

XXVII.—*Researches on the Phosphates of Calcium, and upon the Solubility of Tricalcic Phosphate.*

By ROBERT WARINGTON, Junr.

THE original object of this investigation was to ascertain the solubility of the phosphates of calcium employed in agriculture, more particularly under the conditions to which they would be subject after mixture with the soil. Other points of interest soon, however, arose in the course of experiment; the subject thus spread beyond its intended limits, and in the present communication the agricultural part of the question is left still very incomplete.

The plan proposed, was to determine, in the first place, the solubility of pure, artificially prepared phosphates, and next the solubility, under similar circumstances, of the impure phosphates available for agriculture. Tricalcic phosphate was chosen as the first subject of experiment; its preparation in the pure state was thus a primary object.

Mitscherlich tells us, that when chloride of calcium is added to ordinary disodic phosphate, the latter being maintained in excess, the precipitate formed is tricalcic phosphate, while the solu-

tion becomes acid from the production of monosodic phosphate. Berzelius, on the contrary, states, that the precipitate formed under these conditions is not tricalcic phosphate, but the octocalcic triphosphate, which he has elsewhere described. All experimenters agree, that when the operation is reversed, and disodic phosphate is poured into an excess of chloride of calcium, the precipitate is neither tricalcic nor octocalcic, but dicalcic phosphate.

In following out Mitscherlich's plan, very different results were obtained to those which he describes; a series of experiments was therefore instituted as to the result of mixing disodic phosphate and chloride of calcium.

I. A solution of ordinary disodic phosphate was slowly poured into pure chloride of calcium. The turbidity occasioned by the first drops of the sodium-salt disappeared on agitation;* on a further addition the precipitate soon became permanent, and the solution at the same time distinctly acid. On standing, the precipitate became decidedly crystalline, while the surface of the liquid was covered with floating crystals; these when examined under the microscope were found to have the form of rhombic prisms. The chloride of calcium had been maintained in excess throughout the experiment. The precipitate was thoroughly washed by decantation. On drying it appeared as a crystalline powder, possessing a somewhat nacreous lustre. Analysis yielded the following results:—

EXPERIMENT 1.—*a.* 5·05 grains of the ignited salt gave 4·11 grs. CaCO_3 , and 4·27 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

b. 10·52 grs., gave 8·50 grs. CaCO_3 .

c. 4·88 grs., gave 13·30 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$.

EXPERIMENT 2.—Another specimen prepared in an exactly similar manner to the above. A portion of the moist precipitate was redissolved; it gave 7·41 grs. CaCO_3 , and 7·84 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

	Theory.	Experiment I.			Experiment II.
		<i>a.</i>	<i>b.</i>	<i>c.</i>	
2CaO	44·10	45·58	45·25	—	45·28
P ₂ O ₅	55·90	54·08	—	54·27	54·72
	<hr/> 100·00	<hr/> 99·66			<hr/> 100·00

The salt was therefore dicalcic phosphate, containing, however, an excess of lime, amounting to rather more than 1 per cent.

* According to H. Rose, dicalcic phosphate is slightly soluble in chloride of calcium.

The methods of analysis employed were twofold. As they are the same as were used throughout the investigation, a short description seems necessary. In the first method the lime was precipitated by oxalate of ammonium from an acetic acid solution of the phosphate, the filtrate concentrated, and the phosphoric acid precipitated by magnesia. In using this method, a correction was always made for the bulk of the filtrate and washings from the magnesia precipitate, .008 gr. being added to the weight of $\text{Mg}_2\text{P}_2\text{O}_7$ for each ounce of fluid. The amount of lime obtained in this plan of analysis appears to be a little above the truth, the error apparently amounting to 1—3-tenths per cent. of the precipitate. Qualitative analysis showed that it contained a trace of phosphoric acid.

The second method consisted in the precipitation of the phosphoric acid by acetate of uranium, the precipitate being washed, by decantation, with hot water containing a little acetate of ammonium, then dried, ignited, and weighed.

II. We have seen that the result of adding disodic phosphate to an excess of chloride of calcium is the formation of dicalcic phosphate; we now turn to the next experiment, in which chloride of calcium was added to an excess of disodic phosphate.

As disodic phosphate possesses a distinct alkaline reaction, it is evident that the precipitate first formed on addition of chloride of calcium, must originate under alkaline conditions. As, however, more of the calcium-salt is added, this alkaline reaction disappears, and the fluid finally becomes acid. The precipitates obtained in the operation are thus formed under a variety of circumstances. The attempt was made to examine separately the phosphates produced at the different periods of the reaction.

EXPERIMENT 1.—The chloride of calcium was added in such quantity that the fluid remained distinctly *alkaline* after standing. A portion of the washed precipitate, redissolved, gave 3.92 grs. CaCO_3 and 3.12 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 2.—Another specimen, prepared as above, gave 2.71 grs. CaCO_3 and 2.12 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 3.—Chloride of calcium added so that the solution after standing appeared perfectly *neutral*. A portion of the washed precipitate gave 5.08 grs. CaCO_3 and 4.15 grs. $\text{Mg}_2\text{P}_2\text{O}_7$:

		Theory.	I. alkaline.	II. alkaline.	III. neutral.
8CaO	51.26	52.37	52.80	51.73
3P ₂ O ₅	48.74	47.63	47.20	48.27
		<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Tricalcic phosphate contains 54.19 per cent. of lime.

It appears then that the precipitate produced when the phosphate of sodium was used in greatest excess, was not tricalcic phosphate, but more nearly approached in composition the octocalcic triphosphate of Berzelius, the proportion of lime being, however, somewhat excessive; and that when the chloride of calcium was used in rather larger quantity, the liquid after standing being neutral, not alkaline, the composition of the precipitate approached still more nearly to this formula.

The nature of the precipitate, formed after the solution became *acid*, next engaged attention.

