

VI.—*On the Extraction of pure Phosphoric Acid from Bones, and on a new and anomalous Phosphate of Magnesia.* By WILLIAM GREGORY, Esq., M.D., F.R.S.E., Professor of Chemistry in the University of Edinburgh.

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I.—*On the Preparation of Pure Phosphoric Acid.*

THE usual methods of obtaining pure phosphoric acid by the oxidation, with nitric acid, or by combustion, of pure phosphorus, are well known; but, although they yield a pure product, yet, as the phosphorus must be prepared from phosphoric acid, it is obvious that we shall derive a great advantage from any method of purifying easily and cheaply the phosphoric acid from bones, instead of first reducing it to phosphorus, and then re-oxidizing it. In practice, phosphorus is made from the superphosphate of lime, and it is from the same salt that phosphoric acid may be most economically prepared.

Two processes, already given for this purpose, are worthy of notice. It is to be borne in mind, that the superphosphate of lime is the soluble compound obtained by acting on burnt bones with sulphuric acid and water, and filtering to separate the sulphate of lime.

In the first process, the solution of superphosphate is neutralized with ammonia or carbonate of ammonia, which precipitates all the lime in the solution, with about one-fourth of the phosphoric acid, as bone phosphate; while three-fourths of the acid are converted into phosphate of ammonia. The filtered liquid being evaporated, deposits crystals of that salt, which, when purified, are decomposed by heat in a platinum crucible; the ammonia and a great part of the water being expelled, while the phosphoric acid, with one equivalent of water, or metaphosphoric acid, is left. The objections to this process are the following:—The salt, when heated, melts, spirts much in boiling, becomes viscid, and froths up to a most inconvenient degree, requiring vessels of platinum of a large size for small quantities of material. Secondly, a very high and long continued heat is required to expel all the ammonia; and at that temperature, a portion of phosphorus is reduced by the hydrogen of the ammonia, and corrodes the platinum, leaving a blue stain of phosphuret of platinum. Besides this, the purest phosphate of ammonia often contains a trace of organic matter, which causes the glass of phosphoric acid, thus prepared, to be disfigured by carbonaceous particles. At least I have always seen black particles in the phosphoric acid made by this process. It is obvious, that if carbon be present, we have an additional source of reduced phosphorus; and if the black particles are phosphuret of platinum, then they

shew that the platinum has been strongly corroded. In short, this method, save on a very small scale, is so objectionable, that it is seldom employed except for illustration.

The second process is one recently proposed, I believe, by LIEBIG, founded on the fact, that the whole lime may be removed from the superphosphate of lime, by the addition of sulphuric acid to the concentrated solution. This causes it to become quite thick from the large quantity of sulphate of lime produced. Cold water being added, the whole is filtered, and the filtered liquid and washings again concentrated and filtered from any sulphate of lime deposited during the evaporation. The concentrated liquid is again tested for lime by sulphuric acid, and if no change ensues, the lime has been entirely removed, as I ascertained by the proper tests. The solution now contains only the whole phosphoric acid of the bones, the magnesia which they always contain, and more or less free sulphuric acid. I have described this process thus far minutely, because, up to this point, it is the same as that which I recommend; and it is in the mode of separating the magnesia that the advantage of my process consists.

LIEBIG acts on the concentrated acid solution, brought to the consistence of syrup, by alcohol, which dissolves the phosphoric acid, leaving undissolved the greater part of the phosphate of magnesia, and depositing the last traces when allowed to stand. I cannot ascertain whether this operation is to be performed before or after the sulphuric acid has been expelled by heat; but I find, that after expelling the sulphuric acid, a transparent and colourless glass is obtained, which dissolves perfectly in boiling water, and the solution concentrated to a syrup, and treated with alcohol, yields a solution containing much magnesia, and which, on standing for weeks, deposits nothing. It is very probable that the alcohol did not succeed in separating the magnesia in my experiments, because the phosphoric acid was in some one of its modifications, different from that in which LIEBIG employed the same method. But I have not yet been able to manage that process so as to answer the purpose intended; and, even if it did succeed better, it is well known that alcohol, at its present price, cannot be used in this country on the large scale. I therefore endeavoured to find means of dispensing with its use, and I began by studying the properties of the soluble glass above mentioned, which contains only phosphoric acid, water, and magnesia.

