45·62; loss, 14·57%).

The ammonium zinc phosphate monohydrate first formed evidently decomposed on standing into the anhydrous compound; consequently the following attempt was made to prevent such decomposition by rapid removal of ammonia with hydrochloric acid.

(*c*) 3·4 G. of zinc chloride in 100 c.c. of water were added to 350 c.c. of solution containing 15 g. of diammonium phosphate and 25 c.c. of ammonia (*d* 0·88). Concentrated hydrochloric acid was slowly added from a burette with stirring until a permanent precipitate was formed in considerable amount.* The mixture then stood cold for 10 mins. (Found : ZnO, 42·02; P_2O_5, 36·50; NH_3, 8·61; loss on ignition, 21·92. Calc. for NH_4ZnPO_4,H_2O : ZnO, 41·44; P_2O_5, 36·15; NH_3, 8·65; loss, 22·40%).

The analysis shows the product to be mainly monohydrate. It decomposes into the anhydrous compound on standing in contact with its mother-liquor at either 20° or 100° [Found : (i) after 1½ months at room temperature, (ii) after 3 days on water-bath : loss on ignition, (i) 15·58, (ii) 15·19; ZnO, (i) 45·08, (ii) 45·55. Calc. for NH_4ZnPO_4 : loss, 14·57; ZnO, 45·63%].

Expt. E (*Theory, p.* 857). A solution containing 8·8 g. of $CoCl_2,6H_2O$ and 0·42 g. of zinc chloride in 100 c.c. of water was precipitated hot with a solution of 40 g. of diammonium hydrogen phosphate in 200 c.c. of water. After being kept hot for 5 days, the precipitate was entirely crystalline (Found : CoO, 33·22; ZnO, 6·39; P_2O_5, 37·22; loss on ignition, 23·20. Calc. for $5{\cdot}3NH_4CoPO_4,H_2O + 1{\cdot}0NH_4ZnPO_4,H_2O$: CoO, 33·37; ZnO, 6·39; P_2O_5, 37·18; loss, 23·04%).

Expt. F (*Theory, p.* 857). *Potassium Metal Phosphate Monohydrates,* $KMPO_4,H_2O$.—These compounds, when ignited over the Bunsen burner, suffered loss considerably in excess of that calculated on the assumption that they were monohydrates. In some cases they were nearly dehydrated in an air-oven before ignition, and the total loss was then approximately correct; it seemed probable, therefore, that partial hydrolysis occurred during direct ignition, with subsequent volatilisation of the potassium oxide liberated. This was confirmed by comparing an analysis of the ignited product with that of the original substance. Potassium cobalt phosphate monohydrate was ignited : 0·2992 g. gave 0·2698 g. of residue, which was found to contain 37·35% phosphoric oxide. This corresponds to 33·69% phosphoric oxide in the original solid, which agrees with the value found directly for the solid before ignition, and also with theory for $KCoPO_4,H_2O$, showing that the high loss on ignition was not due to loss of phosphoric oxide.

A sample of the potassium nickel phosphate monohydrate after ignition, when the loss of weight was 9·46%, contained potassium oxide equivalent to 20·98% in the fresh compound, while a determination made on the compound which had not been ignited gave a value of 22·26%, in agreement with theory. This shows that the high losses on ignition are really due to loss of alkali.

The methods of preparation and analyses of the several compounds are shown below :

Magnesium. A solution of 6 g. of magnesium chloride hexahydrate in 50 c.c. of water was added to 300 c.c. of solution containing 30 g. of dipotassium hydrogen phosphate and 30 g. of potassium chloride. After 3 days at 60—70°, the *phosphate* had become crystalline (Found : K_2O, 26·59; MgO, 22·55; P_2O_5, 40·36; loss on ignition, 10·73. $KMgPO_4,H_2O$ requires K_2O, 26·69; MgO, 22·86; P_2O_5, 40·24; loss, 10·20%).