Chloride of calcium was poured into phosphate of sodium till the liquid became faintly acid; the clear solution was then decanted and the addition of the calcium continued. The precipitate which now fell was highly crystalline, and formed streaks on the side of the beaker wherever the stirring rod had passed. On standing, the sides of the vessel were covered with small crystals. The salt thus obtained was washed and analysed.

A portion of the moist precipitate, redissolved, gave 3.69 grs. CaCO₃ and 3.97 grs. Mg₂P₂O₇.

	Theory.	Experiment (acid solution).
2CaO	44.10	44.86
P ₂ O ₅	55.90	55.14
	<hr/> 100.00	<hr/> 100.00

There can be no doubt from this proportion, that the crystalline precipitate from the acid solution was dicalcic phosphate. As analysis showed the salt to be nearly pure, a water-determination was further made.

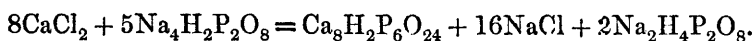
8.73 grs. of the vacuum-dried salt, lost on ignition 2.30 grains, or 26.35 per cent.; the formula Ca₂H₂P₂O₈.4H₂O, demands 26.16 per cent. of water. Dried at 100° the salt contained 23.72 per cent. of water; less than one equivalent was therefore lost at this temperature. The composition of this salt is exactly that of

300 R. WARINGTON, JUN., ON THE PHOSPHATES OF CALCIUM

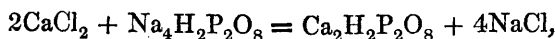
Boedeker's phosphate. According to Raewsky,* the salt prepared as above contains one equivalent less water than that found in the present case.

It appears then, that when chloride of calcium is gradually added to a solution of disodic phosphate, the precipitate first formed is octocalcic triphosphate; and this reaction continues until the solution becomes acid; the precipitate after this ceases to be octocalcic, and becomes dicalcic phosphate.

The origin of the acid reaction is evident. Octocalcic phosphate can only be produced by the simultaneous formation of monosodic phosphate:



The cause of the acid reaction observed when disodic phosphate is poured into chloride of calcium is not so evident. If the calcium-salt formed be nothing but dicalcic phosphate, the reaction is simply:



and the formation of an acid phosphate is not admitted. I believe the true explanation lies in the acid character of dicalcic phosphate. If this salt in its moist condition is examined by delicate litmus paper, the reaction is always found to be faintly acid, however thoroughly it may have been washed. When we remember that this salt is dissolved to a considerable extent in the liquid during its formation, a part of the precipitate distinctly crystallising out, we shall, I think, allow that we have here a sufficient explanation of the phenomenon.

It is interesting to observe that while disodic phosphate is of an alkaline nature, dicalcic phosphate possesses faint acid properties.

When dicalcic phosphate is boiled in water, the solution becomes strongly acid; according to Boedeker† the salt is decomposed under these circumstances, and both monocalcic and tricalcic phosphate are produced.

The crystalline form of the dicalcic tetrahydrated phosphate has been examined by Professor Church. He describes the crystals as thin rhomboïdal plates, of which the diagonally opposite acute angles are sometimes truncated, hexagonal forms being thus produced. This truncation seems to be occasionally

* Compt. rend. xxvi, 205.

† Quoted, Storer, Dict. Solubilities, in loco.

hemihedral, and then may proceed up to the diagonal between the obtuse angles; from this change triangular forms arise. Other modifications are also met with.

When dicalcic phosphate, freshly precipitated and washed, is treated with solution of disodic phosphate, the crystalline character of the precipitate disappears, and it becomes octocalcic triphosphate. In an experiment in which the phosphate of sodium was renewed several times, and left in contact some days, the resulting salt had the composition 52·02 per cent. CaO and 47·98 per cent. P_2O_5 .

III. The next experiment was an attempt to convert dicalcic phosphate into the tricalcic salt by dissolving it in hydrochloric acid and pouring the solution into excess of ammonia.

EXPERIMENT 1.—Solution of dicalcic phosphate reprecipitated by pouring into ammonia—4·26 grs. of the ignited salt gave 3·95 grs. $CaCO_3$ and 3·18 grs. $Mg_2P_2O_7$.

EXPERIMENT 2.—Solution of a phosphate containing 47·96 per cent. CaO, reprecipitated by ammonia—4·34 grs. gave 3·99 grs. $CaCO_3$ and 3·28 grs. $Mg_2P_2O_7$.

	Theory.	I.	II.
8CaO	51·26	51·92	51·48
3P ₂ O ₅	48·74	47·75	48·34
	<hr/> 100·00	<hr/> 99·67	<hr/> 99·82

The salt obtained was thus octocalcic triphosphate. The ammonia had failed to convert the dicalcic phosphate into tricalcic.

To test the decomposing power of the ammonia to its utmost, the salt obtained in Experiment 1, was again redissolved and poured into strong ammonia. The washed precipitate was analysed with the following result—

a. 8·80 grs. of the ignited salt gave 7·99 grs. $CaCO_3$ and 6·64 grs. $Mg_2P_2O_7$.

b. 5·93 grs. gave 14·28 grs. $2U_2O_2 \cdot P_2O_7$.

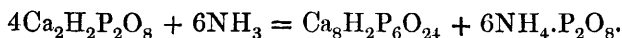
	Theory.	a.	b.	a. recalculated to 100 parts.
8CaO	51·26	50·84	—	51·30
3P ₂ O ₅	48·74	48·26	48·00	48·70
	<hr/> 100·00	<hr/> 99·10	<hr/>	<hr/> 100·00

The octocalcic phosphate was thus unaltered by ammonia. Berzelius has a statement to the same effect.

