211. Studies of Phosphates. Part II. Orthophosphates of the Type $M_3(PO_4)_2,xH_2O$.

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In the course of the experiments on ammonium magnesium phosphate (preceding paper) some normal phosphates of the above type were obtained. Since these compounds unexpectedly showed the phenomenon of " glowing " when ignited, we have prepared and examined a number of them (Expt. A). They are by no means easy to obtain in a satisfactory crystalline condition, owing partly to their insolubility, coupled with the slowness with which crystallisation occurs, and partly to the numerous other compounds which may result from small alterations in experimental procedure. Few are recorded in the literature.

We have prepared $Mg_3(PO_4)_2,22H_2O$; $Mg_3(PO_4)_2,8H_2O$; $Co_3(PO_4)_2,8H_2O$; $Co_3(PO_4)_2,4H_2O$; $Ni_3(PO_4)_2,8H_2O$; $Zn_3(PO_4)_2,4H_2O$. All glow on ignition, with the exception of the zinc compound. The octahydrates of the cobalt and nickel phosphates are red and green respectively, indicating that all the metal is kationic, while the cobalt phosphate tetrahydrate is pale blue. The bearing of these facts on possible structures of the compounds is discussed later (p. 873). The more highly hydrated magnesium salt was prepared and analysed by Stein and Tollens (*Annalen*, 1877, **187**, 79), and the conditions necessary for its formation have been re-examined recently by Zinzadzé (*Compt. rend.*, 1932, **194**, 1498). At ordinary temperatures, it is unstable with respect to the octahydrate, as shown by de Schulten (*Bull. Soc. min.*, 1903, **26**, 81), though it may remain for long periods without change, especially when dry.

The octahydrate occurs naturally as the mineral " bobierrite," and was prepared artificially by de Schulten (*loc. cit.*). The supposed heptahydrate of Schaffner (*Annalen*, 1844, **50**, 145) was almost certainly the octahydrate.

De Schulten (*Bull. Soc. min.*, 1904, **27**, 100) could not obtain the octahydrated zinc compound, the tetrahydrate (mineral " hopeite ") always resulting. Mellor's statement (" Comprehensive Treatise, etc.," IV, 658) that the octahydrate was obtained is erroneous. We have also failed to obtain it. The tetrahydrate was prepared by Debray (*Ann. Chim. Phys.*, 1861, **61**, 419) and Heintz (*Annalen*, 1867, **143**, 356); it was probably Skey's " pentahydrate " (*Chem. News*, 1870, **22**, 61).

It is doubtful whether the *cobalt* octahydrate has hitherto been prepared in such good crystalline form as ours, if at all; Ephraim and Rossetti (*Helv. Chim. Acta*, 1929, **12**, 1025) describe it, but give no details or analysis. They obtained the analogous nickel compound, but our method gives a better product.

We have not succeeded in preparing well-crystallised normal phosphates of manganese, copper, or cadmium. The compounds prepared by Heintz (*Pogg. Ann.*, 1848, **74**, 449), Erlenmeyer and Heinrich (*Annalen*, 1877, **190**, 191), and by Ephraim and Rossetti (*loc. cit.*) are in all probability somewhat impure octahydrated manganese phosphate. The last authors did not analyse their preparation, as they considered it to be an already well-known compound. Debray (*loc. cit.*; *Compt. rend.*, 1861, **52**, 44) claimed to have prepared copper phosphate octahydrate, but Ephraim and Rossetti (*loc. cit.*) were unable to obtain a normal cupric phosphate, and a tricadmium phosphate has never been described.

Basic Copper Phosphate.—The basic copper phosphate, $Cu_4P_2O_9$, has been obtained as a 1·2 and a 1·6 hydrate (Expt. B) under conditions which it was hoped would yield the normal phosphate. The first is well crystallised and the second microcrystalline. Both appear to be definite *compounds*; they are green but of distinct shades. The monohydrate, crystallising in octahedra, occurs as the mineral libéthenite and has been prepared by Debray (*loc. cit.*), and the compound $Cu_4P_2O_9,1{\cdot}5H_2O$, described by Ephraim and Rossetti (*loc. cit.*) as a greenish-white microcrystalline (" little rods ") powder, may have been the same as our $Cu_4P_2O_9,1{\cdot}6H_2O$.

