

THE ACTION OF WATER UPON THE PHOSPHATES OF CALCIUM.¹

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INTRODUCTION.

IT HAS been shown by a number of investigators² that each of the three phosphates of calcium is decomposed or hydrolyzed by water. The dicalcium compound, however, at ordinary temperatures is decomposed to a much less extent than either of the others. The investigations which have so far been made on the action of water upon the phosphates of calcium were conducted, for the most part, under widely different conditions with respect to temperature, time of digestion, purity of product, etc. The experiments described in this paper were undertaken for the purpose of making a comparison of the decomposing action of water upon the three phosphates³ under uniform conditions; and in addition, to obtain data upon the effect of some other calcium salts and of carbon dioxide upon the hydrolysis or decomposition which takes place. The calcium salts chosen are those most commonly present in the principal natural and artificial fertilizers. Their action upon the phosphates, which they accompany, is not clearly understood, although a great many important observations upon the subject have been made.

Tricalcium phosphate, prepared by precipitation, is non-crystalline, and a reasonably pure and crystalline product, with well defined characteristics of a definite molecular species, has not been prepared. It is significant that crystallized tricalcium phosphate does not itself occur in nature,⁴ but only as a mixture or in combination with other substances.

Both monocalcium and dicalcium phosphates (or their hydrates) separate in crystalline form as definite, well characterized compounds, from solutions containing an excess of phosphoric

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² For references see this Journal, **26**, 885 (1904).

³ The occurrence of the so-called tetracalcium phosphate, $\text{Ca}_4\text{P}_2\text{O}_8$, in practically pure condition as crystals in a slag has been observed by Otto (*Chem. Ztg.*, **18**, 235 (1887)) and, mixed with other substances, by several observers, *vide*, Wiley and Krug (*J. Anal. Chem.*, **5**, 685 (1891)), but it does not appear to have been recognized as formed in the wet way, and, therefore, need not be further considered here.

⁴ *Vide*, Groth: *Tabellarische Übersicht der Mineralien*, p. 71: "Dasselbe gilt — in dem als Hauptbestandtheil wohl das normale Calciumphosphat $(\text{PO}_4)_2\text{Ca}_3$ anzunehmen ist, welches man bisher in der Natur noch nicht in reinem Zustande kennt: würde dasselbe regulär krystallizirt, so wäre —."

acid. It has been frequently observed that monocalcium phosphate is, in part at least, decomposed in water, and that in general the extent of the decomposition depends upon the proportion of water to solid phosphate.¹ Judging from the statements in the literature, dihydrate of dicalcium phosphate is the compound which, at ordinary temperatures and conditions, is the stable one over the widest range of concentration of the supernatant acid solution. Rindell,² however, observed that this substance was slightly decomposed by water.

The phosphates used in this investigation were obtained in original sealed packages from Kahlbaum. The tricalcium compound was a white powder in which no crystalline structure could be detected by a microscopical examination. The dicalcium compound was finely powdered, but remnants of crystals were readily detected by the microscope, and the monocalcium compound was in small but well-formed crystals. While it was certain that these samples were reasonably free from other contaminations, they were all found to contain more phosphoric acid than would be required by the respective formulas for tri-, di- or monocalcium phosphate. While this detracts from the value of the data obtained from the point of view of absolute measurements, it cannot be regarded as materially affecting the significance of the results for demonstrating the nature of the reaction between the several phosphates and water. From their nature it is impracticable to obtain tri- or monocalcium phosphate free from an excess of either base or acid, and consequently the absolute values of the solubility effects are of minor importance as compared with the order of magnitude and general direction of the effects.

In order to obtain uniformity all of the solutions were prepared at the same time, as nearly as practicable, by weighing into 8-ounce sterilizer bottles the desired amounts of the phosphate and the other calcium salts. In every case 200 cc. of distilled water were added. The bottles were kept in a large water-bath maintained at 25° C., but were removed at intervals and shaken by hand. The bottles containing the solutions which were treated with carbon dioxide were taken from the bath at each introduction of the gas and a rapid stream of it passed through the solutions for one minute.

