of the same concentration. Thus formaldehyde added to distilled water in the proportion of 1 : 40,000 had diminished to 1 : 160,000 in twenty-eight days, while in a parallel experiment with milk it showed the same diminution in two days.

Stronger solutions are much more stable. Formaldehyde in water 1 : 1000 showed no appreciable loss in five months. The rate of disappearance of formaldehyde from milk containing 1 : 1,000 was practically the same as from water containing 1 : 5,000.

The rate of disappearance did not seem to be affected by allowing the milk to become sour before adding the formaldehyde.

The hydrochloric acid and ferric chloride test for formaldehyde in milk is sensitive to a dilution of 1 : 250,000. Sourness of the milk does not in itself diminish the delicacy of the reaction, but when milk is preserved by means of formaldehyde the latter will have largely disappeared before the milk becomes sour. In all of the cases here studied, however, distinct reactions were obtained at least as long as the milk remained sweet and of normal appearance. That these results indicate a less rapid disappearance of formaldehyde than was found by Rivas or by Bigelow is thought to be due mainly to the greater delicacy of the test as modified for our experiments, though doubtless differences in laboratory temperature and in the nature of the milk used may also have affected the results.

The gallic acid test is much more delicate than the hydrochloric acid and ferric chloride test and gives more conclusive results with samples which have stood until the formaldehyde has largely disappeared.

QUANTITATIVE LABORATORY, COLUMBIA UNIVERSITY,
NEW YORK, October, 1905.

THE PHOSPHATES OF CALCIUM. I.[1]

BY F. K. CAMERON AND A. SEIDELL.

Received October 16, 1905.

WHEN the phosphates of calcium are brought into contact with water they are partially decomposed, owing to hydrolysis. At ordinary temperatures this decomposition generally proceeds at a very slow rate, and in consequence equilibrium conditions

---

[1] Published by permission of the Secretary of Agriculture.

have probably been attained in but very few of the experiments which have been described hitherto.

The purpose of this investigation was to determine the composition of the resulting solutions and the solids in contact with them in the system water (H_2O), lime (CaO), and phosphoric acid (P_2O_5), under conditions of final equilibrium at a definite temperature and throughout a wide range of concentration. The temperature selected was 25°, and the concentration of phosphoric acid (P_2O_5) varied up to nearly 540 grams per liter of solution, the concentration with respect to lime varying in consequence to a maximum of 77 grams per liter.

Several series of solutions were prepared by adding so-called tricalcium phosphate, dicalcium phosphate or monocalcium phosphate to solutions of phosphoric acid. After prolonged standing or heating, the containing bottles were rotated for some time in a water-bath kept at a constant temperature. When the contents of the bottles were to be analyzed, they were allowed to stand until the solid material had settled. A weighed amount of the solution was made up to definite volume and aliquot portions were taken for analysis. By subtracting the sum of the weights of the lime and phosphoric acid contained in a given volume of solution from the total weight of the solution, the weight of the water present was determined.

In the analyses the lime was determined by taking an aliquot, adding a large excess of ammonium oxalate and heating to incipient boiling. Ammonia water in excess was then added and the solution kept for some time on the hot plate at a temperature just below boiling. If the solution remained turbid, more ammonium oxalate was added until it was certain that this salt was present in excess, and a granular precipitate settled to the bottom of the vessel, leaving a clear supernatant solution. When it appeared necessary, the filtered and washed calcium oxalate was redissolved and again precipitated in the usual way. In this way a satisfactory separation of the phosphoric acid from the lime was effected and the latter was then determined in the usual manner, weighing as oxide. The phosphoric acid was determined by the volumetric method of the Association of Official Agricultural Chemists.[1]

---

[1] Bull. No. 46, Division of Chemistry, U. S. Dept. Agriculture (1899), p. 11.

As equilibrium is reached at quite a slow rate, several series of mixtures were made by different methods.

Series A.—To solutions of phosphoric acid of concentrations up to about 200 grams per liter, Kahlbaum's tricalcium phosphate was added until a solid residue was left which did not dissolve even after long standing.

Series B.—To solutions of phosphoric acid of the above concentration dicalcium phosphate was added until a solid residue was left.

Series C.—Monocalcium phosphate containing an excess of phosphoric acid was added to water until a solid persisted. The results of this last series have already been published.[1] Owing to a typographical error in misplacing a decimal point the results for calcium, as printed, are one-tenth the correct value. Making the correction, it is possible to calculate approximately, from the data given, the ratio of phosphoric acid to calcium in the solid residue, although exact ratios cannot be calculated since the specific gravities of the solutions were not determined.