These basic phosphates are clearly very complex, but we think there are several distinct compounds rather than solid solutions as suggested by Mellor (*op. cit.*, III, 288, 289). The production of such basic phosphates of copper is in conformity with the known tendency of this metal.

The Original Amorphous Precipitates.—The amorphous precipitate first obtained on addition of a soluble phosphate to solutions of salts of the bivalent metals dealt with in the present paper are generally supposed to consist of the normal phosphates, $M_3(PO_4)_2,xH_2O$, although the final crystalline precipitate may be of the type NH_4MPO_4,xH_2O (cf. Expt. C). Crystallisation of the precipitates begins soon after their formation, so that it is certain that the products actually analysed had already undergone some change. In view of this fact, it is probable that the precipitates initially obtained with magnesium, manganese, cobalt, nickel, zinc, and cadmium were the normal phosphates of these metals.

The fact that the first amorphous precipitate obtained in the operations is essentially of the type $M_3(PO_4)_2,xH_2O$ is of some practical importance in connexion with estimations of phosphoric acid or of metals which are based upon precipitation of compounds of the type NH_4MPO_4,xH_2O.

With the magnesium compounds the change to the ammonium type occurs with or without excess of phosphate, and for this reason, precipitation of ammonium magnesium phosphate works equally well for the estimation of either magnesium or phosphoric acid. This is not the case with manganese, cobalt, zinc, or cadmium. In the estimation of these metals after precipitation as NH_4MPO_4,xH_2O ($x = 0$, with zinc) crystallisation is facilitated by using a considerable excess of diammonium hydrogen phosphate. A small excess of the latter and much ammonium chloride serves equally well and is preferable in some ways, since excess of ammonium phosphate is not always easy to remove by washing. If there is an excess, not of phosphate, but of metal, then it is very difficult to get these heavy-metal phosphates to crystallise, but it can be done if sufficient ammonium chloride is used. Ishibashi (*Mem. Coll. Sci. Kyoto, A*, 1929, **12**, 23) has worked out methods for estimating phosphoric acid as ammonium manganese or zinc phosphate, but the original amorphous precipitates will not become crystalline unless the ratios NH_4Cl/MCl_2 in the solutions are at least 75 and 50, respectively, whereas for precipitation as ammonium magnesium phosphate it need not be greater than 7.

The heat evolution of the normal phosphates on " glowing " was determined by the same method as employed for the pyrophosphates in Part I: per g.-mol. of $M_3(PO_4)_2$, it was very similar to that liberated per g.-mol. of the corresponding $M_2P_2O_7$ (Expt. D).

Structures of Phosphates of the Type $M_3(PO_4)_2$.—It is clear from the general similarity with respect to glowing which exists between the orthophosphates and the pyrophosphates that the structures of both " glowed " and " unglowed " orthophosphates must be intimately related to those of the corresponding pyrophosphates.

Instead of the glowed orthophosphates of cobalt and nickel having the non-ionic colours of the pyrophosphates, they are respectively purple-red, and greenish-yellow, rather like $(NH_4MPO_4,H_2O)_4$, which indicates that the bivalent metal is partly kationic and partly anionic. The unglowed anhydrous orthophosphates of the same two metals are similarly much too blue and brown to have a purely non-ionic structure according to our views. The colours are, in fact, more like those of compounds containing only anionic cobalt or nickel, but definitely more purple and green respectively, as is seen readily on comparison with the royal-blue and brown preparations of $(KCoPO_4)_4$ and $(KNiPO_4)_4$, obtained by dehydration of the hexa- or mono-hydrates.

