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THE ESTIMATION OF PHOSPHORIC ACID.

By ALFRED SMETHAM, F.C.S., &c.

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THE experiments which I propose to bring before your notice this evening resulted from a statement made by Messrs. Teschemacher and Smith, in a pamphlet which they issued during the past year on the Estimation of Phosphoric Acid, wherein they gave in detail the process which they at present use in their laboratory, and also an account of some experiments which they had conducted on the solubility of ammonio-magnesian phosphate in ammonia water. By these experiments they came to the conclusion, which had previously been arrived at by other chemists, that this salt is totally insoluble in water containing $\frac{1}{3}$ th of its bulk of $\cdot 880$ ammonia. In striking contrast with this conclusion is the high solubility which was found by Fresenius; which, however, I believe he has since found occasion to modify. As the conclusion of Teschemacher and Smith seemed to me at variance with what we should expect, and as, moreover, their experiments were conducted in a very crude manner, viz., by dissolving and reprecipitating ammonio-magnesian phosphate a great number of times, whereby they found that the resulting magnesian pyrophosphate weighed more than the precipitate obtained in the usual course from the same quantity of phosphate, I started the following set of experiments in the hope of setting the matter at rest.

A solution of phosphate was prepared by dissolving 50 grammes of pure phosphate of soda in a litre of water, which solution was used throughout the experiments.

Experiment I.—40 c.c. phosphate solution were mixed with 95 c.c. water, 40 c.c. of $\cdot 880$ ammonia were added, and the phosphoric acid precipitated with 25 c.c. magnesia mixture, which allowed a good excess of magnesia. The solution was allowed to stand for 66 hours in a covered beaker in the laboratory when the resulting precipitate was filtered through a close Swedish filter, washed clean with ammonia water (1 in 4), dried, ignited and weighed. This yielded $\cdot 6385$ grammes of $Mg_2P_2O_7$.

The filtrate was evaporated to a small bulk in a water-bath, and the phosphoric acid contained in solution determined by precipitation with ammonia, care being taken to ascertain the purity of the precipitate. On ignition it yielded $Mg_2P_2O_7$, $\cdot 0020$ grammes.

The yield of pyrophosphate is $\cdot 0064$ grammes in excess of the theoretical quantity, due probably to the fact that the phosphate had effloresced. This, however, is immaterial.

Experiment II. was conducted in a precisely similar manner, but with the following quantities.

40 c.c. phosphate solution.
25 c.c. magnesia mixture.
114 c.c. $\cdot 880$ ammonia.
321 c.c. water.
<hr style="width: 100%; border: 0; border-top: 1px solid black; margin: 0;"/> 500 c.c.

* We regret that the publication of this interesting Paper should have been postponed so long.

This yielded a precipitate of $Mg_2P_2O_7$, weighing $\cdot6350$ grammes.

The filtrate on evaporation gave $Mg_2P_2O_7$, $\cdot0060$ grammes.

Experiment III.—In this experiment the quantities taken were:—

40 c.c. phosphate solution.
25 c.c. magnesia mixture.
120 c.c. $\cdot880$ ammonia.
815 c.c. water.

1000 c.c.

The pyrophosphate obtained from the experiment was $\cdot6250$ grammes. And on evaporating the filtrate a further quantity weighing $\cdot0160$ grammes was obtained.

From these experiments it is evident that ammonio-magnesian phosphate is perceptibly soluble in ammonia water, but not to the extent originally stated by Fresenius. Instead of an addition of one milligramme of pyrophosphate for every 54 c.c. of solution it would be necessary to add only one milligramme for every 100 c.c. by the first experiment, and by the second one milligramme for every 84 c.c. for ammonia water 1 in 4, and by the third experiment 1 milligramme for every 62 c.c. of 1 in 8 ammonia water. It is possible that the excess of magnesium may have slightly diminished the solubility, but as in practice the excess is always present, this is, as far as the present experiments are concerned, immaterial.

But even supposing that the solubility of ammonio-magnesian phosphate in ammonia water was *nil*, it by no means follows that the other substances which are present during the precipitation in the ordinary course by the citric acid process do not increase the solubility and, therefore, Teschemacher and Smith's statement that no allowance should be made for the solubility is far from conclusive. That this is so is proved by the following experiments.

Experiment IV.—To test the influence of citric acid the following quantities were taken and proceeded with as in Experiment I.

40 c.c. phosphate solution.
95 c.c. water.
40 c.c. $\cdot880$ ammonia.
25 c.c. magnesia mixture.
5 grammes of citric acid.

200 c.c.

This yielded a precipitate which, when converted into pyrophosphate, weighed $\cdot6315$ grammes.

The filtrate from this was evaporated in a platinum dish, ignited, dissolved in HCl, the P_2O_5 precipitated by addition of ammonia in a small bulk. This yielded $\cdot0065$ grammes $Mg_2P_2O_7$.

Experiment V.—This was conducted to ascertain the effect of iron in the presence of citric acid in preventing precipitation. The quantities of solution were the same as in Experiment I., but $\cdot35$ grammes of ferrous sulphate and 2 grammes citric acid were dissolved in the water previous to precipitation.

