XVII. *New experiments on some of the combinations of phosphorus.*
By Sir H. Davy, *L.L.D. F.R.S. Vice Pres. R. I.*

Read April 9, 1818.

In a paper published in the Transactions of the Royal Society, for 1812, I have detailed a number of experiments on phosphorus, from which I deduced the composition of some of its compounds with oxygen, with hydrogen, and with chlorine. Since the appearance of this paper, various researches have been brought forward on the same subject, in which some results, differing very much from each other, and from mine, are stated. I ventured to conclude that the phosphoric acid contained double the quantity of oxygen to that in the phosphorous acid; and that phosphoric acid contained about $\frac{3}{5}$ of its weight of oxygen.

M. Berzelius considers the oxygen in phosphoric acid to be 128.17, and M. Dulong, 124.5, the phosphorus being 100. M. Dulong and M. Berzelius suppose the quantity of oxygen in phosphorous acid to be to that in phosphoric acid as 3 to 5.

The motive which immediately induced me to resume the enquiry respecting the phosphoric combinations, was M. Dulong's paper. This ingenious chemist has not only endeavoured to establish new proportions in the known compounds of phosphorus, but has likewise attempted to prove the existence of two new acids of phosphorus; and has denied several facts which I considered as sufficiently established.

The details which I have to lay before the Society in the following pages, will serve to correct and fix, I hope, with tolerable accuracy, the proportional number or equivalent of phosphorus, and at the same time will show the truth of the general series of proportions that I assigned to its compounds. In a case where my conclusions differ so materially from those of M. BERZELIUS and DULONG, it may be supposed that I have not adopted them without considerable caution; and I have preferred my own results to theirs, only because they have been confirmed by minute and repeated experiments.

I was certain from various experiments, made both long ago and recently, and the results of which had been confirmed by Mr. BRANDE, that the proportion of oxygen, which M. DULONG assigns to phosphoric acid, is considerably smaller than that denoted by the combustion of small quantities of phosphorus in oxygen gas. I knew that minute portions of phosphuretted hydrogen were separated from phosphorus by voltaic electricity; and it occurred to me as possible, that water might be formed in the combustion of phosphorus, and separated from the phosphoric acid when it entered into saline and metallic combinations. To ascertain if this were the case, I passed phosphorus to saturation through red hot lime in a green glass tube connected with a mercurio-pneumatic apparatus: the combination took place with vivid ignition; but no elastic fluid was produced. A portion of the phosphuret of lime formed, was introduced into a tray of platinum, and heated in a glass retort filled with oxygen gas; the phosphuret of lime burnt brilliantly, and became partly converted into *phosphate of lime;* but on restoring the original temperature of the retort, there was no appearance of *vapour* or of *moisture.*

Having examined the phosphate of lime formed in this operation, and satisfied myself that it was the same as that formed by other methods, it became evident that there were no sources of error in the experiments on the combustion of phosphorus in oxygen gas, arising from the formation or separation of water; and the only circumstance which could be urged against the accuracy of processes on this combustion, was the small quantity of materials* on which they had been made.

The vividness and rapidity of the combustion of phosphorus, renders it impossible to burn considerable quantities of phosphorus in the common way in glass vessels. Phosphuret of lime burns much more slowly and less intensely. I endeavoured to ascertain the quantity of oxygen absorbed by a given weight of phosphorus converted into phosphuret of lime; but the experiment did not succeed. Though the phosphuret of lime was in fine powder and distributed over a large surface, yet the phosphate of lime which formed and fused on the exterior, defended the interior of the phosphuret from the action of the oxygen, and prevented its combustion.

After various unsuccessful trials to convert considerable quantities of phosphorus into phosphoric acid by combinations containing oxygen, I at last thought of a very simple mode of burning phosphorus, which answered perfectly.

Phosphorus requires a considerable heat for its volatilization. By inclosing it in a small tube, so constructed that the phosphorus can burn in vapour only from the aperture of

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* A source of error might be suspected in carbon combined with phosphorus; but I have been convinced by experiments made on the action of chlorine on the phosphorus I employed, that it contained no appreciable quantity of carbon. I suspect that what is often taken for carburet of phosphorus, is in reality a red oxide.

the tube, large quantities of it may be burnt by the heat of a spirit lamp in a retort filled with oxygen, and the absorption of oxygen and the quantity of phosphoric acid formed may be minutely ascertained.

