THE SOLUBILITY OF CALCIUM PHOSPHATES
IN CITRIC ACID.

BY A. A. RAMSAY.

(Chemical Laboratory, Department of Agriculture, Sydney, N.S.W.)

MODERN writers on theoretical chemistry and particularly those who have written on Agricultural Chemistry, have either stated directly or have in other cases implied, that, excluding basic slag, calcium and phosphoric acid exist in three states of combination, namely mono-, di- and tricalcic phosphate, and that the former is soluble in water, the second is insoluble in water but soluble in ammonium citrate (or citric acid), while the third form is insoluble both in water and in ammonium citrate (or citric acid). That this is so is further confirmed by the general acceptance of the use of ammonium citrate solution, to differentiate between "reverted phosphate" (dicalcic phosphate) and tricalcic phosphate. On this matter Aikman¹ writes: "value of reverted phosphate....At first it was thought that it was impossible to estimate its quantity by chemical means. This difficulty has been overcome and it is generally admitted that the ammonium citrate process furnishes an accurate means of determining its amount." The above statement implies that the ammonium citrate dissolves the dicalcic phosphate and that the tricalcic phosphate is insoluble in ammonium citrate. In Thorpe's *Dictionary of Applied Chemistry*² the following statement occurs: "Phosphates that are soluble in ammonium citrate may be safely regarded as assimilable by plants; in America they are regarded as of almost equal value with water soluble phosphate; that they are so always is certainly open to doubt. Phosphates that are insoluble in ammonium citrate are often effective as manure. Ammonium citrate thus gives no safe distinction between assimilable and non-assimilable phosphates, though it affords a useful approximate means of determining

¹ Aikman, *Manures and Manuring*, p. 391.² Thorpe, *Dictionary of Applied Chemistry* (latest edition), Vol. II, p. 549.

278 *The Solubility of Calcium Phosphates in Citric Acid*

'reverted' phosphate in superphosphate. As a measure of ready availability in basic slag a 2 % solution of citric acid has now superseded ammonium citrate."

To test some of these statements, and to add to our knowledge on the subject, it was decided to purchase or to prepare Tricalcium phosphate, and then to ascertain its behaviour towards the prescribed citric acid solution. Citric acid was chosen, as in modern practice this solvent has taken the place of ammonium citrate, and the results are similar so far as my experiments have gone.

In the analytical work, connected with the experiments about to be described, lime had been determined by three methods:

(a) Adding sulphuric acid and evaporating till a considerable crop of crystals of gypsum has formed. Cool, add alcohol, filter, wash, ignite, and weigh as CaSO_4 ¹.

(b) Dissolve in hydrochloric acid and add ammonia till precipitate just begins to form. Redissolve this in a drop of hydrochloric acid, add ammonium oxalate in excess and then acetate of soda. Allow to settle, filter, wash, dry, ignite, and weigh as CaO ². I find that when this method is followed, the lime precipitate always contains minute quantities of phosphoric acid, which is greater the larger the amount of lime used and precipitated. For accurate determinations this must be determined and deducted. It has been found preferable to precipitate the lime with excess of ammonium oxalate in a solution to which acetic acid has been added. When this is done mere traces of phosphoric acid occur in the lime precipitate.

(c) Girard's method or Reynoso's modification of this, of removing the phosphoric acid in nitric acid solution by means of tin-foil, filtering and precipitating the lime by ammonium oxalate³. It was found that the filtrate from the stannic acid and phosphoric acid compound contains small amounts of tin which must be removed by sulphuretted hydrogen before precipitating the lime. Phosphoric acid has been determined by precipitating with molybdate reagent. Dissolving the precipitate in ammonia and precipitating with magnesia mixture, following the method adopted in *The Fertilisers and Feeding-stuffs (Methods of Analysis) Regulations 1908*⁴.

¹ Wiley, *Principles and practice of Agricultural Analysis*, Vol. II, p. 21.

² Fresenius, *Quantitative Chemical Analysis*, Vol. I, p. 188.

³ Crookes, *Select methods of Chemical Analysis*, p. 499.

⁴ *Fertilisers and Feeding Stuffs Regulations*, 1908. Board of Agriculture. Fisheries Leaflet No. 18, p. 17.

The calculations involved are based upon the following considerations: dicalcic phosphate contains 1 part CaO ·1607 parts water of crystallisation, 1·26786 parts P_2O_5 ; tricalcic phosphate contains 1 part CaO with ·84524 parts P_2O_5 ; calcium hydrate contains 1 part CaO with ·3214 parts water.

In mixtures containing di- and tricalcic phosphates, when the total CaO and total P_2O_5 are determined the amounts of di- and triphosphate is calculated as follows:

$$\begin{array}{ll}
 \text{Let} & x = \text{CaO existing as dicalcic phosphate,} \\
 \text{and} & y = \text{CaO existing as tricalcic phosphate;} \\
 \text{then} & x \times 1\cdot26786 = P_2O_5 \text{ existing as dicalcic phosphate,} \\
 \text{and} & y \times \cdot84524 = P_2O_5 \text{ existing as tricalcic phosphate.} \\
 & 1\cdot26786x + \cdot84524y = \text{total phosphoric acid found} \dots\dots\dots(1), \\
 & x + y = \text{total lime found} \dots\dots\dots(2).
 \end{array}$$

Solving these equations the values of x and y are obtained.

In mixtures containing dicalcic phosphate ($CaHPO_4 \cdot 2H_2O$), tricalcic phosphate ($Ca_3P_2O_8$) and calcium hydrate ($CaOH_2O$), having determined the total CaO, total P_2O_5 and water, the following is the method adopted:

$$\begin{array}{ll}
 \text{Let} & x = \text{CaO as dicalcic phosphate,} \quad y = \text{CaO as tricalcic phosphate,} \\
 & z = \text{CaO as calcium hydrate.} \\
 & \cdot1607x + \cdot6428y + \cdot3214z = \text{total water determined} \dots\dots\dots(1), \\
 & x + y + z = \text{total lime determined} \dots\dots\dots(2), \\
 & 1\cdot26786x + \cdot84524y = \text{total } P_2O_5 \text{ determined} \dots\dots\dots(3).
 \end{array}$$

From (1) obtain value of z in terms of x and substitute in (2), equate this with (3) and obtain value of x . y and z are then found.

The following three samples, Nos. 1, 2, and 3, of phosphate of lime were obtained by purchase.

No. 1. Phosphate of lime in a 1 lb. bottle and of English manufacture.