Manganese. 5 G. of $MnCl_2,4H_2O$ in 50 c.c. of water were added to 250 c.c. of solution containing 100 g. of dipotassium hydrogen phosphate. 2 G. of hydroxylamine hydrochloride

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* The p_H of the liquid was 8·5—9; it was still distinctly ammoniacal.

were added to prevent oxidation, and the mixture was kept at 60—70° for 15 hours (Found : K_2O, 22·73; MnO, 34·27; P_2O_5, 34·31; loss on ignition direct, 9·68; loss on partial dehydration in air-oven and then ignition, 8·77. $KMnPO_4,H_4O$ requires K_2O, 22·72; MnO, 34·29; P_2O_5, 34·29; loss, 8·69%).

Cobalt. (*a*) 3 G. of $CoCl_2,6H_2O$ in 50 c.c. of water were added to 200 c.c. of solution containing 100 g. of dipotassium hydrogen phosphate. The mixture stood at room temperature until the blue precipitate had become purple-pink and crystalline (at least 3 months) (Found : K_2O, 21·55; CoO, 35·57; P_2O_5, 33·74; loss on direct ignition, 9·82; loss on partial dehydration and then ignition, 8·56. $KCoPO_4,H_2O$ requires K_2O, 22·31; CoO, 35·53; P_2O_5, 33·64; loss, 8·53%).

(*b*) A similar cobalt chloride solution was added to 600 c.c. of solution containing 300 g. of dipotassium hydrogen phosphate. The *monohydrate* is quickly deposited in the crystalline condition at room temperature from the blue solution so obtained (Found : CoO, 35·72; P_2O_5, 33·53; loss, 10·14%).

Nickel. 3 G. of the hydrated chloride in 50 c.c. of water were added to 250 c.c. of solution containing 20 g. of dipotassium hydrogen phosphate and 20 g. of potassium chloride; after 2 days at 60—70° the precipitate had become crystalline (Found : K_2O, 22·26; NiO, 35·10; P_2O_5, 33·85; loss on direct ignition, 9·46; loss on ignition after partial dehydration, 9·26. $KNiPO_4,H_2O$ requires K_2O, 22·34; NiO, 35·44; P_2O_5, 33·69; loss, 8·54%).

Copper. 4 G. of the chloride dihydrate in 50 c.c. of water were added to 300 c.c. of solution containing 200 g. of dipotassium hydrogen phosphate. After 4 days at 60—70° the precipitate was entirely crystalline (Found : K_2O, 21·65; CuO, 36·97; P_2O_5, 32·83; loss on ignition, 8·39. $KCuPO_4,H_2O$ requires K_2O, 21·83; CuO, 36·91; P_2O_5, 32·92; loss, 8·35%).

This *compound* is pale blue; the residue after ignition is pale green.

Cadmium. 4 G. of cadmium chloride in 50 c.c. of water were added to 350 c.c. of solution containing 250 g. of dipotassium hydrogen phosphate. After 1 day at 60—70° the precipitate was entirely crystalline (Found : K_2O, 17·59; CdO, 48·69; P_2O_5, 27·04; loss on ignition, 6·62. $KCdPO_4,H_2O$ requires K_2O, 17·80; CdO, 48·55; P_2O_5, 26·84; loss, 6·81%).

Zinc. Potassium zinc phosphate monohydrate could not be prepared. Attempts under the conditions utilised in the preceding cases resulted in the formation of either the anhydrous salt or an amorphous precipitate. Precipitation in the cold gave either the anhydrous phosphate or, when small quantities of dipotassium phosphate in large dilution (2 litres) were used, the tetrahydrate of trizinc phosphate.

The potassium metal phosphate monohydrates all form thin, more or less rectangular, plate-like crystals, which scintillate exactly like the corresponding ammonium compounds with which they are almost certainly isomorphous.

Expt. G (*Theory, p.* 858). *Potassium Metal Phosphate Hexahydrates,* $KMPO_4,6H_2O$.—*Magnesium and nickel.* These two compounds can readily be prepared by the addition, at room temperature, of a solution of 40 g. of dipotassium hydrogen phosphate in 100 c.c. of water to one containing 3 g. of the appropriate hydrated chloride in 200—300 c.c. After standing for about 10 days at room temperature, the precipitate becomes completely crystalline. The magnesium compound (Found : K_2O, 16·90; MgO, 15·13; P_2O_5, 26·78; loss on ignition, 41·30. Calc. for $KMgPO_4,6H_2O$: K_2O, 17·68; MgO, 15·13; P_2O_5, 26·65; loss, 40·53%) formed fair-sized prisms, showing some geniculate twins, while the *nickel* compound (Found : K_2O, 15·39; NiO, 24·77; P_2O_5, 23·80; loss on ignition, 36·24. $KNiPO_4,6H_2O$ requires K_2O, 15·66; NiO, 24·84; P_2O_5, 23·61; loss, 35·91%) was obtained as aggregates of large prismatic crystals of indefinite shape.