The identification of the solid phases in contact with the solutions was an essential feature of the investigation. For this purpose microscopic examinations were made in some instances, but the chemical analyses were made in all cases. The solids could not be separated from the adhering solution, and so portions of the solids, together with the adhering liquid, were removed, weighed and analyzed for the amounts of lime and phosphoric acid present. The water was then known by difference. The composition of the solid phases in contact with the solutions was determined by an algebraic formulation.

Suppose P to represent the total phosphoric acid found in the solid residue and adhering solution, P_1 the phosphoric acid actually in the solid, P_2 the phosphoric acid dissolved in the adhering solution, and L, L_1, L_2 the corresponding values for lime. Then

$$P = P_1 + P_2 \qquad (1)$$

and

$$L = L_1 + L_2. \qquad (2)$$

Suppose W represent the total water found in the solid and adhering solution, W_1 the water combined in the solid, and W_2 the water in the adhering solution. Then

$$W = W_1 + W_2. \qquad (3)$$

---

[1] This Journal, **26**, 1454 (1904).

If the ratio between the water and the phosphoric acid in the solid W_1/P_1 be taken as m and the ratio to lime W_1/L_1 be taken as n (m and n being constants readily calculated from the formula of the substance) then substituting in (3), it follows that

$$W_2 = W - m\ P_1 \tag{4}$$

or

$$W_2 = W - n\ L_1. \tag{5}$$

Then

$$\frac{P_2}{W_2} = \frac{P_3}{W_3} \tag{6}$$

and

$$\frac{L_2}{W_2} = \frac{L_3}{W_3}, \tag{7}$$

where P_3, L_3 and W_3 represent the phosphoric acid, lime and water respectively in any given volume of the supernatant solutions, whose compositions have been determined. Substituting (1) and (4) in (6), it follows that

$$\frac{P - P_1}{W - mP_1} = \frac{P_3}{W_3}$$

whence

$$P_1 = \frac{PW_3 - P_3W}{W_3 - mP_3}, \tag{8}$$

and similarly

$$L_1 = \frac{LW_3 - L_3W}{W_3 - nL_3}. \tag{9}$$

The absolute values of P_1 and L_1 are of little interest, but their ratio will determine the nature of the solid in the residue, hence

$$\frac{P_1}{L_1} = \frac{(PW_3 - P_3W)\ (W_3 - nL_3)}{(W_3 - mP_3)\ (LW_3 - L_3W)}.$$

For monocalcium phosphate [$CaH_4(PO_4)_2.H_2O$], $n = 0.9643$, $m = 0.3800$ and $P_1/L_1 = 2.5$; for dicalcium phosphate ($CaHPO_4.2H_2O$), $n = 0.8035$, $m = 0.6338$ and $P_1/L_1 = 1.3$; for tricalcium phosphate [$Ca_3(PO_4)_2$], n and m disappear and $P_1/L_1 = 0.85$. These ratios are sufficiently wide apart in magnitude to make the identification of the corresponding phosphates an easy matter, and consequently in applying the above formula to the experimental data only four-place logarithms were used and in the tabulated results the ratios are given only to the first decimal place.

It will be seen from the table that the analyses of the solid phases in contact with the solutions yielded a constant ratio (P_2O_5 : CaO) of about 1.3, which is the ratio for dicalcium phosphate, $CaHPO_4.2H_2O$. That equilibrium conditions had been realized was assured, for in Series *A* the solid initially added to the acid solutions was tricalcium phosphate, and finally the solid was dicalcium phosphate; and in Series *C* the solid initially used was monocalcium phosphate, and finally the solid was dicalcium phosphate; while in Series *B*, dicalcium phosphate was dissolved in phosphoric acid solution and the solid in excess again proved to be dicalcium phosphate. Thus starting from solids in which the ratio of P_2O_5 to CaO is greater than, equal to, or less than 1.3, the ratio finally obtained in all cases was 1.3, showing that a solid containing P_2O_5 to CaO in this ratio is the stable phase in each case, and it is safe to conclude that dicalcium phosphate is the solid phase over the range of concentration in the three series. It should be further pointed out that the points on the diagram, in which the abscissas are CaO per liter and ordinates P_2O_5 per liter, all lie on a smooth curve, another indication that equilibrium had been reached.