This sample was found by analysis to contain:

Lime (CaO)	48·26
Phosphoric acid (P_2O_5)	43·26
Water	8·48
	<hr/>
	100·00

	Per cent.
Loss in weight on drying in desiccator over sulphuric acid in 16 hours ...	1·036
Loss in weight on drying in desiccator over sulphuric acid in 112 hours ...	1·620
Loss on drying at 100° C. in 2 hours, 2·37 % in 4 hours	2·37
Loss on ignition	8·47

280 *The Solubility of Calcium Phosphates in Citric Acid.*

By calculation the lime and phosphoric acid exist as :

	CaO	H ₂ O	P ₂ O ₅	Water	
Dicalcic phosphate (CaO) ₂ H ₂ OP ₂ O ₅	5·842	0·939	7·407	—	= 14·188
Tricalcic phosphate (CaO) ₃ P ₂ O ₅ ...	42·418	—	35·853	—	= 78·271
Water of crystallisation ...	—	—	—	7·541	= 7·541
	48·260	0·939	43·260	7·541	100·000

If the water of crystallisation present be contained in the dicalcic phosphate only and none with the tricalcic phosphate we would have

	CaO	H ₂ O	P ₂ O ₅	Water (theory require 7·512)	
Dicalcic phosphate (CaO) ₂ H ₂ OP ₂ O ₅ ·8H ₂ O ...	5·842	0·939	7·407	7·541	= 21·729
CaHPO ₄ ·4H ₂ O					
Tricalcic phosphate Ca ₃ P ₂ O ₈ ...	42·418	—	35·853	—	78·271
	48·260	0·939	43·260	7·541	100·000

But as the tricalcic phosphate might also contain some water of crystallisation, the first statement is probably more correct.

The above sample therefore appears to be a mixture of 14·188 % di- and 78·271 % tricalcic phosphate with water of crystallisation.

No. 2. Calcii Phosphas B.P., purchased locally.

Upon analysis the following figures were obtained :

Lime (CaO) ...	...	...	40·15
Phosphoric acid (P ₂ O ₅) ...	...	...	47·52
Water ...	...	...	12·33
			100·00

	Per cent.
Loss in weight on drying in desiccator over sulphuric acid for 16 hours	1·184
Loss in weight on drying in desiccator over sulphuric acid for 112 hours	1·620
Loss on drying at 100° C. : 2 hours 3·46 %, 6 hours 3·51 %, 9 hours ...	3·60
Loss on ignition ...	12·35

By calculation the lime and phosphoric acid are found to exist in the following combination :

	CaO	H ₂ O	P ₂ O ₅	Water	
Dicalcic phosphate (CaO) ₂ H ₂ OP ₂ O ₅	32·142	5·166	40·751	—	= 78·059
Tricalcic phosphate (CaO) ₃ P ₂ O ₅ ...	8·008	—	6·767	—	= 14·777
Water of crystallisation ...	—	—	—	7·164	= 7·164
	40·150	5·166	47·518	7·164	= 100·000

If all the water of crystallisation be contained in the dicalcic phosphate only, the dicalcic phosphate present would conform to the formula

$(\text{CaO})_2\text{H}_2\text{OP}_2\text{O}_5$ 1.4 H_2O or CaHPO_4 0.7 H_2O . This preparation therefore appears to be a mixture of 78.059 % dicalcic phosphate and 14.777 % tricalcic phosphate with water of crystallisation.

No. 3. Calcii Phosphas B.P., also purchased locally.

Upon analysis the following figures were obtained :

Lime (CaO)	41.15
Phosphoric acid (P_2O_5)	42.20
Water	16.65
	<hr/> 100.00

	Per cent.
Loss in weight on drying in desiccator over sulphuric acid 16 hours	1.920
Loss in weight on drying in desiccator over sulphuric acid 112 hours	2.760
Loss on drying at 100°C . : 2 hours 5.38 %, 4 hours 5.38 %, 6 hours 5.45 %, 11 hours	5.52
Loss on ignition	16.66

By calculation we find the lime and phosphoric acid exist in the following combination :

	CaO	H_2O	P_2O_5	Water	
Dicalcic phosphate $(\text{CaO})_2\text{H}_2\text{OP}_2\text{O}_5$...	17.554	2.821	22.256	—	= 42.631
Tricalcic phosphate $(\text{CaO})_3\text{P}_2\text{O}_5$...	23.596	—	19.944	—	= 43.540
Water of crystallisation	—	—	—	13.829	= 13.829
	<hr/> 41.150	<hr/> 2.821	<hr/> 42.200	<hr/> 13.829	<hr/> 100.000

Assuming that all the water of crystallisation is associated with the dicalcic phosphate only, this would conform to the formula

The above sample therefore appears to be a mixture of 42.631 % dicalcic phosphate with 43.540 % tricalcic phosphate with water of crystallisation.

None of these three compounds are what they purport to be, but are mixtures of varying amounts of di- and tricalcic phosphates.

Having been unsuccessful in procuring pure tricalcium phosphate by purchase, the preparation of this substance was undertaken, following recognised authorities.

Roscoe and Schorlemmer¹ state: "pure calcium phosphate $\text{Ca}_3\text{P}_2\text{O}_8$ is obtained as a white precipitate by adding an excess of common sodium phosphate to an ammoniacal solution of chloride of calcium." This method was adopted by Warrington² in preparing pure tricalcic phosphate for his investigations on the action of water on this substance.

¹ *Treatise on Chemistry*, Vol. II, Part I, p. 205.

² "On the decomposition of tricalcium phosphate by water," *Journal Chemical Society*, Vol. XXVI (entire series), p. 983.

282 *The Solubility of Calcium Phosphates in Citric Acid*

The method was followed and the product obtained was marked as phosphate No. 4.

