V. A final experiment was made by dissolving 10 grms. KI in 30 cc starch-water. 20 cc of this solution were placed in the first comparison-tube, 10 cc concentrated  $H_2SO_4$  in the second, and both treated with carbonic acid. The tubes were exposed to direct sunlight. In a few minutes the first comparison-tube exhibited a brown coloration, and after several hours a carmine-red precipitate was formed. After being allowed to stand over night, the red precipitate was still present, but another also, of a darker hue, lay above. On allowing the carbonic acid to flow through both precipitates for 6 hours, in the sun-light, they disappeared, and the original brown coloration only was visible. During this part of the experiment, the iodide and starch, it will be noted, were not mixed with the acid. Finally, they were driven over, when immediate decomposition ensued, and a large amount of iodide was set free.

CONCLUSIONS :—1st. In the absence of air and presence of carbonic acid, decomposition of an acid solution of potassium iodide occurs, when the concentration has attained to some point between one-third and one-tenth the weight of the water employed. 2d. During the course of these experiments, a compound of starch has been formed which, from its deportment with reagents, and more especially from its turning blue on absorption of oxygen, may probably be regarded as a *hydriodide of starch*. An attempt would have been made to study it further, had it not been for the difficulty of satisfactorily isolating a body which changed so readily on exposure to air, into ordinary starch iodide.

XVII.—UPON AMMONIUM NITRITE, AND UPON THE BY-PRODUCTS Obtained in the ozonisation of Air by Moist Phosphorus.

## By ALBERT R. LEEDS.

As long ago as 1848, Dr. T. Sterry Hunt threw out the suggestion, that the nitrogen of the atmosphere is really composed of two equivalents of the element, sustaining towards each other the same relations as the two equivalents in nitrous oxide. He supposed that the group NNO is not a simple oxide, but an anhydrous amide, or nitryl, derived from the ammonium nitrate by the removal of  $2H_2O$ , and capable, when passed over a mixture of lime and potash at a sufficiently high temperature, of regenerating ammonia and a nitrate.\*

<sup>\*</sup> American Jour. Sci., May, 1848, p. 407.

monium nitrite which undergoes a precisely similar decomposition under the influence of heat, losing  $2H_2O$  and evolving NN, nitrogen gas. It would appear that Prof. G. C. Schaeffer had independently arrived at a similar conclusion concerning the dual nature of nitrogen, holding the same view as Dr. Hunt, that it is the nitryl of ammonium nitrite, and capable of forming this body by assuming again the elements of water.\*

In 1862, Schönbein published an extensive series of experiments upon the generation of ammonium nitrite from water and atmospheric air under the influence of heat. † Unacquainted, apparently, with speculations by which the formation of ammonium nitrite in this manner had been anticipated on theoretical grounds, he announced his own discovery as in the highest degree remarkable and hitherto entirely unexpected. He states that his own labors in this direction, were animated by the consideration that this salt is so readily decomposed under the influence of heat, into water and nitrogen, that it might, under suitable circumstances, be likewise readily regenerated from the same bodies. These circumstances he found to consist in the contact of water, converted into vapor at various temperatures, with atmospheric air, and attributed the combination principally to the heat employed. No other phenomena, according to Schönbein, were concerned in the generation of ammonium nitrite under these circumstances, and those which regulated its formation when various bodies, like hydrogen, hydrocarbons, fats, wood, coal, etc., were burned in air.

It is not necessary to enter into the details of his experiments, further than to remark, that in none of them, apparently, was the precantion taken, to use air which had been purified from its preexistent ammoniacal and nitrons compounds. This manifest source of error was at once pointed out by Bohlig, ‡ who never succeeded, in whatever way or at whatever temperatures, the experiment was conducted, in obtaining the reactions of ammonium nitrite when purified air was employed, but readily obtained them when, under like conditions, common air was used. In opposition to these results of Bohlig, Prof. Liebig maintained in the same journal, the trustworthiness of Schönbein's observations, contending that the fact was sufficiently proven by the very numerous and varied experiments of Schönbein, and disregarding the valid objection, that in none of

<sup>\*</sup> Chemical and Geological Essays, T. S. Hunt, 2d Ed., p. 472.

<sup>†</sup> Ann. der Chem. u. Pharm., 1862, Vol. exxiv, p. 1.

