967. The Stability of Calcium Hydrogen Phosphate Precipitated from Solutions of Calcium Nitrate and Phosphoric Acid.

By D. H. Booth and R. V. Coates.

Calcium hydrogen phosphate dihydrate was precipitated from a solution of calcium nitrate and phosphoric acid by neutralization with 4 moles of ammonia per mole of P_2O_5. This dihydrate was converted into more basic phosphates if it was retained in contact with the solution and the pH was raised above 4 by further addition of ammonia. The rate of conversion was increased by an increase of temperature and the presence of fluoride ions in solution. When there were fluoride ions in solution the final product was always pentacalcium fluoride trisphosphate and the conversion rate was increased by the absence of Ca^{2+} ions in solution. When fluoride ions were absent, the final product varied from tetracalcium hydrogen trisphosphate through tricalcium bisphosphate hydrate to pentacalcium hydroxide trisphosphate, according to the other experimental conditions. The various water-insoluble calcium phosphates obtained were identified by *X*-ray powder diffraction and quantitative chemical analysis.

Table 1 below lists the names and formulæ of the water-insoluble calcium phosphates in order of increasing basicity. The abbreviations given will be used in Tables in the Experimental section.

Table 1.

Compound	Formula	Molar ratio, CaO : P_2O_5	Abbreviation
Calcium hydrogen phosphate dihydrate	$CaHPO_4,2H_2O$	2	CHPh
Calcium hydrogen phosphate	$CaHPO_4$	2	CHP
Tetracalcium hydrogen trisphosphate trihydrate	$Ca_4H(PO_4)_3,3H_2O$	$2\frac{2}{3}$	4CHPh
Tricalcium bisphosphate hydrate	$Ca_3(PO_4)_2,xH_2O$	3	3CPh
Pentacalcium hydroxide trisphosphate	$Ca_5(OH)(PO_4)_3$	$3\frac{1}{3}$	5C(OH)P
Pentacalcium fluoride trisphosphate	$Ca_5F(PO_4)_3$	$3\frac{1}{3}$	5CFP

The most basic calcium phosphate [$Ca_5X(PO_4)_3$; X = F or OH] is a definite crystalline compound of known structure (cf. *e.g.*, refs. 1—3), but the distinct existence of the slightly less basic compounds $Ca_4H(PO_4)_3,3H_2O$ and $Ca_3(PO_4)_2,xH_2O$ has often been queried, mere calcium deficiency in the " apatite " structure being proposed. However, although complete structural analyses for these two materials have not yet been made their lattice

---

[1] St. Naray-Szabo, *Z. Krist.*, 1930, **75**, 387.
[2] Mehmel, *Z. Krist.*, 1930, **75**, 323.
[3] Posner, Perloff, and Diorio, *Acta Cryst.*, 1958, **11**, 308.

types are known: that of $Ca_4H(PO_4)_3,3H_2O$ differs from that of apatite;[4] that of $Ca_3(PO_4)_2,xH_2O$ is isomorphous with apatite but discrete.[5] Moreover, our own studies confirm that the basicity of the calcium phosphates changes in discrete steps, and not smoothly once calcium hydrogen phosphate is passed.

The precipitation and stability of (water-insoluble) calcium hydrogen phosphate (dihydrate and anhydrous) from various water-soluble phosphates have been studied by several workers[6-9] as they are of considerable technical importance in the manufacture of some fertilizers. Results have, in general, been contradictory and conflicting, owing frequently to poor understanding and characterization of the reaction products. It can be seen from Table 1 that there are six possible water-insoluble products which may occur singly, or as several together.

Accordingly, the following experiments were made as an initial study in the precipitation of water-insoluble phosphates to determine the conditions under which the calcium hydrogen phosphates are precipitated and under which they are converted into the more basic calcium phosphates. In addition, the presence in the solution of fluoride ions was examined to find how they affected the production of the apatite phase, since in certain phosphate processes the formation of pentacalcium fluoride trisphosphate is undesirable as it represents a return to the original phosphate source.

