

XL.—*On the Decomposition of Tricalcic Phosphate by Water.*

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SEVERAL chemists have remarked that when monocalcic or dicalcic phosphate is acted on by water, and especially if they are boiled with it, decomposition takes place, and the phosphate splits up into a more acid and a more basic compound. Thus, according to Boedeker, dicalcic phosphate is resolved by boiling with water into monocalcic and tricalcic phosphate. In no case, as far as I am aware, has the formation of a product more basic than tricalcic phosphate been observed. In 1866 I communicated to the Society some researches on the phosphates of calcium (*Journ. Chem. Soc.* [2], iv, 296), and I then stated that when tricalcic phosphate is boiled with water, it is itself decomposed, the solution becoming distinctly acid. It became at once evident that the observations already alluded to dealt only with the earlier stages of the action of water on the phosphate. I therefore, as soon as possible, commenced experiments to ascertain the ultimate action of water upon tricalcic phosphate; the results I now lay before the Society.

The tricalcic phosphate used in the following operations was prepared by pouring pure chloride of calcium into a very dilute solution of disodic phosphate, plus one equivalent of ammonia; the alkaline phosphate was kept in excess during the precipitation. The tricalcic phosphate produced was washed by decantation till no chlorine was found in the washings. All analyses of phosphates were made, unless the contrary is stated, by dissolving an unweighed quantity of the moist phosphate in hydrochloric acid, precipitating lime with oxalate of ammonium from an acetic acid solution, and afterwards the phosphoric acid with magnesia; the relation of lime to phosphoric acid was then calculated. As I was dealing with substances containing only lime and phosphoric acid, this method was, of course, admissible, and possessed several advantages.

*First Series of Experiments.*—Tricalcic phosphate, prepared as above, was analysed, a portion then placed in a flask, and boiled for two hours with distilled water. The solution obtained was distinctly, though not strongly acid; it contained very little lime, but a more considerable quantity of phosphoric acid. The residue was again boiled with a fresh supply of water for two hours; the solution obtained was far less acid than in the first instance. After decanting the solution, the residue was again boiled with fresh water; and this operation was repeated till the phosphate had been boiled for twenty-four hours, the water being changed every two hours. The residual phosphate was then analysed. The percentage results were as follows:—

	Phosphate taken.	First solution in boiling water.	Phosphate remaining after 24 hours' boiling.
Lime .....	54·37	25·87	56·33
Phosphoric acid..	45·63	74·13	43·67
	100·00	100·00	100·00

Tricalcic phosphate contains, theoretically, 54·19 lime, and 45·81 phosphoric acid per cent. There is not enough lime in the first solution to form monocalcic phosphate, which would contain (as metaphosphate) 28·28 per cent. The action of the boiling water has clearly been to diminish the proportion of phosphoric acid in the phosphate operated on.

*Second Series of Experiments.*—Another specimen of tricalcic phosphate was treated in the same manner as before, save that the water was changed every four hours, and the boiling continued for forty hours.

	Phosphate taken.	First solution in boiling water.	Phosphate remaining after 40 hours' boiling.
Lime .....	54·78	19·09	56·69
Phosphoric acid..	45·22	80·91	43·31
	100·00	100·00	100·00

The constitutional water of the residual phosphate was in this case determined; the phosphate dried at 100° lost 2·20 per cent. on ignition.

The results in this series are quite similar to those of the previous experiments, the decomposing action of the water being, however, pushed a little further. All the above experiments were made in 1866; the following have been recently completed.

*Third Series of Experiments.*—These were not very successful, owing to the distilled water containing a trace of copper, which gradually accumulated in the phosphate boiled in it. The boiling was continued for twenty hours, the water being changed every two hours; the experiment was then prematurely stopped.

	Phosphate taken.	Phosphate remaining after 20 hours' boiling.
Lime .....	54·95	56·09
Phosphoric acid.....	45·05	43·91
	100·00	100·00

The constitutional water in the boiled phosphate was 2·05 per cent.

According to the figures just given, the decomposition of the phosphate would seem to be less than in the previous experiments; it was, however, probably nearly as great, as in this case the lime must have been to a small extent replaced by copper.