We may then safely affirm that whenever dicalcic phosphate,

302 R. WARINGTON, JUN., ON THE PHOSPHATES OF CALCIUM

octocalcic triphosphate, or any phosphate of intermediate composition, is precipitated from solution by ammonia, the salt obtained will be the octocalcic triphosphate; a tricalcic phosphate cannot be obtained in this manner. The following is probably a type of the reaction :—



Professor Church suggested at an early period of the research that the octocalcic triphosphate written by Berzelius $\text{Ca}_8\overset{\text{O}}{\underset{\text{O}}{\text{P}}}_6$, doubtless contained water of constitution. The following experiments were made on the specimen last described.

2·64 grains, vacuum-dried, lost on ignition ·255 grs., or 9·65 per cent. The formula $\text{Ca}_8\text{H}_2\text{P}_6\text{O}_{24}\cdot 4\text{H}_2\text{O}$, requires 9·34 per cent of water.

33·28 grs., dried at 100° for several days, lost on ignition 1·79 grs., or 5·37 per cent. The formula $\text{Ca}_8\text{H}_2\text{P}_6\text{O}_{24}\cdot 2\text{H}_2\text{O}$, demands 5·81 per cent.

In the last experiment, the salt continued to lose weight very slowly in the water-bath; a part of the two equivalents of water is thus apparently removed at this temperature.

It might seem probable, that this phosphate, formed in an ammoniacal solution, would contain no water of constitution but ammonia in its place; unlike, however, the magnesium-salt produced in similar conditions, this is not the case.

Octocalcic triphosphate may of course be written $2\text{Ca}_3\text{P}_2\text{O}_8$. $\text{Ca}_2\text{H}_2\text{P}_2\text{O}_8$.

Octocalcic triphosphate is neutral to litmus, or acid to the faintest possible degree; on boiling with water, the solution becomes strongly acid.

IV. We shall now turn to the experiments relating to tricalcic phosphate.

Tricalcic phosphate may of course be prepared by adding trisodic phosphate to any neutral solution of calcium. The phosphate employed in the determinations of solubility was made either by adding one equivalent of caustic ammonia to a known amount of ordinary phosphate of sodium, and pouring this solution into chloride of calcium: or by simply mixing a considerable excess of ammonia with the phosphate of sodium, and adding chloride of calcium in quantity not quite sufficient to precipitate all the phosphoric acid. Berzelius, indeed, states that the latter method, when phosphate of ammonium is employed, yields only octocalcic phosphate; and the direction he

gives for preparing this salt is to add ammonia to diammonic phosphate, and then precipitate half the phosphoric acid with chloride of calcium.* Yet we have on his own authority, that when ammonia is added to diammonic phosphate, *triammonic phosphate* separates as a crystalline magma if the solutions are strong. If then, the addition of an excess of ammonia converts the diammonic into triammonic phosphate, how can the subsequent addition of chloride of calcium fail in producing a tricalcic phosphate?

The following are analyses of tricalcic phosphate prepared by different methods:—

EXPERIMENT 1.—Disodic phosphate, plus one equivalent of ammonia, poured into chloride of calcium — 9·89 grs. of ignited salt gave 9·32 grs. CaCO_3 and 6·77 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 2.—Salt prepared as above—9·88 grs. gave 9·32 grs. CaCO_3 and 6·79 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 3.—Excess of ammonia added to disodic phosphate, and chloride of calcium poured in, but not in excess. A portion of the moist precipitate gave 7·34 grs. CaCO_3 and 5·40 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 4.—Salt prepared as in No. 3; only half the phosphoric acid precipitated. A portion of the moist precipitate gave 10·06 grs. CaCO_3 and 7·44 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 5.—A large excess of ammonia added to diammonic phosphate; chloride of calcium then added in quantity sufficient to precipitate only a very small part of the phosphoric acid. A part of the washed precipitate gave 11·12 grs. CaCO_3 and 8·32 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

EXPERIMENT 6.—Salt prepared as No. 5; a somewhat larger proportion of chloride of calcium used, yet less than half the phosphoric acid precipitated. A specimen of the washed precipitate gave 8·75 grs. CaCO_3 and 6·32 grs. $\text{Mg}_2\text{P}_2\text{O}_7$.

	Theory.	I.	I. Recalculated to 100 parts. †	II.	II. Recalculated to 100 parts. †	III.	IV.	V.	VI.
3CaO ..	54·19	52·77	54·65	52·83	54·58	54·33	54·25	53·90	54·78
P ₂ O ₅ ..	45·81	43·78	45·35	43·96	45·42	45·67	45·75	46·10	45·22
	100·00	96·55	100·00	96·79	100·00	100·00	100·00	100·00	100·00

* Of course, if chloride of calcium were poured into diammonic phosphate, and ammonia *afterwards* added, the octocalcic triphosphate would result. Berzelius' direction is however explicit, that the ammonia is to be added *before* the chloride of calcium.

† Though all the phosphates were washed by decantation till no chlorine was

The phosphate produced in each of these experiments was thus tricalcic phosphate. Phosphate of ammonium, after mixing with excess of ammonia, is seen to have produced tricalcic phosphate when partially precipitated by chloride of calcium.

A determination of water was made in the specimen obtained in experiment No. 4. 6.72 grs. of the vacuum-dried salt lost, on ignition, .69 grs. or 10.26 per cent.; the formula $\text{Ca}_3\text{P}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, demands 10.40 per cent. of water. Dried at 100° till it ceased to lose weight, the salt still contained 6.35 per cent. of water; less than one equivalent was therefore lost at this temperature.

This experiment agrees with the determination of Berzelius, who states the amount of water to be two equivalents.

Tricalcic phosphate is neutral to litmus paper; if, however, it be boiled with water, the solution becomes distinctly acid. This is a strange reaction, and invites investigation. We have indeed seen that on boiling dicalcic and octocalcic triphosphate, the same phenomenon occurs; with these, however, the formation of an acid salt admits of ready explanation, while in the case of tricalcic phosphate, the splitting up into a basic and an acid salt is certainly hard to understand.