The composition of precipitates was obtained by *X*-ray powder diffraction analysis, supplemented where necessary by chemical analysis of the products.

EXPERIMENTAL

A solution of calcium nitrate and phosphoric acid containing 1·11 moles of P_2O_5 per l. and having a CaO : P_2O_5 molar ratio of 3·4 was prepared. 10·0 ml. portions of this solution were added severally to 200, 1000, 2500, and 5000 ml. of water. The pH was measured, by using glass and calomel electrodes, as 5% ammonia solution was added in 1 ml. portions.

When the first equivalence point at pH 4·5 had been passed, a permanent precipitate appeared and the pH fell below 4·5. On the addition of further ammonia the pH increased, but it fell again after a minute's stirring to a value which remained steady. This effect continued until the second equivalence point was reached. After the second equivalence point had been passed the precipitate was filtered off and submitted to *X*-ray analysis (see Appendix).

Fig. 1 shows the pH–titration curves obtained, and Table 2 gives the composition of the precipitate obtained in this experiment.

Several experiments were carried out in which 300 ml. portions of the solution containing 1·11 moles of P_2O_5 per l. were neutralized with gaseous ammonia in a beaker equipped with a baffle and a powerful stirrer (agitation at 1000 r. p.m.). At intervals during the neutralization two samples were simultaneously withdrawn from the beaker; these were filtered, and the solids were washed with the minimum quantity of water. One solid was then washed with acetone, air-dried, and analysed by *X*-ray diffraction.

TABLE 2.

Titration of solutions containing $Ca(NO_3)_2$ and H_3PO_4 with NH_3 to second equivalence point.

Titrn. no.	Initial soln. (mole of P_2O_5 per l.)	*X*-Ray analysis of precipitate
1	0·0022	CHPh absent, 20% of 5C(OH)P, remainder 4CHPh or 3CPh
2	0·0045	As above, but with 65—70% of 5C(OH)P
3	0·0112	As above, but with 80% of 5C(OH)P
4	0·0558	Precipitate completely CHPh

The filtrate from the other sample was analysed for P_2O_5 and NH_3, and the pH of the

---

[4] Brown, Lehr, Smith, and Frazier, *J. Amer. Chem. Soc.*, 1957, **79**, 5318.

[5] Wallaeys and Montel, *Bull. Soc. chim. France*, 1959, 496.

[6] Montel, *Bull. Soc. chim. France*, 1953, 506.

[7] Brosheer and Lenfesty, *J. Agr. Food Chem.*, 1958, **6**, 827.

[8] Bassett, jun., *Z. anorg. Chem.*, 1907, **53**, 34, 49; 1908, **59**, 1.

[9] Kurmies, *Phosphorsaure*, 1953, **13**, 57.

solution was measured. Ammonia was determined by distillation into standard acid. The solid phase was dissolved in acid and the P_2O_5 content obtained by the vanadomolybdate colour method.

A " neutralization curve " was obtained from the results by plotting the reduction in

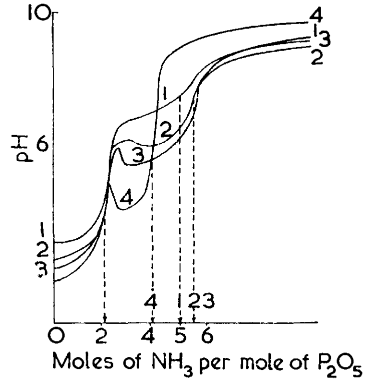


FIG. 1. Neutralization of dilute solutions of H_3PO_4 and $Ca(NO_3)_2$ with NH_3. P_2O_5 contents: (1) 0·0022, (2) 0·0045, (3) 0·0112, and (4) 0·0558 mole l.$^{-1}$.