In the present instance, the quantity of phosphoric acid contained in the first extract by boiling water, and also that in the last extract, was determined. 300 c.c. of the first solution gave 1·485 gram  $2U_2O_3 \cdot P_2O_5$ . If we calculate the phosphoric acid as tricalcic phosphate for the sake of comparison, we have here an apparent solubility of tricalcic phosphate of 1 in 4651 of boiling water. The amount of phosphoric acid taken up by the water would probably have been still greater, had the quantity of tricalcic phosphate operated on borne a larger proportion to the water; even this solubility is comparatively very high, being almost equal to the solubility of tricalcic phosphate in a 10 per cent. solution of chloride of ammonium. Of the last solution, obtained by boiling for two hours at the end of the twenty hours' series, 1000 c.c. gave only

·0035 gram  $2\text{U}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ , corresponding to a solubility of 1 of tricalcic phosphate in 657,332 of water. The insolubility here shown is greater than I should expect; I have, however, no second experiment on the subject. It is evident, from these results, that the work done by the water is nearly all effected in the earlier stages of its action.

*Fourth Series of Experiments.*—These experiments were made on a larger scale; the boilings were conducted in a capacious Bohemian flask. The proportion of phosphate to water was, in this case, about 4 grams to 1 litre; in the earlier experiments, the proportion of phosphate to water was rather smaller.\*

After the experiment had proceeded some time, it was found that when the solutions from the later boilings were evaporated nearly to dryness in a platinum basin over a spirit lamp, they exhibited a marked alkaline reaction. This was soon traced to the glass of the flask, as, when distilled water alone was boiled in the flask for two hours, the same reaction was manifested on concentration. As it might reasonably be argued that the phosphate was partly decomposed by the alkali from the glass, an experiment was made with the same phosphate in a silver beaker covered by a porcelain dish. The results were as follows:—

	Phosphate taken.	Boiled in silver 29 hours.	Boiled in glass		
			19 hours.	27 hours.	50 hours.
Lime . . . . .	54·93	56·43	56·20	56·44	56·93
Phosphoric acid . . . . .	45·07	43·57	43·80	43·56	43·07
	100·00	100·00	100·00	100·00	100·00

\* An incident of the experiment seems worth recording as a word of warning to others.

I wished to ascertain the point at which the watery extract ceased to contain free acid, and to this end evaporated from time to time 100 c.c. of the decanted liquor in a platinum basin, and when concentrated to a single drop tested it with litmus paper. I found, to my surprise, that the watery extract after eighteen hours' boiling, when treated in this manner, still turned litmus paper scarlet. As a matter of precaution, I evaporated 100 c.c. of the distilled water employed, and found that it gave an equally acid residue. Some distilled water kindly supplied by Dr. Gilbert, which had been prepared with great care from rain water, also turned litmus paper scarlet when evaporated nearly to dryness in a platinum basin. A drop of chloride of barium revealed the cause of these perplexing reactions. The acid was sulphuric acid, arising from the argand gas-flame over which the basin was supported on a wire gauze. When the distilled water was evaporated over a spirit lamp, no reaction was obtained with chloride of barium, and the last drop of the concentration had only a faint acid reaction, probably due to impurities in the methylated spirit used.

It appears from these figures, that tricalcic phosphate is decomposed by water in a silver vessel as effectually as in a glass one.

The phosphate which had been boiled for 50 hours, contained 1.96 per cent. of constitutional water.

By long boiling, tricalcic phosphate loses its gelatinous character and becomes a finely divided substance, subsiding very slowly. No crystalline character was detected under the microscope. The boiled phosphate dissolves in acids less readily than tricalcic phosphate.

There is a considerable uniformity in the analyses of boiled phosphate. Omitting the third experiment in which copper was present, the mean proportion of lime to phosphoric acid in six analyses, is 56.50 : 43.50, while the determinations of constitutional water range from 1.96—2.20 per cent. Do these numbers agree with any formula?