If acetic or hydrochloric acid is poured on moist tricalcic phosphate in such quantity that a small portion of the salt is left undissolved, the solution, if filtered, will deposit crystals of dicalcic phosphate; while the residue left undissolved by the acid will be converted into the same salt, and on standing assume its characteristic crystalline form. The crystals are larger when acetic acid has been made use of; indeed, by following this method, crystals of considerable size may be obtained.

Having narrated the experiments which were made as to the preparation, the composition, and properties of the phosphates of calcium, we arrive now at the experiments touching the solubility of tricalcic phosphate; the trials to be here related deal exclusively with the pure, freshly precipitated phosphate.

It is quite possible that precipitated tricalcic phosphate may possess somewhat different solubilities, when prepared by different methods; this difference can, however, scarcely be great. The present experiments are at all events comparable with each other,

found in the washings, the analysis in several cases failed to reach 100 parts. In determinations of solubility the portion of precipitate taken was always submitted to several additional washings.

all having been made with similarly prepared phosphate, and most of them from the same specimen, the analysis of which has been given in Section IV Experiment 4.

It will be seen in every case that the solubility has been determined by precipitation of the phosphoric acid with uranium; the solubility is thus reckoned from the amount of *phosphoric acid* dissolved. The uranium method was adopted as admitting of immediate use, without previous removal of lime; and also because the great weight of the uranium renders the estimation of small quantities of phosphoric acid comparatively easy.

V. The first experiment was upon the solubility of tricalcic phosphate in pure water. As the presence of carbonic acid is known to increase the solubility of this salt, the precaution was taken of boiling the distilled water for some time before use. The phosphate and water were allowed to digest in the cold for several days, with occasional agitation; the solution was then filtered, a weighed amount of the filtrate evaporated to a small bulk, and the phosphoric acid determined by uranium.

EXPERIMENT 1.—Tricalcic phosphate with boiled water, 6 days; temperature when filtered, $8\cdot2^{\circ}$.—18,000 grains of solution gave $\cdot50$ grs. $2\text{U}_2\text{O}_3\cdot\text{P}_2\text{O}_7$, or $\cdot2173$ grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 82,823.

EXPERIMENT 2.—Residue from above with boiled water, 6 days; temperature on removing solution 6° .—18,000 grs. gave $\cdot41$ grs. $2\text{U}_2\text{O}_3\cdot\text{P}_2\text{O}_7$, or $\cdot1782$ grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was thus 1 in 101,010.

EXPERIMENT 3.—Tricalcic phosphate and boiled water, 10 days; temperature when filtered $6\cdot2^{\circ}$.—18,000 grs. gave $\cdot49$ grs. $2\text{U}_2\text{O}_3\cdot\text{P}_2\text{O}_7$, or $\cdot213$ grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 84,515.

The solubility of tricalcic phosphate in pure water is thus seen to be quite insignificant, the mean of the three experiments being 1 in 89,449.

The solution of tricalcic phosphate gives after some time a faint precipitate with oxalate of ammonium. The phosphoric acid can, however, be immediately detected, either by nitrate of silver, acetate of uranium, or by Fresenius' iron-test; the last is indeed a most delicate reaction for phosphoric acid. Ammonia produces no change in the solution.

When a considerable quantity of the solution of tricalcic phosphate is evaporated almost to dryness, the concentrated fluid will

be found to have a distinct acid reaction. This decomposition of the phosphate has been already noticed.

VI. The next determination was the solubility in a solution of chloride of ammonium. The presence of ammonium-salts has been long known to increase the solubility of tricalcic phosphate; few definite results seem, however, to have been published. The subject possesses an agricultural interest, since a part of the effect of ammonium-salts as manure, is thought by some to be due to their solvent power for phosphates.

The chloride of ammonium in these experiments was dissolved in boiled water; care was taken to neutralize with ammonia the slight acid reaction which chloride of ammonium usually possesses.

EXPERIMENT 1.—Tricalcic phosphate in 1 per cent. solution of chloride of ammonium, 20 days*; temperature when filtered 11° .—18,052 grs. of solution gave 2.08 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .904 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 19,969.

EXPERIMENT 2.—Tricalcic phosphate in 1 per cent. chloride of ammonium, 20 days; temperature when filtered, 12.3° .—18,052 grs. of solution gave 2.17 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .943 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 19,143.

EXPERIMENT 3.—Another specimen of tricalcic phosphate in 1 per cent. chloride of ammonium, 11 days; temperature when filtered 7° .—18,052 grs. of solution gave 2.10 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .9128 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was thus 1 in 19,776.

EXPERIMENT 4.—Tricalcic phosphate in 10 per cent. solution of chloride of ammonium, 16 days; temperature when filtered, 17.3° .—8235 grs. of solution gave 4.38 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 1.904 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 4325.

The results of these trials give a mean solubility of 1 in 19,629, in a 1 per cent. solution of chloride of ammonium; and a solubility of 1 in 4325 in a 10 per cent. solution of this salt. The addition of the ammonia salt had thus greatly increased the solvent power of the water.

The solution in chloride of ammonium is not rendered turbid by ammonia, unless the quantity added is considerable; the phosphate is at the best only very imperfectly precipitated.

Neither phosphate of sodium nor chloride of calcium produces any precipitate when employed alone, but if added with ammonia,

* The long periods mentioned here, and in other places, were not generally the result of choice, but convenience.

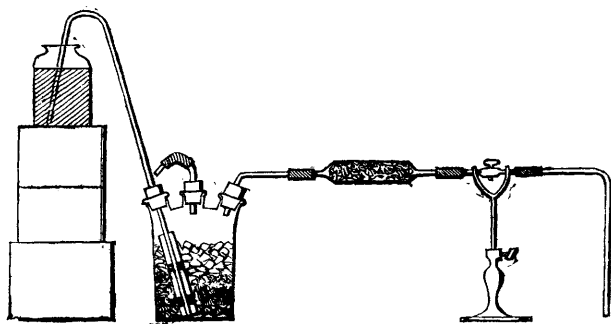
nearly the whole of the tricalcic phosphate is precipitated. Thus an ammoniacal solution containing an alkaline phosphate will never contain more than a trace of lime, however great may be the amount of ammoniacal salt present; and the converse is true, though to a less degree, of an ammoniacal solution containing an excess of lime.