<sup>‡</sup> Ann. d. Chem. u. Pharm., 1863, Vol. cxxv, p. 21.

these same experiments had purified air been employed. Even to the present day, the generation of ammonium nitrite from atmospheric air and water by the aid of heat, is taught in text-books as an admitted fact, and that, too, after Zabelin, in 1864, \* and Carius, † ten years later, had repeated, with exceeding care, and verified Bohlig's observations. In particular, Carius employed most elaborate precautions, using only air and water which had been most carefully purified. The water was evaporated both with a rapid and a slow change of atmosphere; at various temperatures, from the common to 100°; both alone and after addition of baryta, the baryta being devoid of nitrogen compounds; in contact with platinum spirals, and diffused over a great surface of purified cotton wool—in no case was ammonium nitrite formed  $\ddagger$ 

‡ NOTE.-Since the above was written, a paper has been published by A. v. Loesicke (Arch. Pharm. [3], 14, 54-58, and Chemiker Zeitung, No. 9, 1879). Inasmuch as I have no access to either of these journals, I can only quote from the abstracts (Jour. Chem. Soc., April, 1879, p. 298, Chem. News, Vol. xxxix, p. 150). It is stated in the Journal abstract, that "the author has corroborated Schoenbein's statement, that the evaporation of water in air produces ammonium nitrite, and gives the results of experiments to determine the conditions of its formation. It is found that ammonium nitrite is always formed when water evaporates freely, and the lower the temperature, the larger is the quantity produced ; but the formation is prevented if the evaporation takes place in a narnow-necked flask. In another series of experiments, it was observed that one liter of water, evaporated to a small bulk, yielded ammonia equivalent to 0.148 part in 100,000 parts of water; 1 liter, evaporated to small bulk at 40°-50°, yielded ammonia equivalent to 0.5823 part of nitric acid per 100,000 of water : and lastly, 5 liters of water, allowed to evaporate spontaneously, yielded ammonia equivalent to 2.9608 nitric acid per 100,000 parts of water. This last experiment shows the influence that the evaporation of rain-water and dew can have on the nourishment of plants ; and it has been found that if a leaf be moistened and allowed to dry, nitrous acid is produced, and that in dew from leaves, ammonium nitrite can be easily detected."

With reference to these observations, it is to be remarked :--1st. In the absence of any reference to the essential precautions of excluding the access of nitrogenized atmospheric particles, atmospheric ammonia and nitrous compounds, it is fair to infer that these precautions were not taken, and in that case, the experiments of Bohlig, Zabelin and Carius, which contradict the hypothesis of Schoenbein, must be regarded as unshaken and conclusive. 2d. The rise of temperature, especially under such circumstances as would establish a current of vapor from the surface of the liquid, would diminish the rate of absorption of nitrogenous bodies from the surrounding atmosphere. Cooling the evaporating liquids would operate in a two-fold manner; in the first place, by augmenting the coefficient of solubility of the atmospheric ammoniacal com-

<sup>\*</sup> Ann. d. Chem. u. Pharm., cxxx, p. 82.

<sup>+</sup> Ann. d. Chem. u. Pharm., clxxiv, p. 1.

It is of the highest importance therefore :

I. To exclude the possibility of the conversion of water under the influence of heat in contact with atmospheric air, from among the number of possible sources of ammonium nitrite and nitrous compounds.

II. In cases of rapid oxidation, like the combustion of H, \* hydrocarbons,  $\dagger$  fats, phosphorus  $\ddagger$  and other bodies in the air, if it be true that ammonium nitrite is formed, irrespective of any nitrogen compounds pre-existent in the atmosphere, the origin of this ammonium nitrite is to be looked for in other causes than the conjunction of atmospheric air and water-vapor under the influence of heat. §

III. The same remark applies if any ammonium nitrite is formed by the slow oxidation of phosphorus in contact with air and water. The very numerous and laborious experiments by which Schönbein appears to have established the fact of the formation of ammonium nitrite under these circumstances, have caused its universal acceptance. Bohlig following Schönbein, attributed the production of

pounds; and, secondly, by greatly increasing the length of time required for the spontaneous evaporation of so large a bulk as 5 liters of water.

