however, that no such concentration of the soil moisture with respect to phosphoric acid can be attained as is necessary for the continued existence of monocalcium phosphate, and that it must promptly and quite completely "revert" when added to the soil. It is obvious, therefore, that the relative values of the two phosphates as manures can not be entirely accounted for by the marked difference in their respective solubilities and consequent "availability," as has often been supposed.

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THE PHOSPHATES OF CALCIUM. II.[1]

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In the foregoing paper the equilibrium conditions in the system lime (CaO)-phosphoric acid (P_2O_5)-water, have been found for solutions which are comparatively quite concentrated with respect to both lime and phosphoric acid. It has been shown that for concentrations of P_2O_5 above 317 grams per liter the stable solid phase at 25° C. is monocalcium phosphate, and below that concentration down to 20 grams per liter the solid phase is dicalcium phosphate. The object of the present investigation was to find the equilibrium conditions for still lower concentrations of phosphoric acid and of lime and, especially in view of some preliminary experiments by Dr. Seidell, to find whether there might be a series of solutions, all of which can exist in equilibrium with tricalcium phosphate.

Several series of solutions were prepared by adding lime-water (Series M) or dicalcium phosphate (Series N) to solutions of phosphoric acid. The containing bottles were rotated in a constant temperature bath for about three months. After the analyses of the solutions had been made, it was found that between the end solutions of the foregoing paper and the most concentrated solutions of the present series there was a very large range for which there were no data. Another series (Series P) was prepared by adding dicalcium phosphate to somewhat more concentrated solutions of phosphoric acid than had been used in Series N. These solutions were rotated in the constant temperature bath

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for about ten weeks during the past summer. The temperature, however, was often somewhat above 25° and it was impossible to keep it constant. Possibly for this reason, the solutions were somewhat richer in lime than would be expected from the extrapolated curve in the foregoing paper.

The method of analysis for lime and phosphoric acid has been recently given by Jarvinen.[1] The sample for analysis is added slowly to a boiling solution of oxalic acid and ammonium oxalate (10 cc. N ammonium oxalate and 5 cc. 2N oxalic acid diluted to 50 cc.), and then a 1 per cent. ammonia solution is added, drop by drop, to alkalinity. The precipitate of calcium oxalate is filtered, washed, dried, and ignited in the usual way. The filtrate is analyzed for phosphoric acid by the usual ammonium-magnesium phosphate method.

No correction was made for the small quantities of solution which adhered to the solid, and as the solutions were very dilute and were removed by means of suction this error is very small.

The results obtained from the several series are given in the following table:

COMPOSITION OF AQUEOUS SOLUTIONS OF LIME AND PHOSPHORIC ACID

No.	Series.	CaO per liter solution. Grams.	P_2O_5 per liter solution. Grams.	Ratio: P_2O_5/CaO in solid phase.
1	P	7.61	19.96	1.3
2	P	6.51	16.52	1.2
3	P	5.01	12.82	1.3
4	P	3.42	8.16	1.3
5	P	2.42	5.75	1.2
6	P	1.58	3.66	1.2
7	N	0.544	1.516	1.2
8	N	0.400	1.108	1.1
9	N	0.291	0.773	1.1
10	N	0.232	0.662	1.1
11	N	0.145	0.381	1.0
12	M	0.062	0.109	0.9
13	M	0.049	0.088	0.9
14	M	0.034	0.015	0.8
15	M	0.587	0.013	0.4
16	M	0.789	0.012	0.4

The ratio of P_2O_5/CaO in dicalcium phosphate, $CaHPO_4$, is 1.27 and the first six solutions in the table evidently represent solutions in equilibrium with that solid. Solutions 7 to 14 inclusive are in equilibrium with a solid phase for which the ratio

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[1] *Z. anal. Chem.*, **43**, 559 (1904).

P_2O_5/CaO varies from 1.17 to 0.85. The solid phases over this range are evidently solid solutions. Solution 14 contains only 15 parts per million of P_2O_5 and 34 parts per million of lime, and it will be noticed that the ratio P_2O_5/CaO in the solid phase is 0.85. This ratio for tricalcium phosphate $[Ca_3(PO_4)_2]$ is 0.84. Solutions 15 and 16 show markedly alkaline reactions to phenolphthalein, solution 13 an acid reaction, while solution 14 was almost neutral. Thus if lime-water is just neutralized with phosphoric acid and then if equilibrium conditions are obtained, the solid phase will be tricalcium phosphate or a solid solution of almost the same composition. The analytical methods are not delicate enough to determine whether there is a range of solution in equilibrium with tricalcium phosphate, although it may be stated that such a range would be extremely small in extent.

For very low concentrations of phosphoric acid there is quite a large quantity of lime in solution, while the solid phase here again is undoubtedly a solid solution. One of the solids comprising the first solid solution may safely be assumed to be dicalcium phosphate, but it is impossible to say what the other solid is. In the case of the second series of solid solutions one solid is lime. It may be, too, that there is only one series extending over the whole range, in which case the solids are dicalcium phosphate and lime.

Theoretically, there should be a point of intersection of the curve along which the solid is dicalcium phosphate and that along which the solid is the solid solution. At that point we should have present dicalcium phosphate, the solid solution of the limiting composition, liquid and vapor, and with the temperature fixed there would be an invariant point. It may be seen from the table that the composition of the limiting solid solution is quite close to that of dicalcium phosphate, and the analytical difficulties have made it impossible to determine the exact composition of the solid solution. The table shows, however, that the ratio P_2O_5/CaO in the limiting solid solution must be above 1.10 and below 1.27, and it shows that the composition of the liquid solution at that point lies between 0.40 and 0.54 gram CaO per liter, and between 1.11 and 1.52 grams P_2O_5 per liter.

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