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THE ACTION OF WATER AND SALINE SOLUTIONS UPON  
CERTAIN SLIGHTLY SOLUBLE PHOSPHATES.<sup>1</sup>

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INTRODUCTION.

THE solubilities, so-called, of the slightly soluble phosphates have been frequently determined. The recorded data are, however, very conflicting and have little more than historical interest. The phosphates of iron, aluminum, and calcium are all substances which react with water, or are hydrolyzed, yielding, as one of the products of the reaction, phosphoric acid, which is much more soluble than the phosphate itself, and, at the same time, the hydroxide of the metal or possibly a basic phosphate, generally less soluble than the original phosphate. The solutions always contain free acid. It is not strictly correct, therefore, to speak of the solution, resulting from the action of water upon one of these phosphates, as a solution of the phosphate; rather it is a solution of the decomposition products, and the phosphate itself is, in many cases, present in negligible quantities only.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

The relative masses of the solid phosphate and the solvent have a marked effect upon the amount of hydrolysis that takes place, and, therefore, upon the concentration of the resulting solution with respect to the phosphoric acid dissolved, owing, apparently, to the fact that the basic product of the hydrolysis has a marked effect in reducing the solubility or further hydrolysis of these phosphates. The extent of hydrolysis is markedly affected by the temperature. Finally, the reaction between the phosphates and water, at ordinary temperatures, is usually a rather slow one, final equilibrium conditions probably being approximated only after many days of contact. These facts have not been recognized or they have been generally ignored in work upon these phosphates, and consequently it will not be necessary to consider the earlier work except incidentally as it bears upon details of this investigation.

The work recorded in the following pages has all been done with artificially prepared material. The investigation will be extended to include phosphates occurring in nature, as well as a number of other artificially prepared phosphates. For assistance in the experimental work, described in this paper, acknowledgment is due Dr. Atherton Seidell, who is continuing the investigation along certain lines, which will be described in a later communication.

#### EXPERIMENTAL METHODS.

In some of the experiments, the results of which are given in the following pages, large quantities of solution were used. In the majority of cases the procedure employed was to weigh the solid phosphate into a bottle and then add 200 cc. of water or solution. It is believed, however, that the relationships are more clearly seen by calculating the results to the basis of 1 gram of solid phosphate and varying amounts of solvent.<sup>1</sup> Eight-ounce sterilizer bottles, tightly closed with rubber stoppers, were found to be very convenient. The bottles were completely immersed in a constant temperature-bath which varied less than 1° C. during the experiment. In some cases the bottles were occasionally shaken by hand, but in others they were placed in a submerged

<sup>1</sup> That this procedure is justifiable was shown by two series, in one of which 2, 4 and 10 grams of iron phosphate were in contact with 40, 80 and 200 cc. of water, respectively for ten days, and in the second series double the amounts of phosphate were in contact with the same amounts of water. In both series the amount of  $\text{PO}_4$  per liter dissolved and the acidity were found to be constant for the series within the limits of error of experimentation.

rotating cradle, driven by an electric motor, and the contents thus kept constantly agitated. When the solutions had remained in the constant temperature-bath the desired length of time, the bottles were placed in an upright position for twenty-four hours, or longer, to permit the suspended solid particles to subside, as far as possible, and then the supernatant solutions were passed through filters. An aliquot part of the clear filtrate, usually 100 cc., was then titrated with a standard solution of potassium hydroxide free from carbonates, using phenolphthaleïn as indicator, to determine the "acidity" of the solution. The results, when given, are always expressed as the number of cubic centimeters of tenth-normal potassium hydroxide solution required to neutralize a liter of the solution. The phosphoric acid was then precipitated, in the usual way, as phosphomolybdate, and estimated gravimetrically as magnesium pyrophosphate, or occasionally by titrating the yellow phosphomolybdate precipitate with a standard solution of alkali. In a few cases the dissolved phosphoric acid was present in such small quantities that it was found desirable to estimate it by a colorimetric method. In determining the phosphoric acid present in those solutions which also contained considerable amounts of potassium chloride, potassium sulphate or sodium nitrate, by precipitation as phosphomolybdate, it was important to see if the solubility of the phosphomolybdate precipitate was increased by the presence of the soluble salt to such a degree as to affect materially the results and necessitate a correction. To this end a solution of sodium phosphate was prepared, containing 0.0782 gram  $\text{PO}_4$  per liter. To three separate portions potassium chloride, potassium sulphate and sodium nitrate, respectively, were added in the proportions of 75 grams per liter, and the solutions analyzed by the usual procedure. The results are given in Table I, from which it appears that any effect that the added salt may produce is within the usual error of manipulation.

TABLE I.—INFLUENCE OF ADDED SALTS ON THE PRECIPITATION OF THE PHOSPHOMOLYBDATE.

Salt added, 75 grams per liter.	$\text{PO}_4$ found, grams per liter.
.....	0.0782
KCl	0.0776
$\text{K}_2\text{SO}_4$	0.0784
$\text{NaNO}_3$	0.0778

The dissolved bases, whenever estimated, were determined in a separate aliquot part of the solution by standard methods.

#### IRON PHOSPHATE.

The phosphates of iron used in this work were precipitated by adding solutions of sodium hydrogen phosphate to solutions of ferric nitrate. Two products were prepared. In the preparation of one of these products the resulting supernatant solution, which is always acid, was carefully neutralized by the addition of sodium carbonate solution. Both precipitates were carefully washed a great number of times (about 100 times) by trituration and decantation with both hot and cold water until no traces of nitrates could be detected in the wash liquid by the phenoldisulphonic acid method. When thus prepared, both the products gave, with water, solutions more or less acid. The first product prepared in the slightly acid solution and designated as *iron phosphate* (A) showed a relative excess of phosphoric acid over that required by the formula  $\text{FePO}_4$ , while the second product, prepared by neutralizing with sodium carbonate and designated as *iron phosphate* (B), showed, on analysis, a percentage of iron greater than that required by the formula. Product (A) was perfectly white when first prepared, but later acquired a faint yellow tinge. The color of product (B) was white or pale yellow when first prepared and while yet moist, but on drying and standing it changed to a decided yellow.

The preparation of a product which would contain just the proportions of iron and phosphoric acid required by the formula  $\text{FePO}_4$  is, of course, possible, though somewhat difficult.<sup>1</sup> A product containing an excess of the acid might be washed with successive portions of pure water until the residue had, on analysis, the desired composition. On the other hand, a product containing an excess of the base might be washed with successive portions of a solution of phosphoric acid. As the result of several experiments a curve could be readily constructed from which, by interpolation or extrapolation, the correct proportions of salts could be approximated, which would yield a precipitate of the desired composition. Other methods could undoubtedly be devised. From lack of attention to temperature and concentration condi-

<sup>1</sup>"Sur les phosphates de sesquioxyde de fer et d'alumine," by M. Millot, *Compt. Rend.*, **82**, 89 (1876).

tions the directions found in the literature for the preparation of this substance are generally unsatisfactory.