To get rid of all traces of ammonia upon the surfaces of vessels, is a problem of almost insuperable difficulty so long as laboratory operations must be performed in common air. In this connection we would call to mind the experiments of Faraday, \* who was greatly perplexed by obtaining ammonia, on heating hydrogen gas in contact with potassium and zinc. The vessels and substances had been purified, and every precaution exercised, which the almost matchless skill of that incomparable experimental philosopher could devise, and yet Faraday abandoned the research, confessing his inability to satisfactorily account for the appearance of ammonia under these circumstances. Additions to our knowledge since that time, may render it not presumptuous to suggest the cause above given.

\* Saussure (Annales de Chemie, 1xxi, 282).

† Boettger (Jahresb. d. Phys. Vereins, zu Frankfurt a.M., 1860, 1861, p. 69)

‡ Schoenbein (Ann. der Chem. u. Pharm., Vol. exxiv, p. 6).

§ In the case of hydrogen, Zoeller and Grete have shown, by the burning of very large volumes of perfectly pure hydrogen in completely purified air, that small amounts of ammonium nitrite are produced, and have demonstrated the presence of ammonia and nitrous acids in the water formed in the course of the combustion, by many concordant and quite satisfactory tests.—(Ber. der deutsch. chem. Gesell., 1877, Vol. x, p. 2,144.)

|| See Carius, Ann. der Chem. u. Pharm., 1874, Vol. clxxiv, p. 43.

<sup>\*</sup> Quart. Jour. Sci., x)x, 16.

ammonium nitrite during the slow oxidation of moist phosphorus, to the action of the ozone formed at the same time. Carius by elaborate proofs, has demonstrated that ozone, which was prepared by electrolysis in such a manner as to be entirely free from nitrogen compounds, and even from hydrogen gas, was entirely devoid of action upon nitrogen in the presence of vapor of water. In order to make the experiments comparable to those in which ozone is liberated at the same time with a disengagement of heat, as in the case of the electrical discharge, the ozone was brought by Carius into contact with nitrogen and water vapor at all temperatures short of those at which ozone undergoes dissociation into ordinary oxygen-in every case with negative results. The ozone prepared by electrolysis was preferred to that obtained by the electrical discharge, since, as both Soret \* and Carins have shown, ordinary oxygen prepared from potassium chlorate, and containing from 1 to 2 p. c. of nitroger, vields, when ozonised by the electrical discharge, small, but determinable amounts of nitrous acid. Still later, Berthelot + has investigated the accuracy of the statement made by Schönbein, I that ozone combines with free nitrogen, in presence of alkalies, at ordinary temperatures, to form nitrous compounds.

Schönbein found in 3,000 liters of air, powerfully ozonised by phosphorus, then washed with water, the washings treated with lime water, and the resulting calcium compound decomposed by potassium carbonate, an amount of nitric acid corresponding to 5 grms. of nitre. Berthelot collected in a number of flasks over water, oxygen ozonised by the silent discharge, until the flasks were three-fourths filled. The surplus water was then allowed to run out completely, its place being supplied by atmospheric air, and some pure baryta water introduced in each flask. After standing over night, all traces of ozone had completely disappeared. But the baryta water contained no traces of nitrogen compounds; the wash-water did. Similar results were obtained with the air ozonised by phosphorus, and completely washed before contact with baryta water.

Quite independently of the work done by other observers, an extended series of experiments had been instituted upon the phenomena which accompanied the ozonisation of moist air by means of phosphorus. In the earlier trials, attention was limited to the question whether oxidised compounds of nitrogen were produced or no. Sub-

<sup>\*</sup> Compt. Rend., lvi, 390.

<sup>+</sup> Compt. Rend., 1877, Vol. lxxxiv, p. 61.

<sup>‡</sup> Denkschrift ueber das Ozon, p. 16, Basel, October, 1849.

sequently the research was made to include all other by-products. It was deemed important to purify and measure the air used and the ozone formed; to determine the amount of phosphorus consumed, and of phosphoric and phosphorons acid produced; and, in case they were really present and it were possible to estimate them, the amounts of nitrogen compounds, of hydrogen peroxide and ozone, remaining in solution in the jar- and wash-waters. Lest it be thought needless to have re-investigated these points, the following reasons for so doing may be mentioned:

I. Preliminary trials had shown that, if formed at all, there were grounds for supposing that these products were comparable in minuteness to the nitrogen compounds pre-existent in the atmosphere.

