

ART. XIX.—On Nitrification;* by S. W. JOHNSON.

Formation of nitrogen compounds in combustion.—Sausure first observed (Ann. de Chimie, lxxi, 282), that in the burning of a mixture of oxygen and hydrogen gases in the air, the resulting water contains ammonia. He had previously noticed that nitric acid and nitrous acid are formed in the same process.

Kolbe (Ann. Chem. u. Pharm., cxix, 176) found that when a jet of burning hydrogen was passed into the neck of an open bottle containing oxygen, reddish-yellow vapors of nitrous acid or nitric peroxyd, were copiously produced on atmospheric air becoming mingled with the burning gases.

Bence Jones (Phil. Trans., 1851, ii, 399), discovered nitric (nitrous ?) acid in the water resulting from the burning of alcohol, hydrogen, coal, wax, and purified coal-gas.

By the use of the iodid of potassium starch-test (Price's test), Boettger (Jour. für Prakt. Chem., lxxxv, 396,) and Schönbein (ibid., lxxxiv, 215,) have more recently confirmed the result of Jones, but because they could detect neither free acid nor free alkali by the ordinary test-papers, they concluded that nitrous acid and ammonia are simultaneously formed—that, in fact, *nitrite of ammonia* is generated in all cases of rapid combustion.†

* The substance of this paper was orally presented to the National Academy of Sciences, in August, 1868.

† Nitrous acid does not appear when the combustible contains sulphur, since it is decomposed at high temperatures by sulphurous acid.

Meissner (Untersuchungen über den Sauerstoff, 1863, p. 283,) was unable to satisfy himself that either nitrous acid or ammonia is generated in combustion.

Finally, Zabelin (Ann. Chem. u. Ph., cxxx, 54), in a series of careful experiments, found that when alcohol, illuminating gas and hydrogen burn in the air, nitrous acid and ammonia are very frequently, but not always formed. When the combustion is so perfect that the resulting water is colorless and pure, only nitrous acid is formed; when, on the other hand, a trace of organic matters escapes oxydation, less or no nitrous acid, but in its place ammonia appears in the water, and this under circumstances that preclude its absorption from the atmosphere.

Zabelin gives no proof that the combustibles he employed were absolutely free from compounds of nitrogen, but otherwise, his experiments are not open to criticism.

Meissner's observations were indeed made under somewhat different conditions; but his negative results were not improbably arrived at simply because he employed a much less delicate test for nitrous acid than was used by Schönbein, Boettger, Jones and Zabelin.*

We must conclude then, that nitrous acid and ammonia are usually formed from atmospheric nitrogen during rapid combustion of hydrogen and compounds of hydrogen and carbon. The quantity of these bodies thus generated is, however, in general so extremely small as to require the most sensitive reagents for their detection.

Formation of nitrogen compounds at low temperatures.—Schönbein was the first to observe that nitric acid may be formed at moderately elevated or even ordinary temperatures. As is well known he obtained several grams of nitrate of potash by adding carbonate of potash to the liquid resulting from the slow oxydation of phosphorus in the preparation of ozone.

More recently he believed to have discovered that nitrogen compounds are formed by the simple evaporation of water. He heated a vessel (which was indifferently of glass, porcelain, silver, &c.), so that water would evaporate rapidly from its surface. The purest water was then dropped into the warm dish in small quantities at a time, each portion being allowed

* Meissner rejected Price's test in the belief that it cannot serve to distinguish nitrous acid from hydric peroxyd. He therefore made the liquid to be examined alkaline with a slight excess of potash, concentrated to small bulk and tested with dilute sulphuric acid and ferrous sulphate, (Unters. ü. d. Sauerstoff. p. 233). Schönbein had found that iodid of potassium is decomposed after a little time by concentrated solutions of hydric peroxyd, but is unaffected by this body when dilute, (Jour. für prakt. Chem. lxxxvi, p. 90.) Zabelin agrees with Schönbein that Price's test is decisive between hydric peroxyd and nitrous acid. (Ann. Chem. u. Ph., cxxx, p. 58.)

to evaporate away before the next was added. Over the vapor thus generated was held the mouth of a cold bottle until a portion of the vapor was condensed in the latter.

The water thus collected gave the reactions for nitrous acid and ammonia, sometimes quite intensely, again faintly, and sometimes not at all.

