III.—Upon the Invariable Production, not only of Ozone and Hydrogen Peroxide, but also of Ammonium Nitrate, in the Ozonation of Purified Air by Moist Phosphorus.

By Dr. A. R. Leeds.

As the result of very numerous quantitative experiments performed two years ago, and published in the Journal American Chemical Society, **I**, 145, and *Chemical News* for August, 1879 ("Upon ammonium nitrite, and upon the by-products obtained in the ozonation of air by moist phosphorus"), I gave the proofs of the statement contained in the heading of this article, and the determination of the amounts of the three substances formed. Forthwith, under the title "Is ozone produced during the atmospheric oxidation of phosphorus?" (*Chemical News*, **40**, 96) Mr. Kingzett, without waiting to disprove any of the above propositions by experiment, asserted that "*There is no known process of slow oxidation which has been established to produce ozone*," and that the gaseous body which I had obtained and experimented upon, was altogether peroxide of hydrogen. Mr. Kingzett insisted that the long series of wash-bottles and purifiers, which I had used to absorb and hold back as far as possible the hydrogen peroxide, did not militate at all against his assumption, for the reason that peroxide of hydrogen suspended in a vesicular condition, might pass through all the washing liquids and constitute the only active agent in the escaping gas. How greatly Mr. Kingzett's views have altered may be seen from the fact ("Report upon the atmospheric oxidation of phosphorus, etc.," *Journal Chemical Society*, December, 1880) that the points most dwelled upon by him in this last paper are, that the escaping gas contains no peroxide of hydrogen whatsoever, but consists entirely of ozone, and that "the peroxide of hydrogen formed in the process is entirely deposited in the water contained in the oxidisers; and if it cannot escape condensation in the aqueous spray and vapor of the oxidisers, it cannot be expected to escape solution in five wash-bottles."

Since the statements of Mr. Kingzett now, are diametrically opposed to those which he made when he attacked my results in the beginning, I think it will facilitate the labors of future workers in this field, if I present a brief summary of the facts hitherto established.

When I first entered upon the study of the phenomena exhibited in the aerial oxidation of moist phosphorus (October, 1878), the first difficulty encountered arose from the unsatisfactory character of the apparatus previously employed, and the impossibility of obtaining a stream of oxidised air containing a uniform and definite percentage of ozone. These difficulties disappeared when it was ascertained that the volume of ozone produced, under given conditions, was a definite function of the temperature, and might accordingly be expressed by a curve, having its origin at 6° C., at which temperature the production was nul, and arriving at its maximum at 24°, from this point falling off again rapidly. The manipulation was rendered easy by the phosphorus ozonator, described along with the volume-temperature experiments (JOURNAL AMERICAN CHEMICAL SOCIETY, **I**, 8, and *Chem. News*, **40**, 157). These results were referred to by Mr. Kingzett in the *Chemical News* for August, 1879, and yet in his earlier experiments performed long subsequently (February, 1880), he states that he obtained no satisfactory evidence of the production of ozone, and but little evidence of the production of peroxide of hydrogen. Later on, when working in summer weather, Mr. Kingzett obtained better results, and discovered that his previous failures had been due to his having conducted the experiments at too low temperatures.

In plotting the volume-temperature curve, the water in the jars of the ozonator was replaced by a solution of potassium bichromate and sulphuric acid of such strength, that the surface of the phosphorus was kept clean without undergoing the danger of ignition from too concentrated acid and too rapid oxidation. Mr. Kingzett states that "such a method of experiment obviously precluded examination for peroxide of hydrogen in this solution, in which the phosphorus was partially submerged," and explained why he found the relation of peroxide of hydrogen to ozone at 1 : 400.

The comment of Mr. Kingzett would have been only too just if I had looked, or proposed to look, in an acidified potassium bichromate bath for undecomposed hydrogen peroxide. But Mr. Kingzett, who criticised both papers at length (*loc. cit.*), must have known at that time, a year and a half ago, though apparently he has since forgotten, that I did not employ such a method. The potassium bichromate bath was employed in the determination of the volume-temperature curve of the evolved ozone only, and in that investigation no attempt was made to determine the hydrogen peroxide formed. That question was taken up at great length in the subsequent paper upon "Ammonium nitrite, and the by-products obtained in the ozonation of air by moist phosphorus." In the experiments therein detailed, and in which the determination of the hydrogen peroxide in the ozonising chambers and in the various wash-waters is expressly considered, not merely water, but water especially purified for the purpose, was employed. This and many other precautions were essential at that time, when the exact nature and extent of the sources of error were unknown. And since these sources of error are not even alluded to, nor suitable precautions to obviate them taken by Mr. Kingzett in his paper, it will be necessary to emphasize them here.