On submitting this product (No. 4) to chemical analysis the following data was obtained:

Lime (CaO)	52.93
Phosphoric Acid (P ₂ O ₅)	41.44
Water (combination and constitution)	5.68
	<hr/> 100.05
	Per cent.
Loss on drying at 100° C. in 2 hours	1.91
Loss on drying at 100° C. in 6 hours	1.95
Loss on ignition	5.68

By calculation the lime and phosphoric acid probably exist as:

	CaO	P ₂ O ₅
Dicalcic phosphate	4.590	5.819
Tricalcic phosphate	42.142	35.621
Lime (free)	6.198	—
	<hr/> 52.930	<hr/> 41.440

Assuming that the water present is associated only with the dicalcic phosphate and with the lime as hydrate, the formula of the dicalcic phosphate present is (CaO)₂H₂OP₂O₅4H₂O or CaHPO₄2H₂O. Thus:

	CaO	Water of constitution	P ₂ O ₅	Water of crystallisation	
Dicalcic phosphate (CaO) ₂ H ₂ OP ₂ O ₅ 4H ₂ O	4.590	0.738	5.819	2.950	= 14.097
Tricalcic phosphate (CaO) ₃ P ₂ O ₅	42.142	—	35.621	—	= 77.763
Calcium hydrate CaOH ₂ O	6.198	1.992	—	—	= 8.190
	<hr/> 52.930	<hr/> 2.730	<hr/> 41.440	<hr/> 2.950	<hr/> = 100.050

This preparation therefore is not pure tricalcic phosphate, but is a mixture of 77.76 % tricalcic phosphate, 14.10 % dicalcic phosphate and 8.19 % calcium hydrate.

The method given in the *British Pharmacopœia*¹ for the preparation of tricalcium phosphate, by dissolving bone ash in hydrochloric acid and precipitating with ammonium hydrate was next tried.

The preparation thus obtained was marked No. 5, and upon analysis gave the following data:

Lime (CaO)	53.05
Phosphoric acid (P ₂ O ₅)	41.17
Water	5.78
	<hr/> 100.00

¹ *The British Pharmacopœia* (Spottiswoode and Co., London), 1891, p. 87.

By calculation the lime and phosphoric acid would probably exist as:

	CaO	P ₂ O ₅
Dicalcic phosphate ...	4.547	5.765
Tricalcic phosphate ...	41.887	35.405
Lime (free) ...	6.616	—
	53.050	41.170

Assuming that the water present is associated only with the dicalcic phosphate, and with the lime as hydrate, the formula of the dicalcic phosphate present would be $(\text{CaO})_2\text{H}_2\text{OP}_2\text{O}_5\cdot 4\text{H}_2\text{O}$ or $\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$.

Thus:

	CaO	Water of constitution	P ₂ O ₅	Water of crystallisation	
Dicalcic phosphate (CaO) ₂ H ₂ OP ₂ O ₅ ·4H ₂ O ...	4.547	0.731	5.765	2.923	= 13.966
Tricalcic phosphate (CaO) ₃ P ₂ O ₅ ...	41.887	—	35.405	—	= 77.292
Calcium hydrate CaOH ₂ O ...	6.616	2.126	—	—	= 8.742
	53.050	2.857	41.170	2.923	= 100.000

This preparation is not pure tricalcic phosphate, but is a mixture of 77.29 % tricalcium phosphate, 13.97 % bicalcium phosphate and 8.74 % calcium hydrate.

A second attempt was made to prepare pure tricalcium phosphate by dissolving bone ash in hydrochloric acid and precipitating with ammonium hydrate, following the method of the *British Pharmacopœia*, but washing the precipitate till free from chlorides with very dilute ammonium hydrate as was done in the old analytical method of determining phosphoric acid as tricalcic phosphate.

The product obtained after drying and igniting was marked No. 6. Upon analysis the product was found to consist of:

Lime (CaO) ...	56.15
Phosphoric acid (P ₂ O ₅) ...	43.85
	100.00

Since the above is most probably a mixture of di- and tricalcic phosphate with free lime, it is impossible from the data given to calculate the percentage of each, since several such mixtures could be calculated having 56.15 % CaO and 43.85 % P₂O₅.

Since 43.85 P₂O₅ requires 51.997 CaO to form tricalcic phosphate, and 34.664 CaO to form dicalcic phosphate, the free lime may be anything between 56.15 minus 51.997 = 4.153 and 56.15 minus 34.664 = 21.486. If however the free lime be 7.00 % (which is about that

284 *The Solubility of Calcium Phosphates in Citric Acid*

present in the hydrated product previously discussed (No. 5) we would have:

	CaO	P ₂ O ₅	
Dicalcic phosphate ...	5.46	6.92	= 12.38
Tricalcic phosphate...	43.69	36.93	= 80.62
Lime (free) ...	7.00	—	= 7.00
	56.15	43.85	= 100.00

When time permits I hope to investigate the question of the estimation of the free lime actually present in such a mixture as the above, but it is evident that the product obtained by this method is not tricalcic phosphate as is usually stated and as it is assumed to be.

Experiments were next made to prepare tri- and dicalcic phosphates from pure phosphoric acid (H₃PO₄) by the addition of three equivalents and of two equivalents respectively of lime (CaO). The solution of phosphoric acid used was prepared by taking about 32 grams pure phosphorus pentoxide, dissolving in water and making up to 500 c.c. Gravimetric analysis showed that the 500 c.c. solution contained 31.66 grams phosphoric acid (P₂O₅).

Tricalcium phosphate preparation No. 7.

For the preparation of this 243 c.c. of the above mentioned solution of phosphoric acid containing 15.386 grams P₂O₅ were taken and to this was added 18.203 grams pure freshly ignited lime (CaO). A further small quantity of lime was added in the form of lime-water, the idea being to have a faint excess of lime—which excess could be easily washed out by water. Owing to an absence from Sydney, the precipitate formed was not separated from the liquid portion for about a fortnight after the addition of the lime to the phosphoric acid.

This precipitate when dried weighed 36.22 grams, and was marked preparation No. 7. The filtrate and washings contained lime but no phosphoric acid and measured 1000 c.c. On evaporation, the filtrate and washings yielded 0.53 gram lime (CaO).

Dicalcium phosphate preparation No. 8.

To 243 c.c. of the phosphoric acid solution mentioned above containing 15.386 grams P₂O₅, 12.135 grams pure lime (CaO) (equivalent to 2 molecules of lime) were added.

This mixture also stood for a fortnight before filtering. 19.63 grams dried preparation (No. 8) were obtained.

The filtrate (without the washings) which measured about 500 c.c. was evaporated. When boiling commenced, the clear fluid became milky, and a precipitate separated out. Evaporation was continued

till bumping was severe. The precipitate was filtered off, washed well with water, and on drying weighed 2.210 grams. This was marked preparation 8A. The filtrate from which the last mentioned preparation (8A) was obtained, was further evaporated on the water bath to small bulk but not to dryness. On standing for two days the mass crystallised. This mass was placed on a filter paper and washed with water. The washings contained much lime and phosphoric acid. The filter paper and contents were placed in a water oven to dry but the paper blackened and then charred. This last product therefore appears to be an acid calcium phosphate; the weight would be about 1.1 gram.

The result of the chemical analyses of these various preparations will now be given.