When the above method was applied to manganese, potassium manganese phosphate monohydrate was obtained; with cobalt and copper, the original amorphous precipitates persisted indefinitely, and zinc gave an amorphous precipitate which sometimes changed into the crystalline anhydrous potassium zinc phosphate. Cadmium yielded complex crystalline products which are discussed in Part III (p. 881).

Expt. H (*Theory, p.* 858). *Anhydrous Ammonium Cobalt Phosphate.*—A solution of cobalt chloride on the addition of diammonium hydrogen phosphate gives a bulky pale pinkish or bluish amorphous precipitate changing slowly on gentle warming into a dense compound of a royal-blue colour, which is then readily converted into ammonium cobalt phosphate monohydrate. This second change appears to occur more readily than the first, which makes it almost impossible to isolate the dark blue compound in a pure state. The first change cannot be completed before the second has begun if one uses more than about 0·5 g. of hydrated cobalt chloride, and half this amount is better. The best conditions for the isolation of the dark blue compound depend upon two factors: (1) only a small amount of diammonium hydrogen phosphate, not more than twice the calculated quantity, should be used, a large excess tending to promote the formation of the monohydrate; (2) excess of ammonium chloride exercises a stabilising influence on the blue compound.

Many unsuccessful attempts were made to isolate the compound in a pure condition under these conditions. On the rare occasions when a comparatively pure specimen was obtained, it decomposed on washing with hot water; washing with hot 5% ammonium nitrate solution (to supply the stabilising ammonium ion), followed by hot absolute alcohol, was tried, but failed.

One of the most successful attempts was made as follows : 25 C.c. of solution containing 0·21 g. of hydrated cobalt chloride and 1 c.c. of *N*-hydrochloric acid were precipitated with 1·5 g. of diammonium hydrogen phosphate, dissolved in a small amount of hot water. When kept hot, the pale blue amorphous precipitate quickly became dark blue and was then rapidly filtered off, washed several times with hot water, and pressed between smooth-surfaced, rather hard filter-paper. (Considerable change into the thin plates of the monohydrate occurred during the treatment.) It was then placed in a weighed crucible and dried to constant weight, after which the loss on ignition was 19·4%. The preparation therefore contained almost exactly equal parts of hydrated and anhydrous ammonium cobalt phosphate. In spite of this, it showed strong glowing and shrinking—easily seen in daylight—on ignition over the Bunsen burner. It follows that the pure dark blue anhydrous phosphate must glow very strongly on ignition, since the monohydrate is almost non-glowing.

Expt. I (*Theory, p.* 858). *Solid Solutions in Ammonium Zinc Phosphate of the Corresponding Magnesium, Cobalt, and Cadmium Salts.*—These were all prepared by adding a solution containing 3·4 g. of zinc chloride and an appropriate amount of the chloride of the other metal in 100 c.c. of solution to one containing 15 g. of diammonium hydrogen phosphate in 200 c.c. of solution. The temperature of the solutions was 90—100°, and the total volume after admixture about 300 c.c. The precipitate was filtered off directly it had crystallised. With the cobalt mixtures a ZnO : CoO ratio of less than 5 : 1 was insufficient to prevent the visible formation of some ammonium cobalt phosphate monohydrate. In Table II, compositions (A) and (B) have been calculated on the assumption that the metal other than zinc was present as the anhydrous compound and as the monohydrate respectively.

TABLE III.