The accompanying sketch (Pl. XVIII.) will give an idea of the apparatus. The neck of the little curved tube, or small distilling retort, after the phosphorus is introduced, is drawn out, and an aperture left of about $\frac{1}{10}$ of an inch; it should not be smaller, or it becomes choaked by the phosphoric acid formed. Regulating the heat by raising or lowering the spirit lamp, the combustion may be carried on slowly, or rapidly, at pleasure.

Operating in this way, I have often burnt from 5 to 10 grains of phosphorus without any accident, and ascertained exactly the quantity of oxygen absorbed: there is only one source of error—a quantity of phosphorus remains in the upper part of the tube, which cannot be burnt except by a greater heat than the retort will bear; and it is difficult to ascertain the precise weight of this, as the tube always unites with some phosphoric acid where it is red hot at its mouth; but this can be only a trifling source of error.

In these experiments, and in all the others detailed in this paper, I received much useful assistance from Mr. FARADAY of the Royal Institution; and much of their value, if they shall be found to possess any, will be owing to his accuracy and steadiness of manipulation.

EXPERIMENT I.

Six grains of phosphorus. The small tube with the phosphorus weighed before the combustion 56.5 grains; after the combustion 50.9; so that it had increased $\frac{4}{10}$; and this increase was in great measure from phosphorus that had escaped combustion; and when this was burnt out by a strong red heat, the increase of weight of the tube was under $\frac{1}{10}$; so that at least 5.9 of phosphorus had been converted into acid: 23.5 cubical inches of oxygen were absorbed: thermometer being at 46° FAHRENHEIT; barometer 29.6 inches.

EXPERIMENT II.

Ten grains of phosphorus. The glass tube containing the phosphorus weighed 103.1 grains; after the experiment 95.6; but much phosphorus remained unconsumed. After the tube had been heated to redness, it weighed 94 grains; so that at least 8.4 grains of phosphorus were consumed in the first process. The absorption of gas was 34 cubical inches. Barometer 29.8, thermometer 47°.

EXPERIMENT III.

Ten grains of phosphorus. By weighing the tube after the experiment, and then distilling and burning the residual phosphorus, it was found that 9.1 grains of phosphorus had been burnt, which had absorbed 35.25 cubical inches of oxygen. Barometer 29.7, thermometer 49° FAHRENHEIT.

I give these experiments as the most accurate I have made. The pressure and temperature vary so little, that the corrections for them are of no importance. Supposing that 100 cubical inches of oxygen (the barometer being between 29.8 and 29.6, and the thermometer between 46° and 49° FAHRENHEIT) weigh 33.9 grains, phosphoric acid will be composed, according to the first result, of 100 phosphorus to 135 oxygen;

according to the second, of 100 to 137.2; and according to the third, of 100 to 131.3: the mean will be 100 to 134.5.

The light of the phosphorus burning in vapour in these experiments was excessively bright; yet the top of the retort never became softened; and the phosphoric acid, which increased the weight of the tube, principally combined with the glass at the aperture where it was red hot. I cannot but consider this process of burning phosphorus in the gaseous state in a great excess of oxygen, as the most accurate mode that has yet been devised for ascertaining the composition of phosphoric acid. In this instance no phosphorous acid, as I ascertained by direct trials, is formed from the vapour; and no substances are concerned except those that actually combine. M. DULONG's method of ascertaining the composition of phosphoric acid, appears to me much too complicated to afford any results approaching to accuracy. He first combines copper wire with phosphorus, by passing phosphorus over it by means of a stream of hydrogen gas; he then dissolves his phosphuret of copper in nitric acid, and determines the quantity of phosphoric acid formed by precipitation: in all of which processes sources of error may exist.

M. BERZELIUS's methods of ascertaining the composition of phosphoric acid, that of reviving gold from its oxide by means of phosphorus, and that of determining the quantities of phosphate and muriate of silver formed from perphosphorane, or the perchloride of phosphorus, appear to me still more exceptionable; yet his results on the quantity of oxygen approach nearer to mine than those of M. DULONG.