Our explanation of these facts is that the unglowed orthophosphates have the structure $M^{\cdot\cdot}\left[PO_4 \overset{M}{\underset{M}{}} PO_4\right]''$, in which one M atom is kationic with zero covalency, the complex anion having a structure almost identical with that of the non-ionic $M_2P_2O_7$ (see Part I) except that two PO_4''' groups take the place of the $P_2O_7^{IV}$ group. On glowing, this compound passes into $M_2^{\cdot\cdot}\left[M \begin{matrix} PO_4\,M\,PO_4 \\ PO_4\,M\,PO_4 \end{matrix} M\right]^{IV}$, in which there are two $M^{\cdot\cdot}$ kations and one complex quadrivalent anion. This anion is related to the neutral molecule $(M_2P_2O_7)_2$ in precisely the same way as the anion $[M_2(PO_4)_2]''$ is related to the neutral $M_2P_2O_7$. On this basis the reason for the mixed colour of the polymerised orthophosphates is at once clear. It is not so clear, however, why the unglowed orthophosphates do not have the same obvious mixed colour. We can only suggest that, although the unco-ordinated $M^{\cdot\cdot}$ ion is red (cobalt) or green (nickel), its colouring power is weak compared to that of the same ions when hydrated, so that it is the much more intensely coloured anions which chiefly determine the colour of the unglowed orthophosphates. In the glowed orthophosphates, however, there are two kations for one anion, and the former are able to exert a marked effect on the colours of the compounds.

$Mg_3(PO_4)_2,22H_2O$ can be obtained in large crystals and shows in a striking way the effect of the size of particles on the character of the "glowing" which occurs on ignition. The glow of these large crystals is seen with difficulty in the dark, whereas the incandescence of the finely ground substance is visible in ordinary daylight. A similar relationship holds for the finely divided amorphous cobalt phosphate and its crystalline octahydrate.

The red and green colours of the octahydrated cobalt and nickel phosphates indicate that all the metal is kationic. The structure $[(H_2O)_2Co(H_2O)_2Co(H_2O)_2Co(H_2O)_2]^{VI}(PO_4''')_2$ enables all the metal atoms to have a co-ordination number of 4. Such linkage of metal atoms in polynuclear kations through water molecules has already been assumed by Bassett and Croucher (J., 1930, 1784). Direct experimental proof that it can occur has been obtained recently (Bassett and Sanderson, J., 1932, 1855). In the 22-hydrated magnesium compound we seem to have a somewhat similar structure in which the three magnesium atoms are 6-co-ordinated, the co-ordination being partly to double water molecules as so frequently appears to occur with magnesium.

Zinc phosphate tetrahydrate resembles the compounds $(NH_4MPO_4,H_2O)_4$ of Part I in crystalline form. It is obtained, as are they, in glittering rectangular plates, and in view of the marked tendency for the zinc phosphates to be of condensed types, we assign to it a structure in which the kation is the same as that present in the octahydrated trimetal phosphates, while the anion is that present in compounds of type $(NH_4MPO_4,H_2O)_4$. The cobalt tetrahydrate certainly belongs to an entirely different type, since it is a " glowing " form. Its crystalline form is unlike that of the zinc compound, and its pale bluish colour suggests that it is a non-ionic form.

There are several interesting points in connexion with the amorphous normal phosphates. It is sometimes considered that the water content of such products is entirely indefinite, but we cannot subscribe to that view in the present case, although we admit that adsorption and the presence of considerable amounts of secondary products in admixture cause the analytical figures to deviate considerably from those of pure compounds. When allowance is made for this, it is clear that the amorphous precipitates were essentially of the type

$M_3(PO_4)_2,xH_2O$, except for copper (see p. 872). The indications are also that the degree of hydration of the normal compounds is definite, but varies from case to case. For magnesium and cobalt it was very close to that of the known crystalline octahydrates, but for both manganese and nickel it was near to that required for a dodecahydrate. Such compounds of these metals are unknown in the crystalline condition. Other manganese preparations appeared to be mixtures of 6- and 7- or 6- and 8-hydrates. The zinc and cadmium precipitates appear to be tetrahydrates, corresponding to the known crystalline hydrate of the former. The case of cobalt is interesting. It might have been expected that the amorphous octahydrate would correspond to the crystalline octahydrate, *but it was the wrong colour.* This puzzled us greatly till we found that the dry powder, after being kept for about ten months in corked specimen tubes, had become pink—just like the crystalline octahydrate—and with very little change in its water content (Expt. C). We conclude from this that the pale blue amorphous octahydrate is a non-ionic isomeride of the pink octahydrate into which it slowly turns. This change sometimes appears to be quite rapid, and occasionally a pink amorphous tricobalt phosphate seems to be precipitated directly.

EXPERIMENTAL.

The analytical methods employed were the same as in Part I.

Expt. A (*Theory, p.* 871). *The Normal Phosphates,* $M_3(PO_4)_2,xH_2O$.—*Magnesium* ($x = 22$). This forms large rhombohedral plates. The method of preparation given in the literature is satisfactory.