By simply exposing a piece of filter paper for a sufficient time to the vapors arising from pure water heated to boiling and pouring a few drops of acidified iodid of potassium-starch-paste upon it, the reaction of nitrous acid was obtained. When paper which had been impregnated with dilute solution of pure potash was hung in the vapors that arose from water heated in an open dish to 100° F. it shortly acquired so much nitrite of potash as to react with the above named test.

Lastly, nitrous acid and ammonia appeared when a sheet of filter paper, or a piece of linen cloth, which had been moistened with the purest water, was allowed to dry at ordinary temperatures, in the open air or in a closed vessel. (*Jour. für Prakt. Chem.*, lxvi, 131). These experiments of Schönbein are open to criticism and do not furnish perfectly satisfactory evidence that nitrous acid and ammonia are generated under the circumstances mentioned. Bohlrig has objected that these bodies might be gathered from the atmosphere where they certainly exist, though in extremely minute quantity.

Zabelin, in the paper before referred to (*Ann. Ch. Ph.*, cxxx, p. 76), communicates some experimental results which, in the writer's opinion, serve to clear up the matter satisfactorily.

Zabelin ascertained in the first place that the atmospheric air contained too little ammonia to influence Nessler's test, which is of extreme delicacy and which he constantly employed in his investigations.

Zabelin operated in closed vessels. The apparatus he used consisted of two glass flasks, a larger and a smaller one, which were closed by corks and fitted with glass tubes, so that a stream of air entering the larger vessel should bubble through water covering its bottom and thence passing into the smaller flask should stream through Nessler's test. Nextly, he found that no ammonia and (by Price's test) but doubtful traces of nitrous acid could be detected in the purest water when distilled alone in this apparatus.

Zabelin likewise showed that cellulose (clippings of filter paper or shreds of linen) yielded no ammonia to Nessler's test when heated in a current of air at temperatures of 120° to 160° F.

Lastly, he found that when cellulose and pure water together

were exposed to a current of air at the temperatures just named, ammonia was at once indicated by Nessler's test. Nitrous acid, however, could be detected, if at all, in the minutest traces only.

The reader should observe that Boettger and Schönbein, finding in the first instance by the exceedingly sensitive test with KI and starch-paste, that nitrous acid was formed, when hydrogen burned in the air, while the water thus generated was neutral in its reaction with the *vastly less sensitive* litmus test-paper, concluded that the nitrous acid was united with some base in the form of a neutral salt. Afterward, the detection of ammonia appeared to demonstrate the formation of nitrite of ammonia. Schönbein's explanation of the mode in which this salt may be generated, viz., by the direct union of water and nitrogen, seems to have perfectly satisfied the chemical critics.*

This theory has, however, nothing to warrant it, even in the way of probability. If traces of nitrite of ammonia can be produced by the immediate combination of these exceptionally abundant and universally diffused bodies at common temperatures, or at the boiling point of water, or lastly in close proximity to the flames of burning gases, then it is simply inconceivable that a good share of the atmosphere should not speedily dissolve in the ocean, for the conditions of Schönbein's experiments prevail at all times and at all places so far as these substances are concerned.

The discovery of Zabelin that ammonia and nitrous acid do not always appear in equivalent quantities or even simultaneously, in no wise conflicts with any of Schönbein's facts. A quantity of free nitrous acid that admits of recognition by help of Price's test would not necessarily have any effect on litmus or other test for free acids. There remains then no necessity of assuming the generation of nitrite of ammonia, and the fact of the separate appearance of the elements of this salt demands another explanation.

The writer is not able perhaps to offer a fully satisfactory explanation of the facts above adduced. He submits, however, some speculations which appear to him entirely warranted by the present aspects of the case, in the hope that some one with the time at command for experimental study, will establish or disprove them by suitable investigations.

He believes that in no case can free nitrogen unite directly

* Zabelin was inclined to believe that his failure to detect nitrous acid in some of his experiments where organic matters intervened, was due to a power possessed by these organic matters to mask or impair the delicacy of Price's test, as first noticed by Pettenkofer and since demonstrated by Schönbein in case of urine.

with water, but in the conditions of all the foregoing experiments, it enters combination by the action of *ozone*, as Schönbein formerly maintained and was the first to suggest. Ozone is formed not only in all rapid combustions but also in the slow oxydation of organic matters (paper and linen.)

Pincus has lately published some observations which any chemist may readily verify, that demonstrate the formation of ozone in combustion at high temperatures. It is only necessary to hold a cold, clean and dry beaker glass for a few seconds over a jet of pure hydrogen burning from a metal tube with a flame $\frac{1}{8}$ of an inch high, and then to smell of its contents. The ozone odor is most plainly perceived. The same result may be obtained from a small flame of alcohol or of a stearine candle.—(Die Landwirthschaftlichen Versuchs-stationen, ix, 473.)