VII. We now pass to the solubility of tricalcic phosphate in water saturated with carbonic acid gas. Boussingault has abundantly shown that carbonic acid gas exists in field soils to a considerable extent, and especially where the organic matter is large in quantity; the solvent power of water holding this gas in solution becomes therefore an important item in soil economy.

The experiments under this head were made in the following manner. The phosphate, diffused through water, was contained in a pint bottle, which it nearly filled, and carbonic acid was made to bubble slowly through the mixture. The passage of the gas produced sufficient motion to keep the phosphate in suspension.

The apparatus used for generating a constant stream of gas was constructed from an ordinary Woulfe's bottle. As the apparatus admits of easy construction, and was found to answer well, it may be worth while describing.

A Woulfe's bottle, of about 30 ozs. capacity, is furnished through one of its necks with a syphon of considerable height; the short leg of the syphon is outside the bottle, and dips into a vessel of strong hydrochloric acid. The bottom of the Woulfe's bottle is filled with pumice, or pieces of broken earthenware; upon the pumice is placed a quantity of broken marble; the centre neck of the bottle is fitted with an india-rubber tube terminating in a



glass stopper. The remaining neck is connected with a wide tube filled with fragments of chalk (to purify the gas from hydrochloric acid), beyond which is placed a glass stop-cock and delivery tube.

Suppose the stop-cock closed, then on removing the stopper from the tube in the central neck, and applying suction with the lips, the syphon will be filled. The stopper is then replaced, and, if the apparatus be tight, the acid remains stationary in the syphon. On now opening the cock of the delivery tube, air passes out; the acid descends the syphon, rises through the pumice, and immediately attacks the marble; but only just the quantity of gas is produced which the position of the stop-cock allows to escape, for when more is evolved, the pressure on the surface of the acid forces it to descend to a lower level, and pass up the syphon to the acid reservoir. A constant stream of gas is thus obtained of almost any required rapidity.

When the apparatus is no longer required, the stop-cock is closed, the acid reservoir lowered, and the bottle emptied of acid by pressure from the lips applied to the tube attached to the central neck.

The limb of the syphon within the Woulfe's bottle is surrounded by an outer tube to prevent small bubbles of gas from entering the syphon. Fresh acid and marble are readily supplied as wanted.

The solutions in carbonic water were brought on to the filter by means of a glass syphon provided with a stop-cock, fitted by a cork into the neck of the bottle containing the liquid to be filtered. The filter was carefully covered to hinder access of air.

EXPERIMENT 1.—Tricalcic phosphate in water; carbonic acid passed ten hours; height of barometer at the end of the operation 29·034 inches;* temperature when filtered 5·3°†. 8095 grs. of solution gave 10·36 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 4·503 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1797.

EXPERIMENT 2.—Tricalcic phosphate in water; gas passed fourteen hours; height of barometer at the end of the operation 30·136 inches; temperature when filtered, 9·3°. 7281 grs. of solution gave 10·04 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 4·364 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1668.

* The height of the barometer has been corrected for temperature in every case.

† Unfortunately the temperature was not registered at the time of passing the gas, save in a few cases only; the degrees mentioned above refer to the temperature of the solution when filtered the following day.

EXPERIMENT 3.—Tricalcic phosphate in water; gas passed fourteen hours; height of barometer 29·082 inches; temperature when filtered, 9·3°. 8075 grs. of solution gave 9·80 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 4·26 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1895.

EXPERIMENT 4.—Residue from preceding experiment treated as before; gas passed twelve hours; height of barometer 29·887 inches; temperature on filtering, 7·3°. 8044 grs. of solution gave 10·30 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 4·477 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1796.

The mean of these experiments gives a solubility of 1 in 1789, at a mean pressure of 29·535 inches, and a temperature of *about* 10°.*

According to Bischof, the solubility of moist tricalcic phosphate in carbonic water is 1 in 1102. Lassaigue, as the result of one experiment, gives the solubility as 1 in 1333 at the temperature of 10° and ordinary pressure.

I will just note, that in an experiment with a phosphate which had been dissolved and re-precipitated, a solubility as high as 1 in 1540 was obtained. The barometer in this experiment stood at 30·136 inches; the temperature was *about* 12°. The conditions were, indeed, precisely the same as those of Experiment 2.

The solution of tricalcic phosphate in carbonic water possesses a slight acid reaction. The addition of ammonia only occasions a faint milkiness. Disodic phosphate produces an immediate precipitate. Chloride of calcium is without effect.

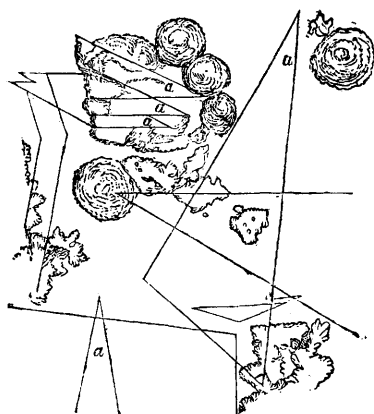
When the solution is heated, no considerable precipitation of phosphate takes place till the temperature has reached about 80°; the precipitation is then very sudden.† A large proportion of the carbonic acid may thus be expelled without separating the phosphate. Strong solutions naturally become clouded at a lower temperature than weaker ones.