For this investigation it was not deemed worth while to attempt the preparation of a product of any particular composition, as the analytical results would be no criteria whatever as to the constitution of the amorphous product obtained, and no other satisfactory means to this end suggested themselves. Since, therefore, the product which must be employed is of an indefinite nature and the possibility of its exact reproduction a matter of doubt, it was considered more desirable to investigate two products of compositions on either side of that indicated by the formula  $\text{FePO}_4$ . The absolute value of the figures obtained for the solubility or decomposition of these iron phosphates have, at most, but a secondary interest. Their importance lies primarily in their comparative values and to show the order of magnitude which might be expected from products of analogous origin or composition.

The analysis of the iron phosphate was made with considerable difficulty, especially the iron determinations. The most satisfactory method was to reduce the iron and titrate with a standard solution of potassium permanganate, but, as others have found,<sup>1</sup> the reduction of the iron is accomplished with difficulty. The water contained in both products could not be accurately determined directly, since a constant weight could not be reached even at the highest temperature obtainable in a large combustion furnace.

Lachowicz<sup>2</sup> has published a very interesting paper on the behavior of ferric phosphate in the presence of water and saline solutions. He quotes a number of authorities as to the preparation of iron phosphate, himself investigates several methods, and concludes that a precipitate corresponding to the formula  $\text{FePO}_4$  can only seldom be obtained. He gives the results of several authorities as to the solubility of iron phosphate in water, with and without dissolved carbon dioxide, and calls attention to the observations of Senft<sup>3</sup> that ammonium humate increases the solu-

<sup>1</sup> "On the Composition of Ferric Phosphate," by G. W. Waine, *Chemical News*, **36**, 132 (1877).

<sup>2</sup> *Monatsh. Chem.*, **13**, 357 (1892).

<sup>3</sup> *Gesteins- und Boden-Kunde*, 329 (1877). Senft's experiments, however, prove nothing conclusive as to the action of the humic acid, since his observations are easily accounted for by the free or hydrolyzed base necessarily present.

bility, to those of Luna<sup>1</sup> that the presence of potassium, sodium and ammonium salts also increases the solubility, and that of Kosbitscheff<sup>2</sup> that calcium carbonate, and especially the bicarbonate, increases the solubility. Lachowicz concluded from his experiments that although water *dissolves* very little iron phosphate it *decomposes* it to a considerable extent, and that the amount of the decomposition is dependent upon the relative masses of the phosphate and the water in contact with it. These conclusions are confirmed by the more elaborate experiments described in this paper. It was also shown by Lachowicz that the effect of water upon the phosphates was decreased by iron hydroxide. Saturating the water with carbon dioxide produced no appreciable effect in its action on the iron phosphate, an observation made also by Gerlach,<sup>3</sup> who found further that when calcium carbonate was mixed with either iron or aluminum phosphate in water that carbon dioxide caused an increased amount of calcium to go into solution without producing any noticeable effect upon the amount of dissolved phosphoric acid. A most interesting and suggestive set of experiments was performed by Lachowicz to show the influence of various salts in solution upon iron phosphate as compared with the action of pure water, but his conclusions in this matter cannot be accepted as more than suggestions for further experiments, since the solutions were in contact with the solid for only twenty-four hours, an entirely insufficient time for the true effects to become established. It appears, from Lachowicz's experiments, and is confirmed by this investigation, that the sulphates of the alkali metals increase the amount of phosphoric acid in the solutions as do salts which themselves hydrolyze with the formation of alkaline solutions, such as the carbonates or acetates of the alkalis. This action of hydrolyzed bases is most strikingly brought out in the case of disodium phosphate, which markedly increases the solubility of the iron phos-

<sup>1</sup> Heiden's "Lehrbuch der Düngungsmittel," 2nd Ed., p. 494. Luna's observations, however, are not confirmed by the work of Lachowicz or the present investigation.

<sup>2</sup> Sutherst (*Chem. News*, 85, 157 (1902); *Agric. Gaz.* (London), 55, 204 (1902)) found that lime increased the solubility of the phosphates of iron and aluminum, but thinks "it is essential that the lime should be in the form of hydrate, the carbonate being of no value whatever." H. J. Patterson (Penna. Dept. Agric. Bull. No. 94 (1902)) has made some very interesting observations on this subject from an agricultural point of view, from which it would appear that the solubility was increased by lime or the organic matter of soils. An opposite result, however, might have been expected from the research of Gerlach, cited in the text.

<sup>3</sup> *Landw. Versuchs-sta.*, 46, 201 (1895).

phate, although, at first thought, a decreased solubility might be expected, due to the formation of a common ion. It is common knowledge that solutions of the alkali hydroxides will dissolve iron phosphates, as will also, though less readily, solutions of free mineral acids. Gerlach<sup>1</sup> found that oxalic acid was a more effective solvent than citric acid, which, in turn, was much more effective than acetic acid: in the presence of an excess of free iron hydroxide the solvent action of oxalic acid was unaffected, while that of citric acid was much lowered, and acetic acid did not dissolve enough phosphoric acid to be detected. Lachowicz studied the action of humic acid (?), but his experimental results hardly warrant his conclusion that this substance increases the solubility of iron phosphate, since the observed effects were more probably due to the free bases, also present in the solution, as a result of the hydrolysis of the supposed humates.<sup>2</sup> His experiments at 100° C. show, as might be expected, that temperature has a large influence on hydrolysis, but they are also unsatisfactory on account of the time element.

#### IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

*Iron Phosphate (A).*—The average of a number of analyses of this product gave 51.26 per cent. PO<sub>4</sub>, 27.20 per cent. Fe, corresponding to a mixture containing 73.31 per cent. FePO<sub>4</sub>, with an excess of 5.15 per cent. PO<sub>4</sub>.

TABLE II.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.  
Temperature, 25° C.

Cc. water per gram of solid.	Grams PO <sub>4</sub> per liter of solution.			
	Series I. One minute shaking; twenty-four hours settling.	Series II. One day shaking; twenty-four hours settling.	Series III. Four days shaking; twenty-four hours settling.	Series IV. Seven days shaking; twenty-four hours settling.
10	0.214	0.267	0.286	0.320
50	0.086	0.107	0.118	0.142
200	0.027	0.041	0.047	0.056
800	0.010	0.013	0.016	0.020

Several series of experiments were made with this substance to obtain an idea as to how rapidly equilibrium would be ap-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> See also the work of Schneider (*Ztschr. anorg. Chem.*, 5, 84 (1894); 7, 386 (1894)), who studied not only the action of ammoniacal solutions of humus upon iron phosphates, but also that of alkalis and carbonates. From his experiments it seems that the solubility of the phosphate is increased by ferric chloride or ferrous sulphate, probably on account of the free hydrolyzed acid which these salts yield.

proached when it was brought into contact with water at 25° C. The results obtained from four of these series are given in Table II, from which it appears that phosphoric acid was still going into solution in considerable amounts after seven days of contact, no matter what the proportion of water to solid might be. Two more series at this same temperature were then examined at intervals of twelve and forty-three days, the results being given in Tables III and IV.

TABLE III.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER. Temperature, 25° C. Time of contact, twelve days, with frequent agitation.

Cc. water per gram of solid.	Gram PO <sub>4</sub> dissolved per liter.	Acidity.
5	0.512	78.0
10	0.391	60.4
20	0.283	48.2
33.3	0.215	34.0
40	0.189	33.4
60	0.152	26.9
80	0.120	21.9
100	0.107	19.1
200	0.070	12.8
400	0.042	8.0

TABLE IV.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER. Temperature, 25° C. Time of contact, forty-three days, with constant agitation.