II. Since the time of Schönbein, the experiments of Goppelsröder and Carins had shown that the ozonisation of ammonia would produce ammonium nitrite and nitrate and hydrogen peroxide.

III. We could not discover that in experiments previously made upon the ozonisation of air by phosphorus, the air had been previously purified.

IV. It was important to determine whether any ammonia or nitrons acid existed at the close of the operation, or whether they were completely oxidised to nitric acid. The explanations of the reactions would depend largely upon the determination of these factors.

The phosphorus-ozonator, described in Vol. I, p. 8, of this JOUR-NAL, was employed throughout the whole course of this investigation. In the first series of experiments, ordinary air drawn from outside the laboratory, was used. 'The jars in some cases contained common distilled water, in other cases, the bichromate mixture made as described in article alluded to. The ozonised air was aspirated through the kerite-tubing, from the last bell, into a wash-bottle containing aqua puriss. (re-distilled and free from every trace of ammonia), and then into one or more Peligot-tubes containing neutral solution of potassium iodide. Only on titration was the solution of potassium iodide made acid. The reason for this precaution is given (JOUR. AMER. CHEM. Soc., Vol. I, p. 78), where it is shown that a stream of air or oxygen passing through an acidified solution of potassium iodide, greatly increases the amount of iodide set free. The nitric acid in the wash-bottle was determined by reduction with pig-iron, the precautions being employed which are stated (PROCEED-INGS AMER. CHEM. Soc., Vol. II, No. 4, 1878).

	Air	Used.		Total Ozone in mgrm.	Total Ozone in cc.	V. p. c. of Air.	Total HNO3.	HNO3 p. c.
<b>27</b>	liters	(over	H <sub>2</sub> O)	_	—		0.111	0.000318
108	"	"	"		—	—	0.444	0.000318
45	"	(over	CrO <sub>3</sub> )	13.61	6.37	0.014	0.314	0.00054
85	"	(over	H <sub>2</sub> O)	77.07	36.09	0.039	0.333	0.000303
90	"	(over	CrO <sub>3</sub> )	71.91	33.67	0.037	0.610	0.00054

TABLE I .- NITRIC ACID FORMED WITH NON-PURIFIED AIR.

In the following trials, the air was purified by aspiration through a tube one-half meter in length, packed with cotton-wool, then through three Peligot-tubes, the first containing aq. puriss., the second soda solution, the third sulphuric acid. The soda employed in this and other trials was some made from sodium, and which had been repeatedly proven to be free from nitrogenous bodies. The sulphuric acid yielded to metadiamidobenzol no trace of nitrous acid, nor any ammonia on neutralization and reduction. Ordinary distilled water was employed in the jars.

TABLE II.-NITRIC ACID FORMED WITH PURIFIED AIR (AQ. PUR.).

Air Used.	Total	Total	V. p. c.	Total	HNO3
	Ozone.	Ozone.	of Air.	HNO <sub>3.</sub>	p. c.
262 liters (over H <sub>2</sub> O)	мдям. 261.8	104.16 cc.	0.04	мд <b>рм</b> . 1.11	0.000328

In an experiment similarly arranged, except that hydrant water was used in the jars, 0.3964 grm. of ozone was produced. The wash-water contained 0.37 mgrm. of nitric acid, and 1.3 mgrm. of hydrogen peroxide. The latter would correspond to 0.00039 per cent. of the total weight of the air used.

In the foregoing experiments, the percentage of nitric acid as compared with the weight of the air passed over, appears quite constant. This is true whether water or bichromate mixture was employed, although with the latter the percentage was somewhat higher. The ozone had been manufactured for a variety of purposes, and these percentages were not calculated until after all the determinations were concluded, when an unexpected closeness of agreement between the results was developed. Although this agreement pointed to a constantly operating cause, yet, by reason of the extreme minuteness of the amounts of nitric acid, it was deemed safer provisionally to assume that the agreement was really due to a constant source of error. A scheme was therefore drawn up, which should include the sources of error and the substances to be determined to the best of our knowledge. As others may detect features in which our methods were at fault, or essential precautions were overlooked, this scheme is given below :

I. Use of a measured amount of aq. puriss., in the jars.

II. Complete straining and washing of the air by means of cotton-wool, aq. puriss., NaOH and  $H_2SO_4$ , both shown to be free from nitrogen.