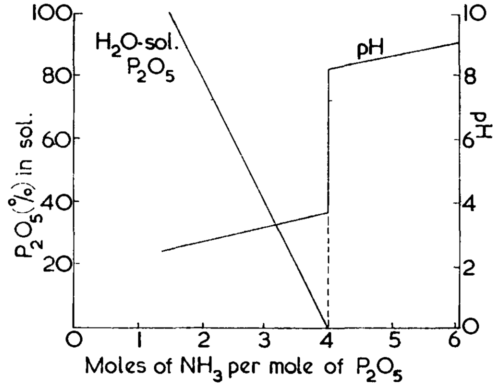


FIG. 2. Precipitation of $CaHPO_4,2H_2O$ by addition of NH_3. Rate of addition 0·01, 0·03, 0·05, or 0·06 mole/min. Temp., 26°, 70°, or 90°.

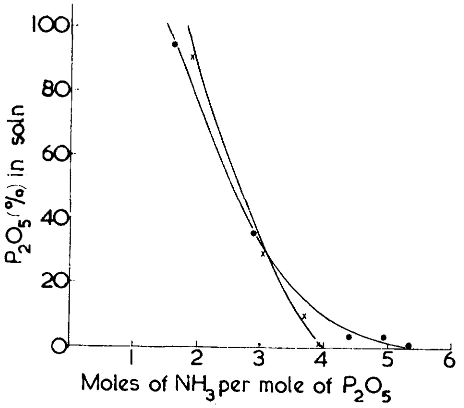


FIG. 3. Influence of fluoride ion on the precipitation of $CaHPO_4,2H_2O$ (cf. Fig. 2). Molar ratio CaO : P_2O_5 3·4 and F : P_2O_5 0·83. P_2O_5 content 1·11 moles l.$^{-1}$. × At 26°; ● at 70°.

P_2O_5 content of the solution against the moles of ammonia added per mole of P_2O_5; pH change was also plotted. The neutralizations were made at rates of 0·01, 0·03, 0·05, and 0·06 mole of NH_3 per min. and initial temperatures of 26°, 70°, and 90°. The curves obtained were all similar and are therefore given combined in Fig. 2.

If the precipitated $CaHPO_4,2H_2O$ was left overnight in the beaker before being submitted for X-ray analysis it was found to have been partially, or in some cases largely, converted into an apatite. Further experiments were therefore carried out by starting with precipitated $CaHPO_4,2H_2O$.

The salt $CaHPO_4,2H_2O$ (2 moles l.$^{-1}$) was added to a solution containing ammonium nitrate (4 moles l.$^{-1}$) and calcium nitrate (1·5 moles l.$^{-1}$), and the suspension was agitated. This system simulates the conditions existing at the completion of precipitation of $CaHPO_4,2H_2O$ from a $Ca(NO_3)_2$–H_3PO_4 solution containing an excess of calcium. The pH of the suspension was maintained at 8 by the addition of ammonia and samples were removed at intervals and analysed by X-ray diffraction after the usual washing and drying.

This experiment was carried out at 20° and 50°. The results are given in Table 3, which shows the relative amounts of $Ca_3(PO_4)_2,xH_2O$ and $Ca_5OH(PO_4)_3$, obtained.

TABLE 3.

The rate of conversion of $CaHPO_4,2H_2O$ into $Ca_5OH(PO_4)_3$ at pH 8; calcium ions present in solution.

At 20°				At 50°			
Time (hr.)	CHPh (%)	3CPh (%)	5C(OH)P (%)	Time (hr.)	CHPh (%)	3CPh (%)	5C(OH)P (%)
1	100	—	—	½	100	—	—
2	100	—	—	1	100	—	—
3	100	—	—	1½	80	←— 20 —→	
6	95	←— 5 —→		2	60—70	←— 30—40 —→	
22½	70	←— 30 —→		3	20	←— 80 —→	
24	40—45	←— 55—60 —→		4	5—10	←— 90—95 —→	
27	2—3	60—70	25—35	5	2—3	65—70	30—35
30	Trace	55—65	35—45	6	Nil	55—60	40—45
48	Nil	25—30	70—75	22½	Nil	10—15	85—90

The above two experiments were repeated but this time the solution phase did not contain calcium. The resulting rate of disappearance of $CaHPO_4,2H_2O$ is shown in Table 4.

TABLE 4.