Cc. water per gram of solid.	Gram PO <sub>4</sub> dissolved per liter.	Acidity.
25	0.302	69.4
60	0.257	56.0
85	0.136	36.0
140	0.099	30.0
200	0.080	24.5
800	0.029	17.1

Some experimental evidence was obtained which indicated that phosphoric acid was still going into solution even after forty-three days contact with constant agitation of the mixture of solid and liquid. These tables show, however, the same general order of relative solubilities for different proportions of water to solid at the end of the several periods of time, and since the absolute value of the solubility figures for final equilibrium conditions are not of any special significance, and it was improbable that they would

bring out any relations not shown by the figures obtained within a convenient period of time, it was not deemed advisable to make further efforts to obtain final equilibrium conditions with this compound.

The figures given in the foregoing tables show conclusively that the greater the proportion of water in contact with iron phosphate the less was the concentration of the resulting solution with respect to phosphoric acid, although an easy and obvious calculation will show that the actual total amount which went into solutions increased with increased proportions of water.

In Tables III and IV are also given the acidity per liter of the solutions which also show that the larger the proportion of water to solid the less, relatively, was the decomposition, although actually it was greater. The titration figures themselves are given in these and the other tables in view of the lack of a satisfactory agreement with the gravimetric results. A calculation from the acidity figures, given in Tables III and IV of the equivalent amounts of phosphoric acid in the solutions, on the assumption that phosphoric acid is dibasic towards phenolphthaleïn, indicates, as do the figures determined gravimetrically, that an increasing proportion of solvent to solid phosphate takes into solution an actually increasing amount of phosphoric acid, yet *relatively* less is dissolved. The iron in the solutions, though its presence could in some cases be detected, contrary to the experience of Lachowicz, was not in sufficient quantities to admit of accurate estimation.

A series was determined also at 39° C., the results being given in Table V.

TABLE V.—IRON PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER. Temperature, 39° C. Time of contact, sixteen days, with constant agitation.

Cc. water per gram of solid.	Gram PO <sub>4</sub> dissolved per liter.	Acidity.
50	0.267	42
200	0.109	18
1000	0.033	6

The gravimetric determinations show that the higher temperature tended to increase somewhat the extent of the reaction between the water and the iron phosphate, as might have been expected. This conclusion is apparently contradicted by the acidity

found, which is lower in the series run at the higher temperature, the significance of the acidity becoming thus even less explicable.

#### IRON PHOSPHATE (A) IN AQUEOUS SOLUTIONS OF SALTS.

Solutions of varying concentration with respect to sodium nitrate were put in contact with the iron phosphate, three different proportions of solution to solid being used. The results are given in Table VI.

TABLE VI.—IRON PHOSPHATE (A) IN SOLUTIONS OF SODIUM NITRATE.  
Temperature, 25° C. Time of contact, forty days, with continuous agitation.

Grams NaNO <sub>3</sub> per liter.	Gram PO <sub>4</sub> dissolved per liter.	Acidity.
One gram solid per 20 cc. solution.		
0	0.3500	....
5	0.2237	73.2
25	0.1912	97.4
75	0.1622	118.4
150	0.1451	128.6
300	0.1084	130.6
One gram solid per 40 cc. solution.		
0	0.2175	....
5	0.1786	57.0
25	0.1558	74.0
75	0.1331	84.0
150	0.1124	88.0
300	0.0776	90.0
One gram solid per 100 cc. solution.		
0	0.1250	....
5	0.1130	33.0
25	0.0976	41.0
150	0.0615	50.0
300	0.0482	51.0

It will be seen that, no matter what the proportion of solution to solid may have been, with increasing concentration of sodium nitrate there was a decrease in the amount of phosphoric acid dissolved, but an increase in the acidity. So far no satisfactory explanation of these facts has been suggested.

In Table VII are given the results obtained by treating the iron phosphate (A) with solutions of potassium chloride. In

TABLE VII.—IRON PHOSPHATE (A) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature. 25° C.			
Grams KCl per liter.	Gram PO <sub>4</sub> dissolved per liter.	Gram Fe dissolved per liter.	Acidity.
One gram solid per 20 cc. solution			
0.0	0.3500	.....	....
0.111	0.2256	.....	57.6
0.272	0.2011	.....	59.4
0.444	0.1689	.....	64.9
5.0	0.1127	0.0429	119.6
25.0	0.0905	0.0480	174.2
75.0	0.0820	0.0540	209.2
150.0	0.0871	0.1020	224.0
300.0	0.0871	0.1420	234.0
One gram solid per 40 cc. solution.			
0.0	0.2175	.....	....
5.0	0.09296	0.0152	84.0
25.0	0.07690	0.0168	114.0
75.0	0.05685	0.0200	128.0
150.0	0.05284	0.0320	139.0
300.0	0.04280	0.0700	141.0
One gram solid per 100 cc. solution.			
0.0	0.1250	.....	....
5.0	0.0602	0.0128	44.0
25.0	0.0448	0.0144	58.0
75.0	0.0374	0.0168	66.0
150.0	0.0314	0.0248	68.0
300.0	0.0268	0.0376	69.0

these series, however, besides determining the amount of phosphoric acid and the acidity, the amount of iron in the solutions was also determined.

Here again it will be observed that with all the proportions of solution to solid phosphate an increasing concentration with respect to the potassium chloride was accompanied by a decrease in the concentration of dissolved phosphoric acid and an increase in the acidity: also the amount of iron dissolved increased. It would thus appear that the acidity of the solution was causally connected with the amount of iron dissolved, but in what manner is not clear, especially, as will presently appear, an opposite conclusion is indicated by the experiments with calcium phosphate. Calculating the acid equivalent of the iron found and adding the acid

equivalent of the phosphoric acid found on the assumption that both are trivalent, the sum does not account for the acidity actually found.

TABLE VIII.—SOLUBILITY OF IRON PHOSPHATE (A) IN SOLUTIONS OF POTASSIUM SULPHATE.

Temperature, 25° C. Time of contact, nineteen days.		Acidity.
Grams $K_2SO_4$ per liter.	Gram $PO_4$ dissolved per liter.	
One gram solid per 20 cc. solution.		
3	0.320	76.0
6	0.344	93.0
25	0.366	141.0
50	0.372	171.0
75	0.367	194.0
150	0.364	233.0

In Table VIII are given the results obtained in solutions of potassium sulphate, from which it will be seen that the presence of this salt somewhat increases the amount of phosphoric acid entering solution, thus confirming the conclusion of Lachowicz. The acidity of the solution is markedly increased with increasing amounts of the potassium sulphate.

IRON PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

*Iron Phosphate* (B) —The results of a large number of fairly concordant analyses gave 44.33 per cent.  $PO_4$  and 32.61 per cent. Fe, corresponding to a composition of 70.47 per cent.  $FePO_4$ , 12.37 per cent.  $Fe(OH)_3$  and 17.16 per cent.  $H_2O$ .

This basic phosphate was treated with varying amounts of water, as already described under phosphate (A). No iron could be detected in the solutions and on account of the small amounts of phosphoric acid available for determination, the well-known colorimetric method was used.<sup>1</sup> The results are given in Table IX.