Magnesium ($x = 8$). This hydrate is formed when the foregoing hydrate is left in contact with the mother-liquor. This change usually begins after about a fortnight and is complete in about 5 weeks. The octahydrate retains its water when heated to 100°. It formed small radial aggregates of minute prisms which seemed as though they would have had the diamond shape, characteristic of the other octahydrates, had they been formed under more favourable conditions [Found: after 3 weeks, H_2O, 40·26; after 5 weeks, MgO, 30·04; H_2O, 37·00. Calc. for $Mg_3(PO_4)_2,8H_2O$: MgO, 29·74; H_2O, 35·38%].

Cobalt ($x = 8$). This forms diamond-shaped crystals which are pink when small and red when large enough; it is stable at 100°. It was obtained by the following four methods, the last two giving larger crystals.

(*a*) 3 G. of cobalt chloride hexahydrate in 50 c.c. of water were added to 10 g. of dipotassium hydrogen phosphate dissolved in 400 c.c. of water; the mixture was heated until the precipitate became dark blue (5—10 minutes), and was then set aside over-night [Found: CoO, 44·38; P_2O_5, 27·53; H_2O, 28·18. $Co_3(PO_4)_2,8H_2O$ requires CoO, 44·03; P_2O_5, 27·79; H_2O, 28·08%]. If the heating is too prolonged, conversion of the dark blue crystals ($KCoPO_4$) into pink normal phosphate is slow and may take some days; the use of only 5 g. of dipotassium hydrogen phosphate avoids this.

(*b*) As in (*a*), but the potassium phosphate was replaced by 10 g. of crystallised disodium hydrogen phosphate.

(*c*) A similar cobalt solution was added to 50 g. of disodium hydrogen phosphate dissolved in 500 c.c. of water; the mixture stood at room temperature for six months with frequent shaking.

(*d*) 4·8 G. of cobalt chloride in solution were added to 3·6 g. of dipotassium hydrogen phosphate and 40 g. of potassium chloride dissolved in 2 litres of water; the mixture stood cold for a month with frequent shaking.

Attempts made to obtain the other normal phosphate octahydrates by the above methods were unsuccessful owing to the original amorphous precipitate failing to crystallise, except in the case of zinc, in which either anhydrous potassium zinc phosphate or normal zinc phosphate tetrahydrate was obtained.

Cobalt ($x = 4$). This compound was obtained as pale blue rosettes of thin prisms in the course of the experiments with pyridine (see Part I, Expt. M). The data of a second experiment (*b*) are given in parentheses. (*a*) 3·2 (12·0) G. of crystallised cobalt chloride dissolved in 150 (280) c.c. of water were added to 350 (420) c.c. of the pyridine–phosphoric acid mixture mentioned in Expt. M. Crystallisation of the precipitate was complete after 3 days' heating on the water-bath in each case [Found: (*a*) CoO, 51·58; P_2O_5, 33·08; H_2O, 15·74. (*b*) CoO, 51·63; P_2O_5, 33·16; H_2O, 15·47. Calc. for $Co_3(PO_4)_2,4H_2O$: CoO, 51·25; P_2O_5, 32·35; H_2O, 16·40%].

Nickel ($x = 8$). This was also obtained by the pyridine method in the form of fair-sized, green, diamond-shaped rhombs. Initially the solution was quite clear, the crystals only separating slowly as the pyridine evaporated. A mixture was prepared by adding a solution of 12 g. of nickel chloride hexahydrate in 580 c.c. of water to 420 c.c. of the pyridine–phosphoric acid mixture. Crystallisation of the precipitate was complete after 4 days' heating on the water-bath [Found : NiO, 43·25; P_2O_5, 27·73; H_2O, 28·68. Calc. for $Ni_3(PO_4)_2,8H_2O$: NiO, 43·92; P_2O_5, 27·84; H_2O, 28·28%].

The octahydrates glow under precisely similar conditions and to about the same degree as the corresponding $NH_4MPO_4,6H_2O$ compounds (Part I, Table I).