The formation of ozone in all cases of slow oxydation at common temperatures is in analogy with its appearance during the eremacausis of phosphorus, and if antozone really exists and is the genetic complement of ozone as is indicated so strongly by the researches of Schönbein and Meissner, we must consider the case pretty well made out in theory, for hydric peroxyd which is held to be the result of the union of antozone with water, is formed in so many instances of slow oxydation of metals and organic bodies that Schönbein felt justified in assuming its production, or that of a corresponding organic antozonid in them all.—(Jour. für. prakt. Chem., xcvi and xcix.)

In Schönbein's experiments before mentioned, where paper or linen were not employed, the dust of the atmosphere probably supplied the organic matters.

The first result of the oxydation of nitrogen is nitrous acid alone (at least Schönbein and Bohlign detected no nitric acid), when the combustion is complete as in case of hydrogen, or when organic matters are excluded from the experiment. Nitric acid is a product of the subsequent oxydation of nitrous acid. When organic matters exist in the product of combustion, as when alcohol burns in a heated apparatus yielding water having a yellowish color, it is probable that nitrous acid is formed, but is afterward *reduced* to ammonia.

The reduction of nitrates to nitrites by various organic matters was announced by Schönbein several years ago. He found that all the vegetable and animal albuminoids, gelatine, and most of the carbohydrates, especially starch, glucose and milk-sugar (but not cane sugar) had this effect.—(Jour. für. prakt. Chem., lxxxiv, p. 207.) Zabelin in the article before cited, refers to Schönbein as authority for the fact that these organic

bodies reduce nitrites to *ammonia* and ultimately to nitrogen and although we have not been able to find such a statement in those of Schönbein's papers to which we have had access, it is entirely credible and in accordance with numerous analogies.

Pelouze could find no nitrates (nor nitrites?) in the drainings of dung-heaps. Lawes, Gilbert, and Pugh, detected no trace of nitrites in moist mixtures of ignited earth, with bean-meal, starch and saw-dust, over which ozone (&c., by phosphorus,) was passed daily for several months. (Trans. Roy. Soc., 1861, p. 496.) Boussingault states that mixing quick-lime or carbonate of potash with garden soil prevents nitrification and causes the development of ammonia. (Agronomie, etc., iii, p. 200.) In these cases the readily oxydable matters were in excess of active oxygen; the process was therefore a *putrefactive and reducing one*, and although nitrites may have been and doubtless were formed on the surface, where oxygen was in excess, they were deoxydized in the interior of the mass.

Zabelin alludes to this reduction of nitrites by organic bodies not with the purpose of accounting for the formation of ammonia from nitrous acid, but to explain why he failed to detect nitrous acid in some of his experiments. Apparently firm in the conviction that nitrite of ammonia was in all cases formed, he says, "I believe that at the high temperature of our experiments the nitrite of ammonia produced was decomposed into ammonia that was carried off and into nitrous acid which mostly remained in the water of the flask, where it was probably further decomposed, under oxydation of the linen or the paper. Therefore it was found only in traces while ammonia was very easy to identify." He says further, "By our experiments in the burning of illuminating gas and alcohol we have recognized the same action of organic matters on nitrites; nay, nitrous acid gradually decomposed in their presence at ordinary temperatures; the water at the same time acquired the power of decolorizing iodized starch." (Ann. Chem. Pharm., cxxx, 85.) Now ammonia speedily bleaches starch made blue by iodine, and thus Zabelin's observations sustain our hypothesis.

If, as thus appears extremely probable, ozone is developed in all cases of oxydation both rapid and slow, then every flame and fire, every decaying plant and animal, the organic matters that exhale from the skin and lungs of living animals or from the foliage and flowers of plants, especially, perhaps, the volatile oils of cone-bearing trees, are indirectly, means of converting a portion of free nitrogen into nitrous and nitric acids, or ammonia.

In the interesting experiment of Mr. Loew, where pure water evaporating from the surface of paper which has been impregnated with alloxan, gives rise to the formation of ammonia as is indicated by the red color of murexyd supervening, (this *Journal*, xlv, p. 29,) the explanation we have offered, accounts for the facts observed as well as the hypothesis of Schönbein. We assume eremacausis of the moist paper, perhaps of the alloxan itself, to take place, ozone and by it nitrous acid to be formed, the latter being subsequently reduced to ammonia.