The rate of conversion of $CaHPO_4,2H_2O$ into $Ca_4H(PO_4)_3,3H_2O$ at pH 8; calcium ions absent from solution at 50°.

Time (hr.)	⅓	1½	2¾	4	6
X-Ray analysis:					
CHPh (%)	98	60—65	15	0	0
4CHPh (%)	2—3	35—40	85	100	100

At 20°, change was very slow. After 30 hr., only 5% of 4CHPh was detected.

Experiments were carried out in which fluoride was added as potassium fluoride to the solution containing 1·11 moles of P_2O_5 per l., which was then neutralized as described above. Two neutralizations were carried out, at 20° and 70°, samples being taken at intervals for chemical and *X*-ray analyses. At 20° the " neutralization curve " and the *X*-ray analysis of precipitates showed apatite formation had not taken place up to the point of complete precipitation of $CaHPO_4,2H_2O$. At 70°, however, $Ca_5F(PO_4)_3$ was being formed in the final stages of precipitation. Fig. 3 shows the precipitation curves at 26° and 70°, for comparison with Fig. 2 where no fluoride was present. Analyses of the precipitates are given in Table 5.

From the *X*-ray and chemical analyses it was concluded that the apatite produced was completely $Ca_5F(PO_4)_3$, with no $Ca_5OH(PO_4)_3$ at any stage of the neutralization. The calcium was determined by EDTA titration, and fluorine by the method of Willard and Winter.[10]

The experiments starting with precipitated $CaHPO_4,2H_2O$ were repeated, this time with fluorine added to the solution phase. With calcium present in the solution phase, the rates of formation of $Ca_5F(PO_4)_3$ were obtained at 20° and 50°; the results are given in Table 6.

TABLE 5.

Neutralization at 70° with gaseous NH_3. Solution concentration 1·11 moles P_2O_5 per l.; mole ratios 3·4 for CaO : P_2O_5, 0·83 for F : P_2O_5.

Sample no.	Moles of NH_3 added per mole of P_2O_5	pH of H_2O-sol. part	*X*-Ray analysis of ppt.	Mole ratio: F : P_2O_5	Mole ratio: CaO : P_2O_5
1	1·3	2·3	—	—	—
2	2·9	2·7	—	—	—
3	4·4	3·95	CHP only	—	—
4	4·95	4·6	85—90% of 5CFP	0·63	3·2
5	5·31	6·6	95% of 5CFP	0·65	3·3
6	—	7·9	All 5CFP	0·64	3·2
7	6·09	8·4	All 5CFP	—	—

When calcium was absent from the solution, the rate of conversion of $CaHPO_4,2H_2O$ was greatly increased, as is shown in Table 7.

---

[10] Willard and Winter, *Ind. Eng. Chem. Anal.*, 1933, **5**, 7.

TABLE 6.

Rate of formation of $Ca_5F(PO_4)_3$. Solution pH 8. (Solution contains $Ca(NO_3)_2$ 1·5 moles, NH_4NO_3 4 moles, KF 0·25 mole, and $CaHPO_4,2H_2O$ 2 moles.)

At 20°					At 50°				
	X-Ray analysis of ppt.					*X*-Ray analysis of ppt.			
Time (hr.)	CHPh (%)	CHP (%)	5CFP (%)	CaF_2 (%)	Time (hr.)	CHPh (%)	CHP (%)	5CFP (%)	CaF_2 (%)
½	98	0	2	s.t.	20/60	100	0	t	s.t.
1	↓	0	↓	t	35/60	85—90	0	10—15	s.t.
1½		0		t	50/60	35—40	20	40—45	s.t.
2	96	0	4	t	1¼	5	5	90	t
3	5—10	0	90—95	0	2	2—3	0	97	t
4	5	0	95	0	3	0	0	100	t
5	3	0	97	0	6	0	0	100	t
6	0	0	100	0					
7	0	0	100	0					

t = trace. s.t. = slight trace.

TABLE 7.

Solution pH 8. Solution contains 4 moles of NH_4NO_3 and 0·025 mole of KF, at 20°.