The facts which I endeavoured to establish respecting chlorine, in a paper published in the Philosophical Transactions for 1810, show that the proportional or equivalent volume in which chlorine combines, is to that in which oxygen combines, as 2 to 1; and it follows, that 10 grains of phosphorus in forming the white sublimate, or perchloride, ought to combine with between 76 and 80 cubical inches of chlorine.

In experiments that I formerly made on this subject, by admitting chlorine to phosphorus in exhausted vessels, and ascertaining the absorption by introducing solution of chlorine, I overrated the absorption. I did not at that time know, what I have since ascertained, that a solution of chlorine in water, *apparently* saturated with chlorine, by agitation with it in long narrow vessels, will still take up more, by exposure to a great surface of chlorine in larger vessels. Under all circumstances, it is difficult to gain very precise results in experiments on the action of phosphorus on chlorine. Mercury acts so rapidly upon chlorine, that it cannot be employed in experiments in which the absorption is to be determined. When common water is used, some of the gas is absorbed by the water, and, the sublimate being a very volatile substance, its vapour always increases the volume of the residual gas. Some aqueous vapour likewise, in experiments over water, enters with the gas, which forms a volatile hydrate, the effect of which is likewise to diminish the apparent absorption of chlorine.

I have always found the absorption greatest, when I have operated in small retorts, connected by small stop-cocks with the vessel containing the chlorine, over water. Making the proper corrections for the absorption by the water, the apparent absorption has been from 35 to 38 cubical inches for every 5 grains of phosphorus.

M. Dulong's two methods of ascertaining the quantity of chlorine in the sublimate, appear to me at least as objectionable as his process for determining the composition of phosphoric acid, and liable to great errors: the first from the uncertainty of the absolute quantity of chlorine admitted; and the second, from the loss arising from the vapour of the sublimate, which must be carried off by the current of chlorine. How great a deficiency may originate from the last circumstance, is shown by the following experiment: 5 grains of phosphorus were converted into sublimate by chlorine in great excess, the remaining chlorine was displaced by passing common air through the vessel for some time, till not the slightest smell of chlorine could be perceived; the retort was then weighed, and a current of air passed through it. Though this current could hardly have replaced the air contained in the retort, yet the loss of weight was 1.7 grains, and copious vapours were produced in the atmosphere. In a second trial of the same kind, there was a greater loss of weight, and by barely exhausting the retort, and then again admitting air, there was a loss of $\frac{7}{10}$ of a grain.

When chlorine is made to act upon phosphorus over mercury not carefully dried, some muriatic acid gas is always formed; but when the mercury has been recently boiled, no effect of this kind is produced, and the vapour in the gas, forms a minute quantity of a liquid hydrate of the perchloride which by more water, is converted into muriatic and phosphoric acids, as I proved by some very delicate experiments; so that there is certainly no hydrogen denoted in phosphorus by the action of chlorine, and in their mutual action a mere binary compound of the two substances is formed.

After reflecting much upon the methods of combining chlorine and phosphorus, so as to gain correct results, it occurred to me, that in operating over water, and introducing a perfectly saturated solution of chlorine to absorb the vapour of the sublimate and of its hydrate formed from the water in the chlorine, I should gain a result nearly correct. I made an experiment in this way on 4 grains of phosphorus, in a retort containing 13 cubical inches. I ascertained the absorption, introduced into the retort a tube, containing about half a cubical inch of saturated solution of chlorine, and suffered the fluid slowly to act upon the sublimate, cooling the retort by immersion in water; I then ascertained the degree of the second absorption, which was nearly a cubical inch and a half. I likewise ascertained that water had its powers of dissolving chlorine diminished, and not increased, by uniting with phosphoric and muriatic acids, so that the apparent absorption must have been less than the real one. Adding the second absorption to the first, and making the proper corrections, the quantity of chlorine uniting to 4 grains of phosphorus was 31.9 cubical inches; barometer being 30.1 inches, and thermometer 46° FAHRENHEIT.

Rather a larger proportion would be given, if the correction for the presence of vapour had been made for some of the other experiments: and the result agrees exactly with the mean deduced from the absorption of oxygen in the formation of phosphoric acid; for, assuming that 100 cubical inches of chlorine weigh 76.5 grains, then the sublimate will consist of 1 of phosphorus to nearly 6 of chlorine; and taking the composition of phosphoric acid from this datum, it would consist of 100 of phosphorus and 135 of oxygen.