¹ Stoklasa · *Listy Chem.*, **13**, 203, 240, 273. Abstract *J. Chem. Soc.*, **58**, 695 (1890). The original papers are not accessible to us.

² *Compt. Rend.*, **134**, 112 (1902).

There were three series of 24 bottles each, corresponding to the tri-, di- and monocalcium phosphate respectively. The bottles in each series formed two groups of twelve each, identical in all respects save the presence of carbon dioxide in one group of each series and its absence from the other. The bottles were withdrawn from the constant temperature bath in groups and aliquot portions of the clear solutions taken for analysis.

All figures in the tables are in grams per liter. No correction for water or adhering acid was made in weighing the original phosphates.

Tricalcium Phosphate.—Warington¹ showed that tricalcium phosphate containing slightly more calcium than required by the formula was decomposed by boiling in water for two hours to such an extent that the solution contained about three times as much phosphoric acid as calcium. The decomposing action was possessed to a lesser extent by cold water. He also found that the amount of phosphoric acid which water would extract depended on the relative masses of the phosphate and water that are brought together. These observations have been verified by the experiments described in a recent paper from this laboratory. The material which was used in the experiments there recorded contain, like Warington's, a slight excess of calcium. The analysis of the material showed it to correspond to 85.07 per cent. calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, 0.14 per cent. calcium hydroxide, $\text{Ca}(\text{OH})_2$, and 14.69 per cent. moisture.

The material used for the experiments recorded in the present paper corresponded to 87.22 per cent. calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, 2.83 per cent. phosphoric acid, H_3PO_4 , and 9.98 per cent. moisture. A comparison of the results obtained with the two compounds is given in Table I, the figures for the compound containing an excess of calcium being interpolated from results already published. These figures not only show that the nature of the particular product used determined the composition of the solution and that the phosphate which originally contained the larger proportion of phosphoric acid yielded the more acid to the solution, but an inspection of the figures brings out the important fact that in the last series the amount of phosphoric acid, PO_4 , entering solution is less than would be expected from the excess of acid in the original phosphate above that required by the formula $\text{Ca}_3(\text{PO}_4)_2$.

¹ *J. Chem. Soc.*, **26**, 953 (1873).

TABLE I.

Grams phosphate per liter.	Grams PO_4 dissolved per liter.	
	Sample containing an excess of Ca.	Sample containing an excess of PO_4 .
5	0.068	0.109
10	0.113	0.189
20	0.185	0.324
40	0.310	0.558

From these results it is apparent that all determinations of the solubility of tricalcium phosphate, which have so far been made, are open to objection. The products which have been used vary among themselves, according to their source and preparation, to as great, if not a greater, extent than the samples which were used for the preceding experiments, and the absolute values of the results obtained can, therefore, have very little value as physical constants.

The results of the analyses of the series of solutions prepared with the Kahlbaum tricalcium phosphate, together with calcium sulphate or calcium carbonate and without, in distilled water previously boiled to eliminate dissolved carbon dioxide and then cooled rapidly, and in distilled water containing carbon dioxide, are given in Table II.

TABLE II.—ACTION OF WATER AND SOLUTIONS UPON TRICALCIUM PHOSPHATE. TIME OF CONTACT, THIRTY-FIVE DAYS.

Grams $\text{Ca}_3(\text{PO}_4)_2$ per liter.	Without CO_2 . Grams per liter of		With CO_2 . Grams per liter of	
	Ca.	PO_4 .	Ca.	PO_4 .
With water alone.				
5	0.014	0.109	0.085	0.239
10	0.019	0.189	0.114	0.344
20	0.031	0.324	0.114	0.481
40	0.050	0.558	0.134	0.738
In contact with solid calcium sulphate.				
5	0.620	0.113	0.646	0.217
10	0.640	0.205	0.659	0.315
20	0.644	0.360	0.662	0.451
40	0.666	0.623	0.682	0.715
In contact with solid calcium carbonate.				
5	0.034	trace	0.352	trace
10	0.073	"	0.354	"
20	0.106	"	0.327	"
40	0.134	"	0.306	"

The average of sulphate determinations for the saturated calcium sulphate solutions gave 2.087 grams CaSO_4 per liter of solution without CO_2 , and 2.029 grams CaSO_4 per liter of solution with CO_2 . The calcium determinations as given in the above table for these solutions are to be corrected for 0.614 and 0.597 gram Ca, dissolved as calcium sulphate in the solutions free from and containing carbon dioxide, respectively, in order to obtain the amounts of calcium which were dissolved as phosphate.