At that time, and even now, the generation of ammonium nitrite by evaporation of water was, and is taught, as an established fact. If this were indeed the case, the ozonising chambers present the most favorable conditions for its generation, and the nitrite thus formed would give the same reaction as hydrogen peroxide or ozone, when we came to titrate the water in the ozonisers with an acidified solution of potassium iodide. The elaborate experiments of Bohlig, Zabelin and Carius, however, have shown that this is not true, and that the alleged formation of ammonium nitrite by evaporation of water in air, never takes place when adequate precautions are taken to exclude from the evaporated water, the ammoniacal compounds pre-existent in the atmosphere. Fortunately, therefore, this source of error was not inherent in the experiments themselves, and it only remained to guard against it by very complete washing of the air drawn through the ozonator.

Again, Goppelsröder and Carius had shown that when ammonia is brought into contact with ozone, it is decomposed with the formation of ammonium nitrite and nitrate, and peroxide of hydrogen. It was essential, therefore, that the phosphorus should be in contact with water from which every trace of ammonia had been expelled. If this were not done, the origin of any ammonium compounds or hydrogen peroxide, found among the products of the reaction, would be rendered doubtful. It was for this reason that all the water employed in my experiments, in which a determination of the hydrogen peroxide was attempted, was *aqua purissima*, that is, water redistilled until it did not give the slightest reaction for ammonia when treated with Nessler's reagent.

Moreover, while the oxidation of water to hydrogen peroxide by *free* ozone had been abundantly disproved, yet there appeared to be much reason for supposing that during the aerial oxidation of moist phosphorus, a formation of hydrogen peroxide actually took place. If this were true, its origin could not be ascribed to a secondary action due to the ozone first formed, but to the same series of changes as those which led up to the oxidation of the oxygen molecule itself. The only sufficient assignable cause was the formation of nascent oxygen, or oxygen in the atomic condition, such as it must necessarily enter into during some moment of the chemical change, when a substance of uneven quantivalence, like phosphorus, undergoes oxidation. That oxygen in an uncombined or monatomic condition, might peroxidise the water molecule, while oxygen already combined in a triatomic molecule might not, appeared to be a legitimate hypothesis. That nascent oxygen might oxidise the nitrogen molecule at the same time, and generate, in the presence of water, ammonium nitrate, I regarded likewise as a not improbable supposition. For this reason, excessive care was taken to preclude the presence of atmospheric ammoniacal or nitrous compounds, both in the air drawn through the ozonator, and also in the water brought into contact with the phosphorus in the ozonator jars.

The mental picture which was formed at that time of the sequence of phenomena to be studied, was embodied in the following equations, the last three being imagined as contemporaneous:

(1.) $P_4 + O_{14} = P_2O_5 + P_2O_3 + 2O_2 + O + O$.
(2.) $O_2 + O = O_3$.
(3.) $HOH + O = HOOH$.
(4.) $NN + 2H_2O + O = NH_4NO_3$.

The experiments performed now two years ago, and the repetition of which, though in an imperfect manner and with the neglect of essential precautions, constitute the substance of Mr. Kingzett's report to the Chemical Society above alluded to, were framed with a view of testing the truth or falsity of the above propositions. What these experiments actually were, may be seen by inspection of the accompanying scheme of them, which, with one exception, was followed to the letter :

I. Use of a measured amount of aqua purissima in the ozonator jars.

II. Complete straining and washing of the air by means of cotton wool, aqua purissima, caustic soda and sulphuric acid, both of the latter previously tested and shown to be free from nitrogen compounds.

III. Height of the phosphorus cakes before and after the experiments.

IV. Amount of ammonia in the jar-water at the close of the experiment.

V. Amount of the nitrites and nitrates, as determined by reduction.

VI. Amount of nitrous acid, as determined by metadiamidobenzole.

VII. Amounts of phosphoric and phosphorous acids, and of *hydrogen peroxide in the jar-water* (ozonising chambers).

VIII. Estimation of ammonia, nitrates and nitrites, nitrous acid alone, phosphoric acid, phosphorous acid and hydrogen peroxide, in the water used to wash the escaping products of ozonation.