III. Weight of phosphorus cakes before and after the experiment.

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

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

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

VII. Amounts of phosphoric and phosphorus acids and of hydrogen peroxide in the jar-water.

VIII. Estimation of  $H_3N$ , (HNO<sub>3</sub> and HNO<sub>2</sub>), HNO<sub>2</sub>,  $H_3PO_4$ ,  $H_3PO_5$  and  $H_2O_2$ , in the wash-water after ozonising ("ozone-wash-water").

IX. Similar estimations, except of the phosphorus compounds, in the solutions employed to wash the air (" air wash-water ").

X. Measurement of total volumes of air used, and of ozone after its escape from the ozone wash-water.

In order to compensate for the increase of suction necessitated by so many wash-bottles, the standards and discs carrying the phosphorus were raised nearly to top of the bells.

This required the employment of 11 liters of aq. puriss. in the jars. After 420 liters of air had been aspirated, the jar-water was poured into three tall cylinders, the precipitate, mostly lead phosphate, allowed to settle, and the water and precipitate analyzed separately. The weight of the phosphorus cakes at beginning of the experiment was 111.646 grms., at the close 54.284 grms. The total amount of ozone which passed out of the ozone wash-bottle, was 0.8046 grm., or an average of 1.92 mgrm. ozone per liter of air, the temperature varying during the course of the six days consumed in the experiment, between 18° and 21°. This would correspond to 71.29 grms. of phosphorus consumed, for each gramme of ozone produced. Probably the consumption would be in a somewhat different ratio at the temperature of maximum evolution (24°), and with bichromate mixture in the jars.

#### PHOSPHORIC AND PHOSPHOBOUS ACIDS.

The amount of phosphoric acid  $(H_sPO_4)$  existing in solution in the jar-water, was 178.02 grms.; in combination with the lead as triplumbic phosphate, 0.939 grms.; and the comparatively small amount carried over into the ozone wash-water was 0.252 grm., making a total of 179.24 grms.

The large amount of phosphoric acid is itself a valuable product, and capable either of being used directly or of being easily reconverted into phosphorus. Hence, its formation cannot be considered as a drawback upon this method of ozonising. The phosphorous acid in the jar-water was 2.57 grms., in the ozone wash-water, 0.013 grm.

## AMMONIA, NITROUS AND NITRIC ACIDS.

(a.) In air wash-water. — The entire ammonia derived from washing 420 liters of air, was .03 mgrm., corresponding to 6 parts in 100 million. No nitrous acid could be detected by means of metadiamidobenzol; nitric acid not determined.

(b.) In jar-water.—50 cc of the jar-water rendered alkaline with pure soda, and distilled in a purified retort, yielded 0.08 mgrm.  $H_3N$ , corresponding to 17.60 mgrms. ammonia in the 11 liters. A like portion, similarly treated, gave, on reduction with pig-iron, 0.14 mgrm.  $H_3N$ , or in the total jar-water, 0.0308 grm. Both  $NH_4NO_2$ and  $NH_4NO_3$  should yield on reduction twice the amount of ammonia which they give when the ammonia is determined directly. In the above determination, the amount which was found falls short of the theoretical by a difference quite within the errors of experiment.

Since phosphorous acid was contained in the jar-water, it became important to determine whether this body, when distilled in neutral or slightly alkaline solution, with pig-iron, would yield a distillate capable of effecting the Nessler reagent. Some phosphorous acid was therefore prepared from phosphorus trichloride, and the experiment tried, but the results obtained negatived the above hypothesis.

No nitrous acid was detected. The nitric acid, as deduced from the ammonia found directly and after reduction, amounted to 0.0489 grm., or 0.0089 per cent. of the total weight of the air used.

(c.) In ozone wash-water.—The ammonia obtained by direct distillation amounted to 0.075 mgrm.; by reduction, to 0.315 mgrm.; this would leave for the ammonia, corresponding to the nitric acid, 0.24 mgrm. (equivalent to 0.88 mgrm. HNO<sub>s</sub>), a result three times greater than the ammonia corresponding to the base, instead of twice, as should have been.

No nitrous acid was found by the use of metadiamidobenzol.