Zinc ($x = 4$). This was obtained by the pyridine method as large, thin, rectangular plates. The precipitate obtained by adding 290 c.c. of solution containing 3·4 g. of zinc chloride to 210 c.c. of the pyridine–phosphoric acid mixture became completely crystalline after 4 hours' heating on the water-bath. We append for comparison analyses of the same compound prepared by Graham's method (*loc. cit.*) (supposed to give $ZnHPO_4,H_2O$, see Part I, p. 859) and by de Schulten's method (*loc. cit.*) :

	ZnO, %.	P_2O_5, %.	H_2O, %.
Prepared by pyridine method	53·41	31·36	15·97
„ „ Graham's method	53·31	31·17	16·23
„ „ de Schulten's method	53·12	—	16·37
Calc. for $Zn_3(PO_4)_2,4H_2O$	53·30	30·99	15·71

Expt. B (*Theory p.* 872). *Basic Copper Phosphate*, $Cu_4P_2O_9,xH_2O$.—(1) $x = 1·2$. This *hydrate* was obtained as large rectangular prisms, bottle-green in colour, by the pyridine method. 12 G. of copper chloride dihydrate in 580 c.c. of water were added to 420 c.c. of the pyridine–phosphoric acid mixture, and after 3 days' heating on the water-bath the precipitate was completely crystalline (Found : CuO, 65·89; P_2O_5, 29·87; H_2O, 4·35. $Cu_4P_2O_9,1·2H_2O$ requires CuO, 66·06; P_2O_5, 29·46; H_2O, 4·48%).

(2) $x = 1·6$. Small aggregates of minute green crystals were obtained when a solution containing 7·2 g. of crystallised disodium hydrogen phosphate in 3·5 litres of water was added to one of 7·5 g. of copper sulphate crystals in 4 litres of water, and the mixed solutions kept for a month at room temperature (Found : CuO, 65·09; P_2O_5, 28·91; H_2O, 5·80. $Cu_4P_2O_9,1·6H_2O$ requires CuO, 65·09; P_2O_5, 29·03; H_2O, 5·89%). The colour of this *compound* is quite distinct from that of the foregoing hydrate—there is much less yellow mixed with the green. It is not a question of the size of the crystals, for when the large crystals of the first hydrate are ground, the difference still remains.

Expt. C (*Theory, p.* 872). *The Original Amorphous Precipitates.*—The precipitates were obtained in the cold by mixing solutions of the metal chloride with twice the amount of phosphate calculated for $M_3(PO_4)_2$. They were washed with water, followed by alcohol and ether, as in our standard procedure with crystalline preparations.

Magnesium. 12 G. of hydrated chloride in 400 c.c. of water were used with 400 c.c. of disodium hydrogen phosphate solution, since the precipitate crystallised too rapidly if ammonium phosphate was used (Found : MgO, 27·51; P_2O_5, 33·67; loss on ignition, 39·82%). MgO : P_2O_5 = 2·90 : 1. The composition approximates to that of $Mg_3(PO_4)_2,8H_2O$.

Manganese and copper. 6 G. of the hydrated chlorides dissolved in 400 c.c. of water were used, and an equal volume of diammonium hydrogen phosphate solution.

The analytical data for the manganese salt were :

	MnO, %.	P_2O_5, %.	Loss on ignition, %.	Mol. ratio, MnO/P_2O_5.
Found	34·46	23·78	41·72	2·90
„	44·94	30·15	24·74	2·98
„ (Na_2HPO_4 used)	44·03	29·74	25·91	2·96
Calc. for :				
$Mn_3(PO_4)_2,12H_2O$	37·27	24·88	37·85	—
$Mn_3(PO_4)_2,7H_2O$	44·29	29·53	26·20	—
$Mn_3(PO_4)_2,6H_2O$	46·00	30·67	23·32	—

The copper salt gives a molecular ratio CuO/P_2O_5 = 3·63 (Found : CuO, 53·45; P_2O_5, 26·30; loss, 20·62%; CuO : P_2O_5 = 3·63 : 1).

Cobalt. (*a*) 5 G. of crystallised chloride in 300 c.c. of water were mixed with 300 c.c. containing twice the calculated amount of diammonium hydrogen phosphate and 10 c.c. of 2*N*-hydrochloric acid [Found : CoO, 40·89; P_2O_5, 29·87; H_2O, 29·19. Calc. for $Co_3(PO_4)_2,8H_2O$: CoO, 44·03; P_2O_5, 27·79; H_2O, 28·18%]. (*b*) As for manganese, but disodium hydrogen phosphate was used (Found : CoO, 43·54; P_2O_5, 28·62; H_2O, 27·86%). All the precipitates were light blue. After 10 months in corked specimen tubes, preparations (*a*) and (*b*) had become pink and then contained 28·63 and 26·32% H_2O.