TABLE IX.—IRON PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER. Temperature, 25° C.

Cc. water per gram of solid.	Gram $PO_4$ per liter of solution.
66.6	0.072
100.0	0.061
200.0	0.037
400.0	0.033

<sup>1</sup> See West-Knights; *Analyst*, **5**, 197 (1880); Lepierre; *Bull. Soc. Chim.*, (3), **15**, 1213 (1896); Lepierre; *Ibid.*, (3), **25**, 800 (1901); Jolles and Neurath; *Monatsh. Chem.*, **19**, 5 (1895); 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).

It will be observed that the less the proportion of water to solid the greater is the concentration of phosphoric acid, but the actual amount dissolved from a given weight of solid becomes greater as the proportion of water increases. The solutions obtained were distinctly acid.

IRON PHOSPHATE (B) IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

TABLE X.—IRON PHOSPHATE (B) IN SOLUTIONS OF POTASSIUM CHLORIDE. Temperature. 25° C. Time of contact, fifteen days, with continuous shaking.

Grams KCl per liter.	Gram PO <sub>4</sub> per liter observed.	Gram PO <sub>4</sub> per liter corrected. <sup>1</sup>
One gram solid per 200 cc. solution.		
0	0.037	0.037
3	0.009	0.011
5	0.007	0.009
15	0.008	0.012

In Table X are shown the results obtained when the solid is kept in contact with solutions of varying concentrations with respect to potassium chloride. It will be observed that the potassium chloride enormously decreased the amount of PO<sub>4</sub> which went into solution, although Lachowicz found that practically no effect was produced by this salt, and the generalization of Luna<sup>2</sup> is also contradicted. The solutions in all cases were acid. Here also the amounts of phosphoric acid in solution were so small that it was found advisable to determine them by the colorimetric method. The figures given for the amounts of phosphoric acid in solutions, containing considerable quantities of

<sup>1</sup> The presence of considerable amounts of soluble salts influences the readings in the colorimetric determination of phosphoric acid; therefore Mr. J. G. Smith made some experiments on the subject. The influence of potassium chloride, in the concentrations used in the work described in the text, on the readings due to the phosphomolybdate coloration is shown in the following table:

Grams KCl per liter,	PO <sub>4</sub> parts per million of solution.			
0	5.0	10.0	15.0	20.0
3	4.7	8.0	12.3	15.8
5	4.6	8.2	10.9	13.7
15	4.0	7.2	10.1	12.5

It will be readily seen that increasing amounts of potassium chloride decrease the phosphomolybdate coloration, the effect being more marked in the higher concentrations with respect to phosphates. This effect is, however, small as compared with the enormous decrease produced by potassium chloride on the solubility of the iron phosphate as is shown when the results, given in the text as found, are corrected for the influence of the potassium chloride on the determination by interpolation from the results given in this table.

<sup>2</sup> *Loc. cit.*

potassium chloride, are not very satisfactory as to their absolute values, due unquestionably to errors of determination for such small quantities in the presence of relatively large quantities of other dissolved substances. The figures show, however, that even small quantities of potassium chloride greatly reduce the solubility of the phosphate as compared with the action of pure water, but that relatively large quantities of the potassium chloride produce but little more effect than do the smaller quantities.

#### ALUMINUM PHOSPHATE.

Aluminum phosphate was prepared in a similar way to that employed for iron phosphate. Three products were obtained: Aluminum phosphate (A) was prepared by adding dissolved sodium phosphate to a solution of aluminum sulphate and washing repeatedly with hot and cold water until the washings were free from sulphates. Aluminum phosphate (B) was prepared by adding a solution of ammonium phosphate to a solution of aluminum sulphate, partially neutralizing the supernatant acid solution with ammonium carbonate, decanting and washing the residue repeatedly until the presence of sulphate could no longer be detected in the washings. The residue still contained traces of ammonia, however, and the material was, therefore, strongly heated over the blast-lamp. Aluminum phosphate (C) was prepared by adding dissolved sodium phosphate to aluminum sulphate in the presence of sodium acetate.

There has been no work on the phosphates of aluminum, such as that of Lachowicz on the phosphates of iron, from which one might predict the action of water upon them, other than occasional observations that it behaved similarly to iron phosphate, but was less resistant than the latter to the action of water or saline solutions. The presence of carbon dioxide in the solution appears to have no appreciable effect upon the amounts of aluminum or phosphoric acid dissolved even when lime or magnesia is present.<sup>1</sup> The solubility is increased by the hydroxides of potassium or sodium, and to a lesser extent by free mineral acids. Gerlach found that oxalic and citric acids were about equally effective and much more so than acetic acid in bringing phosphoric acid into solution and that free aluminum hydroxide, while greatly re-

<sup>1</sup> Gerlach: *Loc. cit.*

ducing the action of the acetic acid, did not affect that of the oxalic or citric acids. Schneider<sup>1</sup> states that the solubility is increased by aluminum chloride or aluminum sulphate.

## ALUMINUM PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

*Aluminum Phosphate (A).*—Analysis of the product showed it to contain 77.42 per cent.  $\text{PO}_4$  and 21.49 per cent. Al. whereas the formula  $\text{AlPO}_4$  requires 77.80 per cent.  $\text{PO}_4$  and 22.20 per cent. Al. Two series with varying proportions of water were run at 25° C. for twenty-one days and forty-eight days respectively, the results obtained being given in Table XI.

TABLE XI.—ALUMINUM PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Temperature, 25° C. Time of contact, twenty-one days, with continuous agitation.

Cc. water per gram of solid.	Gram $\text{PO}_4$ per liter.	Acidity.
25	0.6789	116.4
75	0.2477	45.2
175	0.1172	23.3
425	0.0589	13.0
800	0.0343	8.7

Time of contact, forty-eight days, with continuous agitation.

Cc. water per gram of solid.	Gram $\text{PO}_4$ per liter.	Gram Al per liter.	Acidity.
50	0.3886	0.0359	70.0
100	0.2110	0.0157	38.8
250	0.0968	0.0079	19.7
600	0.0516	0.0065	12.7
4000	0.0113	0.0033	4.2
8000	0.0049	.....	2.1

From these figures it will be seen that the phosphoric acid goes into solution quite slowly and that it is improbable that a final state of equilibrium was reached even after forty-eight days of contact. Both series show that while a greater amount of phosphoric acid goes into solution with the greater proportion of water to solid, the concentration of the resulting solution is less and the acidity also is less. The same statements would probably hold, moreover, for the aluminum, as shown in the figures obtained for the series carried forty-eight days.

<sup>1</sup> *Ztschr. anorg. Chem.*, 5, 87 (1894).

TABLE XII.—ALUMINUM PHOSPHATE (A) IN VARYING PROPORTIONS OF WATER.

Temperature, 35° C. Time of contact, thirty days, with continuous agitation.

Cc. water per gram of solid.	Gram PO <sub>4</sub> dissolved per liter.
25	0.889
50	0.503
100	0.274
200	0.131

In Table XII are given the results obtained with aluminum phosphate (A) in contact with varying proportions of water at 35° C., which show that the reaction between the phosphates goes either farther or more rapidly at the higher temperature.