IX. Similar estimations, except of the phosphorus compounds, in the solutions used to wash the entering air.

X. Measurement of total volumes of air used, and of ozone after its escape from the water employed in washing.

With regard to the first two heads of this scheme, it is to be noted that the *proof* of the exclusion of all compounds of nitrogen from the substance entering into the reaction, was essential to establishing this vital fact—that any nitrogen compounds found among the *products* were the results of chemical changes induced in the process of ozonation itself. That this preliminary proof was of the highest importance was shown by the results of the investigation; it was found that while no ammonium nitrite was present in the water of the ozonising chambers or in the wash-water, of ammonium nitrate a considerable amount (27.39 mgrms) was present in the first, and a determinable quantity (0.31 mgrm) even in the latter. Until adequate experimental evidence, therefore, is adduced to the contrary, the formation of ammonium nitrate during the ozonation of purified air by moist phosphorus, is to be regarded as a fact which cannot be overlooked, and one which demands an explanation in any theoretic account of the chemical phenomena involved.

Mr. Kingzett, however, does not even contemplate the possibility of the nitrogen, which is relatively the most abundant of the substances present, taking part in the reaction. To say nothing of the fact that his arrangements for washing the air were inadequate, there is no proof given that the water used by him in contact with the phosphorus was pure. If it was ordinary distilled water, it certainly was not pure, but contained the very body (ammonia) which was the worst possible impurity, so far as the question at issue was concerned. Not to speak of the discovery of Goppelsröder and Carius, that ammonia is converted by ozone into hydrogen peroxide and the nitrate and nitrite of ammonia. No experiment is narrated by Mr. Kingzett in which he sought to determine whether nitrous acid was present or not, in any of the liquids examined. In the entire absence of such tests, his determinations of the amounts of hydrogen peroxide, etc., are correspondingly incomplete. That this is not hypocriticism, is shown by the fact that the dense white fumes which are seen in the ozonising chambers, at one time were attributed by Schönbein to ammonium nitrite.

By referring to the seventh head of the scheme, it will be seen that the determination of hydrogen peroxide in the ozonising chambers was expressly mentioned, and as preliminary to this determination, experiments were made upon the possible influence of phosphorous acid upon the titration for the peroxide, and elaborate pains were taken to prove the absence of nitrous acid in the water examined. My surprise was very great on finding, after the publication of the paper, that while the hydrogen peroxide in the wash-water, and every other point in the scheme had been determined, this particular estimation had been overlooked. For this reason, in every communication written subsequently, I have never committed myself to any statement as to the total amount of hydrogen peroxide produced, knowing that it was the sum of three quantities:

1st. That referred to under the seventh head, which remains behind in the jar-water.

2d. That carried forward in a state of aerial suspension, and partly detained by the wash-water.

3d. That escaping along with the ozone in the evolved gas.

Mr. Kingzett has called my attention to the oversight in carrying out this important part of the general scheme, and has made some estimations of the amounts of hydrogen peroxide in the ozonising chambers. Unfortunately, from his use of an acidified solution of potassium iodide as a reagent for titrating the evolved gas, and from his having employed a fan to blow the air through the apparatus without indicating the method of measuring the air, I am unable to use his results.

In my own experiment, in which 56 liters of purified air were drawn through the ozonator, the jars containing pure water, the amount of ozone in the evolved gas was 44.47 mgrms; that of hydrogen peroxide in the jar-water, 35.69 mgrms. This would give for the ratio of the ozone to the hydrogen peroxide, in this particular experiment, 1 : 0.8, or by molecules ($O_3 = H_2O_2$), as 1 : 0.8.

In my earlier paper (August, 1879), the amount of ozone in the evolved gas bore to the amount of peroxide of hydrogen, the ratio of 400 : 1. In these experiments, it was supposed that a long series of wash-bottles was sufficient to wash out the aerially suspended hydrogen peroxide, and hence the number, 400 : 1, was taken as expressing the relation between the total quantities in the gas, after its escape from the ozonising chambers. No statement was made, either then or subsequently, as to the total amount of hydrogen produced (owing to my original oversight in failing to determine it in the water of the ozonising chambers), but only to the amount in the evolved gas.

Subsequently, after much more elaborate experiments (*Chem. News*, **42**, 19), this assumption was found to be false, and that after passing not only through the wash-bottles, but a length of sulphuric acid dryers, so great that every trace of moisture was removed, the ratio of the ozone to the hydric peroxide in the *evolved gas*, was far less than 400 : 1. In the last and best agreeing series of trials, it was as 51 : 31, or 1 : 0.67. The ratio of the ozone to the water formed by the decomposition of the hydrogen peroxide with the aid of heat (at 200°) was 51 : 18, or approximately 3 : 1. This ratio was accidentally given instead of the former, in stating the result of the trials (*loc. cit.*)