To ascertain the composition of phosphorous acid, I used a new method, that of converting the perchloride of phosphorus, or perphosphorane by phosphorus, into the chloride which affords phosphorous acid by the action of water. This is easily done by heating them together in a close retort; and it enables us to determine with certainty, which opinion is correct, *that* assuming the oxygen in phosphorous acid to be 3, or *that* which supposes it to be 2.5, the oxygen in phosphoric acid being 5.

5 grains of phosphorus were converted into perchloride in a small retort of the capacity of 6 cubical inches: it was necessary to exhaust this retort twice to remove the residual common air mixed with the chlorine, and some perchloride must have been lost during this process. A small quantity of chlorine, which could have been little more than sufficient to compensate for the loss, remained in the retort. 5 grains of phosphorus were introduced, and the retort suffered to remain filled, principally with common air; heat was very slowly applied; all the phosphorus, except an atom not so big as the head of a small pin, disappeared, and a little of the sublimate still remained, when the retort burst from the expansion of the vapour of the new chloride formed; but the chloride found on the fragments was pure, and held no phosphorus in solution.

A second experiment was made in a retort of the capacity of 11 cubical inches. 5 grains of phosphorus were converted into perchloride: the retort was twice completely exhausted, by which at least a grain and a half or two grains of perchloride must have been lost. 5 grains of phosphorus were introduced; a little of the sublimate was lost by falling into the stop-cock of the retort; yet the conversion of the phosphorus by heat into the liquor was almost complete; there remained only a minute fragment. In this experiment, however, the liquor held phosphorus in solution. When this phosphorus was precipitated by water, and obtained with the fragment by sublimation in a small glass tube, it did not equal $\frac{7}{10}$ of a grain, and was no more than could be expected from the loss of the sublimate.

These two experiments prove distinctly that the oxygen in phosphorous acid is half that in phosphoric acid; for if the proportion had been that which M. DULONG and M. BERZELIUS indicate, 1.67 grains of phosphorus, at least, ought to have remained after the action of the sublimate.

A collateral experiment was made. 32.7 grains of the fluid chloride, made by passing phosphorus through corrosive sublimate in great excess, were acted on by water, and precipitated by nitrate of silver; the precipitate was immediately separated from the fluid, after it had been greatly diluted with distilled water. Distilled water was then repeatedly passed through it, and it was dried and fused, when it weighed 98.4 grains; which, allowing 24.5 per cent. of chlorine in horn silver, would give the composition of the fluid chloride as 24.108 of chlorine, and 8.592 of phosphorus.

The comparative quantity of precipitate in this experiment was so much less than I had found in a former experiment, that, notwithstanding the care with which the process had bee conducted, I resolved to make some more experiments of the same kind. In the first, in which the decomposition by water was made in a small bottle, from which no vapour could escape, and in which I superintended the weighing and drying of the horn silver formed, with the greatest care, 18.4 of the liquid chloride afforded only 54.5 of chloride of silver, which agrees as nearly as could be expected with the former experiment. In two other experiments, made with equal care, and in which the liquid was poured into a solution of nitrate of silver, 6 grains gave 17.1 of horn silver, and 29.4 gave 89.9 of fused horn silver.

In examining minutely the circumstances of the action of the liquid chloride, or solutions containing phosphorous and muriatic acids, or nitrate of silver, I found no difficulty in explaining the cause of the error in the former experiments. Phosphorous acid acts upon nitrate of silver, and more rapidly in proportion to its concentration, and gradually produces a copious precipitate from it; so that if there be an excess of nitrate of silver, and the precipitate be not immediately separated from the solution, there is always a considerable increase of weight. M. DULONG, and M. BERZELIUS, whose experiments agree with my former ones, *may* have been misled by a precipitation from the nitrate of silver by phosphorous acid, as I am sure *I* was. M. BERZELIUS does not state how he prepared his liquid chloride of phosphorus; but M. DULONG, who objects to my process by corrosive sublimate, and employs, instead of it, the action of chlorine on phosphorus in forming his fluid, must have been exposed to other sources of error. He speaks of acting on dry phosphorus by dry chlorine; but it must be always extremely difficult to free a gas that cannot be kept over mercury, of all its vapour; and as perchloride always forms during the action of phosphorus on chlorine, a part of which produces a fluid, and easily volatile hydrate with water, and soluble in ll proportions in the liquid chloride, this process must be very liable to error. I have never been able to form the perchloride, even from chlorine slowly passed through muriate of lime, without producing a small quantity of liquid hydrate of perchloride, which, when the solid perchloride was converted into liquid by more phosphorus, rose in vapour with it, and which, containing nearly a double quantity of chlorine, (for the water forms a very small part of it) occasions the precipitation of a much larger quantity of horn silver than the pure chloride formed from corrosive sublimate.