If the solution of tricalcic phosphate in carbonic water be exposed to air at common temperatures, a crystalline film is formed on the surface after some hours. The crystals were examined under the microscope, and found to agree in form with tetrahydrated dicalcic phosphate. If the crystalline film when fully developed is separated by filtration, and the solution again allowed

* The room becoming warmer towards the end of the day, the temperature when the gas was last passed would be a little greater than the temperature of the solution when filtered on the following morning.

† The boiling was conducted in a flask nearly filled by the solution.

to stand, no more crystals of dicalcic phosphate are deposited, but the film is composed entirely of a net-work of small botryoidal masses. If this film be also removed, the next deposit will be found to contain another new form, consisting of comparatively large globular aggregations. This form survives the reticulations, and continues to be deposited as long as any film is produced. If the carbonic solution of tricalcic phosphate is allowed to stand some days, all three forms may be found in one film.



I am indebted to Professor Church's kindness for the sketch which accompanies the present description, and also for much help in the microscopical observations. The sketch represents a film containing all three forms; the reticulated substance is however somewhat imperfectly developed. The crystals marked *a* are those of dicalcic phosphate.

During the slow deposit of these various substances, the fluid loses its acid reaction and becomes alkaline to red litmus. I think I may state, that no dicalcic crystals are formed after the solution has acquired an alkaline reaction.

An attempt was made to identify the various forms by analysis; the quantity operated on being necessarily very small, the results must be taken with some reservation.

A crust composed mainly of dicalcic crystals, but containing a little of the reticulated form, gave .35 grs. CaCO_3 , and .37 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 45.36 per cent. of lime and 54.64 per cent. of phosphoric acid, a composition nearly approaching dicalcic phosphate.

A later crust, made up of the reticulated and globular forms, gave .44 grs. CaCO_3 , and .37 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 51.01 per cent. of lime, and 48.99 per cent. of phosphoric acid, a proportion almost exactly that of octocalcic triphosphate.

A still later crust, composed mainly of the globular body, gave .59 grs. CaCO_3 , and .45 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 53.44 per cent. of lime, and 46.56 per cent. of phosphoric acid; a proportion approaching that of tricalcic phosphate.

These analyses, I think, establish the fact, that the crystals first formed are dicalcic phosphate, but the precise nature of the two other forms remains uncertain; we only see that each successive crust contains a greater proportion of lime than the preceding, and that the last, composed mainly of the globular body, has apparently reached the condition of tricalcic phosphate. The reticulated form is probably an octocalcic or heptocalcic triphosphate.

When the solution of the phosphate has ceased to produce crusts by exposure to air, a certain amount of solid matter still remains in solution, and is deposited on boiling. A solution which had ceased to form a deposit, even at a summer temperature, was concentrated by evaporation and analysed in the ordinary way; it gave $\cdot 60$ grs. CaCO_3 , and $\cdot 18$ grs. $\text{Mg}_2\text{P}_2\text{O}_7$; or per cent. 74.50 parts of lime, and 25.50 parts of phosphoric acid. There was, therefore, as might naturally be expected, a considerable excess of lime left in the solution. This most likely existed as carbonate; indeed we shall see further on, that a solution of carbonate of calcium in carbonic acid possesses, like this solution, a distinctly alkaline reaction; a perfect proof is, however, wanting.

The decomposition of tricalcic phosphate during the evaporation of its carbonic solution, is perfectly analogous to the decomposition of the same phosphate already referred to as taking place in its acetic and hydrochloric solutions. Dicalcic phosphate, in either case, crystallises out, while the solution retains the excess of lime.

The formation of several distinct deposits from a carbonic solution during its exposure to air is interesting in a geological aspect, as it seems very probable that by a similar action a variety of mineral substances may be produced by the action of carbonic water on one or two simple compounds.

VIII. The next series of experiments was upon the solvent power of ammonium-salts in the presence of carbonic acid gas.

EXPERIMENT 1.—Tricalcic phosphate in 1 per cent. chloride of ammonium solution; gas passed 10 hours; height of barometer 29.034 inches; temperature when filtered, 6.8° . 8122 grs. of solution gave 14.14 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 6.146 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was therefore 1 in 1321.

EXPERIMENT 2.—Tricalcic phosphate as above; gas passed 12 hours; height of barometer 29.663; temperature when filtered 12.3° . 7649 grs. of solution gave 12.77 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or 5.55 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility was thus 1 in 1377.

The mean solubility from these experiments will be 1 in 1349, at a pressure of 27·348, and a temperature of about 12°.

The addition of chloride of ammonium greatly increased the solubility in pure water; its addition to water saturated with carbonic acid has produced comparatively small result. As Experiment 1 was made under precisely the same circumstances as the first experiment in Section VII., the exact effect of the ammonium-salt can be calculated. We find, then, that for 100 dissolved by the ammonium-solution, 73·5 were dissolved by the pure carbonic water.

On heating the solution of phosphate no deposit takes place till the thermometer reaches about 88°. The chloride of ammonium, though dissolving more, thus holds the phosphate longer in solution than pure carbonic water.

IX. The next point experimented on was the influence of certain ingredients of soil upon the solubility of phosphate of calcium; and first of limestone. What effect would the presence of limestone in a soil have upon the solubility of tricalcic phosphate? The first trial was concerning the amount of pure carbonate of calcium which water saturated with carbonic acid was capable of dissolving.

The quantity of carbonate dissolved in the aerated water was determined by boiling the carbonic solution, adding hydrochloric acid, evaporating the whole fluid in a platinum basin, then treating with excess of sulphuric acid, and, after ignition, weighing the sulphate of calcium obtained.

EXPERIMENT 1.—Precipitated undried carbonate of calcium in water; gas passed 20 hours; height of barometer at time of last passing, 29·226 inches; temperature when filtered, 18·6°. 8000 grs. of solution gave 10·55 grs. of CaSO_4 , or 7·757 grs. CaCO_3 . The solubility was therefore 1 in 1031.