ZnO/MO (mols.) in solid analysed.		Composition, %.			ZnO/MO (mols.) in solid analysed.		Composition, %.		
		Found.	Calc. (A).	Calc. (B).			Found.	Calc. (A).	Calc. (B).
Magnesium.					Cadmium.				
3·5 : 1	Loss *	15·80	13·37	17·33	10 : 1 (approx.)†	Loss	14·46	14·24	15·00
5·23 : 1	MgO	3·74	3·77	—	11·38 : 1	CdO	5·77	5·71	—
	ZnO	39·66	39·77	—		ZnO	41·35	41·05	—
	P_2O_5	41·36	41·32	40·66		P_2O_5	39·09	38·97	38·67
	Loss	15·27	15·14	16·54		Loss	14·24	14·27	14·95
Cobalt.					Manganese.				
4·94 : 1	CoO	7·14	7·12	—	10 : 1	Loss	14·99	14·69	15·46
	ZnO	38·30	38·17	—	Copper.				
	P_2O_5	40·10	40·06	39·38	10 : 1	Loss	14·79	14·59	15·36
	Loss	14·87	14·66	16·10	Nickel.				
					10 : 1	Loss	15·48	14·62	15·40

* Loss = loss on ignition, throughout.

† The precipitate was kept hot rather long.

Cobalt and magnesium form anhydrous ammonium phosphates fairly readily, cadmium with some difficulty, manganese, copper, and nickel not at all.*

Expt. J (*Theory, p.* 858).—When ammonium cobalt phosphate monohydrate was heated to 130—140°, rapid decomposition occurred with a loss of about 14%. At the point where a total loss of weight of about 14·5% had occurred, the solid remaining had a composition which approximated to that required for loss of all the water of crystallisation and half the ammonia; *e.g.*, in one experiment at 130°, after a loss of weight of 14·68% had occurred, the residue contained 5·56% of ammonia, while the figures calculated on the above basis would be : loss of weight, 13·94; NH_3 in residue, 5·20%. Beyond this point the rate of loss of weight became

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* This explains the absence of a brown stage (NH_4NiPO_4) in the precipitation of nickel as NH_4NiPO_4,H_2O with diammonium hydrogen phosphate.

much slower and only ceased after many days, when all ammonia had been lost and a composition corresponding to $CoHPO_4$ reached. The time required for this at 130° was not determined, but 24 days were required at 180° (Found : loss on ignition of residue, 5·83. Calc. for $CoHPO_4$: 5·81%).

Ammonium cobalt phosphate monohydrate was also heated in concentrated ammonium nitrate solution to temperatures ranging from 200° to 240° to see if the large excess of ammonium ion would stabilise the anhydrous ammonium cobalt phosphate, but if the monohydrate was heated for only 1 hour, decomposition was incomplete, while heating for 3 hours caused almost complete conversion into cobalt hydrogen phosphate.

Expt. K (*Theory, p.* 858). *Anhydrous Potassium Metal Phosphates. Preparation of Cobalt and Zinc Salts.*—20 C.c. of a solution containing 0·7 g. of the metal chloride were added to a solution of 14 g. of dipotassium hydrogen phosphate in 40 c.c. of water, and the mixture was kept hot (over a small flame) for 1—2 hours until the precipitate had become dense and crystalline. A few pink crystals of normal cobalt phosphate octahydrate were visible in the cobalt preparation (Found : CoO, 39·28; K_2O, 22·47; P_2O_5, 36·39; loss on ignition, 1·47. Calc. for $KCoPO_4$: CoO, 38·86; K_2O, 24·35; P_2O_5, 36·77%), and account for the loss of water on ignition. The zinc preparation probably contained a little unchanged amorphous material (Found : ZnO, 40·86; K_2O, 21·67; P_2O_5, 35·41; loss on ignition, 1·68. Calc. for $KZnPO_4$: ZnO, 40·78; K_2O, 23·61; P_2O_5, 35·60%).

The compounds both appear as aggregates of small prisms. The cobalt compound has a royal-blue colour, is not easily hydrated, and is much more stable than the corresponding ammonium compound. Its formation with dipotassium hydrogen phosphate would justify the assumption, even if other evidence were lacking, that the dark blue compound similarly produced with the diammonium salt should be formulated as NH_4CoPO_4.

The other anhydrous potassium metal phosphates were obtained (in slightly impure condition owing to loss of potassium oxide) by ignition of the corresponding hexa- or mono-hydrates.