These various experiments on the combination of phosphorus with oxygen and chlorine, sufficiently agree with each other to afford the means of determining the proportion in which phosphorus combines with other bodies, or its equivalent number considered as an element.

If the absorption of oxygen be considered as offering the data, and phosphoric acid be supposed to consist of two proportions of oxygen, and one of phosphorus, the number representing the proportion in which phosphorus combines, will be 22.3. If phosphoric acid be considered as consisting of four proportions of oxygen, the proportional number or equivalent of phosphorus will be 44.6.

If the absorption of chlorine in forming phosphorane be made the datum, the number will be the same, 22.2, or the double 44.4. If the quantity of horn silver formed from the liquid chloride, taking the mean of all the experiments, be assumed as the datum, the number would be 23.5, or the double 47: the mean of all these proportions is 22.6, or the double 45.2; or taking away decimals, 45.

In referring to the analyses which have been made of the different combinations of phosphoric acid, for the purpose of ascertaining if they correspond with this number, I found the data so uncertain and so discordant, that it was impossible to form any conclusions from them. The phosphate of soda, as is well known, has alkaline properties; yet, according to M. Berzelius, it contains but 17.67 of soda to 20.33 of acid; whereas it ought to contain, according to the proportion indicated by my experiments (if neutral) nearly an equal weight of soda. M. Berzelius mentions several combinations of baryta and lime with phosphoric acid, of which only two approach to a correspondence with the number I have given for phosphorus; that containing 45.5 of acid to 48.7 of lime; and that containing 39.1 of acid to 60.8 of barytes. New researches are required to explain the anomalies presented by the phosphates.

I shall give three experiments on the quantity of hydrate of potassa necessary for saturating given quantities of phosphoric acid made from given weights of phosphorus.

18 grains of phosphorus converted into phosphoric acid by combustion in oxygen, required for its saturation 47 grains of dry hydrate of potassa.

5.7 grains of phosphorus converted into acid, required 14.7 of hydrate of potassa.

5 grains of phosphorus converted into perchloride, demanded, to produce perfect neutralization, 68 grains of hydrate of potassa.

These three experiments agree so well with each other, and with the proportionate number gained from the absorption of chlorine and oxygen by phosphorus, that it is impossible not to put confidence in them.

If 13.1 be considered as the quantity of hydrate of potassa required to neutralize the phosphoric acid formed in the last experiment, and the 54.9 of hydrate remaining, be supposed to contain 43 grains of potassa, then the chlorine required to expel the oxygen from the potassa would be rather more than 40 cubical inches.

We owe to the ingenuity of M. DULONG the discovery of an acid, which he names the hypophosphorous acid, and which he supposes to contain half the quantity of oxygen in the phosphorous acid. I have satisfied myself as to the correctness of his views respecting the existence of this acid, and the properties of its compounds; but I cannot regard the method he has adopted for its analysis as entitled to confidence. He takes a given quantity of hypophosphite of soda, acts upon this by chlorine, converts the excess of chlorine into muriatic acid, precipitates by nitrate of silver and earthy salts, and from the comparison of all these data, in which some substances of uncertain composition may be concerned, draws his conclusions.

I have found that the neutral hypophosphite of barytes, when acted on by heat in close vessels, is converted into acid phosphate of barytes, disengaging an elastic fluid, which is almost entirely the hydrophosphoric gas, or phosphuretted hydrogen saturated with phosphorus. I say *almost entirely*, because in the beginning of the process, a little gas spontaneously inflammable is produced, and a minute quantity of moisture appears: and when the heat is raised to redness, a very little phosphorus is produced, probably from the decomposition of a part of the phosphoric gas. Now supposing the quantity of phosphoric acid in phosphate of baryta known, and the quantity of phosphorus in phosphuretted hydrogen known; it is very easy, from an accurate experiment on the decomposition of the hypophosphite of baryta, to learn the composition of hypophosphorous acid.