Nickel, zinc, and cadmium. If twice the calculated quantities of diammonium hydrogen phosphate were used, the precipitates crystallised so rapidly that the amorphous stage could not be isolated. If only two-thirds of the calculated amount were used, isolation was possible; otherwise the conditions of precipitation were much the same as in the case of manganese and copper. Analyses relate to the three metals respectively (M = Ni, Zn, or Cd).

MO	38·09	50·50	61·21
P_2O_5	25·73	30·30	24·11
Loss on ignition	36·25	19·62	15·44
MO/P_2O_5	2·82	2·91	2·81

A solution of 5 g. of cadmium chloride in 100 c.c. of water was mixed with one containing 55 g. of sodium phosphate dodecahydrate. The mixture (600 c.c.) was heated on the water-bath for one hour: the precipitate was then microcrystalline [Found: CdO, 68·96; P_2O_5, 25·51; loss on ignition, 4·19; Na_2O (by diff.), 1·34%; CdO/P_2O_5 = 2·99].

These figures disagree with de Schulten's statement (*Bull. Soc. chim.*, 1899, **1**, 472) that $2CdHPO_4,Cd_3(PO_4)_2,4H_2O$ resulted when a solution of disodium hydrogen phosphate was added to a hot solution of cadmium chloride or sulphate, but as he gives no details of the concentrations used, it was not possible to repeat his conditions.

Experiment D (*Theory, p.* 872).

Phosphate used.	Rise of temp. per g. solid and average.		Diff. between "glowed" & "unglowed" phosphate.	Sp. heat of "glowed" phosphate.	Calc. rise * of temp. when "glowing" occurs.	Heat evolution due to 2 g.-mols. $M_3(PO_4)_2$ polymerising (cals.).
"Unglowed" $Mg_3(PO_4)_2$	3·73° 3·78 3·79	3·77°				
"Glowed" $[Mg_3(PO_4)_2]_2$	3·27 3·29	3·28	0·49°	0·22	101°	11,730
"Unglowed" $Co_3(PO_4)_2$	1·40 1·40	1·40				
"Glowed" $[Co_3(PO_4)_2]_2$	0·95 1·01	0·98	0·42	0·22	87	14,030
"Unglowed" $Ni_3(PO_4)_2$	2·93 2·97	2·95				
"Glowed" $[Ni_3(PO_4)_2]_2$	1·54 1·47	1·50	1·45	0·25	264	48,310

* Rise in temperature = (Diff. between "glowed" and "unglowed") (Water equivalent)/(Specific heat of glowed phosphate). Water equivalent of apparatus, 45·5 calories. The "glowed" samples were obtained by heating over a Bunsen burner, followed by short ignition over the blowpipe.

Details of preparations.

Compound "unglowed."	Phosphate used for prepn.	Temp. and time of heating.	Loss of water, %, after heating.	Loss of water on ignition, % of original solid.
$Mg_3(PO_4)_2$	$Mg_3(PO_4)_2,22H_2O$	550° for 1½ hours	59·44	60·13
$Co_3(PO_4)_2$	$Co_3(PO_4)_2,8H_2O$	550° ,, ,,	28·40	28·63
$Ni_3(PO_4)_2$	$Ni_3(PO_4)_2,8H_2O$	560° ,, ,,	27·54	28·44

SUMMARY.

1. Improved methods are given for obtaining several orthophosphates of the type $M_3(PO_4)_2,xH_2O$ in a crystalline condition.
2. The nature of the amorphous precipitates which are first formed has been examined.
3. These compounds "glow" on ignition in the same way as do the pyrophosphates $M_2P_2O_7$ considered in Part I.
4. The heat evolution is closely similar in amount for the ortho- and the pyro-phosphate of the same metal.
5. Two new hydrates of $Cu_4P_2O_9$ have been obtained.
6. The glowing of the orthophosphates can be accounted for satisfactorily in a similar manner to that used for the pyrophosphates in Part I.

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