Expt. L (*Theory, p.* 858).—Addition of cobalt chloride solution to a concentrated solution of dipotassium hydrogen phosphate (1 g. in 2 c.c. of water) produced a deep blue liquid. The mixture was kept at 70° for a short time after the addition of sufficient cobalt chloride solution to cause some anhydrous potassium cobalt phosphate to separate. This was removed, leaving a fine blue solution. A U-tube, immersed in cold water, similar to that described by Donnan and Bassett (*loc. cit.*), contained the heavier blue solution, prepared as described, in the lower part, and the lighter colourless dipotassium hydrogen phosphate solution above. The boundaries were quite well defined and could be easily marked. The distance between the electrodes was about 28 cm., and the *P.D.* across them was 33 volts. The boundary of the blue layer had moved 1·4 cm. towards the anode in 4 hours. The blue solutions obtained with copper and diammonium and dipotassium hydrogen phosphates gave similar results. Nickel gave a greenish-yellow colour with dipotassium hydrogen phosphate, somewhat similar to that obtained from the chloride and concentrated hydrochloric acid, which also travelled towards the anode. The colour produced was probably due to the presence of green nickel kations and brown anions. Cobalt and nickel did not give solutions with diammonium hydrogen phosphate of sufficient stability for use in this manner.

The results justify the ascription of these various colours to complex anions containing the bivalent metals.

Expt. M (*Theory, p.* 859). *Preparation of Compounds,* $MHPO_4,xH_2O$.—A solution containing 1 mol. of pyridine and 0·5 mol. of phosphoric acid per litre was prepared and used as precipitating agent, sometimes supplemented by additional pyridine. Crystallisation of the precipitates took 3—16 days at room temperature, coarsely crystallised products being then obtained. The p_H of most of the pyridine mixtures from which compounds were obtained was about 5. In the following four cases 12 g. of the hydrated metal chloride dissolved in a small amount of water were added to 420 c.c. of the pyridine–phosphoric acid solution. In the preparation of the magnesium compound ($x = 7$) an additional 100 c.c. of pure pyridine were added, and in that of the corresponding trihydrate an additional 50 c.c., and water to a total volume of 1200 c.c.

In the preparation of the manganese compound ($x = 3$), 10 g. of hydroxylamine hydrochloride were added to prevent oxidation. The magnesium compound ($x = 3$) was obtained after 2 days' digestion in the water-bath of the mixture in a loosely stoppered bottle; the other three compounds were obtained at room temperature.

The *cobalt* preparations were not quite pure. The presence of a small amount of $Co_3(PO_4)_2,8H_2O$ is indicated in Prepn. I, and Prepn. II might contain some

Compound and appearance.		Composition, %.		
		MO.	P_2O_5.	Loss on ignition.
$MgHPO_4,7H_2O$. Long prisms.	Found	17·04	—	54·66
	Calc.	16·39	—	54·79
$MgHPO_4,3H_2O$. Large diamond-shaped rhombs.	Found	22·98	40·82	35·62
	Calc.	23·17	40·72	36·12
$MnHPO_4,3H_2O$. Very fine, large, flesh-coloured prisms, truncated to give six-sided plates.	Found	34·79	34·82	30·72
	Calc.	34·63	34·63	30·73
$CoHPO_4,2H_2O$. Aggregates of small purple-red plates.	Found Prepn. I	40·06	36·48	23·55
	„ II	40·86	37·59	22·18
	Calc.	39·27	37·18	23·56

$2CoHPO,Co_3(PO_4)_2,4H_2O$, which has not itself been obtained, though the corresponding manganese and cadmium compounds have.

No hydrogen phosphates of nickel, copper, zinc, or cadmium could be obtained by the pyridine method. Nickel gave no precipitate at room temperature, and the hot solution gave the normal phosphate; copper gave on heating a basic phosphate. Zinc gave, both hot and at room temperature, $Zn_3(PO_4)_2,4H_2O$, while cadmium gave, either hot or cold, $2CdHPO_4,Cd_3(PO_4)_2,4H_2O$.