I made two experiments on this subject; in one, 50 grains of dry hypophosphite of barytes were used, and the distillation conducted in a small glass tube. About 23.25 cubical inches of gas were produced. The loss of weight of the apparatus could not be ascertained, as unluckily a little of the phosphate was lost; a small portion of phosphorus was deposited in the upper part of the tube, from the decomposition of a minute quantity of the bi-phosphuretted gas; but this could not have equalled the $\frac{4}{10}$ of a grain, as the tube only lost $\frac{4}{10}$ by being heated to whiteness.

In the second experiment, 29 grains of the hypophosphite were used, and the loss of weight only ascertained, which was 3.5 grains. To be able to form any opinion as to the composition of the hypophosphorous acid, it was necessary to ascertain the composition of the phosphate of baryta produced in these experiments; which was easily done by precipitating a given quantity of the hypophosphite of barytes by sulphate of soda in solution. 15 grains of hypophosphite of barytes, in an experiment very carefully made, afforded 11.3 of sulphate of barytes. Now, supposing this sulphate of barytes to contain 7.4 of baryta, the hypophosphite would consist of 7.4 of baryta, and 7.6 of hypophosphorous acid; and 13.1 of the acid phosphate of baryta, formed from its decomposition, would contain 5.7 phosphoric acid, and 7.4 baryta. And in the experiment in which 29 grains of hypophosphite of baryta were decomposed, supposing the whole loss of weight to be owing to perphosphuretted hydrogen given off, and this gas to be composed of 22.5 of phosphorus to 4 of hydrogen, or of 5.29 hydrogen to 29.76 phosphorus, and the 25.5 of acid phosphate remaining composed of 14.47 baryta nearly, and 11.03 phosphoric acid, adding the 29.76 of phosphorus to the 4.72 in the phosphoric acid, and subtracting 39, the quantity of oxygen required to form water with the 5.24 of hydrogen, the hypophosphorous acid may be conceived to be composed of 7.69 phosphorus, and 2.54, which denotes rather less than half the oxygen in phosphorous acid: i. e. as 7.43 to 1.5, an approximation nearer than could have been expected.

Assuming the composition of the phosphuretted gas to be what is stated in the preceding page, which agrees very nearly with an experiment which I formerly made, the first experiment on the quantity of gas disengaged would give a proportion of oxygen rather less than that which has been just calculated upon; but it must be remembered, that a certain quantity of common phosphuretted hydrogen is produced, which containing less hydrogen in a given volume, would sufficiently explain the difference of result.

M. DULONG has advanced an ingenious opinion, that the hypophosphorous acid *may be considered* as a triple compound of hydrogen, oxygen, and phosphorus. There is another view which may be taken of its composition, namely, that it may be a compound of phosphoric acid and perphosphuretted hydrogen. Phosphuretted hydrogen, as may be deduced from some experiments of M. DULONG, has the properties of a very weak alkali; and when expelled from the neutral hypophosphites, they become acid. This view agrees very well with the equivalent, or proportional numbers, which represent phosphoric acid and phosphuretted hydrogen. If it be adopted, the hypophosphites must be considered as triple compounds, analogous to the salts containing fixed alkali and earths, or ammonia and earths combined with acids.

M. Dulong imagines that the acid formed by the slow combustion of phosphorus in the air, and which I have supposed to be a mixture of phosphorus and phosphoric acids, is a peculiar acid, a chemical compound of phosphorous and phosphoric acids, which he names phosphatic acid. I cannot say that his arguments give much probability to this opinion. This substance has no crystalline form, no marked character which distinguishes it from a mere mixture of phosphorous and phosphoric acids; and as far as my experiments have gone, it is far from uniform in its composition; and phosphorous and phosphoric acids mixed together, produce a substance of exactly the same kind.