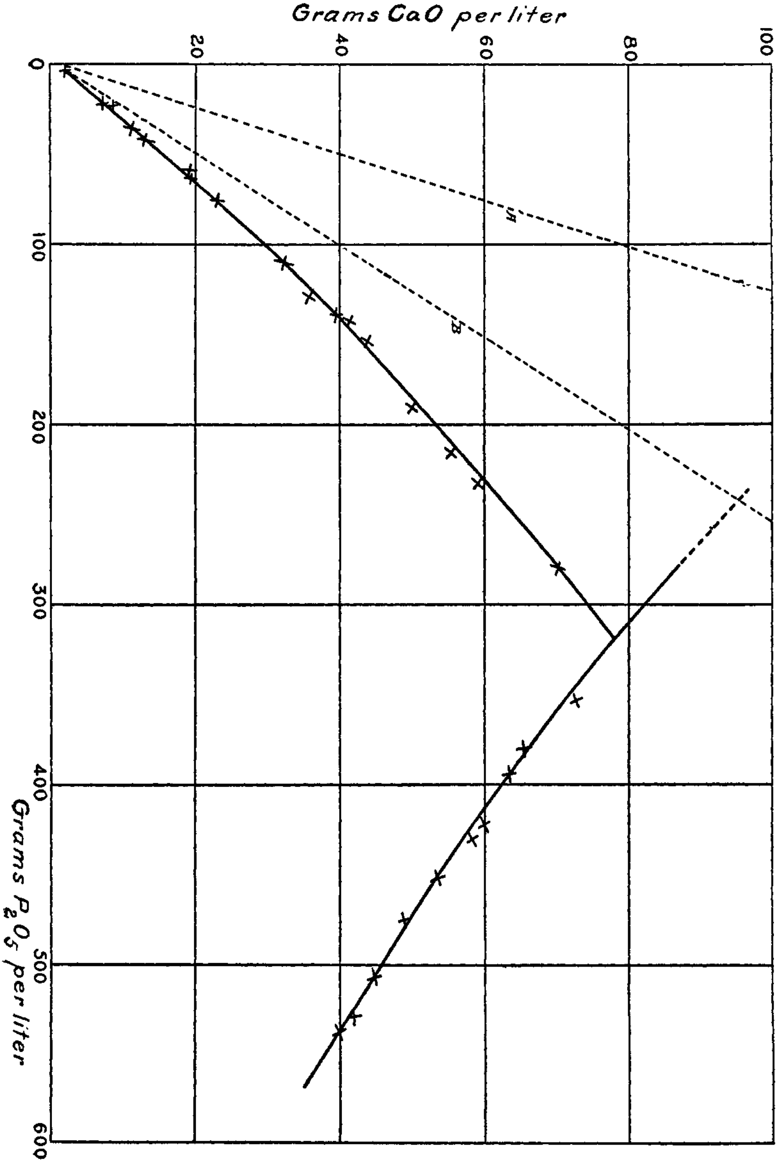
Two further series of solutions were prepared, using more concentrated solutions of phosphoric acid than those employed in the first three series. In one case, Series *D*, the solid added initially was monocalcium phosphate, while in the other case, Series *E*, the solid added was dicalcium phosphate. The analyses of the solid phase show that in every case it was undoubtedly monocalcium phosphate [$CaH_4(PO_4)_2.H_2O$], the ratio of P_2O_5 to CaO varying but little from the calculated ratio 2.5. That equilibrium had been reached was indicated by the fact that the points obtained from two differently prepared series all lay on a smooth curve; also in Series *D* monocalcium phosphate goes into solution as such and the solid phase remaining has the same composition as the solid originally added, while in Series *E* there is a complete change in the composition of the solid from dicalcium phosphate to monocalcium phosphate.

The results obtained from the several series are given in the following table, and the concentrations of the solutions are represented in the accompanying chart.

Composition of Aqueous Solutions of Lime and Phosphoric Acid.

Series.	CaO per liter solution. Grams.	P_2O_5 per liter solution. Grams.	Ratio P_2O_5/CaO in solid.
A	1.71	4.69	1.2
C	7.48	22.39	1.4
A	8.10	23.37	1.3
A	11.57	36.14	1.3
C	12.88	41.24	1.5
A	18.77	59.35	1.3
C	19.25	63.03	1.4
A	23.31	75.95	1.2
C	23.69	79.10	1.5
A	32.41	109.8	1.3
A	35.90	129.8	1.3
A	39.81	139.6	1.3
A	40.89	142.7	1.3
A	43.82	154.6	1.3
B	49.76	191.0	1.4
B	55.52	216.5	1.3
B	59.40	234.6	1.4
B	70.31	279.7	1.5
E	72.30	351.9	2.4
E	69.33	361.1	2.4
E	65.46	380.3	2.4
E	63.53	395.1	2.4
E	59.98	419.7	2.6
E	59.25	424.6	2.4
D	57.74	428.0	2.6
D	53.59	451.7	2.2
D	48.78	475.3	2.2
D	44.52	505.8	2.3
D	41.86	528.9	2.4
D	39.89	538.3	2.5

When the results for concentrations in solution are plotted (see Fig.) it will be seen that they fall upon two curves. The curve representing the series of solutions in contact with dicalcium phosphate as solid phase, shows an increasing concentration of lime with increasing concentration of phosphoric acid, while on the contrary the curve representing the series of solutions in contact with monocalcium phosphate as solid phase, shows a decreasing concentration of lime with increasing concentration of phosphoric acid. Both curves approximate straight lines, although there is evident a slight curvature in the one representing the solutions in contact with dicalcium phosphate. The intersection of the two curves at which point both mono- and dical-


Grams CaO per liter
0
20
40
60
80
100
Grams P_2O_5 per liter
100
200
300
400
500
600
A
B

cium phosphate are stable solid phases in contact with the solution, is found by interpolation to represent a concentration of approximately 77 grams lime and 317 grams phosphoric acid per liter of solution, the solution having a specific gravity of approximately 1.29 as compared with pure water at the same temperature.