The results contained in Table II show, in general, the direction of the changes in the decomposition or hydrolysis of tricalcium phosphate produced by the two calcium salts and carbon dioxide. It is seen that calcium sulphate augments the decomposition when no carbon dioxide is present; slightly decreases it when carbon dioxide is present, while calcium carbonate retards it. Carbon dioxide increases the amount of PO_4 dissolved in the solutions of water alone and the saturated calcium sulphate solutions, but has no other effect than to increase the amount of calcium in the solutions in contact with calcium carbonate. It appears that solutions of neither calcium carbonate nor bicarbonate have any marked solvent or decomposing action upon the calcium phosphate.

Georgievics¹ studied the action of carbon dioxide on tricalcium phosphate. He experimented with quantities of material only one-tenth as large, per liter of water, as used in the work here described. He concluded that tricalcium phosphate is transformed into dicalcium phosphate and dissolved as such in solutions treated with a slow stream of carbon dioxide for twenty-four to forty-eight hours, but he also states that tricalcium phosphate dissolves as such in solutions of calcium bicarbonate.

An examination of the figures in Table II will show that the ratio of the reacting weight of calcium to that of phosphoric acid in solution steadily increases with increase of the mass of solid phosphate, and does not remain constant. Georgievics was probably misled, on account of the small quantities of solid phosphate he used producing but slight differences in the solutions, into thinking this ratio was constant and approximately that required by the formula for dicalcium phosphate. Only traces of phosphoric acid were found in the solutions containing calcium bicarbonate, which invalidates Georgievics' further assumption that under such circumstances tricalcium phosphate dissolves as such.

¹ *Monatsh. für Chem.*, 12, 566 (1891).

Dicalcium Phosphate.—The action of water on dicalcium phosphate has recently been investigated by Rindell,¹ who employed a product having a composition closely approximating that represented by the formula $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$. He found that the ratio of the quantities of lime and phosphoric acid dissolved is practically constant and independent of the relative amounts of solid and solvent used. This ratio, however, in molecular quantities, as calculated from Rindell's results, was 1.68 instead of unity, indicating that when hydrated dicalcium phosphate is subjected to the action of water a decomposition takes place, and that a condition of equilibrium is reached, the solution containing an excess of phosphoric acid.

The sample of dicalcium phosphate used for the experiments, described in this paper, gave, on analysis, Ca 29.06 per cent., PO_4 70.84 per cent., corresponding to 98.71 per cent. dicalcium phosphate and 1.23 per cent. phosphoric acid. The results presented in Table III for the solutions of this product in water alone show, as do Rindell's, that the amount of calcium and phosphoric acid dissolved is practically independent of the proportion of phosphate to water used. The ratio of the molecular quantities of calcium, Ca, to phosphoric acid, PO_4 , dissolved is, however, 1.32 instead of 1.68, as found by Rindell.

The difference in the molecular ratios of the calcium to phosphoric acid in solution in the two cases is probably due to the nature of the sample employed. In the latter case an excess of phosphoric acid above that necessary to combine with the calcium was shown by the analysis to be present. One might, therefore, expect the ratio in this latter case to be the larger, whereas, actually, it was less.

The results of the experiments upon the conduct of dicalcium phosphate in contact with pure water and when in contact with an excess of calcium sulphate, or calcium carbonate, as well as similar solutions treated with carbon dioxide, are given in Table III.

The average of sulphate determinations in the saturated calcium sulphate solutions gave 2.108 grams CaSO_4 per liter of solution without CO_2 , and 1.941 grams CaSO_4 per liter of solution with CO_2 . The calcium determinations as given are to be corrected for 0.620 and 0.571 gram of calcium dissolved as calcium sul-

¹ *Compt. Rend.*, 134, 112 (1902).