Preparation No. 7 (3 equivalents CaO : 1 equivalent P_2O_5) was found to consist of:

Lime (CaO)	48.61
Phosphoric acid (P_2O_5)	42.48
Water	8.91
	<hr/> 100.00

By calculation the above numbers correspond to a mixture of:

	CaO	H ₂ O	P_2O_5	Water	
Dicalcic phosphate $(CaO)_2H_2OP_2O_5...$	3.297	0.530	4.180	—	= 8.007
Tricalcic phosphate $(CaO)_3P_2O_5 ...$	45.313	—	38.300	—	= 83.613
Water of crystallisation (H_2O) ...	—	—	—	8.380	= 8.380
	<hr/> 48.610	<hr/> 0.530	<hr/> 42.480	<hr/> 8.380	<hr/> = 100.000

If all the water of crystallisation be associated with the dicalcic phosphate, the composition of this would correspond to the formula $(CaO)_2 \cdot H_2O \cdot P_2O_5 \cdot 15.8H_2O$ or $CaHPO_4 \cdot 7.9H_2O$.

If as is more probable, the water of crystallisation is shared by both di- and tricalcic phosphates, and assuming that $CaHPO_4 \cdot 2H_2O$ is the particular form of dicalcic salt present, then the formula of the tricalcic phosphate present is $(CaO)_3P_2O_5 \cdot 1.29H_2O$. Thus:

Dicalcic phosphate $(CaO)_2H_2OP_2O_5 \cdot 4H_2O ...$	10.127
Tricalcic phosphate $(CaO)_3P_2O_5 \cdot 1.29H_2O ...$	89.873
	<hr/> 100.000

Preparation No. 8 (2 equivalents of CaO : 1 equivalent P_2O_5) was found to consist of:

Lime (CaO)	46.36
Phosphoric acid (P_2O_5)	41.77
Water	11.87
	<hr/> 100.00

286 *The Solubility of Calcium Phosphates in Citric Acid*

By calculation the above appears to consist of:

	CaO	H ₂ O	P ₂ O ₅	Water	
Dicalcic phosphate (CaO) ₂ H ₂ OP ₂ O ₅	6.116	0.983	7.754	—	= 14.853
Tricalcic phosphate (CaO) ₃ P ₂ O ₅ ...	40.244	—	34.016	—	= 74.260
Water of crystallisation	—	—	—	10.887	= 10.887
	46.360	0.983	41.770	10.887	= 100.000

If the whole of the water of crystallisation be contained in the dicalcic phosphate only, then the formula of this would correspond to (CaO)₂H₂OP₂O₅11H₂O, but if, as is more probable both the di- and tri-salts contain water of crystallisation, and if the di-phosphate be CaHPO₄2H₂O the tricalcic phosphate would correspond to the formula Ca₃P₂O₈ 1.61H₂O. Thus:

(CaO) ₂ H ₂ OP ₂ O ₅ 4H ₂ O	...	...	18.785
(CaO) ₃ P ₂ O ₅ 1.61H ₂ O	...	...	81.215
			100.000

Preparation No. 8A was found upon analysis to consist of:

Lime (CaO)	...	...	41.386
Phosphoric acid (P ₂ O ₅) ...	...	...	50.596
Water	...	...	8.018
			100.000

By calculation the above appears to be a mixture of:

	CaO	H ₂ O	P ₂ O ₅	Water	
Dicalcic phosphate ...	36.949	5.938	46.846	—	= 89.733
Tricalcic phosphate ...	4.437	—	3.750	—	= 8.187
Water of crystallisation ...	—	—	—	2.080	= 2.080
	41.386	5.938	50.596	2.080	= 100.000

If all the water of crystallisation be associated with the dicalcic phosphate only, its formula would correspond to (CaO)₂H₂OP₂O₅0.35H₂O. The tricalcic phosphate would be Ca₃P₂O₈.

It was considered probable that in the last experiments (preparations No. 7 and No. 8) hydrolysis of the salts originally produced might easily have occurred, owing to the lapse of time between the mixing of the lime and phosphoric acid, and the separation of the precipitates formed, from the fluid portion. It was therefore decided to repeat this portion of the work, and to remove the precipitate formed after the lapse of an hour. Preparation of the solution of phosphoric acid (H₃PO₄):

About 43 grams pure phosphorus pentoxide was dissolved in water and made up to 500 c.c.

A titration of this to methyl-orange, using caustic soda, gave

41.54 grams P_2O_5 . Quadruplicate gravimetric determinations gave 41.664 grams P_2O_5 present in the 500 c.c. solution.

Preparation of tricalcic phosphate from 3 equivalents CaO to 1 equivalent P_2O_5 preparation No. 9.

225 c.c. of the above phosphoric acid solution containing 18.745 grams P_2O_5 were taken. 22.1796 grams pure freshly ignited lime prepared by igniting pure calcium carbonate was weighed out. About 100 c.c. of water was added to the lime, then the phosphoric acid added, stirred well, and allowed to stand with frequent stirring for one hour.

The precipitate was filtered off and dried at $100^\circ C$.

Product obtained by mixing $\frac{1}{2}$ equivalents of CaO with 1 equivalent P_2O_5 preparation No. 10.

11.2644 grams pure lime prepared as above described was weighed out. To this was added about 100 c.c. water, and 171.5 c.c. phosphoric acid solution containing 14.2816 grams P_2O_5 . The mixture was well stirred at frequent intervals during an hour. At the end of that time the precipitate was filtered off, washed well with water, and dried at $100^\circ C$. The weight of the product obtained was 20.74 grams.

Upon analysis preparation No. 9 was found to contain:

Lime (CaO)	50.12
Phosphoric acid (P_2O_5)	42.36
Water	7.52
	<hr/> 100.00

By calculation the above lime and phosphoric acid corresponds to $3CaO : P_2O_5$ or pure tricalcium phosphate. The water of crystallisation present indicates that the formula of the tricalcic phosphate is $Ca_3P_2O_8 \cdot 1.384H_2O$ or $8Ca_3P_2O_8 \cdot 11H_2O$.

This preparation when dried at $125^\circ C$. has apparently the composition of $Ca_3P_2O_8 \cdot 1.3H_2O$ or $10Ca_3P_2O_8 \cdot 13H_2O$.