It has been noted by many investigators that when monocalcium phosphate is added in large amount to water, agitation, long standing, or rise of temperature will cause a precipitate of dicalcium phosphate to form. This fact suggests the possibility of monocalcium phosphate existing in meta-stable equilibrium in contact with a solution containing less phosphoric acid than that required by the triple point as charted. Experiments showed that such meta-stable conditions could be obtained rather readily, but no attempt was made to see how far the monocalcium curve could be extended.

The two dotted lines on the diagram indicate the systems in which the ratio $P_2O_5:CaO$ is the same as in the compounds $CaHPO_4$ and $CaH_4(PO_4)_2$, respectively. The line *A* does not cut the curve representing the solution in equilibrium with solid dicalcium phosphate and hence it is impossible at the temperature 25° to obtain a solution in equilibrium with a solid of the composition $CaHPO_4.2H_2O$. On the other hand, the line *B* cuts the curve representing the solutions in equilibrium with monocalcium phosphate, but the point of intersection is in a field unstable with respect to dicalcium phosphate. It is therefore possible, theoretically, to obtain a solution of monocalcium phosphate in equilibrium with monocalcium phosphate of the composition $CaH_4(PO_4)_2.H_2O$.

Tricalcium phosphate, when brought into contact with water, always gives a solution with an acid reaction,[1] this fact having been observed many years ago by Warington.[2] Repeated washing of the solid residue finally leaves a product which yields a solution neutral to litmus, but containing a smaller ratio of P_2O_5

---

[1] Apatite, of which a number of specimens from different sources have been examined, always gives a solution with an alkaline reaction. But many specimens of South Carolina and Tennessee rock phosphate give solutions with acid reaction to litmus, as does also the precipitated product of the laboratory. It is further worthy of note that when these phosphates which give an acid solution are powdered or precipitated in a finely divided form and are shaken up with a solution of litmus, on settling they carry down all the coloring-matter with them, leaving the supernatant solution clear and colorless, though still quite acid, as can be seen by adding more litmus to the decanted liquor.

[2] *J. Chem. Soc.*, **26**, 983 (1873).

to CaO than that required by the formula $Ca_3(PO_4)_2$. It is possible to precipitate products containing still smaller ratios of P_2O_5 to CaO which yield solutions containing more lime than phosphoric acid and which are alkaline to such indicators as litmus or phenolphthalein. Some preliminary attempts were made to follow the solubility curve for lime in solutions of phosphoric acid of lower concentrations than are given in the table, but owing to the length of time required to reach conditions of equilibrium and the analytical difficulties involved, the reliability of the results obtained was open to doubt and consequently this work was postponed for a separate investigation. Some idea as to the concentrations below which tricalcium phosphate might exist as a stable solid phase was, however, obtained.

A rather dilute solution of sodium phosphate, alkaline to litmus or phenolphthalein, was added to a dilute neutral solution of calcium chloride. After the addition of the first drop or two of the alkaline phosphate solution, the neutral calcium chloride solution became acid, and became more and more acid on further addition of the alkaline solution, as indicated by the color of the added litmus, up to a certain point, then gradually less and less acid, finally becoming alkaline. The points at which the maximum acidity was reached and at which the solution passed from acid to alkaline could not be sharply determined. The precipitated solid obtained by adding various amounts of the phosphate solution to a definite volume of the calcium chloride solution was always found to be dicalcium phosphate whenever the resulting supernatant solution possessed an acid reaction. When the supernatant solution was alkaline, however, the precipitate always contained a larger proportion of lime than is required by the formula for tricalcium phosphate. It became evident, therefore, that either tricalcium phosphate can exist under equilibrium conditions in contact with water over but a very narrow range of concentration or that it exists only as a metastable form in contact with water at room temperature, although the rate of change to a more stable form is probably quite slow.

The results given in the foregoing paragraphs have a special significance for agricultural investigations. It is generally held that monocalcium phosphate is the form contained in superphosphates or "acidulated" phosphates, and that the dicalcium phosphate is the salt of "reverted" phosphates. It is evident, 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.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

THE PHOSPHATES OF CALCIUM. II.[1]

BY F. K. CAMERON AND J. M. BELL.

Received October 16, 1905.

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

---

[1] Published by permission of the Secretary of Agriculture.