Copper. This monohydrated *compound* was obtained by crystallisation from phosphoric acid solution. 62 G. of copper carbonate (found by ignition to be equivalent to 42 g. of oxide) were added to 135 g. of phosphoric acid (*d* 1·75) dissolved in 200 c.c. of water. The resulting mixture was well stirred until evolution of carbon dioxide ceased, and heated for 3 days. The compound formed rosettes of prisms (Found : CuO, 44·80; P_2O_5, 40·20; loss on ignition, 15·41. $CuHPO_4,H_2O$ requires CuO, 44·82; P_2O_5, 39·98; loss, 15·20%); its colour is saxe-blue. Although it has not been described before, yet the corresponding arsenate has (Debray, *Compt. rend.*, 1861, **52**, 44; *Ann. Chim. Phys.*, 1861, **61**, 419).

Cadmium. This compound could not be prepared from phosphoric acid solution. 73 G. of cadmium phosphate (B.D.H., precipitated) were dissolved in 135 g. of hot phosphoric acid (*d* 1·75). The mixture was diluted to 500 c.c. and kept on the water-bath for 24 hours. Although the p_H of the solution was less than 3, the compound produced was $2CdHPO_4,Cd_3(PO_4)_2,4H_2O$ (see Part III). The crystals obtained from more highly acid solutions were hydrolysed to this compound if washed with water, so they were washed with phosphoric acid (1 part of acid, *d* 1·75, to 2 parts of water), the excess of which was then removed by means of acetone. Analysis of the compound so prepared showed it to be essentially $CdH_4(PO_4)_2,2H_2O$ (cf. de Schulten, *Bull. Soc. chim.*, 1889, **1**, 472).

The stability of dicadmium phosphate is small and only to be determined by phase-rule methods, which lay outside the scope of the present investigation.

Expt. N (*Theory, p.* 859).—The electric furnace was heated to the temperatures stated and known weights of $NH_4MgPO_4,6H_2O$ (loss on thorough ignition, 55·21%) were heated for definite periods.

Temp. of furnace.	Period of heating at this temp., hrs.	Loss of wt. of phosphate, %.
510°	4	54·06
550	4	54·62
570	6—8	54·49
570	½	54·36
580	1½	54·47

All the above preparations glowed on subsequent ignition.

Temp. of furnace.	Period of heating at this temp., hrs.	Loss of wt. of phosphate, %.
600—620°	2—2½	55·22
660—670	4—5	55·22

Neither of these two preparations glowed on ignition.

It was concluded from these results that it was not possible to drive off the water completely and obtain a product which would still glow on ignition. All the preparations of unglowed magnesium pyrophosphate used for density determinations and for thermochemical measurements (see below) were obtained by placing the above phosphate in the electric furnace previously heated to 580° and maintaining it at that temperature for ½—1 hour. Slight polymerisation may have occurred even under these conditions. The small amount (about 0·7%) of residual water introduces an uncertainty in the density and thermochemical determinations for which it is impossible to make any allowance.

Expt. O (*Theory, p.* 859). *Density Determinations of Magnesium Pyrophosphate.*—These were made with about 1 g. of solid in a 10-c.c. specific-gravity bottle. The liquid used was alcohol, as it was found that the non-glowed pyrophosphate was attacked somewhat by water during the boiling necessary to expel air.

The densities of three different types of pyrophosphate were determined : (*a*) " unglowed " pyrophosphate from $NH_4MgPO_4,6H_2O$; (*b*) " glowed " pyrophosphate from $NH_4MgPO_4,6H_2O$; (*c*) pyrophosphate from NH_4MgPO_4,H_2O.

Pyrophosphate.	Density found.
(*a*)	2·572; 2·529; 2·572; mean 2·558
(*b*)	3·038; 3·036; mean 3·037
(*c*)	3·006; 3·005; mean 3·006

Each density determination was made on a separately prepared sample.

Expt. P (*p.* 859). *Heat of Solution of Pyrophosphates.*—The rise of temperature produced by solution of a known amount of pyrophosphate in 50 c.c. of concentrated hydrochloric acid was measured, a Dewar flask being used as calorimeter. The " glowed " pyrophosphates only dissolve with difficulty, and for this reason the experiments were performed at 70°. Even then ½ hour was required for solution of the " glowed " magnesium and nickel compounds, though the " unglowed " pyrophosphates dissolved readily.