EXPERIMENT 2.—Carbonate of calcium in water as before; gas passed 24 hours; height of barometer, 29·700 inches; temperature at last passing of gas, 21·3°. 8010 grs. of solution gave 10·87 grs. CaSO_4 , or 7·993 grs. CaCO_3 . The solubility was therefore 1 in 1002.

The mean of these two experiments gives the solubility of carbonate of calcium as 1 in 1016; the height of the barometer being 29·463 inches, and the temperature about 21°.

Bischof tells us that in his experiments the maximum solubility was, at ordinary pressures, 1 in 1000, a result very close to that here obtained.

The solution of carbonate of calcium in carbonic water has a faint alkaline reaction to red litmus, becoming very marked as the paper dries. Ferric oxide is precipitated when perchloride of iron is dropped into the solution, and in other respects it behaves as a weak alkali. These alkaline properties doubtless play an important part in geological transformations.

The carbonate of calcium is of course precipitated from solution when caustic soda or ammonia is added to the liquid; but I was not prepared to find that alkaline carbonates, and even bicarbonates, produced a similar effect. The precipitation with bicarbonate of potassium, or sodium, is not so immediate as with carbonate of sodium, but after a few minutes is apparently as complete.

The carbonic solution of carbonate of calcium does not become turbid when heated, till the temperature has reached about 80° .

X. We pass to the experiments in which tricalcic phosphate was mixed with carbonate of calcium, thus imitating the conditions which occur when a phosphatic manure is applied to a limestone soil.

As both substances were used in the undried state, it was difficult to mix them in any definite proportion; the quantities mentioned are thus only rough approximations.

EXPERIMENT 1.—Tricalcic phosphate, with at least twice its weight of carbonate of calcium, in water; gas passed several days; height of barometer at last passing of gas, 29.881; temperature at same time 19.3° . 7266 grs. of solution evaporated to dryness with slight excess of acetic acid; the residue, after ignition, weighed 8.17 grs. The mass, redissolved, gave .48 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .208 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was therefore 1 in 34,932.

EXPERIMENT 2.—The undissolved residue from previous experiment treated as before; gas passed 22 hours; height of barometer 29.754 inches; temperature when filtered, 19° . 7035 grs. of solution gave .36 grs. $2\text{U}_2\text{O}_2 \cdot \text{P}_2\text{O}_7$, or .156 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was thus 1 in 45,096.

The results here obtained make it evident, that where an excess of carbonate of calcium exists, the amount of tricalcic phosphate dissolved by carbonic water is excessively small; the water becomes saturated with carbonate of calcium, while only a trace of the phosphate enters into solution. In the next experiment the proportion of the carbonate was much smaller.

EXPERIMENT 3.—Tricalcic phosphate and carbonate of calcium, the latter perhaps a twentieth of the former; gas passed 25 hours; height of barometer 29·692; temperature, last time of passing gas, 20·3°. 7741 grs. of solution gave ·38 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or ·165 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was thus 1 in 46,915.

EXPERIMENT 4.—The undissolved residue from Ex. 3 again treated with water, and gas passed 4 hours; the clear liquid was then decanted off. Fresh water was poured on the solid matter, and gas passed for 4 hours; the solution thus obtained was also removed. The residue remaining after this repeated treatment with carbonic water, was put on again; gas passed for 25 hours; temperature of solution, when filtered, 13°. 7600 grs. of solution gave 6·19 grs. of $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or 2·69 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The solubility of the phosphate was thus 1 in 2825.

No appreciable amount of carbonate of calcium was present in the liquid.

We see here, first, that a comparatively very small amount of carbonate of calcium is sufficient to prevent the solution of tricalcic phosphate; next, we see the progressive action of a continued supply of water saturated with carbonic acid upon a mixture of phosphate and carbonate of calcium. At first the carbonate is dissolved, accompanied by only a trace of phosphate; as the action progresses, the carbonate is gradually removed from the mixture; and then, and not till then, the phosphate freely enters into solution.

The bearing of these facts on the chemistry of soils is obvious. Phosphate of calcium will be dissolved by the aerated water of a calcareous soil to only a minute extent, and a phosphatic manure applied to such a soil will be only very slowly diffused throughout it; at least these are the natural deductions from the experiments, supposing always that there are not unknown interfering influences in the conditions of a natural soil.

We may in the same manner conclude, that manures like bone-ash, or coprolite, containing both carbonate and phosphate of calcium, will yield their greatest fertilising effect some time after their application; the solubility of the phosphate becoming greater as the carbonate of calcium is removed.

XI. An experiment was made as to the effect of chloride of ammonium upon the mixture of tricalcic phosphate and carbonate of calcium.

EXPERIMENT 1.—Tricalcic phosphate, with excess of carbonate of calcium, in 1 per cent. solution of chloride of ammonium; gas passed 12 hours; height of barometer 29·378 inches; temperature when filtered 14·3°. 8061 grs. of solution gave 1·00 grs. $2\text{U}_2\text{O}_2\cdot\text{P}_2\text{O}_7$, or ·4346 grs. $\text{Ca}_3\text{P}_2\text{O}_8$. The amount of phosphate dissolved was thus 1 in 18,552.

The chloride of ammonium in this instance has more than doubled the solvent power of the carbonic water.

XII. It was thought that, possibly, the influence of the ammonium-salt in the last experiment might be simply due to a capacity for dissolving carbonate of calcium, owing to which, the liquid never became saturated with this substance; the amount of this salt soluble in chloride of ammonium under the influence of carbonic acid, was therefore determined.

EXPERIMENT 1.—Carbonate of calcium in 1 per cent. solution of chloride of ammonium; gas passed 12 hours; height of barometer 29·425 inches; temperature when gas last passed 13·3°. 8134 grs. of solution gave 11·65 grs. CaSO_4 , or 8·566 grs. CaCO_3 . The solubility was therefore 1 in 950.

This proportion is but slightly greater than that previously found for pure carbonic water.