## ALUMINUM PHOSPHATE (A) IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

TABLE XIII.—ALUMINUM PHOSPHATE (A) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 30° C. Time of contact, thirty days, with continuous shaking.

Grams KCl per liter of solution.	Gram PO <sub>4</sub> dissolved per liter of solution.
One gram solid per 100 cc. solution.	
0	0.287
5	0.270
35	0.266
125	0.249

In Table XIII are given results obtained with the phosphate in contact with solutions of varying concentrations in potassium chloride. The results show that as in the case of the iron phosphates, in the presence of increasing amounts of potassium chloride the amount of phosphoric acid going into solution is steadily decreased.

## ALUMINUM PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

*Aluminum Phosphate (B).*—The analysis of the substance gave 81.33 per cent. PO<sub>4</sub> and 21.16 per cent. Al.

In Table XIV are given the results obtained with the phosphate in contact with several proportions of water. With this product, also, the larger the proportion of water to solid the greater the actual amount dissolved, but the less the concentration of the resulting solution. The results, however, show that the product is much

TABLE XIV.—ALUMINUM PHOSPHATE (B) IN VARYING PROPORTIONS OF WATER.

Temperature, 30° C. Time of contact, thirty-five days. with continuous agitation.

Cc. water per gram of solid.	Gram PO <sub>4</sub> dissolved per liter.
20	0.241
40	0.134
80	0.081

less acted upon by the water than aluminum phosphate (A), and it seems probable that this fact is to be ascribed to some change produced by the heating before the blast-lamp, since it is not to be accounted for by a comparison of the analyses of the two substances.

ALUMINUM PHOSPHATE (B) IN AQUEOUS SOLUTIONS OF SALTS.

TABLE XV.—ALUMINUM PHOSPHATE (B) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 27° C. Time of contact, fifteen days. with continuous agitation.

Grams KCl per liter.	Gram PO <sub>4</sub> per liter.
One gram solid per 20 cc. solution.	
0	0.241
150	0.201
200	0.189
250	0.186
One gram solid per 80 cc. solution.	
0.0	0.081
2.5	0.071
17.2	0.067
60.9	0.065

In Table XV are given results which show that increasing amounts of potassium chloride decrease the amount of phosphoric acid going into solution, as was the case with aluminum phosphate (A), and the phosphates of iron.

TABLE XVI.—ALUMINUM PHOSPHATE (B) IN SOLUTIONS OF POTASSIUM SULPHATE.

Temperature, 35° C. Time of contact, ten days. with continuous agitation.

Grams K <sub>2</sub> SO <sub>4</sub> per liter.	Gram PO <sub>4</sub> per liter.
One gram solid per 20 cc. solution.	
0.0	0.241
5.4	0.218
49.0	0.191
101.4	0.183

Grams $K_2SO_4$ per liter.	Gram $PO_4$ per liter.
One gram solid per 80 cc. solution.	
0.0	0.080
2.5	0.071
7.7	0.068
27.2	0.064
62.5	0.062

Table XVI shows that potassium sulphate, like potassium chloride, reduces or retards the reaction between the water and the solid phosphate. There is in this respect a notable difference between the phosphates of iron and aluminum.

TABLE XVII.—ALUMINUM PHOSPHATE (B) IN SOLUTIONS OF SODIUM NITRATE.

Temperature, 27° C. Time of contact, fifteen days, with continuous agitation.

Grams $NaNO_3$ per liter.	Gram $PO_4$ per liter.
One gram solid per 20 cc. solution.	
0	0.3094
20	0.2988
60	0.2818
140	0.2732
240	0.2220
One gram solid per 80 cc. solution.	
0.0	0.0811
2.5	0.0807
7.5	0.0798
17.5	0.0794
27.5	0.0790
87.5	0.0657

The results obtained with solutions of varying concentrations in sodium nitrate are given in Table XVII, and clearly show that the general effect of this salt is the same as that produced by the other salts studied.

#### ALUMINUM PHOSPHATE (C) IN VARYING PROPORTIONS OF WATER.

This product, on analysis, gave, from two closely agreeing sets of determinations, 48.79 per cent.  $PO_4$  and 19.82 per cent. Al, showing an excess of aluminum over that required by the phosphoric acid found.

The results obtained with this basic phosphate in varying proportions of water are given in Table XVIII. The amount of phosphoric acid in the solution was so small that the colorimetric method had to be used.

TABLE XVIII.—ALUMINUM PHOSPHATE (C) IN VARYING PROPORTIONS OF WATER.

Temperature, 25° C. Time of contact, fifteen days, with constant agitation.

Cc. of water per gram of solid.	Gram PO <sub>4</sub> per liter.
66.66	0.0039
100.00	0.0037
200.00	0.0035
400.00	0.0039

ALUMINUM PHOSPHATE (C) IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

TABLE XIX.—ALUMINUM PHOSPHATE (C) IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 25° C. Time of contact, fifteen days, with continuous agitation.

Grams KCl per liter.	Gram PO <sub>4</sub> per liter found.	Gram PO <sub>4</sub> per liter corrected.
One gram solid per 200 cc. solution.		
0	0.0035	0.0035
5	0.0028	0.0031
15	0.0027	0.0033

The results obtained with two concentrations of potassium chloride are given in Table XIX. These small amounts were determined colorimetrically, making the corrections for the influence of the potassium chloride on the coloration, as was done with the iron phosphate. The hydrolysis of the phosphate in water itself is already so slight that the effect of the potassium chloride is scarcely perceptible.

CALCIUM PHOSPHATE.

The preparation of a calcium phosphate, approximating to the formula Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, is much more readily accomplished than in the case of the phosphate of iron or aluminum. Nevertheless, the product usually obtained, when the attempt is made to prepare the substance by precipitation, seldom corresponds to this formula, but may contain either a smaller or a larger proportion of the base than desired. The "solubility" of the phosphate, as given by different authorities, varies widely. It is dependent on the proportion of base present, whether freshly precipitated, dried or

ignited, whether a natural product, as an apatite, a phosphate rock, bones, etc., as witness the values obtained by Völcker,<sup>1</sup> Warrington,<sup>2</sup> Pollacci,<sup>3</sup> Reichardt,<sup>4</sup> Berthelot<sup>5</sup> and Longuinine,<sup>6</sup> Maly and Donath,<sup>7</sup> Jaffre,<sup>8</sup> Williams,<sup>9</sup> and others. The effect of various acids in increasing the solubility has been studied by Bischof,<sup>10</sup> Crum,<sup>11</sup> and many later investigators, mainly from the point of view of fertilizer analyses. For instance, Paturel<sup>12</sup> found that acetic acid, the presence of which in certain soils was proved, has a relatively greater solvent action than has citric acid. Causse<sup>13</sup> found that the presence of phosphoric acid increases the solubility of either tri- or dicalcium phosphate, the monocalcium salt being formed at ordinary temperatures, but some dicalcium phosphate separating from solutions which were first heated and then re-cooled. Sulphurous acid, according to Gerland,<sup>14</sup> also increases the solubility of tricalcium phosphate. Humic acid, according to Minssen and Jacke,<sup>15</sup> increases the solubility. The presence of calcium carbonate,<sup>16</sup> or calcium sulphate,<sup>17</sup> appears to depress the solubility, while ammonium salts<sup>18</sup> generally increase it, as do some other alkaline salts. That a rise in temperature or the presence of carbon dioxide<sup>19</sup> increases the solubility has been fre-

<sup>1</sup> Report British Assoc. Advancement of Science, 1862, 169; *Jsb. d. Chem.*, **131**, (1862).