## HYDROGEN PEROXIDE.

The ozone wash-water contained 2.01 mgrm. hydrogen peroxide, or 0.00037 per cent. of the total weight of the air passed over. The nitric acid contained in the ozone wash-water, was only 0.000162, or about one-half the percentage of the hydrogen peroxide.\*

Final experiment.—The failure to find in the jar-water an amount of ammonia, on reduction, which would exactly correspond to the nitric acid required to form with the basic annuonia, ammonium nitrate, cast some suspicion on the above results. A final experiment was therefore instituted, in order to settle positively whether any ammonium nitrite could be detected at the close of the operation, and whether all the nitric acid found, existed in combination as ammonium nitrate.

Renewed precautions were therefore instituted to purify the air employed-two columns of glass beads saturated with H<sub>2</sub>SO<sub>4</sub>, being employed in addition to the wash-bottles mentioned in the former trials. The air was forced by a tromp through this long series of purifiers into the ozonator, and drawn out again through the washbottles used to wash and titrate the products, by means of a water air-pump. By this means, the phosphorus cakes were always kept immersed to the same depth in the jar-water. Sliding standards had been discarded in the improved form of ozonator now employed, and the cakes were supported on leaden discs which rested upon little leaden brackets, passing through holes drilled through the sides of the bells, at a small distance above their lower rims. 4,850 cc aq. puriss. were used in the jars; the amount of air passed through the apparatus was 481 liters; the ozone discharged from the ozone wash-water, 0.924 grm. The following table presents a synopsis of the results obtained :

<sup>\*</sup> NOTE.—In Table I, the ammonia found in the ozone wash-waters by reduction is all calculated as  $HNO_3$ . If we, in like manner, convert the total ammonia contained in the air (see Table III) into  $HNO_3$ , it will be found equal to 0.000088 per cent. of the air drawn over; subtracting this from 0.0003 per cent., the amount given for P over  $H_3O$  in Table I, leaves 0.000212 per cent., and this, if regarded not as it was when the experiments were made, as  $HNO_3$ , but as  $NH_4NO_3$ , would give for the true percentage of  $HNO_3$  in Table I, 0.000167 p. c.

#### TABLE III.

### Air wash-water.

Amm	onia.	HNO <sub>2</sub>	HNO <sub>3</sub>	NH 4 NO2	NH 4 NO3				
Before Reduction.	After.								
MGRM.	MGRM.	MGRM.	MGRM.	MGRM.	MGRM.				
0.10	0.15	0.065	0.104	0.092	0.132				
Corresponding in 100 million parts.									
PARTS.		PARTS.	PARTS.	PARTS.	PARTS.				
16	None.	10	17	15	20				
Jar-water.									
MGRM.	MGRM.		MGRM.		MGRM.				
<b>(</b> 1.) 7.76									
(2.) 4.82	11.64	None.	21.57	None.	27.39				
Ozone wash-water.									
0.066	0.198	None.	0.49	None.	0.31				

It will be noted that the ammonia washed out of the atmospheric air, is somewhat in excess of that required to neutralize the nitric and nitrous acids, and it may be queried whether this excess existed in some other form of combination, as the carbonate.

The determination marked (1) of ammonia in the jar-water, was made upon 50 cc. Subsequently the same apparatus was employed as that ordinarily used in water analysis, and after the large amount of soda required to render 500 cc of the jar-water alkaline, was repeatedly distilled with aq. puriss. until it gave no further reaction of ammonia, the 500 cc was added, and the distillations continued. This determination corresponded to 5.82 mgrm. H<sub>3</sub>N in the total jarwater, and is just one-half the amount obtained after reduction. Since the absence of nitrous acid was proven, this result goes far to demonstrate that the ammonia derived from the jar-water, existed there as ammonium nitrate.

But in the ozone wash-water, instead of being one-half, it is only one-third of the amount found on reduction, a result corresponding with that found in the former trial.

Hydrogen Peroxide.—As determined directly upon one portion of the ozone wash-water, this amounted to 2.7 mgrm.; determined after evaporating 30 cc down to 3 cc, it amounted to 2.4 mgrm. The estimation was made by means of sodium hyposulphite and potassium iodide. These reagents could be safely made use of, since the absence of nitrous acid had been previously proven. It was likewise found that the presence of phosphorus acid had no effect upon the titration. If the larger result obtained on titrating directly, be attributed to dissolved ozone, then the amount of ozone in solution would have been 0.44 mgrm. Since, however, the percentage of hydrogen peroxide is diminished by concentration with the aid of heat, the lower result obtained after evaporation, might, perhaps, be more satisfactorily attributed to the loss of hydrogen peroxide than to expulsion of dissolved ozone.