TABLE III.—ACTION OF WATER AND SOLUTIONS UPON DICALCIUM PHOSPHATE. TIME OF CONTACT, THIRTY-EIGHT DAYS.

Grams CaHPO ₄ per liter.	Without CO ₂ , Grams per liter of		With CO ₂ , Grams per liter of	
	Ca.	PO ₄ .	Ca.	PO ₄ .
	With water alone.			
5	0.039	0.090	0.169	0.392
10	0.033	0.116	0.160	0.388
20	0.036	0.117	0.162	0.395
40	0.039	0.131	0.166	0.402
	In contact with solid calcium sulphate.			
5	0.619	0.016	0.683	0.299
10	0.624	0.016	0.690	0.306
20	0.612	0.040	0.687	0.281
40	0.636	0.064	0.687	0.299
	In contact with solid calcium carbonate.			
5	0.110	0.037	0.291	0.084
10	0.110	0.043	0.284	0.089
20	0.119	0.043	0.289	0.080
40	0.120	0.045	0.313	0.081

phate in the solutions free from and containing carbon dioxide, respectively. It is interesting to observe the effect here of the phosphate in decreasing the solubility of the calcium sulphate.

The results in Table III show that, with the possible exception of the saturated calcium sulphate solutions, the decomposition of the dicalcium phosphate depends but slightly upon the relative amounts of solid and solvent which are present. In all cases the addition of carbon dioxide to the solutions has resulted in an increase in the decomposition. The presence of calcium sulphate, as well as of calcium carbonate, decreased the amount of phosphoric acid which dissolved. In the case of the saturated calcium sulphate solutions not treated with carbon dioxide the calcium in solution was only equivalent to that required by the sulphate dissolved. In the solutions treated with carbon dioxide, however, the amount of calcium present was more, and was probably dissolved either as phosphate or bicarbonate. It is to be noted that the calcium sulphate in the solutions treated with carbon dioxide was less than in the solutions not so treated. It, therefore, appears that the solubility of the calcium sulphate itself was decreased by the other calcium salts present.

With regard to the solutions in contact with calcium carbonate it will be observed that in the solutions not treated with carbon dioxide more phosphoric acid was present than in the similar solutions in contact with calcium sulphate. In the solutions treated with carbon dioxide, however, less phosphoric acid was dissolved than in the similar solutions in contact with calcium sulphate. It follows, therefore, that calcium hydrogen carbonate solutions have a more marked action on dicalcium phosphate than do solutions of calcium sulphate alone, but calcium sulphate and carbon dioxide together decompose a larger quantity of phosphate than either of the calcium salts separately.

Monocalcium Phosphate.—It has been stated by Stoklasa¹ that monocalcium phosphate itself is not hygroscopic, but that the hygroscopic nature of the usual preparation is due to free phosphoric acid, which is almost always present. Stoklasa treated preparations of monocalcium phosphate with varying quantities of water. The original papers are not accessible to us, however, and a comparison can not be made of the results obtained by him with those obtained in this investigation.

The preparation which was used for the work described in this paper was well crystallized, but evidently contained free phosphoric acid in considerable excess, as shown by the following analysis: Ca found, 15.17 per cent.; $\text{CaH}_4(\text{PO}_4)$ calculated from Ca found, 88.67 per cent.; PO_4 calculated from Ca found, 71.88 per cent.; PO_4 found, 79.58 per cent.

On account of its greater solubility it was necessary to use larger proportions of the monocalcium phosphate than of the other phosphates to the usual volume of water in order to obtain the solutions in contact with the solid phosphate. The results which were obtained by digesting different quantities of the salt in water and in solutions in contact with solid calcium sulphate are given in Table IV.

TABLE IV.—ACTION OF WATER AND SOLUTION OF CALCIUM SULPHATE UPON MONOCALCIUM PHOSPHATE.