	X-Ray analysis				*X*-Ray analysis		
Time (hr.)	CHPh (%)	5CFP (%)	CaF_2 (%)	Time (hr.)	CHPh (%)	5CFP (%)	CaF_2 (%)
1	98	2	0	4	0	100	Trace
2	60	40	0	5	0	100	Trace
3	10	90	0				

At 50° instantaneous conversion into $Ca_5F(PO_4)_3$ occurred.

To find the effect on the conversion of $CaHPO_4,2H_2O$ into $Ca_5F(PO_4)_3$ at lower pH when calcium is absent from the solution phase, solid $CaHPO_4,2H_2O$ was stirred in a solution of ammonium nitrate containing potassium fluoride at 50°. The pH of the solution had not been raised by addition of ammonia and was initially 6·5, falling to 5 as conversion proceeded. Even under these conditions formation of $Ca_5F(PO_4)_3$ was rapid, being almost complete within 10 min.

DISCUSSION

Table 8 summarises diagrammatically the results of the experiments discribed in the experimental section, showing the products existing under various conditions at different times.

As a solution of calcium nitrate and phosphoric acid is neutralized with ammonia solution, the pH–ammonia-addition curve shows a first equivalence point at 2 moles of NH_3 per mole of P_2O_5 and pH 4 (all curves Fig. 1), corresponding to the formation of calcium tetrahydrogen bisphosphate in solution:

$$Ca(NO_3)_2 + 2H_3PO_4 + 2NH_3 \longrightarrow Ca(H_2PO_4)_2 + 2NH_4NO_3$$

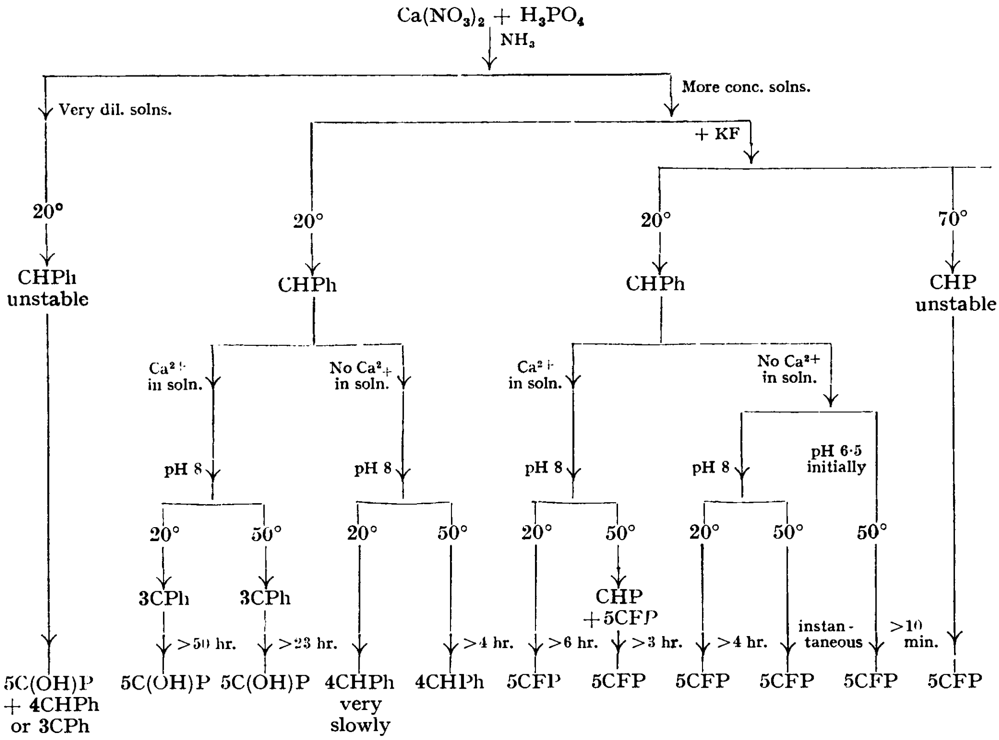
Curve 4 of Fig. 1 for the most concentrated solution in this first experiment shows a second equivalence point at 4 moles of NH_3 per mole of P_2O_5 and pH 6, corresponding to the formation of insoluble calcium hydrogen phosphate dihydrate:

$$Ca(NO_3)_2 + H_3PO_4 + 2NH_3 \longrightarrow CaHPO_4 + 2NH_4NO_3$$

That the precipitate obtained was indeed calcium hydrogen phosphate was confirmed by *X*-ray analysis.