<sup>2</sup> *J. Chem. Soc.*, **19**, 296 (1866); *Ibid.*, **24**, 80 (:S71); *Ibid.*, **25**, 269 (1871); *Ibid.*, **26**, 983 (1873).

<sup>3</sup> *L'Oros*, **19**, 217 (1896); See Abstr., *J. Chem. Soc.*, **72**, ii, 260 (1897).

<sup>4</sup> *Ztschr. anal. Chem.*, **11**, 275 (1872).

<sup>5</sup> *Ann. chim. phys.*, [6], **11**, 350 (1887).

<sup>6</sup> *Ibid.*, [5], **9**, 33 (1876).

<sup>7</sup> *J. prakt. Chem.* [2], **7**, 413 (1873).

<sup>8</sup> *Bull. Soc. Chim.* [3], **19**, 372 (1895).

<sup>9</sup> *Chem. News*, **24**, 306 (1871).

<sup>10</sup> *J. prakt. Chem.* **67**, 39 (1833).

<sup>11</sup> *Ann. Chem. (Liebig)*, **63**, 284 (1847).

<sup>12</sup> *Ann. Agron.*, **20**, 332 (1894).

<sup>13</sup> *Compt. Rend.*, **114**, 414 (1892).

<sup>14</sup> *J. prakt. Chem.* [2], **4**, 97 (1871).

<sup>15</sup> *Bied. Centrbl.*, **29**, 447 (1900).

<sup>16</sup> Warrington: *Loc. cit.*; Pollacci: *Loc. cit.*

<sup>17</sup> *Ann. Chem. (Liebig)*, **198**, 290 (1879); Armsby: *Am. J. Sci.* [3], **12**, 46 (1876).

<sup>18</sup> Warrington: *Loc. cit.*; Ferreil: *Bull. Soc. Chim.* [2], **35**, 548 (1881).

<sup>19</sup> This observation, which was made in 1846 by Dumas[*Compt. Rend.*, **23**, 1018 (1846)] and by Lasaigne (*Compt. Rend.*, **23**, 1019 (1846); *J. Pharm.*, [3], **3**, 11 (1847); **5**, 258 (1849)) and practically every one who has worked with phosphates since, was confirmed in the course of the present investigation. It is remarkable because it might be expected that the increased solubility of the calcium induced by the presence of carbon dioxide would reduce the amount of phosphoric acid entering the solution, in view of the decrease observed in the presence of other calcium salts. Barillé (*Report Pharm.*, 1901, p. 145), who studied the action of carbon dioxide on solutions of tricalcium phosphate at increased pressures, reports that the biphosphate and calcium bicarbonate were formed, but that the bicarbonate decreased the solubility of the biphosphate.

quently observed, citations being too numerous to be given. Practically all observers have noted that the solutions of this substance were always acid and many have pointed out that the solid residue contains more base than before contact with water. It has been shown that when monocalcium phosphate or dicalcium phosphate is dissolved in water, dicalcium phosphate (or the hydrate  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) may separate, leaving free acid as well as some calcium salt in the solution, but on boiling the solution and removing, in part, the acid, either by neutralizing or by decanting and using renewed portions of water, the residue is converted into tricalcium phosphate, or into a mixture with an even greater proportion of base.<sup>1</sup>

From these facts it appears that no matter what compound, or mixture of compounds, containing only calcium and phosphoric acid ( $\text{Ca}_n(\text{PO}_4)_m$ ), be placed in water, there will result free phosphoric acid in the solution with separation of calcium hydroxide. The calcium hydroxide may then react to form a more basic and less soluble phosphate, or simply form a mixture with the phosphate, the solubility of which is decreased by its presence. The system is more interesting and more complex than the corresponding ones for iron and aluminum, respectively, owing to the existence, under certain concentration-temperature conditions, of the definite molecular species, mono-, di-, tricalcium phosphates (or hydrates of them) as solid phases in contact with the solution.<sup>2</sup>

<sup>1</sup> Joly: *Compt. Rend.*, **94**, 529 (1882); **97**, 1480 (1883); Joly and Sorel: *Ibid.*, **118**, 738 (1894); Barillé: *Report Pharm.*, 1897, p. 529; *Chem. Centrbl.*, **1**, 69, 434 (1898); Viard: *Compt. Rend.*, **127**, 178 (1898); Delattre: *Bull. Soc. Chim.* (2), **35**, 358 (1881); Millot: *Ibid.* (2), **33**, 194 (1880); Wibel: *J. prakt. Chem.* (2), **9**, 113 (1874); Aeby: *Ibid.* (2), **9**, 469 (1874); Stoklasa: *Landw. Versuchs-sta.*, **38**, 401 (1891); **44**, 437 (1894); Rindell: *Compt. Rend.*, **134**, 112 (1902); *et. al.*

<sup>2</sup> From an agricultural point of view the above considerations have a special interest. They show that the process of "inversion" of phosphates in the soil to less soluble forms is but a process of hydrolysis, and that no matter what phosphate be put upon the soil the resulting phenomena are essentially the same; phosphoric acid will be continually given off to the soil solution, but in constantly decreasing amounts, or what is perhaps a more useful way to regard it, at a constantly decreasing rate. With any given soil, however, a number of factors enter which affect the rate of solution of the phosphoric acid, so that Schloesing (see excellent memoir of Paturel: *Ann. Agron.*, **28**, 385 (1902)) has suggested that the amount of water-soluble phosphoric acid in a soil is a constant definite characteristic (see also Bull. No. 22, Bureau of Soils, U. S. Dept. of Agr.). It would depend upon the lime and magnesia in the soil (Schloesing: *Compt. Rend.*, **127**, 236, 327 (1898); **131**, 149, 211 (1900); Jacobson: *Ann. Agron.*, **24**, 292 (1898); Schreiber: *Expt. Sta. Rec.*, **7**, 104 (1895); Stahl-Schröder: *Expt. Sta. Rec.*, **4**, 587 (1893); Crawley: *This Journal*, **24**, 1114 (1902)); upon the iron and alumina in the soil (Georgievics: *Monatsh. Chem.*, **12**, 566 (1891)); upon the humus content (Dumont: *Compt. Rend.*, **132**, 435 (1901)); upon the absorptive power of the soil grains (Gerlach: *Landw. Versuchs-sta.*, **46**, 201 (1895)); upon the presence of various soluble salts, etc., and probably the nature of the vegetation.

A number of the systems which these substances form with water are now under investigation in the laboratory. The following experiments were made with a specimen of precipitated calcium phosphate obtained from Eimer & Amend. and, on analysis, this product gave figures agreeing very closely with the formula  $\text{Ca}_3(\text{PO}_4)_2$ .

TABLE XX.—CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN WATER AFTER VARYING PERIODS OF CONTACT.