The precipitate formed was separated by filtration as before, and the filtrate evaporated, ignited, and the phosphoric acid determined by means of the molybdenum process.

This yielded $\text{Mg}_2\text{P}_2\text{O}_7$.0030.

Experiment VI.—The same quantities of the solutions were used in this case, but the ferrous sulphate was increased to .7 grammes, and the citric acid to 5 grammes.

The filtrate was treated as in Experiment V., and yielded $\text{Mg}_2\text{P}_2\text{O}_7$.0065 grammes.

Experiment VII.—This, and the following two experiments were conducted to determine the effect of alumina on the solubility. .5 grammes potash alum and 2 grammes citric acid were dissolved in 95 c.c. water, and the solution made up to the same strength as in Experiment I.

The direct precipitate weighed .6425 grammes $\text{Mg}_2\text{P}_2\text{O}_7$. The filtrate was evaporated, ignited, fused with a little sodic carbonate and the phosphoric acid estimated with molybdenum.

This gave $\text{Mg}_2\text{P}_2\text{O}_7$.0055 grammes.

Experiment VIII.—A similar experiment to the last, but 1.5 grammes of alum and 5 grammes citric acid were used.

The direct precipitate weighed .6340 grammes.

The filtrate treated as in Experiment VII. gave $\text{Mg}_2\text{P}_2\text{O}_7$.0095.

Experiment IX.—A similar experiment to VII. to VIII., but 5 grammes of alum and 5 grammes citric acid were used.

The direct precipitate weighed .6300 grammes, and the filtrate yielded, when treated as before, .0100 grammes.

From these experiments it is evident:—

I. That the presence of citric acid increases slightly the solubility.

II. The presence of iron makes no perceptible difference in this respect, the solubility being determined by the quantity of citric acid present.

III. Alumina increases slightly the solubility, but the quantity dissolved seems to be beyond a certain point determined by the citric acid rather than the alumina present.

IV. That the influence of alumina is not so marked as is generally supposed. The widespread idea that alumina prevents the precipitation is doubtless due to the fact that in the presence of much alumina the precipitate forms very slowly, but the almost complete separation is merely a matter of time.

By subtracting the solubility of ammonio-magnesian phosphate in ammonia water (1 in 4) from the increased solubility due to citric acid and alumina, and dividing by the quantity of citric acid in grammes, we arrive at the quantity of phosphoric acid expressed as $\text{Mg}_2\text{P}_2\text{O}_7$, held in solution by 1 gramme of citric acid.

In making the correction for solubility, I therefore propose to add .001 grammes $\text{Mg}_2\text{P}_2\text{O}_7$ for every 100 c.c. of solution, and in addition to allow .0015 for every gramme of citric acid used in the determination. This would, in a determination where 2 grammes of substance were taken, and the liquid amounted to 250 c.c., and where it was necessary to use 2 grammes of citric acid, amount to .18 per cent. P_2O_5 . The allowance is not great, but it is perceptible, and should in all cases be made.

I have had experience with the citric acid process for many years past, and as I have always found it give excellent results, I may, perhaps, be allowed to sketch the method which I pursue. About two grammes of the finely powdered substance are weighed accurately, transferred to a beaker and decomposed with HCl, and where

necessary a drop or two of HNO_3 . The solution is then evaporated to dryness in a water-bath, taken up with HCl , and after digestion, the insoluble silicious matter is separated by filtration; a weighed quantity of citric acid is added; the solution heated up nearly to boiling point, and a weighed quantity of oxalate of ammonia added. The quantities used must vary with the substance under examination, the knowledge only being acquired by experience, but it is seldom necessary to add more than two grammes citric acid or 2.5 grammes oxalate of ammonia. The free acid is then just neutralised, with dilute ammonia, and acetic acid added, to decidedly acid reaction. The liquid is kept simmering for a few minutes with constant stirring, and after standing a short time the oxalate of lime filtered. Great care must be observed not to have too large an excess of oxalate of ammonia present, as oxalate of magnesia in an ammoniacal solution is somewhat easily precipitated. To the filtrate ammonia of .880 sp. gr. is added to about one-fourth of the bulk, and to the liquid, which must remain clear, or only slowly throw down a small precipitate, due to the magnesia present, magnesia mixture is added in moderate excess. The liquid must be set aside with occasional stirring for the precipitate to form—the time required being principally determined by the quantity of alumina present. It is best, however, to allow it to stand overnight, although in cases where the alumina is absent, or small, the precipitation will be found to be complete in two hours. The precipitate is then separated from the liquid by filtration, dissolved in as little HCl as possible, and reprecipitated with one-third of its bulk of ammonia. After allowing to stand for two hours with occasional stirring, it may be filtered, and after drying converted into $\text{Mg}_2\text{P}_2\text{O}_7$.

The oxalate of lime is converted to CaCO_3 by gentle ignition, weighed, dissolved in HCl , and tested for P_2O_5 , which may be present in small quantities, and which should be determined.