The analysis of preparation No. 10 (from 2 equivalents CaO to 1 equivalent P_2O_5) showed this product to consist of:

Lime (CaO)	44.58
Phosphoric acid (P_2O_5)	44.30
Water	11.12
	<hr/> 100.00

By calculation the above numbers are found to indicate a mixture of di- and tricalcic phosphate. Thus:

	CaO	H ₂ O	P_2O_5	Water	
Dicalcic phosphate ...	15.663	2.517	19.858	—	= 38.038
Tricalcic phosphate ...	28.917	—	24.442	—	= 53.359
Water of crystallisation ...	—	—	—	8.603	= 8.603
	<hr/> 44.580	<hr/> 2.517	<hr/> 44.300	<hr/> 8.603	<hr/> =100.000

288 *The Solubility of Calcium Phosphates in Citric Acid*

The water of crystallisation present appears to indicate that the dicalcic phosphate present corresponds to $(\text{CaO})_2\text{H}_2\text{OP}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ or $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$, and of the tricalcic phosphate $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$. Thus:

	CaO	Water of constitution	P_2O_5	Water of crystallisation	
Dicalcic phosphate $(\text{CaO})_2\text{H}_2\text{OP}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$...	15.663	2.517	19.858	5.034	= 43.072
Tricalcic phosphate $(\text{CaO})_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$	28.097	—	24.442	3.097	= 56.456
	43.760	2.517	44.300	8.131	= 99.528
Water of crystallisation not allotted				...	0.472
					100.000

It appears, therefore, that the product formed by the interaction of 3 equivalents of lime (CaO) on 1 equivalent of phosphoric acid (P_2O_5) yields pure tricalcic phosphate when the precipitate formed is removed from the fluid portion within an hour of the commencement of the reaction. The tricalcic phosphate formed contains water of crystallisation. The amount of this is intermediate between that occurring in the mineral ornithite $\text{Ca}_3\text{P}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, and collophanite $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$. When however 2 equivalents of lime (CaO) are added to 1 equivalent of phosphoric acid (P_2O_5) the resultant product is not dicalcic phosphate, but is a mixture of di- and tricalcic phosphates.

Having now obtained a pure tricalcium phosphate (preparation No. 9), experiments were carried out to ascertain what would be the result of treating (a) pure tricalcic phosphate, (b) tricalcic phosphate plus 25 % pure calcium carbonate, and (c) tricalcic phosphate plus 50 % pure calcium carbonate, with a 2 % citric acid solution in the manner prescribed for determining citrate soluble phosphoric acid¹. Briefly stated, the method is to shake for 30 minutes in a rotary shaker making 30 to 40 revolutions per minute 5 grams of the substance and 500 c.c. of a 2 % citric acid solution.

In these experiments about to be described, the first extraction was made in the prescribed manner. The unexhausted phosphate remaining after the first extraction, was extracted a second time with a further quantity of 500 c.c. of a 2 % citric acid solution for a further period of 30 minutes. This formed the "second" extraction. A third and a fourth extraction was similarly made. At this stage the whole of the lime and the whole of the phosphoric acid had gone into solution.

Experiment (a). Extraction of 5 grams pure tricalcic phosphate containing 50.12 % CaO, 42.36 % P_2O_5 , 7.52 % H_2O with 500 c.c. of

¹ *Fertilisers and Feeding Stuffs Regulations*, 1908. Board of Agriculture. Fisheries Leaflet 18, p. 17.

a 2 % citric acid solution. The results are given in tabular form and are practically self-explanatory.

	Lime		Phosphoric acid		Lime calculated from P_2O_5 found to form with it $Ca_3P_2O_8$	Difference between calculated lime and that actu- ally found
	Grams found cal- culated to 100 grams powder	Expressed in % of total lime present	Grams found cal- culated to 100 grams powder	Expressed in % of total P_2O_5 present		
1st extn, 30 min.	45.45	90.48	38.34	90.96	45.36	+0.09
2nd „ 30 „	3.56	7.09	3.31	7.85	3.92	-0.36
3rd „ 30 „	0.71	1.41	0.34	0.81	0.40	+0.31
4th „ 30 „	0.51	1.02	0.16	0.38	0.19	+0.32
Total ...	50.23	100.00	42.15	100.00	49.87	+0.36
					50.23	
Actually present	50.12	—	42.36	—	—	—

It will be noted that 90.5 % of the lime and 91 % of the phosphoric acid have gone into solution in the first extraction of 30 minutes, and that the lime and phosphoric acid extracted are very nearly in the ratio of $3CaO : P_2O_5$.

In the second extraction it will be seen that there is rather less lime found than would be necessary to produce $Ca_3P_2O_8$ with the phosphoric acid found. This would appear to indicate that the lime and phosphoric acid had gone into solution as a mixture of di- and tricalcium phosphate.

In the third extraction, the lime found is greater than that which would be necessary to form $Ca_3P_2O_8$ with the P_2O_5 found, so that part of the lime found must have gone into solution as calcium citrate. This also appears to have taken place in the fourth extraction.

After four extractions the whole of the lime and the whole of the phosphoric acid have gone into solution.

It should also be noted that under existing methods of analysis this compound (tricalcic phosphate) would be stated to contain 38.34 % "citrate soluble" phosphoric acid out of a total of 42.36 %.

Experiment (b). Extraction of 5 grams of an intimate mixture consisting of 75 % pure tricalcic phosphate and 25 % pure calcium carbonate with 500 c.c. of 2 % citric acid solution.

	gram CaO	gram P_2O_5
3.75 grams tricalcic phosphate containing 50.12 % CaO , 42.36 % P_2O_5 will contain	1.8795	1.5885
1.25 grams calcium carbonate containing 56.00 % CaO , will contain	0.7000	—
	2.5795	1.5885

290 *The Solubility of Calcium Phosphates in Citric Acid*

100 grams mixture $\therefore$ contains $\left\{ \begin{array}{l} 37.59 \text{ grams CaO, } 31.77 \text{ grams P}_2\text{O}_5 \text{ from the phosphate} \\ 14.00 \text{ grams CaO} \text{ from the carbonate} \end{array} \right.$
 51.59 grams CaO, 31.77 grams P₂O₅

Note that in this mixture there is an excess of 14 % of lime.