TABLE IV.

Series I. *Water equivalent of apparatus,* 46 *calories.*

Phosphate used.	Rise of temp. per g. of solid, and average.		Diff. between " glowed " and " unglowed " phosphate.	Sp. heat of " glowed " phosphate.	Calc. rise of temp. when " glowing " occurs.*	Heat evolution (cals.) due to 2 g.-mols. $M_2P_2O_7$ polymerising.
" Unglowed " $Mg_2P_2O_7$, from hexahydrate.	2·98° 2·90 2·95 2·97	2·95°		——	—	—
" Glowed " $(Mg_2P_2O_7)_2$, from hexahydrate.	1·98 †1·97	1·99	—	—	—	—
	2·31 ‡2·26	2·29	0·66°	0·30	101°	13,520
$(Mg_2P_2O_7)_2$, from monohydrate.	1·92 †2·00	1·96	—	—	—	—
	2·36 ‡2·30	2·33	0·62	—	—	—

Series II. *Water equivalent of apparatus,* 45·5 *calories.*

Phosphate used.	Rise of temp. per g. of solid, and average.		Diff. between " glowed " and " unglowed " phosphate.	Sp. heat of " glowed " phosphate.	Calc. rise of temp. when " glowing " occurs.*	Heat evolution (cals.) due to 2 g.-mols. $M_2P_2O_7$ polymerising.
" Unglowed " $Co_2P_2O_7$, from hexahydrate.	1·37 1·28 1·35	1·33	—	—	—	—
" Glowed " $(Co_2P_2O_7)_2$, from hexahydrate.	0·56 0·52	0·54	0·79	0·24	150	20·990
$(Co_2P_2O_7)_2$, from monohydrate.	0·55 0·56	0·56	0·77	—	—	—
" Unglowed " $Ni_2P_2O_7$, from hexahydrate.	2·40 2·42 2·46	2·43	—	—	—	—
" Glowed " $(Ni_2P_2O_7)_2$, from hexahydrate.	1·06	1·06	1·37	0·27	231	36,330
$(Ni_2P_2O_7)_2$, from monohydrate.	1·03 1·00	1·02	1·41	—	238	—

$$* \text{ Rise in temperature} = \frac{(\text{Diff. between `` glowed '' and `` unglowed ''}) \text{ (water equivalent)}}{\text{Sp. heat of `` glowed '' phosphate.}}$$

† Added phosphate at 20°.

‡ ,, ,, ,, 70°.

In Series II the specific heats of the "glowed" phosphates were determined by adding 2 g. at the ordinary temperature to 50 c.c. of water at 70°. In Series I they were obtained by making two measurements of the heat of solution, in one of which phosphate at 20° was added to acid at 70°, while in the other the phosphate as well as the acid had been heated to 70°.

The "glowed" $(Ni_2P_2O_7)_2$ was prepared by gradually heating the hexahydrated ammonium nickel phosphate to 700° and keeping it at that temperature for 12 hours. If heated more strongly, it dissolved too slowly. All the other polymerised pyrophosphates were obtained by heating over a Bunsen burner, followed by short ignition over the blowpipe. Unglowed magnesium and nickel pyrophosphates were prepared as in Expt. N. Since cobalt pyrophosphate polymerises at a comparatively low temperature (470°), a temperature not exceeding 430° must be used.

Owing to the difficulty in removing all water without causing some polymerisation, the heat liberated on solution of the "unglowed" pyrophosphates will be lower than the correct values and will give a low value for the heats of polymerisation.

Expt. Q (*Theory, p.* 860).—Magnesium pyrophosphate was prepared by mixing solutions of sodium pyrophosphate and magnesium chloride. The gelatinous precipitate, after being washed successively with water, alcohol, and ether, was not free from sodium [Found: MgO, 23·44; P_2O_5, 43·35; loss on ignition, 30·10; Na_2O (by diff.), 3·11. $MgO/P_2O_5 = 1{\cdot}9$]. It glowed on ignition, and the intensity of the glow did not alter whether the sodium pyrophosphate used had been prepared at 300° or at 800°.

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[*Received, March 14th,* 1932.]