That a mixture of phosphorous and phosphoric acids should be produced by the slow combustion of phosphorus, is not surprising, when it is considered that this phenomenon is connected with different chemical processes, viz. the action of the vapour of phosphorus upon air, the action of solid phosphorus upon the elastic atmosphere, and upon the air dissolved in the moisture attracted by the acids formed; and, unless vapour be present in the air, the process of the slow conversion of phosphorus into acids soon stops.

I have mentioned in the paper to which I have referred, in the beginning of this communication, that the hydrophosphorous acid is decomposed by heat; and that phosphoric acid, and perphosphuretted hydrogen are the results. In examining the nature of the phosphoric acid formed, I find that it contains water, so that it is a hydrated phosphoric acid. In carefully conducting the experiment, I find likewise, that a small proportion of water is given off with the perphosphuretted gas. I shall give the results of an experiment: 17.5 grains of hydrophosphorous acid were decomposed by heat in a small glass retort carefully weighed; 6.5 cubical inches of elastic fluid were generated, and the loss of the retort was 4 grains. Now, if it be assumed that the hydrate of phosphoric acid * remaining equalled 13.5 grains, and that it contained, according to the law of definite proportions, 1.88 of water, and that the bi-phosphuretted gas weighed 1.937, and consisted of 1.6446 phosphorus, and .2924 hydrogen; then the oxygen in the phosphorous acid will be to the phosphorus as 44 to 66, which is as near a result as can be expected.

For 4 proportions of phosphorous acid are - -	300	or the double	150
and 10 of water - -	170	or	85
which together amount to -	470	or	235
which form 3 proportions of phosphoric acid	315	or	157.5
with 3 of water to form the hydrate -	51	or	25.5
	366		183.0
4 of water decomposed, of which the hydrogen is 8, to form with 45 of phosphorus phosphuretted hydrogen - -	53	or	26.5
3 of water given off - - -	51	or	25.5
making - - - -	470	or	235.

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* I proved it to be a hydrate by heating it with magnesia, when abundance of water was given off from it.

I have no doubt that the acid which I used formerly was drier than the acid employed in this experiment, which will account for the difference of the result. Supposing a hydrophosphorous acid could be procured, containing only the quantity of water sufficient to convert it into dry phosphoric acid, it would consist, as I have stated in my former paper on phosphorus, of four proportions of water, and four proportions of phosphorous acid.

I have adopted throughout the whole of these calculations, the supposition that the hydrogen in water is to the oxygen as 2 to 15; and consequently I have taken the number representing oxygen as 15, which is extremely convenient, as the multiples are simple, 30, 45, 60, &c. Taking the proportion of phosphoric acid in phosphate of potassa, which may be deduced from the experiments, page 329, it appears more convenient to represent the proportional number, or equivalent of phosphorus, by 45, or 45.2, than by 22.5, or 22.6, which gives facility in adopting either hypothesis of the composition of hypophosphorous acid. If it be supposed a simple compound of oxygen and phosphorus, the series of proportions in the acids of phosphorus will be

Hypophosphorous acid, Phosphorus	45	Oxygen 15
Phosphorous acid -	45	Oxygen 30
Phosphoric acid - -	45	Oxygen 60
or hypophosphorous acid 263 -	Phosphoric acid 2 proportions	210
	Phosphuretted hydrogen 1 prop.	53