Curves 1, 2, and 3 are for the more dilute solutions, and all three had their second equivalence points at 5 or more moles of NH_3 per mole of P_2O_5 and pH 6·5—8, indicating that calcium phosphates more basic than calcium hydrogen phosphate were formed.

TABLE 8.



Tetracalcium hydrogen trisphosphate requires $5\frac{1}{3}$ moles of NH_3 per mole of P_2O_5 for complete production:

$$4Ca(NO_3)_2 + 3H_3PO_4 + 8NH_3 \longrightarrow Ca_4H(PO_4)_3 + 8NH_4NO_3$$

Tricalcium bisphosphate requires 6 moles of NH_3 per mole of P_2O_5:

$$3Ca(NO_3)_2 + 2H_3PO_4 + 6NH_3 \longrightarrow Ca_3(PO_4)_2 + 6NH_4NO_3$$

Pentacalcium hydroxide trisphosphate requires $6\frac{2}{3}$ moles of NH_3 per mole of P_2O_5:

$$5Ca(NO_3)_2 + 3H_3PO_4 + 10NH_3 + H_2O \longrightarrow Ca_5(PO_4)_3(OH) + 10NH_4NO_3$$

X-Ray analysis showed the precipitates in these three cases to be mixtures of the more basic phosphates.

From solutions more concentrated than these first four, only calcium hydrogen phosphate dihydrate was precipitated and it could be filtered off, except in the case of a solution containing fluoride ions at 70°. Fig. 2 shows the P_2O_5 solubility curve reaching zero at the theoretical molar $NH_3 : P_2O_5$ ratio of 4. The same line was obtained over the wide range of neutralization rates and temperatures given in the Experimental section. When the calcium hydrogen phosphate dihydrate was retained in contact with the solution existing at the end of precipitation (maintained at pH 8) it was converted into a more basic calcium phosphate, the exact phosphate depending on the solution contents:

(*a*) With no fluoride or calcium ions in solution the calcium hydrogen phosphate dihydrate went to the next more basic phosphate, tetracalcium hydrogen trisphosphate, the rate increasing with increase of temperature.

(*b*) With no fluoride but with calcium ions in solution the calcium hydrogen phosphate dihydrate was converted first into hydrated tricalcium bisphosphate and finally into pentacalcium hydroxide trisphosphate the rate increasing with increase of temperature.

(c) With fluoride ions in solution, the calcium hydrogen phosphate dihydrate was converted into pentacalcium fluoride trisphosphate whether or not there were calcium ions in solution, and even at a pH as low as 6·5. The conversion rate with fluoride ions present was considerably greater than when they were absent. The rate of pentacalcium fluoride trisphosphate production was further increased by the absence of calcium ions in the solution. It is likely that the presence of calcium ions in the solution reduces the solubility of the calcium hydrogen phosphate dihydrate and hence the rate of reaction of the dissolved calcium hydrogen phosphate dihydrate with the fluoride.

At 70° when fluoride ions were in the initial solution, calcium hydrogen phosphate dihydrate was never obtained alone, and the final precipitate at the end of little more than ten minutes was completely pentacalcium fluoride trisphosphate.

Montel[6] showed that calcium hydrogen phosphate dihydrate was converted into pentacalcium fluoride trisphosphate in the presence of a calcium fluoride suspension, although very slowly. With dissolved sodium fluoride present, the conversion was virtually complete in 24 hours, to be compared with the results given here where only a few hours at room temperature were necessary. The difference is due, presumably, to the maintenance of a solution pH of 8 in our experiments, whereas Montel allowed his solution pH to fall as conversion proceeded. At 50°, with the pH initially 6·5 and allowed to fall, conversion was complete within 10 minutes, the final pH being 4·8. Montel did not study fluoride-containing systems at higher temperatures, although he did study fluoride-free hydrolysis at 40°, 50°, and 70° and found the completion times to be considerably reduced, although still measured in days rather than minutes.