But it will be asked, what proof is there that the neutral solution employed in titrating the current of ozone and hydrogen peroxide, would indicate the ozone only and not the peroxide as well? The answer is to be found in the fact that hydrogen peroxide held in vesicular suspension will pass through neutral potassium iodide solution without causing any appreciable decomposition in the latter. This was verified in the following experiment.* "Perfectly pure and dry oxygen was ozonised by one of the 'ozonising elements' (electrical ozonisers), and then drawn through three bulbs, the first containing a solution of neutral potassium iodide, the second water, and the third chromic acid. The latter was connected with an aspirator. As soon as the strongly ozonised oxygen came into contact with the potassium iodide, a very slow current being employed, a yellow coloration made its appearance on the surface of the solution in the first bulb, and above the surface the characteristic white cloud. On increasing the rapidity of the current, this white cloud was drawn through the water and chromic acid into the aspirator, and remained for one or more hours before its absorption was complete. After drawing over six liters of oxygen containing 0.194 grm of ozone, the water was titrated, and found to have absorbed 0.31 mgrm of peroxide of hydrogen. The chromic acid solution was unaffected, showing that the suspended hydrogen peroxide may pass

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* JOURNAL AMERICAN CHEMICAL SOCIETY, **2**, 157.

through it without effecting a decomposition. The same remark applies to a neutral potassium iodide solution put in the place of the chromic acid. The excessively dilute hydrogen peroxide held in a state of aerial suspension, was not able to decompose the neutral iodide during the course of the experiment. Of course, an *acidified* solution could not be employed to absorb the peroxide, since, as above shown, its decomposition occurs under the action of oxygen alone."

The conclusion, therefore, to be drawn from the above result is, that in the ozonation of air by moist phosphorus, the number of molecules of hydrogen peroxide approximates very nearly to an equality with the number which is, *pari passu*, formed of molecules of ozone. That it does not fully equal the number, may possibly be connected with the production, as the third essential result of the action of nascent oxygen under the circumstances studied, of a certain amount of ammonium nitrate. And not only does this relation exist between the amounts of ozone and hydrogen peroxide *produced*, but subsists with little alteration, after the two bodies have been passed through many wash-bottles and have been, for a considerable interval, in contact with one another in the *evolved gas*.

Now that I have reviewed my own labors in this direction, I wish briefly to examine Mr. Kingzett's statements concerning them.

After incorrectly stating that I looked for hydrogen peroxide in an acidified potassium bichromate bath, Mr. Kingzett adds: "Moreover, it is not apparent from his various communications that he subjected his gaseous product to any very special examination. He seems to have relied upon its odor and general characters rather than upon any exclusive properties, as evidence of its nature."

In the first place, with regard to the odor, Mr. Kingzett has apparently overlooked the fact that, unlike his present position, which is that the body evolved is all ozone, and contains no hydrogen peroxide, he maintained at that time the opposite—that the gas evolved was altogether hydrogen peroxide, and contained no ozone. And the only connection in which I have brought forward the smell of ozone, as an important physical quality, was to state that attention to it might have prevented Mr. Kingzett from so positively affirming that a gas which possessed the powerful and unique smell of ozone, was not ozone, but another body, viz: hydrogen peroxide, which is entirely odorless.

In the next place, Mr. Kingzett has brought forward only two tests, which differ from those which I have applied. The first consisted in passing the ozonised air through turpentine, and assuming that the failure of the gas, after its passage, to set free iodine in a potassium iodide solution, demonstrated that it originally contained ozone only. But until it has been shown that hydrogen peroxide suspended in the gaseous current, would not undergo absorption by oil of turpentine as well, the proof is valueless.

That this absorption would probably take place may be inferred from the action of organic liquids in general, for when the current of ozonised gas is passed into alcohol, ether or glycerine (JOURNAL AMERICAN CHEMICAL SOCIETY, **1**, 448), the white cloud entirely disappears, and hydrogen peroxide is found in the liquid. In this respect the organic liquids strikingly differ from solutions of potassium iodide, water, acidified chromates, etc., inasmuch as the latter do not arrest the suspended hydrogen peroxide.

Mr. Kingzett's second novel test consisted in heating the ozonised air to 240°, and assuming that the entire destruction of the active agent at this temperature proved that it was ozone. The information to be derived from heating the gas under proper conditions, is perhaps the most conclusive of any that can be obtained, as to its true nature. But, as Mr. Kingzett has applied the test, he has deprived it of the very conditions essential to its value. For at 240°, not only ozone, but also peroxide of hydrogen is destroyed, and there is nothing in the test as he has applied it, to prove that the active agent was ozone only, or peroxide of hydrogen only, or a mixture of both.