This glass dissolves slowly, but perfectly, in boiling water; but the solution, when again concentrated, and so far deprived of water, that its temperature in an open platinum capsule rises to nearly  $600^{\circ}$ , suddenly becomes turbid, from the separation of a powder, while crystals begin to form in the viscid mass, resembling those which form in honey. When cold, water dissolves these crystals instantly, and leaves undissolved only a heavy white powder, which is a peculiar phosphate of magnesia. I shall return to it presently. It is quite insoluble in water.

As this salt was evidently formed at a certain temperature, I could see no reason why the whole of the magnesia might not be converted into that insoluble form, although, in this first experiment, the filtered liquid was found to contain much magnesia. I therefore again evaporated the filtered solution; and, at the same temperature as before, it again became turbid. I kept up the same heat for fifteen minutes; and when the mass, after cooling, was acted on by water, a large quantity of the insoluble phosphate separated, and the filtered liquid was now found absolutely free from the smallest trace of magnesia. It now clearly appeared that the first heating had been too short, and that it was only necessary to heat long enough to bring every part of the mass to the same temperature.

The process which I recommend, therefore, is as follows:—The glass remaining, after heating to redness in a covered platinum crucible to expel sulphuric acid (after the separation by that acid of all the lime), is to be boiled in water, and the solution evaporated, and, finally, exposed in a platinum capsule for a quarter of an hour, to a heat of from  $595^{\circ}$  to  $600^{\circ}$ , or to that temperature at which the acid begins to volatilize with the water. It must not be heated more strongly, lest the glass should be reproduced. When cold, the mass is to be softened with water, and the solution of pure phosphoric acid filtered from the insoluble phosphate of magnesia. The acid is pure from magnesia, if, when diluted and supersaturated with ammonia, it forms no deposit, especially after standing for one or more days. I have repeated the process six or seven different times, and on no one occasion did the filtered acid contain magnesia, except when I had purposely heated too strongly. This proves that the degree of heat is not difficult to manage. Indeed, after the first experiment I found it unnecessary to use the thermometer, the appearance of the mass furnishing a sufficient guide. It is evident that the above process has the twofold advantage of simplicity and economy.

The quantity of magnesia which separates in the form of the insoluble phosphate is very considerable. It will be very easy to determine exactly the amount of magnesia in bone-earth, by converting it into this salt.

## II. *On a new and anomalous Phosphate of Magnesia.*

This is the salt so often mentioned above, as being separated by a heat of  $600^{\circ}$  from its solution in phosphoric acid. As the salt is perfectly anhydrous, it is obvious that its formation is owing to the separation of water at that high temperature. The analysis of the salt was made by fusing with carbonate of soda, dissolving in diluted hydrochloric acid, adding, for precaution's sake, a little phosphate of soda, and then precipitating by ammonia, collecting the ammoniacomagnesian phosphate on a filter, washing moderately with cold water, drying and igniting. The residue, pyrophosphate of magnesia, was reckoned to contain

36.67 per cent. of magnesia. In three analyses, the per-centage of magnesia in the new salt was found to be 16.78, 16.92, and 15.94. In the last of these I pushed the washing further than in the first two, and I did the same in three more analyses, which yielded 15.12, 15.34, and 15.12, per cent. of magnesia. The mean of the six analyses, all made with portions of salt prepared at different times, is 15.87 per cent. of magnesia. As the salt lost no weight by ignition, it contained no water, and therefore was composed of magnesia and phosphoric acid alone: the absence of lime being previously ascertained. Its composition is therefore,

Magnesia,	.	.	.	.	.	.	15.87
Phosphoric acid,	.	.	.	.	.	.	84.13

The only formula which at all approaches to this composition is  $3 P_2 O_5 + 2 Mg O$ , according to which, it is an acid sesquiphosphate of magnesia. The composition, calculated according to this formula, is,

Magnesia,	.	.	.	.	.	.	16.18
Phosphoric acid,	.	.	.	.	.	.	83.82

Considering the imperfection of the means for determining the amount of magnesia in analyses with precision, there can, I think, be no doubt, that the above formula expresses, empirically, the composition of the salt in question.

But what is the rational formula of this salt? As far as I know, there are no known sesquiphosphates of protoxides. Indeed, the very characteristic of the three known classes of phosphates, is their tendency to form salts with 1, 2, and 3 equivalents of base for 1 of phosphoric acid.