In our experiments, when potassium fluoride was added to the solution phase, only a trace of free calcium fluoride was detected in the solid samples, and no intermediate phosphate between calcium hydrogen phosphate and pentacalcium fluoride trisphosphate (Tables 5 and 6). Kurmies[9] suggests that pentacalcium fluoride trisphosphate is formed from calcium hydrogen phosphate *via* pentacalcium hydroxide trisphosphate, a view which our results would not support. Scharrer, Gericke, and Jung[11] consider the hydroxyl ions in pentacalcium hydroxide trisphosphate are too strongly bound to exchange with fluoride ions, whereas Montel[12] and McCann[13] claim to have obtained such an exchange.

Conclusions.—It is possible to precipitate calcium hydrogen phosphate dihydrate completely from all but very dilute (0·005 g. of P_2O_5 per l.) solutions of calcium nitrate and phosphoric acid neutralized by 4 moles of NH_3 per mole of P_2O_5 over a wide range of temperatures and rates. The precipitate is stable if filtered off at once, but is converted into more basic calcium phosphates if retained in the solution. The rate of conversion increases with increase of temperature, and if fluoride ions are in the solution. At 70° with fluoride ions in solution, calcium hydrogen phosphate cannot be obtained alone.

The chemical analyses were carried out by Miss M. O. Oxborrow and Mr. V. C. Vinyard.

Appendix: X-Ray Powder Diffraction Analysis.—Calcium hydrogen phosphate and calcium tetrahydrogen bisphosphate (both anhydrous and hydrated) give sharp *X*-ray powder-diffraction patterns; there is, thus, no difficulty or ambiguity in determining their occurrence. Laboratory preparations of hydrated tricalcium bisphosphate, tetracalcium hydrogen triphosphate trihydrate, pentacalcium hydroxide trisphosphate, and pentacalcium fluoride trisphosphate give similar, very blurred patterns, corresponding to that of mineral apatite. It is, therefore, very difficult to decide from a laboratory-prepared sample which of these materials is present, or if a mixture of them exists. A distinction is, however, possible if the sample is heated to about 850° for a few hours, and then the *X*-ray pattern again measured.

---

[11] Scharrer, Gericke, and Jung, *Z. Pflanzenernährung, Düng.*, 1953, **60**, 250.
[12] Montel, *Compt. rend.*, 1956, **242**, 1182.
[13] McCann, *J. Biol. Chem.*, 1953, **201**, 247.

Apatites are stable (in the absence of any chemically reacting components) up to at least 1450°. The effects of the heating are to improve crystallinity and increase crystallite size, both of which produce a much sharper *X*-ray powder pattern, similar to that of mineral apatite. Distinctions between fluoro- and hydroxy-compounds are based on fine details of this pattern.

Hydrated tricalcium bisphosphate is dehydrated at ~700° to give β-$Ca_3(PO_4)_2$, of sharp distinguishable *X*-ray powder pattern.

Tetracalcium hydrogen trisphosphate trihydrate decomposes at 850° to a mixture of β-$Ca_3(PO_4)_2$ and β-$Ca_2P_2O_7$; the *X*-ray powder pattern of a heated sample, therefore, consists of a mixture of these two sharp patterns. Since calcium hydrogen phosphate also decomposes to β-$Ca_2P_2O_7$ at 850°, a distinction between hydrated tricalcium bisphosphate and tetracalcium hydrogen trisphosphate trihydrate can be made only if calcium hydrogen phosphate is largely absent from the original sample.

FISONS FERTILIZERS LIMITED, LEVINGTON RESEARCH STATION,
LEVINGTON, IPSWICH, SUFFOLK.

[*Received, April 24th,* 1961.]