Grams $\text{CaH}_4(\text{PO}_4)_2$ per liter.	With water alone. Grams per liter of		With solid CaSO_4 . Grams per liter of	
	Ca.	PO_4 .	Ca.	PO_4 .
40	0.534	29.85	0.572	30.38
80	0.920	54.98	1.051	56.58
120	1.375	84.04	1.463	84.30
160	1.692	105.50	1.797	106.02

¹ *Loc. cit.*

From these data it appears that monocalcium phosphate is greatly decomposed by water, and that the resulting solution is to be regarded as a solution of the decomposition products rather than of the substance itself. The presence of an excess of calcium sulphate does not materially affect the amount of phosphoric acid entering the solution, the slight discrepancies appearing in the table being due much more probably to experimental errors than to real differences. A similar set of solutions was also treated with calcium carbonate in the proportion of 10 grams of the carbonate to a liter of solution with the result that the carbonate was entirely dissolved and the phosphoric acid in solution and the acidity of the solutions were reduced in amounts practically equivalent to the added calcium carbonate. The results are not given, since they show nothing further regarding the action of the solutions.

Duplicate sets of all these solutions were treated repeatedly with carbon dioxide, but the treatment in no case produced any appreciable effect upon the phosphoric acid nor calcium dissolved, nor upon the acidity of the resulting solution and it does not seem worth while to present the results here.

SUMMARY.

From the foregoing data it appears that tricalcium phosphate and monocalcium phosphate are alike in their conduct towards water in that both are very much hydrolyzed and decomposed. With tricalcium phosphate, former study in this laboratory makes it appear improbable that final equilibrium conditions were obtained in the work here described, but with the monocalcium phosphate there can be but little doubt that the results here given do represent final conditions, and that it is safe to say that with both tri- and monocalcium phosphate the amount of decomposition and the concentration of the resulting solution at the temperature employed is dependent upon the proportion of the mass of solid phosphate to the mass of water.¹

Dicalcium phosphate is unlike the mono- and tri-compounds, in that it is, relatively speaking, but slightly decomposed by water, and appears to dissolve mainly as such. In other words, it is the only phosphate of calcium which is stable in water under ordinary conditions.

¹ A systematic study of the concentrations of phosphoric acid which condition equilibrium between solution and mono- and dicalcium phosphate as stable solid phases is now in progress.

The presence of calcium sulphate slightly increases the phosphoric acid dissolved from tricalcium phosphate, produces probably a slight increase with monocalcium phosphate, but a marked decrease with dicalcium phosphate.

The presence of calcium carbonate decreases the phosphoric acid dissolved from all three phosphates.

Carbon dioxide increases the phosphoric acid dissolved from tri- or dicalcium phosphate, but does not appear to affect the action of water upon monocalcium phosphate.

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THE COLORIMETRIC ESTIMATION OF PHOSPHATES; SECOND METHOD.¹

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THE estimation of small amounts of water-soluble phosphates has within the past few years become a matter of considerable interest in sanitary, physiological, and agricultural chemistry, as well as in physico-chemical studies on slightly soluble phosphates. The small amounts available for analysis in many cases led to the adoption of colorimetric instead of gravimetric methods. Quite a number of procedures have been devised during the past few years,² but all have as a basis the development of the yellow color of the phosphomolybdates in acid solution. This phosphomolybdate coloration is influenced somewhat by the presence of larger quantities of other salts, but the chief difficulty lies in the similar and even more intensive coloration produced by the silicomolybdates. The chief aim in the various proposed procedures has been the elimination of the color produced by these silicomolybdates, either by eliminating the silica itself or by means of a differential coloration of the solutions by varying the procedure. Another difficulty met with in dealing with the natural solutions is the disturbing influence of foreign organic coloring-matter. It has, therefore, always been necessary to completely decolorize the solution before proceeding with the colorimetric test.

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² See West-Knights: *Analyst*, **5**, 197 (1880); Lepierre: *Bull. Soc. Chim.* (3), **15**, 1213 (1896); Jolles and Neurath: *Monatsh. Chem.*, **19**, 5 (1898); Jolles: *Arch. f. Hygiene*, **34**, 22 (1899); Woodman and Cayvan: *This Journal*, **23**, 96 (1901); Woodman: *Ibid.*, **24**, 735 (1902); Veitch: *Ibid.*, **25**, 169 (1903); Schreiner: *Ibid.*, **25**, 1056 (1903); **26**, 808 (1904).