The percentage of hydrogen peroxide, as compared with the total weight of the air drawn over, is 0.00038; that of nitric acid in the ozone wash-water only 0.00008. The former agrees quite closely with the result obtained in the previous experiment; the latter is about one-half.

CONCLUSION.—It will be noted that the chief by-product of the ozonisation of moist air by phosphorus, according to our determinations, is not phosphorons acid, but phosphoric acid. It is generally stated that the former of these two substances, is the one principally produced under these circumstances. This may be true in the sense that the phosphorous acid is first formed, and that it gradually is transformed into phosphoric acid under the influence of nascent ozone. This point could not be very readily determined, in the course of the experiments made with the apparatus described above.

It is certainly an error to ascribe, as is done in various text-books, the dense, white fumes seen in the ozonising chambers, to ammonium nitrite—they are chiefly due to phosphoric anhydride.

The above experiments do not permit us to say that no ammonium nitrite was found during any period of the ozonation, they prove merely that no ammonium nitrite could be detected at its close. If, therefore, this body were produced, it must have become oxidized to ammonium nitrate.

As to the reason of the formation of ozone itself under these circumstances, it may be conjectured along with Lamont \* and others, that it is connected with the uneven quantivalencies of the elements taking part in the reaction, which may be represented by the equation  $P_4 + O_{14} = P_2O_3 + P_2O_5 + 2O_3$ . If this hypothesis be true, then we should anticipate the development of ozone whenever oxidation of a perissad occurred at temperatures compatible with the stability of the ozone molecule. Even at the temperature of combustion of hydrogen, this is supposed by C. Than  $\dagger$  to be the case. He explains

<sup>\*</sup> Chem. News, xxviii, p. 236.

<sup>†</sup> Jour. Chem. Soc. [2], Vol. ix, 1871, p. 483; J. pr. Chem. [2], i, 415.

in this manner the presence of the ozone, which he states he has detected in the combustion of hydrogenous substances generally, and its absence in the combustion of carbon.

In entering into new combinations, the oxygen molecules must undergo temporary resolution into their constituent atoms. These, while en route to take up new positsons in other combinations, and animated by their atomic energy, or energy of the nascent state, may either oxidize the oxygen molecule, or the nitrogen, or the molecule of water. In the first case, ozone would be produced; in the second, regarding water as the basic body and NNO as the nitryl, there might be formed, as Hunt has indicated, ammonium nitrate; in the third, hydrogen peroxide.

It gives me much pleasure to acknowledge the co-operation of my assistant, Dr. Edgar Everhart, in the performance of these experiments.

# Abstracts from American and Foreign Journals.

# Berichte der deutschen chemischen Gesellschaft.

Abstractor, P. TOWNSEND AUSTEN, PH. D., F. C. S.

On Betuline, N. FRANCHIMONT (Ber. d. d. chem. Ges., vol. xii, p. 7).-By extraction of birch bark with boiling alcohol, distilling off the alcohol, taking up the residue in water, treating with sodium hydrate, and crystallizing the product from benzol or petroleum ether, betuline was obtained in the form of colorless needles, fusing at 251°. The acetate (fusing at 216°) was made according to Hausmann's method. By saponification with alcoholic potash, betuline was regenerated. F., hence, considers that Hausmann's formulæ,  $C_{38}H_{80}O_{3}$  for betuline, and  $C_{38}H_{38}O(C_{2}H_{3}O_{2})_{2}$  for betuline-acetate, are correct. To produce a hydro-carbon from betuline, by extraction of the elements of water, phosphorous pentasulphide proved to be the best reducing agent. The mixture, on being heated, fused and evolved H<sub>2</sub>S and PH<sub>3</sub>. The operation was hence conducted in a current of carbonic acid. After twelve hours the liquid was distilled off up to 300°. A thick, brown mass was obtained, which, by fractional distillation, drying over calcium chloride, etc., gave a colorless, liquid hydro-carbon. If pure, it would appear to be C13H20. Oxidizing agents, fuming sulphuric acid and nitric acid, acted on this hydrocarbon, but no defined products could be obtained. Hydrochloric acid gas gave no reaction.