Prior to this, I had made use of the same test (JOURNAL AMERICAN CHEMICAL SOCIETY, **2**, 147, and *Chem. News*, **42**, 19), but in a different manner. The ozonised air, after extended washing, was completely dessicated, and then exposed to temperatures running from the ordinary up to 200°. It was shown that as the reaction for ozone diminished with the successive increments of temperature, the quantities of water derived from the decomposition of the suspended hydrogen peroxide, as regularly increased. The numbers obtained by experiment exhibited this diminution of ozone and increment of water, as uniformly as was to be reasonably anticipated in view of the difficult nature of the work. The total amount of water obtained in twelve experiments was 0.0086 grm, corresponding to 0.016 grm hydrogen peroxide ; the total amount of water obtained in blank experiments continued for a much longer time than those reported, and differing from the latter only in the circumstance that the phosphorus cakes were kept submerged beneath the surface of the water in the ozonator jars, was zero. We have seen with what neglect of essential precautions Mr. Kingzett has applied this test. Against my results he has to urge merely his conviction (?) that they were wrong, and that the amounts of water weighed were due to water only, and not to H_2O_2. It is hardly worth while to comment—0.016 grm is a ponderable quantity, the reality of which is capable of experimental proof or disproof, whilst a conviction is not necessarily of any weight except in the mind of its author.

The only experiment which Mr. Kingzett has brought forward in this connection, shows that he has failed to apprehend the real question at issue. He passed a rapid current of air through a solution of hydric peroxide, and inferred that the failure of the air, after its passage, to effect a noteworthy decomposition in an acidified potassium iodide solution, proved (what it did not) that no H_2O_2 could be carried forward when the H_2O_2 was in a *state of aerial suspension.* Mr. Kingzett's experiment is a repetition of a similar one of my own published previously (JOURNAL AMERICAN CHEMICAL SOCIETY, **2**, 154), but illustrates merely the well-known fact that hydrogen peroxide is a difficultly vaporisable body. Mr. Kingzett appears to think that the use of a *rapid* stream of air had some bearing upon the question, and speaks of a spray of peroxide of hydrogen. The phenomena which are under investigation cannot be studied in this manner. The state of vesicular suspension of the hydrogen peroxide is not one which, so far as we are at present aware, can be brought about by mechanical means, but is one which hydrogen peroxide assumes only when it is the immediate result of a previous chemical change. This is its condition when formed in the phosphorus ozonator, and likewise when ozone undergoes decomposition in presence of water, as when it is absorbed by a solution of potassium iodide, and is the origin of the white cloud seen under these circumstances over the surface of the latter. The difference between the two conceptions Mr. Kingzett would have noted, had he been acquainted with what is the most striking reaction which occurs during the ozonation of air by moist phosphorus. This is the permanent white cloud which fills the ozonator, and is carried forward through an extensive series of wash-bottles, and remains sometimes for hours without undergoing absorption, above the surface of the water in an aspirator employed to draw air through the apparatus. This white cloud was the antozone of Schonbein, which he, and after him, Meissner, labored unsuccessfully for so many years to account for. For our knowledge of its true nature we are indebted mainly to Von Babo, and after him to Nasse and Engler, who demonstrated that the so-called antozone is merely hydrogen peroxide, in a state of vesicular suspension. The stumbling-block which rendered of so little value the life-long labors of Meissner upon this question was, that starting out from the well-established fact that hydrogen peroxide is not volatile, he concluded that the clouds could not be due to this substance. As the only alternative, he and Schönbein ascribed them to a peculiar modification of oxygen, other than ozone. There is danger of our giving up ground acquired with great difficulty, and falling back into hopeless contradictions, if we do not keep clearly in mind the distinction between hydrogen peroxide in its ordinary condition, in which it is not volatile, and hydrogen peroxide as suspended at the moment of its formation, in a current of air or aqueous vapor. An atmosphere saturated with aqueous vapor is most favorable to the existence of the hydrogen peroxide in a state of vesicular suspension, but is not essential, since after complete withdrawal of the water vapor, the suspended hydrogen peroxide will still be present.

SUMMARY.

1st. Both ozone and hydrogen peroxide are produced during the ozonation of purified air by moist phosphorus, in the ratio approximately of one molecule of the latter to one of the former.

2d. Both bodies are evolved, the suspended hydrogen peroxide passing through a series of wash-bottles, without undergoing any but a slight absorption, and being present in the evolved gas in nearly the same ratio as that which it held to the ozone, when. originally produced.

3d. Along with these two bodies, and as a necessary part of the same series of reactions, incident originally to the setting free of nascent oxygen, a certain amount of nitrate of ammonia is invariably produced. This last is altogether detained in the water of the ozonator and of the wash-bottles.