Temperature, 25° C. Constant shaking.	
Number of days contact.	Gram $\text{PO}_4$ per liter.
One gram solid per 40 cc. solvent.	
1	0.1989
3	0.2060
8	0.2163
20	0.2288
37	0.2302
81	0.2339

In Table XX are given the results obtained by shaking the phosphate continuously in water at 25° C. for periods varying from one day to eighty-one days. It will be seen that the phosphate hydrolyzed at a constantly diminishing rate. A chart of these results would indicate that equilibrium was practically reached in about thirty-five days, although a small amount of phosphoric acid continued to go into solution, and it is improbable that complete equilibrium was established at eighty-one days. No especial significance can be attached to the absolute values of such figures, since the rate of solution would depend upon so many factors, fineness of the solid particles, vigor of shaking, temperature of solution when first prepared, etc., but the figures are of importance in showing that a very considerable length of time is required to bring about even an approach to equilibrium conditions. In the experiments, the results of which are given in the following tables, the phosphate was left in contact with the solvent for varying lengths of time, until it was believed that equilibrium conditions were approximated sufficiently near to establish the true character of the results sought, and justify their use for comparative purposes. It seems worth while to emphasize here that such comparative figures alone have any significance

when dealing with a substance of the indefinite character possessed by the phosphate with which this work was done. That is, when working with a substance whose composition alone is known, as shown by analysis, but whose constitution, whether it be one distinct molecular species or a mixture, is uncertain. It seems well, moreover, to repeat that the true solubility of the substance is probably very small, practically indeterminate with our present facilities and of but little interest, and that it is the solutions of the hydrolyzed or decomposition products with which one has to deal. Unless a perfectly definite molecular species be under consideration, there is nothing to be gained by waiting for final equilibrium to become established so long as it is clearly understood that considerable lengths of time are required for complete equilibrium, and that the figures obtained are for comparative purposes only.

## CALCIUM PHOSPHATE IN VARYING PROPORTIONS OF WATER.

TABLE XXI.—CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN WATER FREE FROM CARBON DIOXIDE.

Temperature, 25° C. Time of contact, twelve days, frequent shaking.

Cc. of water per gram of solid.	Gram $\text{PO}_4$ per liter of solution.
2.5	1.2293
5.0	0.9049
10.0	0.6805
20.0	0.3825
40.0	0.2156
60.0	0.1668
80.0	0.1315
100.0	0.1131
200.0	0.0679
400.0	0.0427

In Table XXI are given the results obtained from a series of solutions obtained from calcium phosphate in contact with varying proportions of water. It will be observed that here, as in the similar experiments with the phosphates of iron and aluminum, that while the actual amount of phosphoric acid dissolved increases as the proportion of water to solvent increases, the relative concentration of the solution decreases.

## CALCIUM PHOSPHATE IN AQUEOUS SOLUTIONS OF SALTS.

In Tables XXII and XXIII are given the results obtained with

TABLE XXII.—CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN SOLUTIONS OF CALCIUM CHLORIDE WHEN IN THE PROPORTION OF 1 GRAM CALCIUM PHOSPHATE TO 40 CC. SOLUTION.

Temperature, 25° C. Time of contact, five days, with continuous shaking; one day settling.

Grams $\text{CaCl}_2$ per liter.	Gram $\text{PO}_4$ dissolved per liter.
0	0.2185
1	0.1383
5	0.1150
10	0.1050
25	0.0979
50	0.0905
100	0.0797
200	0.0626

TABLE XXIII.—CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN SOLUTIONS OF CALCIUM CHLORIDE, WHEN IN THE PROPORTION OF 1 GRAM CALCIUM PHOSPHATE TO 100 CC. SOLUTION.

Temperature, 25° C. Time of contact, fifteen days, frequent shaking.

Grams $\text{CaCl}_2$ per liter.	Gram $\text{PO}_4$ dissolved per liter.
2.50	0.0684
5.00	0.0604
6.25	0.0600
12.50	0.0548
25.00	0.0511
50.00	0.0502

solutions of calcium chloride, from which it appears that increasing the concentration with respect to the latter salt decreases the amount of phosphoric acid entering the solution.<sup>1</sup>

This effect may possibly be ascribed to the formation of a common ion ( $\text{Ca}^+$ ) from both substances, and a "forcing back" of the solubility of the calcium phosphate or hydrolyzed calcium hydroxide, and in consequence a lessening of the amount of phosphoric acid entering the solution. The same explanation suggests itself for the results given in Table XXIV, showing that increasing amounts of calcium nitrate also decrease the amount of the

<sup>1</sup> The following figures obtained in the course of another investigation, in which N/200 hydrochloric acid was used instead of pure water, may be of interest in this connection. The results show that in the dilute acid, although the absolute solubility is greater, the depressing influence of the calcium chloride is nevertheless quite marked.

CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN N/200 HYDROCHLORIC ACID CONTAINING CALCIUM CHLORIDE WHEN IN THE PROPORTION OF 1 GRAM CALCIUM PHOSPHATE TO 40 CC. SOLUTION.

Temperature, 25° C. Time of contact, five days, with continuous shaking; one day settling.

Grams $\text{CaCl}_2$ per liter.	Gram $\text{PO}_4$ dissolved per liter.
0.00	0.3154
1.00	0.2745
5.00	0.2527
10.00	0.2455
25.00	0.2234
50.00	0.2125
100.00	0.1875
200.00	0.1421

TABLE XXIV.—CALCIUM PHOSPHATE,  $\text{Ca}(\text{PO}_4)_2$ , IN SOLUTIONS OF CALCIUM NITRATE.

Temperature, 25° C. Time of contact, sixteen days, with constant shaking.

Grams $\text{Ca}(\text{NO}_3)_2$ per liter.	Gram $\text{PO}_4$ per liter.
One gram solid to 40 cc. solution.	
0.0	0.2163
1.0	0.1907
5.0	0.1110
10.0	0.1053
25.0	0.1064
50.0	0.1098
100.0	0.1132
200.0	0.1093
One gram solid to 100 cc. solution.	
2.5	0.0598
5.0	0.0452
6.25	0.0404
12.50	0.0223
25.00	0.0045
50.00	trace

phosphoric acid entering the solutions.<sup>1</sup> That calcium sulphate<sup>2</sup> and calcium carbonate<sup>3</sup> have a similar depressing effect has already been noted.

The same line of argument, however, does not appear satisfactory when potassium chloride is used. It might be expected that this salt would increase the solubility of the calcium phosphate and thus increase the amount of phosphoric acid entering the solution. But Table XXV shows a contrary effect. The acidity of the solution is also decreased with increasing concentration with respect to the more soluble salt, but the amount of calcium increases. The effect may be due to the increase in the solubility of calcium hydroxide produced by the potassium chloride, although, as shown by Cabot,<sup>4</sup> the solubility curve for this pair of electrolytes passes through a maximum point and the solubility of calcium hydroxide is actually less, when upwards of 200 grams of potassium chloride per liter are present, than in pure water. Therefore, when formed by the action of the water on the calcium phosphate, calcium hydroxide does not so com-

<sup>1</sup> The acidity of the solutions, however, increased.

<sup>2</sup> *Ann. Chem.* (Liebig), 198, 290 (1879) : Armsby : *Loc. cit.*

<sup>3</sup> Warrington : *Loc. cit.*

<sup>4</sup> *J. Soc. Chem. Ind.*, 16, 417 (1897).