The solution obtained in this experiment did not deposit carbonate of calcium when heated, nor even on long boiling. H. Rose has shown that carbonate of calcium is readily dissolved by a boiling solution of chloride of ammonium, of course with decomposition of the latter.

XIII. The last of the present experiments, was upon the influence of hydrated ferric oxide and alumina on the solubility of phosphate of calcium. As both ferric oxide and alumina are insoluble in water, they can scarcely be expected to prevent the solution of a phosphate: at the same time, by their superior affinity for phosphoric acid, they might succeed in decomposing the phosphate when dissolved, and remove the phosphoric acid from solution.

The plan of the experiment was as follows. Three equal volumes of a solution of tricalcic phosphate in carbonic water were taken; in one, the amount of lime and of phosphoric acid were determined; to the others were added hydrated ferric oxide and hydrated alumina, respectively. Then after digestion for some days, carbonic acid being passed from time to time to maintain a saturated solution, the liquid was filtered, the residue

316 R. WARINGTON, JUN., ON THE PHOSPHATES OF CALCIUM

washed with carbonic water, and the lime and phosphoric acid in the filtrate determined.

EXPERIMENT 1.—8000 grs. of a solution of tricalcic phosphate in carbonic water was found to contain 2·54 grs. $\text{Ca}_3\text{P}_2\text{O}_8$, or 1·163 grs. P_2O_5 and 1·377 grs. CaO ·

EXPERIMENT 2.—To 8000 grs. of the above solution was added some well washed precipitated ferric oxide, and carbonic acid passed from time to time. After two weeks the liquid was separated; it yielded to analysis 2·46 grs. CaCO_3 , or 1·377 grs. CaO , and ·08 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to ·051 grs. P_2O_5 . The ferric oxide was dissolved in hydrochloric acid, and the phosphoric acid it contained determined; it gave 1·74 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or 1·113 grs. P_2O_5 .

EXPERIMENT 3.—8000 grs. of the same solution with freshly precipitated hydrate of alumina, the operation conducted as above. The solution gave 2·35 grs. CaCO_3 , or 1·316 grs. CaO , and ·06 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, equal to ·038 grs. P_2O_5 . The alumina yielded to analysis 1·24 grs. $\text{Mg}_2\text{P}_2\text{O}_7$, or ·793 grs. P_2O_5 ·*

It appears then, that both hydrated ferric oxide and hydrated alumina have the power of decomposing phosphate of calcium very perfectly in a carbonic acid solution. At the end of the action, the whole of the lime remains dissolved as carbonate, while the phosphoric acid has been abstracted and is now combined with the iron or aluminum. In the experiment with oxide of iron, 95·7 per cent. of the phosphoric acid was thus absorbed; with the alumina the absorption was 96·8 per cent.† There are many analogies to this action; the separation of phosphoric acid from its solutions by oxide of tin, and the absorption of arsenious acid by hydrated ferric oxide, will at once suggest themselves.

Viewed agriculturally, this reaction is very important. There are few soils in which ferric oxide is not a considerable ingredient, and it undoubtedly exists chiefly in a hydrated condition; the presence of uncombined alumina is perhaps more problematic. Now will not the oxide of iron in a soil have the same effect on

* The whole of the phosphoric acid was not recovered from the alumina, owing to an unforeseen analytical difficulty.

† Dr. Voelcker states, in one of his papers, that oxide of iron and alumina decompose a solution of monocalcic phosphate, and that tricalcic phosphate, and phosphate of iron, or of aluminium, is produced. The present experiments go further and show that these hydrated oxides are, in the presence of carbonic acid, capable of completely decomposing a basic phosphate, and combining with the whole of its phosphoric acid.

the phosphate of calcium applied in manure as the oxide of iron had in the experiment just considered? As the phosphate of the manure is dissolved and brought in contact with the soil, will not the phosphoric acid be abstracted and become phosphate of iron, while the lime percolates through the soil dissolved in carbonic water?

If this be so, the solubility of phosphate of iron under various conditions becomes of equal importance with the solubility of phosphate of calcium. Fresh light too is thrown on the phenomenon of the absorptive power of soils; a property which is held by some to depend on mere surface attraction, and to be therefore, analogous to the decolorising faculty of charcoal, but which, if these results are borne out by actual experiment on soil, is, at least in the case of phosphoric acid, of a purely chemical nature.

We commenced by saying that the agricultural part of the investigation was as yet very imperfect. I hope on a future occasion to be able to throw some further light on the subject.

Subjoined is a tabular view of the various solubilities determined. Where several experiments have been recorded, the mean only is given.

EXPERIMENTS WITH TRICALCIC PHOSPHATE.

Nature of Solid.	Nature of Fluid.	Pressure. (inches).	Tempe- rature. (centigrade)	Parts of fluid containing 1 part of Tricalcic Phosphate.
Tricalcic phosphate	Boiled water	7°	89,449
Tricalcic phosphate	1 % Chloride of ammonium in boiled water	10°	19,629
Tricalcic phosphate	10 % Chloride of ammonium in boiled water	17°	4,325
Tricalcic phosphate	Carbonic saturated water	29.535	10°	1,789
Tricalcic phosphate	1 % Chloride of ammonium in carbonic saturated water	29.348	12°	1,352
Tricalcic phosphate, plus carbonate of calcium ..	Carbonic saturated water	29.776	21°	42,314
Tricalcic phosphate, plus carbonate of calcium ...	1 % Chloride of ammonium in carbonic saturated water	29.378	16°	18,552

EXPERIMENTS WITH CARBONATE OF CALCIUM.

Nature of Solid.	Nature of Fluid.	Pressure. (inches).	Tempe- rature. (centigrade)	Parts of fluid containing 1 part of Carbonate of Calcium.
Carbonate of calcium	Carbonic saturated water	29.463	21°	1,016
Carbonate of calcium	1 % Chloride of ammonium in carbonic saturated water	29.425	13°	950