Metaphosphoric, or monobasic phosphoric acid, forms salts of the general formula,  $P_2 O_5, M O$ ; and if our salt is to be classed as a metaphosphate, it must be one with the very singular formula  $2 (P_2 O_5, M g O) + P_2 O_5$ ; in which 2 eq. of metaphosphate of magnesia are combined with 1 eq. of anhydrous phosphoric acid, which has either entered the radical of the acid, without increasing its neutralising or assumed a neutral character.

Pyrophosphoric acid, or bibasic phosphoric acid, forms salts of the general formula,  $P_2 O_5, 2 M O$ , or  $P_2 O_5 \left\{ \begin{smallmatrix} M O \\ H O \end{smallmatrix} \right.$ . If our salt be a pyrophosphate, and the temperature appears favourable to its being so, its formula must be  $(P_2 O_5, 2 M g O) + 2 P_2 O_5$ , in which 1 eq. pyrophosphate of magnesia is combined with 2 eq. of anhydrous phosphoric acid, in one of the characters alluded to above.

Lastly, common or tribasic phosphoric acid forms salts of the general formula,  $P_2 O_5, 3 M O$ ;  $P_2 O_5 \left\{ \begin{smallmatrix} 2 M O \\ H O \end{smallmatrix} \right.$  or  $P_2 O_5 \left\{ \begin{smallmatrix} M O \\ 2 H O \end{smallmatrix} \right.$ . If our salt belong to this class, its formula will be  $P_2 O_5 \left\{ \begin{smallmatrix} 2 M g O \\ P_2 O_5 \end{smallmatrix} \right. + P_2 O_5$ . Here, 1 eq. of phosphoric acid, act-

ing as acid, is united to 2 eq. of magnesia, and 1 eq. of phosphoric acid, acting as base, while a third eq. of phosphoric acid acts in another capacity, possibly as a neutral body, like water of crystallization.

In all these supposed formulæ, we have anhydrous phosphoric acid acting in an unusual capacity; and it is evident that, whichever we adopt, the occurrence of the salt is favourable to the doctrine, that the so-called anhydrous acids are not really acids. It is true that, on the old view of phosphoric acid and phosphates, there is nothing startling in a sesqui-phosphate; but, if we adopt this view, we must cast aside all the knowledge recently acquired concerning the phosphates, and which, to a great extent, is established by experiment.

On the whole, the composition of this salt is so anomalous, that we must conclude, either that the received views on the subject of the phosphates are erroneous, or that there exists a fourth modification of phosphoric acid, distinct from the three usually admitted. We might suppose this acid to be  $3 P_2 O_5 = P_6 O_{15}$ , and to be neutralised by 2 eq. base, yielding the formula  $P_6 O_{15}, 2 M O$ .

It is worth while to remark, that, on the theory of compound acid radicals and hydrogen acids, according to which the formula of a tribasic phosphate is  $P_2 O_8, M_3$ , that of a bibasic phosphate,  $P_2 O_7, M_2$ , and that of a monobasic phosphate,  $P_2 O_6, M$ , this salt cannot be represented as a sesqui-metaphosphate, although, as we have seen, it may be so on the old view of acids and salts. The latter makes it  $3 P_2 O_5 + 2 M g O$ ; but the former would require 1 eq. of oxygen more to yield the formula of a sesqui-metaphosphate  $3 P_2 O_6, M g_2$ , the salt containing only  $\left. \begin{matrix} 2 P_2 O_6 \\ P_2 O_5 \end{matrix} \right\} M g_2$ . In this point of view, the existence of the new salt may

turn out to be a serious objection to the above named theory of salts and acids.

The new phosphate is remarkable, among all the salts of magnesia, for its extreme insolubility in water and acids, which is such, that it may be ranked beside sulphate of baryta. This insolubility has hitherto defeated all my efforts to ascertain the precise nature of the acid it contains, and whether that acid be new or not.

As this salt is not only very insoluble, but easily washed, and less hygrometric than any powder I have ever weighed, it would be well adapted for the determination of magnesia, and also of phosphoric acid, if we could, at pleasure, convert these substances into this particular form of combination when mixed with other bodies. The experiments I have made on this subject have convinced me, that there are very great difficulties in the way of this application; but, I trust, they will not be found insuperable. It will, at all events, be easy to determine the amount of magnesia in bones, by converting the magnesia, as in the above process, into this insoluble form.