TABLE XXV.—CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature, 25° C. Time of contact, thirty days, with frequent shaking.

Grams KCl per liter.	Grams $\text{PO}_4$ per liter.	Grams Ca per liter.	Acidity.
One gram solid to 20 cc. solution.			
5	0.3278	0.0357	28.0
25	0.3227	0.0329	27.4
75	0.3193	0.1129	23.6
150	0.2971	0.1286	21.8
300	0.2356	0.1329	17.8
One gram solid to 40 cc. solution.			
5	0.2265	0.0329	17.0
25	0.2224	0.0614	15.0
75	0.2157	0.0672	13.0
150	0.2151	0.0757	11.0
300	0.2137	0.0800	10.0
One gram solid to 100 cc. solution.			
5	0.1280	0.0286	12.0
25	0.1273	0.0329	6.0
75	0.1240	0.0457	4.5
150	0.1126	0.0400	4.0
300	0.1032	0.0415	4.0

pletely separate from the solution if potassium chloride be present, and the depressing action on the solubility of the phosphoric acid which might normally be expected from the hydroxide is shown.

While with increasing concentration of the solution with respect to potassium chloride calcium phosphate is like iron or aluminum phosphate in yielding a decreasing amount of phosphoric acid, and an increasing amount of the base, the calcium salt is different from those of iron and aluminum in that the acidity decreases instead of increases. With sodium nitrate in the solutions the results obtained and given here in Table XXVI were not very satisfactory. The gravimetric determinations of the phosphoric acid found in the solutions indicate that the nitrate has very little effect upon the amount entering solution. The titration figures, however, indicate that the solubility is decreased by the presence of the nitrate, differing in this respect from the results obtained in the case of iron phosphate. But the amount of calcium which enters the solution is markedly increased by the addition of sodium nitrate to the solution.

TABLE XXVI.—CALCIUM PHOSPHATE,  $\text{Ca}_3(\text{PO}_4)_2$ , IN SOLUTIONS OF SODIUM NITRATE.

Temperature, 25° C. Time of contact, thirty days, with frequent shaking.

Grams $\text{NaNO}_3$ per liter.	Gram $\text{PO}_4$ per liter.	Gram Ca per liter.	Acidity.
One gram solid to 20 cc. solution.			
5	0.3073	0.0643	27.8
25	0.2971	0.1572	26.0
75	0.3244	0.1958	24.6
150	0.3142	0.3901	22.8
300	0.3190	0.5916	20.6
One gram solid to 40 cc. solution.			
5	0.1889	0.0329	18.0
25	0.2291	0.0757	16.0
75	0.2372	0.1057	14.5
150	0.2425	0.1343	13.0
300	0.2077	0.1315	11.0
One gram solid to 100 cc. solution.			
5	0.1313	0.0272	8.0
25	0.1300	0.0486	7.0
75	0.1313	0.0600	6.5
150	0.1394	0.0729	6.0
300	0.1404	0.0843	5.0

## SUMMARY.

From the foregoing description it appears that the rate of action of water upon phosphates of iron and aluminum, or upon tricalcium phosphate is very slow, so that neither in this investigation nor, probably, in any yet recorded, have final equilibrium conditions been observed. Free acid accumulates in the solution and a portion of the corresponding base is precipitated. While the free phosphoric acid tends to increase the solubility of the phosphate, the base, even though in solution in correspondingly smaller amounts, exerts a greater effect in decreasing it. Therefore, the addition of increasing amounts of water produces a relatively smaller (though in actual amounts a larger) solution and decomposition of the phosphate. This view is substantiated by the decreased effect observed with calcium phosphate, when calcium chloride or nitrate is present in the solution, but is apparently negated by the increased action of soluble iron salts on iron phosphate and aluminum salts on aluminum phosphate observed by Schneider, although, as these readily soluble salts are them-

selves greatly hydrolyzed with the formation of free acids, it is probable that the effects observed upon the phosphates are due to these free acids.

The relatively decreasing effect of increasing amounts of water may, in part at least, be due to the differences in size<sup>1</sup> of the particles composing the solid phosphate. If there were material differences in the size of the particles and the smaller particles should dissolve or decompose more completely or more rapidly, then, as was observed, the solutions in contact with the larger proportion of water would be the more concentrated. Adsorption phenomena also may very probably play some part in these results, but, if proportional to the concentration of the supernatant solution, they should be in the opposite direction to the results observed.

The presence of potassium chloride in the solution decreases the amount of phosphoric acid obtained from iron, aluminum or calcium phosphate. It increases the amount of iron, aluminum or calcium entering the solution, although so few determinations were made in the case of aluminum that it has not been deemed worth while to give them here.

Potassium sulphate, as previously observed by Lachowicz, increases the amount of phosphoric acid entering the solution from iron phosphate, but decreases the amount entering the solution from aluminum phosphate.

Sodium nitrate decreases the amount of phosphoric acid entering the solution from either iron or aluminum phosphate, but appears to slightly increase the amount yielded by calcium phosphate, while it greatly increases the amount of calcium yielded to the solution by the last-named substance.

The acidity figures given in the foregoing pages are approximations only, since any experimental error in the determination is multiplied at least ten times. The titration of phosphoric acid is not very satisfactory and in the cases of solutions with rather high concentrations of soluble salts is distinctly unsatisfactory. Nevertheless, the figures given are believed to be sufficiently near the true values to warrant publication and to bring out the existing relations. With pure water in contact with the phosphates the acidity of the resulting solutions appears to be in

<sup>1</sup> See Ostwald : *Zischr. phys. Chem.*, **34**, 495 (1900), and Hulett : *Ibid.*, **37**, 335 (1902).

the same direction as the concentration with respect to phosphoric acid, but no satisfactory correlation has been made between the two sets of determinations. In solutions of more soluble salts in contact with the phosphates, no generalization whatever seems justified. Potassium chloride, potassium sulphate and sodium nitrate all increase the acidity of solutions in contact with iron phosphate, while potassium chloride and sodium nitrate decrease the amount of the phosphoric acid in the solution. No correlation of the acidity with the amounts of iron in the solution seems possible, although, as is shown by the solutions of potassium chloride, the base in solution is increased.

In contact with calcium phosphate, potassium chloride and sodium nitrate decreased the acidity of the solution instead of increasing it, as in the case of iron phosphate. In both cases, however, the amounts of calcium in the solutions decidedly increased, and in the case of sodium nitrate the phosphoric acid also.

In so far as observations were made, an increase of temperature increased the decomposition of the solid phosphates in either water or salt solutions.

Owing to the complexity of the reactions involved between the hydrolyzed products and the other solutes, and perhaps also to the fact that definite equilibrium conditions were not under observation, attempts to apply the mass law to the results have not been satisfactory. The hypothesis of electrolytic dissociation has, in many of the cases observed, failed to give a satisfactory explanation.

The importance of the phenomena here described for agricultural and mineralogical studies is obvious. Its discussion will, however, be given at a later stage of the study.

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## A MODIFICATION OF THE FREEZING-POINT METHOD.

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THE usual method of determining molecular weights by measuring the lowering of the freezing-point depends upon slightly supercooling the solution and then allowing ice to form. This is