Our explanation is further sustained by the facts which we possess concerning the part which the organic matters perform in nitrification as it goes on within the soil.

Organic matters are universally recognized as essential in the composts which are employed in saltpeter plantations. Those earths in which nitrification proceeds spontaneously, are in general, characterized by a considerable content of humus. We have precise observations by Boussingault which demonstrate that organic matters are indispensable to nitrification. This investigator in the prosecution of his researches on vegetable nutrition, found in a large series of experiments, that when plants vegetate in calcined earth, neither the plant nor the earth gathers appreciable quantities of nitrogen from the atmosphere, during a period of several months, but when soil containing humus is employed under similar circumstances, either the soil or the plant (in most cases both) assimilate nitrogen to a decided degree.

For example, a lupin vegetating for ninety-seven days in 130 grams of rich garden soil (mixed with pure sand to favor access of air) the whole being confined in a glass case, assimilated 0.0217 grm. of nitrogen, and the soil far from exhibiting loss, during the same period, fixed 0.0454 grm. of this element. (*Agronomie, etc.*, t. 1, p. 339). Of the nitrogen thus gathered from the atmosphere and fixed in a solid form by the soil, only one-ninth existed in the state of nitric acid and ammonia, when the experiment was concluded. We infer that this nitrogen for the most became a constituent of the soil by nitrification induced by the eremacausis of its humus, with the formation of ozone.

The passage of nine-tenths of this fixed nitrogen into a constituent of humus, where it doubtless exists in what we may call organic combination, probably took place by reduction of nitrogen oxyds to ammonia, and subsequent union of the latter with products of the alteration of cellulose in the same way that amid-like bodies have been obtained by Dusart, Schützenberger and P. Thenard, in heating together ammonia with dextrin, starch and glucose, in partial realization of Prof.

T. S. Hunt's idea of the synthesis of gelatine, from a carbohydrate and ammonia.—(Kekulé's *Lehrbuch*, ii, 356.)

Certain experiments executed by Mulder, more than twenty years ago (*Chemistry of Animal and Vegetable Physiology*, p. 673,) confirm the view we have taken. Two of these were "made with beans which had germinated in an atmosphere void of ammonia, and grown in one case in ulmic acid prepared from sugar, and also free from ammonia; and, in the other case, in charcoal, both being moistened with distilled water, free from ammonia. The ulmic acid and the charcoal were severally mixed up with one per cent. of wood ashes, to supply the plants with ash-ingredients. I determined the proportion of nitrogen in three beans and also in the plants that were produced by three other beans. The results are as follows :—

White beans in ulmic acid.			Brown beans in charcoal.		
	Weight.	Nitrogen.		Weight.	Nitrogen.
Beans,	1·465 grm.	50 cub. cent.		1·277	27 cub. cent.
Plants,	4·167 "	160 " "		1·772	54 " "

The white beans, therefore, whilst growing into plants in substances and an atmosphere, both of which were free of ammonia, had obtained more than thrice the quantity of nitrogen that originally existed in the beans; in the brown beans the original quantity was doubled." Mulder believed this experiment to furnish evidence that ammonia is produced by the union of atmospheric nitrogen with hydrogen set free in the decay of organic matters. But the researches of Will have fairly established the impossibility of nascent hydrogen uniting to free nitrogen. The results of the experiments are fully explained by assuming that nitrogen was oxydized in nitrification and no other explanation yet proposed, accords with existing facts.

To sum up, the writer believes that in nature, free nitrogen enters into combination, in all cases, by oxydation, that the agent of oxydation is ozone, that in the soil this ozone originates, for the most part, in the slow oxydation of organic matters, and that ammonia and the organic nitrogen of humus, peat and coal are the result of the reduction of oxyds of nitrogen either in the living organism in the acts of nutrition, or by the organic matters of the dead plant or animal. The union of atmospheric nitrogen and oxygen under the influence of electrical tension has been shown by Meissner to be preceded by the production of ozone. By a long series of critically conducted observations, Daubeny (*Jour. Chemical Soc.*, 1867,) has made probable that ozone appears in the vicinity of active foliage exposed to sunlight, and concludes that the oxygen set free from combination in the plant, is partly ozonized,

as is true of that which separates in the decomposition of permanganates and chromates by oil of vitriol.* The plant, then, appears to be an agent of nitrification when living as well as when dead, and ozone is the result of a molecular change which accompanies the decomposition as well as the formation of oxygen compounds.

Sheffield Laboratory, Dec., 1868.