From these data, and by correction for the slight solubility, the percentages may be calculated.

Warrington has made the statement that oxalate of lime is soluble to a perceptible extent in citrate of ammonia, and in order to ascertain the truth of this statement the following experiment was made: One gramme of pure CaCO_3 was dissolved in HCl , five grammes citric acid added, then two grammes oxalate of ammonia, the liquid (about 100 c.c.) just neutralised with dilute ammonia, and acidified with acetic acid. The precipitation was conducted in a hot solution, and after allowing to stand for a few minutes the liquid was filtered. The filtrate was evaporated in a platinum dish, ignited, the residue dissolved in HCl , and the lime precipitated as oxalate in a very small bulk. This yielded CaCO_3 .0020 grammes.

It must be remembered that the citric acid used (five grammes) is far in excess or that required in an analysis, and supposing the solubility to be entirely due to the citric acid, we should have only .0008 grammes of CaCO_3 dissolved where two grammes citric acid were used. This, with two grammes of substance taken, would only represent .02 per cent. CaO , a quantity so small as to be insignificant, and certainly not exceeding the probable error where a large quantity of lime is present.

In accuracy, the process as described—when all precautions are taken—is unsurpassed by any, and gives strictly reliable results.

When the quantity of phosphoric acid present is small, and the iron and alumina large, the molybdenum process must be used; but with a large percentage of phosphoric acid, the citric acid process is all that can be desired.

Mr. Bernard Dyer said that the process described was one which he had used for several years past, and the results were thoroughly reliable. With regard to the time during which the precipitate stands, he might say that in the case of guanos or bone ashes where the proportion of iron and alumina was slight and the quantity of citric acid small, the precipitation was quite complete within one hour or one and a-half hours at the outside. Where much iron or alumina was present, it was certainly desirable to leave the precipitation for the first time standing overnight. He believed the errors which chemists fell into, and the impossibly high results too often obtained, were due to a great extent to the formation of oxalate of magnesia. He always re-dissolved the precipitate—the trouble was next to nothing, and it only extended the duration of the analysis by one and a-half hours. It was quite possible to make six phosphoric acid determinations in a day by that method.

Mr. Hehner said that the question of phosphoric acid determination was one at which he had worked a good deal, and in which he took much interest. He did not wish to insinuate that Mr. Smetham's and Mr. Dyer's results were incorrect, but if correct they were so only by a fortunate balance of the different errors of the method. Thus the great strength of the ammonia used for precipitating and washing (1 to 3 of strong ammonia) caused a loss by imperfect precipitation and solubility, whilst the proper strength was 1 of strong ammonia to 9 of water, or 1 of ammonia of Fresenius' strength (specific gravity 0.96) to 3 of water. It had long been shown (by Kissel) that any correction for solubility of the ammonium magnesium phosphate in such dilute ammonia ought not to be made, the precipitate being practically insoluble in the dilute ammonia; he thought the correction had been completely dropped. Another cause of error was that the magnesia mixture used by Mr. Smetham was sulphate of magnesia mixture. He thought that had been completely given up, and that it was well understood that from such sulphate mixture basic sulphates almost invariably entered into the phosphate precipitates. He did not see how Mr. Smetham's results went at all to show the solubility of the precipitate in dilute ammonia, as in all of Mr. Smetham's experiments magnesia mixture was invariably present, and it was known that in the presence of magnesia mixture the solubility was very different from that when dilute ammonia only was employed. He considered the molybdic method a far better one, and, after all, the easier and cheaper of the two, no re-dissolving and re-precipitating of precipitates and objectionable corrections for solubilities being required. It certainly allowed of the employment of small quantities of manure only, but if the work was done with due regard to all circumstances there was no chance of error. Most of Mr. Smetham's results were too high, and he attributed this to the presence of sulphate of magnesia in the precipitate and to over-correction.

Mr. Smetham, in reply, said that he had many times worked the molybdate and citric acid processes together on samples of mineral phosphate, and only once had they differed more than 0.2 per cent.; in the majority of cases the difference being within .05 per cent. In the only case in which they differed he found on repeating that the molybdate process was at fault. He differed entirely from Mr. Hehner as to the solubility. Many experiments

had proved that where the quantity of ammonia was lessened, the solubility became greater. He took particular care to prove the purity of the precipitate; he thought it might safely be considered as having been due to the solubility only; the magnesia mixture he used was made with sulphate, but in his ordinary work he always tested the precipitates, and found that they were quite pure, and that was more than could always be said of the molybdate process, by which, when the precipitates were tested, there was a trace of iron carried down. There was more danger of oxalate of magnesia being precipitated than of the basic sulphate, and it was for that reason he put special stress on the necessity of weighing the oxalate of ammonia used. With due care his process gave quite as accurate results as the molybdate process, since it was possible to work with four times the quantity of substance, and errors in weighing, &c., were therefore considerably diminished, and as it was also more expeditious and less expensive, it was to be preferred where many analyses had to be performed.