	Lime		Phosphoric acid		Lime calculated from P ₂ O ₅ found to form with it Ca ₃ P ₂ O ₈	Difference between calculated lime and that actu- ally found
	Grams found cal- culated to 100 grams mixture	Expressed in % of total lime present	Grams found cal- culated to 100 grams mixture	Expressed in % of total P ₂ O ₅ present		
1st extn, 30 min.	44.80	86.82	26.85	84.44	31.77	+ 13.03
2nd „ 30 „	5.31	10.29	4.52	14.21	5.35	- 0.04
3rd „ 30 „	0.82	1.59	0.34	1.07	0.40	+ 0.42
4th „ 30 „	0.67	1.30	0.09	0.28	0.10	+ 0.57
Total ...	51.60	100.00	31.80	100.00	37.62	+ 13.98
					51.60	
Actually present	51.59	—	31.77	—	—	—

It will be noted that 86.8 % of the total lime and 84.4 % of the total phosphoric acid have gone into solution in the first extraction of 30 minutes, and that the lime and phosphoric acid extracted are not in the ratio of 3CaO : P₂O₅. The lime found is 13 grams more than that necessary to form Ca₃P₂O₈ with the P₂O₅ found, and this amount is very nearly the same as that contained in the calcium carbonate, viz. 14 grams.

In the second extraction, the lime and phosphoric acid found are very nearly or are practically exactly in the ratio of 3CaO : P₂O₅ so that apparently the salt dissolved is Ca₃P₂O₈.

In the third extraction, the amount of lime dissolved is nearly twice as much as that necessary to combine with the P₂O₅ found to form Ca₃P₂O₈, indicating that lime which has gone into solution is derived from calcium citrate, as well as from calcium phosphate.

In the fourth extraction, the amount of lime dissolved is nearly 6 $\frac{3}{4}$ times as much as that necessary to form Ca₃P₂O₈ with the P₂O₅ found. This appears to indicate that a larger proportion of the lime which has gone into solution has done so as calcium citrate than as calcium phosphate.

It will be seen also that the so-called "citrate soluble" phosphoric acid has fallen from 91 % to 84.4 % of the total phosphoric acid present.

Experiment (c). Extraction of 5 grams of an intimate mixture consisting of 50 % pure tricalcic phosphate and 50 % pure calcium carbonate with 500 c.c. of a 2 % solution of citric acid.

	gram CaO	gram P ₂ O ₅
2.50 grams tricalcic phosphate containing 50.12 % CaO, 42.36 % P ₂ O ₅ will contain	1.2530	1.0590
2.50 grams calcium carbonate containing 56.0 % CaO will contain	1.4000	—
5.00 grams mixture will contain	2.6530	1.0590
	grams CaO	grams P ₂ O ₅
100 grams of this mixture ∴ contains	25.06 28.00	21.18 —
	53.06	21.18

from the phosphate
from the carbonate

Note that in this mixture there is an excess of 28 % of lime.

	Lime		Phosphoric acid		Lime calculated from P ₂ O ₅ found to form with it Ca ₃ P ₂ O ₈	Difference between calculated lime and that actu- ally found
	Grams found cal- culated to 100 grams mixture	Expressed in % of total lime present	Grams found cal- culated to 100 grams mixture	Expressed in % of total P ₂ O ₅ present		
1st extn, 30 min.	49.45	93.23	17.82	84.26	21.08	+ 28.37
2nd „ 30 „	3.26	6.15	2.87	13.57	2.40	+ 0.86
3rd „ 30 „	0.20	0.38	0.28	1.32	0.33	- 0.13
4th „ 30 „	0.13	0.24	0.18	0.85	0.21	- 0.08
Total ...	53.04	100.00	21.15	100.00	24.02	+ 29.02
					53.04	
Actually present	53.06	—	21.18	—	—	—

It will be noted that 93.2 % of the total lime and 84.3 % of the total phosphoric acid present have gone into solution in the first extraction. The lime extracted is 28.4 grams more than the amount necessary to form Ca₃P₂O₈ with the P₂O₅ found, an amount which is nearly the same as that contained in the calcium carbonate added. In the second extraction the lime found is considerably more than that which would be required to combine with the P₂O₅ found to form Ca₃P₂O₈, indicating that a considerable amount of lime has gone into solution as calcium citrate. In the third extraction the amount of lime found is just about the amount which would be necessary to produce dicalcic phosphate (·22) with the P₂O₅ found. The same remark applies to the amount of lime found in the fourth extraction, the lime and phosphoric acid found are in the proportions in which they exist in dicalcic phosphate.

It will also be noted that here again the so-called "citrate soluble" phosphoric acid has fallen from 91 % as in experiment (a) to 84.3 % of the total phosphoric acid present.

The extraction of mixtures of a higher calcium carbonate content was not tested, as it was considered that in practice few phosphates

292 *The Solubility of Calcium Phosphates in Citric Acid*

would be submitted for the determination of "citrate soluble" phosphoric acid, which would contain more than 50 % calcium carbonate.

Before discussing further the results of these experiments on the action of the prescribed 2 % citric acid solution on tricalcic phosphate and mixtures of these with calcium carbonate, it will perhaps be well to give here, the results of investigations of the action of 2 % citric acid solution on the substances which were sold and purchased as tricalcic phosphate, but which chemical analysis showed to be mixtures of di- and tricalcic phosphates in varying amounts. For this purpose phosphates No. 1 and No. 2 were selected, the former containing 78 % tri- and 14 % dicalcic phosphate, and the latter 78 % di- and 14 % tricalcium phosphate.

The results of these two examinations will now be given.

Extraction of 5 grams of the phosphate of lime (No. 1) with 500 c.c. of a 2 % citric acid solution for 30 minutes.

This powder was shown to consist of:

Dicalcic phosphate CaHPO_4	...	...	14.188
Tricalcic phosphate $\text{Ca}_3\text{P}_2\text{O}_8$	...	...	78.271
Water of crystallisation	...	...	7.541
			<hr/> 100.000

containing lime (CaO) 48.26 % and phosphoric acid (P_2O_5) 43.26 %.

	Lime		Phosphoric acid		Lime calculated from P_2O_5 found to form with $\text{Ca}_3\text{P}_2\text{O}_8$	Difference between calculated lime and that actu- ally found
	Grams found cal- culated to 100 grams sample	Expressed in % of total lime present	Grams found cal- culated to 100 grams sample	Expressed in % of total P_2O_5 present		
1st extn, 30 min.	39.91	82.58	36.16	83.64	42.78	- 2.87
2nd „ 30 „	8.42	17.42	7.07	16.36	8.37	+ 0.05
Total ...	48.33	100.00	43.23	100.00	51.15	- 2.82
					<hr/> 48.33	
Actually present	48.26	—	43.26	—	—	—

In the first extraction this salt appears to have gone into solution as a mixture of tri- and dicalcic phosphates, the tricalcic phosphate predominating, since the lime found is less than that necessary to combine with the P_2O_5 found to form $\text{Ca}_3\text{P}_2\text{O}_8$.