The proportion of lime to phosphoric acid in apatite is 56.79 : 43.21 ; a proportion of lime not quite reached by the mean of these analyses of boiled phosphate, but falling within the extremes. Again, if the fluoride and chloride of calcium in apatite were replaced by an equivalent of hydrate of calcium, the compound would contain 1.79 per cent. of water, a quantity agreeing fairly with the amount of water found in the boiled phosphate. We are therefore led to the formula—



as the one which agrees best with the analyses. We have, however, no certain ground for concluding that the action of boiling water finally results in the formation of such a hydrated oxygen apatite, since we do not know what the still further prolonged action of boiling water might effect. The boiled phosphates contained also, at least in some cases, a little carbonic acid. The phosphate boiled in silver contained a trace of carbonic acid, and that boiled for 50 hours in glass a much more distinct quantity; the alkali from the glass had in this case probably acted as a carrier of carbonic acid to the phosphate. An attempt was made to determine the carbonic acid in this latter phosphate by noting the loss of weight it suffered when fused with bichromate of potassium; the loss obtained was 1.40 per cent. If one equivalent of carbonic acid were added to the formula of hydrated oxygen apatite already given, the compound would contain 4.20 per cent.; this phosphate evidently, therefore, still held the greater part of its *outside* lime as hydrate. If further experiments are made upon the action of water on phosphates, they should clearly be conducted in metallic vessels, and at pressures above that of the atmosphere; the tedious character of the action at ordinary pressures, which allows room for the entrance of impurities, would probably be in this way obviated.

If we cannot certainly conclude that an oxygen apatite has in this case been formed, we have at least brought before us a reaction by

which it is extremely probable that apatite would be produced. If water containing fluorides and chlorides should act at high temperatures and pressures on tricalcic phosphate, it is readily conceivable that the removal of phosphoric acid by the water, and its replacement by chlorine and fluorine, should simultaneously occur, and apatite be thus produced in the wet way.

There is evidence that the decomposing action of water on tricalcic phosphate is not confined to boiling water, but is possessed in a lesser degree by cold water. I have prepared a great number of specimens of the pure phosphates of calcium, and have been very careful to exclude in their preparation all conditions which could give rise to an excess of lime, yet on analysis there has been found, almost without exception, an excess of lime over theory, the excess being often considerable. I attribute this to the fact that all the phosphates were washed by decantation; a plan which ensures the thorough washing of these bulky gelatinous precipitates, but at the same time subjects them to the prolonged action of large volumes of cold water.\* Phosphates of theoretical composition are probably obtainable only by conducting the washing on a Bunsen's filter.

The perplexing irregularities which I have met with in attempting to determine the solubility of tricalcic phosphate in cold water are also explained if the action of water on the phosphate is really one of decomposition, and not one of normal solution. The solubilities I have found have varied from 1 in 35,000, to 1 in 110,000. Experiments strictly duplicate would give perfectly concordant results, but the solubility of different specimens of phosphate would vary, and the same specimen, when repeatedly treated with water, would give decreasing solubilities. Now, if my notion of the action of the water is correct, the amount of phosphoric acid which water will extract from tricalcic phosphate will depend on the extent to which the phosphate has been already acted on by water, and on the relative masses of the phosphate and water that are brought together, both which conditions may in different experiments greatly vary.†

With regard to the solubilities of tricalcic phosphate in carbonic acid water, and in solutions of chloride of ammonium, which I have already

\* In the case of the tricalcic phosphate prepared for the last series of experiments, 11 litres of water were required to wash 13 grams of phosphate, the washing lasting many days.

† My own experiments show a much lower solubility of tricalcic phosphate in water than has been obtained by other chemists; probably their phosphates had not undergone a long previous washing by decantation. Voelcker, who gives the solubility as high as 1 in 12,589, possibly did not employ tricalcic phosphate, as his phosphate was prepared by pouring chloride of calcium into disodic phosphate, a plan which yields octocalcic triphosphate.

published, the results were all obtained before I was aware of the decomposing influence of water; as far as I am able to judge, however, tricalcic phosphate appears to have a definite solubility in these solutions, and is therefore probably dissolved in them unchanged.

Since it appears that all phosphates of calcium less basic than apatite are unstable under the continued action of pure water, it seems probable that a more exact examination of natural phosphates would show that many phosphates now regarded as tricalcic are in fact of a more basic nature.

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