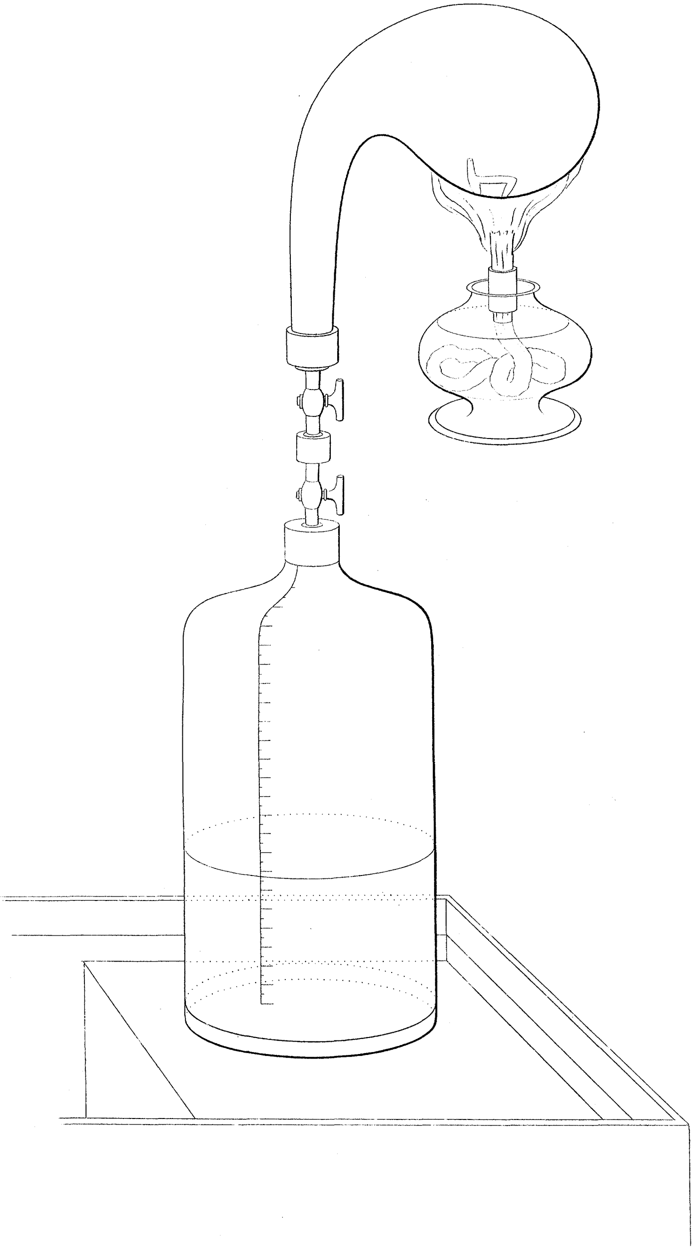
I shall conclude this paper by a few incidental observations on the compounds of phosphorus.

M. DULONG states that no phosphorous acid is formed when phosphorus is burnt in excess of oxygen or atmospheric air;

as, he says, I have asserted. I cannot find that I have any where made such an assertion; but notwithstanding what M. Dulong pretends, the assertion is true, as the following experiment will prove. Half a grain of phosphorus was set fire to in a retort containing 16 cubical inches of common air; the acid products were washed with distilled water, and passed through a filter, and evaporated. When the acid became nearly dry, small globules of phosphuretted hydrogen were disengaged from it, indicating the presence of phosphorous acid. The experiment was repeated two or three times, care being taken to separate the red powder which has been considered as an oxide of phosphorus, and always with the same result.

Whenever phosphorus is inflamed, and suffered to become extinguished in oxygen gas in excess, unless the *product* is strongly heated after the spontaneous combustion is over, *an acid*, of which the hydrate produces phosphuretted hydrogen by heat, is always found in the products; and this acid is probably produced by the action of the solid phosphorus on the phosphoric acid in contact with it. This fact, and the circumstance, that much phosphorus acid is produced by the combustion of phosphorus in rare air, renders it almost certain that the phosphorous acid is a direct combination of phosphorus and oxygen, and destroys an idea which might otherwise be formed from the phenomena of the decomposition of its hydrate, namely, that it is a compound of three proportions of phosphoric acid, and one of phosphuretted hydrogen.

M. Dulong and M. Berzelius speak of freeing phosphorane, or the liquid chloride of phosphorus, from phosphorus,



by distillation. In experiments made in the laboratory of the Royal Institution, in which it has been twice carefully distilled at a low heat, it has still contained minute quantities of phosphorus.

It has been supposed that dry phosphoric acid is fixed at a white heat; but I find that this is not the case: it rapidly rises in vapour at this temperature, and evaporates even at the point of fusion of flint glass: and the hydrate of phosphoric acid is susceptible of being volatilized at a much lower temperature.

In converting the solid sublimate composed of phosphorus and chlorine into the liquid compound, when the phosphorus is first fused in contact with the sublimate, a yellow crystalline mass is formed, which, when acted on by a higher degree of heat, affords the liquid chloride, which rises from it in vapour, and leaves phosphorus behind. It is possible that this yellow solid is a compound of phosphorus and chlorine, containing half as much chlorine as the liquid. Should this be proved to be the case by future experiments, it will give weight to the idea, that the hypophosphorous acid is a binary compound of oxygen and phosphorus.