In the second extraction the phosphate appears to have gone into solution as tricalcic phosphate. There is a very minute excess of lime which probably indicates calcium citrate.

Extraction of 5 grams of the Calcii Phosphas B.P. (No. 2) with 500 c.c. of a 2 % citric acid solution for 30 minutes.

This powder was shown to consist of:

Dicalcic phosphate CaHPO_4	...	...	78.059
Tricalcic phosphate $\text{Ca}_3\text{P}_2\text{O}_8$	...	...	14.777
Water of crystallisation	...	...	7.164
			<hr/> 100.000

containing lime (CaO) 40.15 % and phosphoric acid (P_2O_5) 47.52 %.

	Lime		Phosphoric acid		Lime calculated from P_2O_5 found to form with it $\text{Ca}_3\text{P}_2\text{O}_8$	Difference between calculated lime and that actually found
	Grams found calculated to 100 grams sample	Expressed in % of total lime present	Grams found calculated to 100 grams sample	Expressed in % of total P_2O_5 present		
1st extn, 30 min.	33.18	83.14	30.46	83.00	46.68	- 13.50
2nd „ 30 „	6.73	16.86	8.08	17.00	9.56	- 2.83
Total ...	39.91	100.00	47.54	100.00	56.24	- 16.33
					<hr/> 39.91	
Actually present	40.15	—	47.52	—		

In the first extraction the phosphate experimented with appears to have gone into solution as a mixture of di- and tricalcium phosphate, the dicalcic phosphate predominating.

In the second extraction the lime and phosphoric acid found indicate a dicalcic phosphate, with very minute quantities of tricalcic phosphate.

When di-barium phosphate is dissolved in hydrochloric acid, barium chloride and free phosphoric acid are first produced in accordance with the equation $\text{BaHPO}_4 + 2\text{HCl} = \text{BaCl}_2 + \text{H}_3\text{PO}_4$. According to Newth¹ the addition of an alkali causes precipitation of the phosphate unchanged. The reaction proceeds in two stages—(1) the alkali added (say NaOH) reacts with the free H_3PO_4 forming sodium phosphate, and (2) the sodium of the sodium phosphate takes the chlorine from the barium chloride, and the barium of the barium chloride unites with the phosphoric acid of the sodium phosphate. These reactions are represented by the following equations:

The solution of tricalcic phosphate in acid and its precipitation by an alkali has not been discussed in any text-book or paper that I have had access to, but the following reactions suggest themselves as such as would occur.

Solution in hydrochloric acid would be represented by the equation

¹ Newth, *Manual of Chemical Analysis*, p. 64.

294 *The Solubility of Calcium Phosphates in Citric Acid*

$\text{Ca}_3\text{P}_2\text{O}_8 + 6\text{HCl} = 3\text{CaCl}_2 + 2\text{H}_3\text{PO}_4$. The addition of sodium hydrate would be represented thus:

Were it possible to produce Na_3PO_4 in the reaction we would have:

but as I know of no similar reaction in which Na_3PO_4 is produced but invariably Na_2HPO_4 , no other conclusion seems possible but that free hydrochloric acid is produced which would react at once with the tricalcium phosphate present. In the case of ammonia being the precipitating alkali the following equations might represent what occurs:

or we might have with less ammonia:

if the latter alternative obtains, we would again have free hydrochloric acid, as is apparently the case when sodium hydrate is used, and which would immediately react with the tricalcic phosphate present.

From analogy one might expect the primary action of citric acid on calcium phosphates to be similar to that of hydrochloric acid, and that calcium citrate and free phosphoric acid are produced at least primarily. Thus:

It will be noted that theoretically 5 grams of calcium phosphate would require about 5 grams citric acid for the above reaction whereas in the prescribed method of dissolving calcium phosphates in citric acid solution 10 grams of citric acid are prescribed.

A secondary reaction undoubtedly occurs since the filtrate from the reaction after 30 minutes contains both lime and phosphoric acid. The following equations are suggestions as to what may occur:

When calcium carbonate is dissolved in citric acid solution the addition of phosphoric acid causes no precipitate.

Calcium phosphates dissolve in citric acid solutions, the solution remaining clear. These solutions will then dissolve large quantities of calcium carbonate and still remain clear. On continuing the addition of calcium carbonate, a critical point is reached at which a faint cloudiness or precipitate appears. This is a mixture of calcium phosphate and calcium citrate, but immediately after the cloudiness has become apparent the solution becomes like a magma and calcium citrate is precipitated which contains only traces of phosphoric acid. Apparently then in a mixture of calcium phosphate and citrate lime salts precipitate calcium citrate. Again calcium citrate in aqueous solutions of calcium phosphate renders both lime and phosphoric acid soluble.

The following was tried:

A, Calcium phosphate + 75 c.c. water. B, Calcium phosphate (as in A), calcium citrate, 75 c.c. water. Both were allowed to stand overnight. On filtering aliquots of A and B it was found that filtrate A contained both lime and phosphoric acid while filtrate B contained about 10 times as much lime as filtrate A with only about $3\frac{1}{2}$ times as much phosphoric acid as in filtrate A.

SUMMARY.

The results of these investigations show:

1. The substances sold as "Phosphate of lime" and "Calcii Phosphas B.P." are not pure tricalcic phosphate but are mixtures of di- and tricalcic phosphates.
2. Sodium phosphate (Na_2HPO_4) added to ammoniacal calcium chloride and the resulting precipitate washed with water yields a mixture of di- and tricalcic phosphate and calcium hydrate.
3. Bone ash dissolved in hydrochloric acid and precipitated with ammonia, the precipitate being well washed, yields also a mixture of di- and tricalcium phosphate and calcium hydrate.
4. When three equivalents of lime (3CaO) are made to act on one equivalent of phosphoric acid (P_2O_5) and the resulting precipitate removed with little delay pure tricalcium phosphate is obtained.
5. When two equivalents of lime (2CaO) are made to act on one equivalent of phosphoric acid (P_2O_5) the product is not dicalcic phosphate but is a mixture of di- and tricalcium phosphate.
6. In the case of pure tricalcium phosphate, about 91 % of the total phosphoric acid is soluble in the prescribed 2 % citric acid solution.

296 *The Solubility of Calcium Phosphates in Citric Acid*

in 30 minutes when following the method adopted for the determination of "citrate soluble" phosphoric acid.

7. By the simple addition of calcium carbonate to a pure tricalcic phosphate, the "citrate solubility" of the phosphoric acid is reduced from 91 to 84 %.

8. The availability of the phosphoric acid as judged by the extraction with 2 % citric acid solution is inexact, since the availability of the phosphoric acid in pure tricalcium phosphate is reduced from 91 % to 84.5 % by the addition of 14 % of lime as carbonate, and to 84.3 % by the further addition of 14 % lime as carbonate.

9. The prescribed 2 % citric acid solution is more correctly a solvent for lime than for phosphoric acid, since broadly speaking, the whole of the excess of lime beyond that present as tricalcic phosphate goes into solution in the first 30 minutes' extraction.

10. Pure tricalcic phosphate is largely soluble in 2 % citric acid solution, as are also the so-called tricalcic phosphates produced by the addition of ammonia to acid solutions of tricalcic phosphate, or by the mixing of disodium hydrogen phosphate with ammoniacal calcium chloride. (These are mixtures of di- and tricalcium phosphate in varying amounts.)

11. Since tricalcic phosphate and dicalcic phosphate are both soluble in the prescribed 2 % citric acid solution the statement that dicalcic phosphate can be differentiated from tricalcic phosphate, by means of the selective action of this solvent, is untenable.

It follows that the manurial value of phosphates cannot be determined by a 2 % citric acid solvent in the method prescribed, and it therefore is a matter for consideration whether or not the further use of this method should be continued.

APPENDIX.

A paper by R. Warington¹, published in the *Journal of the Chemical Society*, 1873, has been quoted extensively by authors of text-books on chemistry as the authority on the decomposition of $\text{Ca}_3\text{P}_2\text{O}_8$ on boiling this with water, and the conclusion formed is that $3\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaOH}_2\text{O}$ agrees best with the basic salt produced.

¹ R. Warington, "On the decomposition of Tricalcic Phosphate by Water," *Journal Chemical Society* (Entire Series), Vol. xxvi, p. 983.

$\text{Ca}_3\text{P}_2\text{O}_8$ was prepared by pouring pure CaCl_2 into a very dilute solution of Na_2HPO_4 plus 1 equivalent of ammonia. The alkaline phosphate was kept in excess during precipitation. The triphosphate was washed by decantation till no chlorine was found in the washings. All analyses were made unless the contrary is stated by dissolving an unweighed quantity of moist phosphate in hydrochloric acid, precipitating the lime with ammonium oxalate in acetic acid solution and afterwards the phosphoric acid with magnesia mixture.

The following figures are then given as representing the CaO and P_2O_5 in the phosphates prepared.

	(a)	(b)	(c)	(d)
CaO	54.37	54.78	54.95	54.93
P_2O_5 ...	45.63	45.22	45.05	45.07
	100.00	100.00	100.00	100.00

Warington has apparently assumed that because the ratio of lime to phosphoric acid approximates that of $3\text{CaO} : \text{P}_2\text{O}_5$, the compounds obtained were necessarily tricalcium phosphates, and the possibility of these products being mixtures of di- and tricalcic phosphate, or of these with free lime, appears to have been overlooked.

Let us examine for a moment the figures obtained by Warington.

(a) 54.37 CaO with 45.63 P_2O_5 . Now while theory requires 53.98 CaO to be associated with 45.63 P_2O_5 to form tricalcic phosphate, 54.37 CaO is found present. Therefore we have either

- (1) tricalcic phosphate plus free lime, or
- (2) tricalcic phosphate plus dicalcic phosphate plus free lime.

(2) will obtain if the amount of free lime is at all greater than that required for supposition (1).

(b) 54.78 CaO with 45.22 P_2O_5 . Now theoretically the 45.22 P_2O_5 present would require 53.05 CaO to form $\text{Ca}_3\text{P}_2\text{O}_8$, whereas there is 54.78 CaO present. Again therefore we have either a mixture of tricalcic phosphate and free lime or of di-, tricalcic phosphate and free lime.

(c) 54.95 CaO with 45.05 P_2O_5 . To produce $\text{Ca}_3\text{P}_2\text{O}_8$ from 45.05 P_2O_5 would require 53.30 CaO , and there is actually 54.95 CaO present. Here also we have either (1) a mixture of tricalcic phosphate and lime, or (2) a mixture of di- and tricalcic phosphate and lime.

In the first case a mixture of 98.35 % tricalcic phosphate (containing 53.30 CaO combined with 45.05 P_2O_5) with 1.65 % lime (CaO) would agree with Warington's figures found, viz. 54.95 CaO and 45.05 P_2O_5 . Now if the free lime actually present exceeds 1.65 then di- and tricalcic phosphate must be present and their amounts can be calculated but

298 *The Solubility of Calcium Phosphates in Citric Acid*

only when the figure for free lime present is assumed or is known. Assuming that $(\text{CaO})_2\text{H}_2\text{OP}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ is the dicalcic phosphate present and that the tricalcic phosphate is $\text{Ca}_3\text{P}_2\text{O}_8$ and the lime present as hydrate CaOH_2O the following mixtures will contain 54.95CaO associated with 45.05 P_2O_5 .

	(1)	(2)	(3)	(4)
Tricalcic phosphate ...	97.83	95.27	88.12	81.24
Dicalcic phosphate ...	—	2.12	8.04	13.73
Calcium hydrate ...	2.17	2.61	3.84	5.03
	100.00	100.00	100.00	100.00

and the ratio of lime to phosphoric acid would still be

$$54.95\text{CaO} : 45.05\text{P}_2\text{O}_5.$$

(d) 54.93CaO and 45.07 P_2O_5 . To produce $\text{Ca}_3\text{P}_2\text{O}_8$, 45.07 grams P_2O_5 would require 53.32CaO, whereas 54.93CaO is found present.

The remarks under (c) hold here also.

Since tricalcic phosphate has apparently not been obtained, the conclusions drawn by Warington are not justified.

The formula $(3\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{CaOH}_2\text{O})$ for the resulting product of boiling the above phosphates with water is deduced not from an analysis of the product but again from the ratio of CaO to P_2O_5 , the water of hydration or combination present appears to be more or less problematical.

However, assuming that the above formula approximates the composition of the resulting basic product it appears to be equally possible that this is still a mixture of di- and tricalcic phosphate with lime for $2\text{Ca}_3\text{P}_2\text{O}_8 \cdot 2\text{CaHPO}_4 \cdot \text{CaO}$ or $2(\text{CaO})_3\text{P}_2\text{O}_5 \cdot (\text{CaO})_2\text{P}_2\text{O}_5 \cdot \text{CaOH}_2\text{O}$ would agree equally well with the numbers found.

Further investigations on this matter are therefore desirable.

(Received April 17th, 1916.)