

## THE ATOMATION OF OXYGEN.

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BY ALBERT R. LEEDS, PH. D.

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### FIRST MEMOIR.

The readers of this journal will have noted that ever since the publication of my earliest paper, bearing upon the subject of the Atomation of Oxygen, and entitled "Upon Ammonium Nitrite and upon the By-products obtained in the Ozonation of Air by Moist Phosphorus," Vol. I, p. 145, I have taken the ground that the essential feature in oxidation-processes was the splitting of the oxygen molecule, and the setting free of atomic oxygen, or oxygen in the state of free atoms (sometimes called active or nascent oxygen). I have preferred to employ the term atomic, and the phrase atomation of oxygen, rather than the terms *active* or *nascent*, because ozone is eminently active oxygen, while at the same time it consists of atoms in a combined condition.

The experimental proof of the proposition, that the oxygen must be brought into the atomic condition before it can re-combine to form ozone, hydrogen peroxide, ammonium nitrite, carbon dioxide, etc., is so fully given in the recent paper, "Conversion of Carbon Monoxide into Carbon Dioxide by Active (i.e., Nascent) Oxygen," that it is needless to rehearse it.

My present object is to present two hypotheses differing from the foregoing, the first by Hoppe-Seyler, the second by M. Traube, an animated controversy concerning which has been carried on for many months.

The first publication by Hoppe-Seyler in the Berlin Berichte upon this topic was in 1879, Vol. XII, p. 1551, "Upon the excitement of oxygen by nascent hydrogen." He begins by stating that every investigation undertaken with the object of explaining the life-processes in animals and plants, necessitates the assumption of some adequate source of the activation of oxygen within the organism. He deduces conclusions upon this point from certain phenomena attendant upon putrefaction, and states that the formation

of free hydrogen occurs under these conditions only when oxygen is absent. On the other hand, when oxygen is admitted to putrefying liquids, the nascent oxygen is not only oxidized, but energetic processes of oxidation are set up. The simplest explanation of these facts, according to Hoppe-Seyler, is the assumption that the nascent hydrogen, whilst it itself enters into combination with oxygen, at the same time brings to pass the activation of one or more atoms of oxygen. To test the validity of this hypothesis, Seyler proposes the use of hydrogenized palladium. "From Graham's experiments," he says, "it is known that palladium at ordinary temperatures takes up no oxygen, and one can readily satisfy himself that the ignited foil when placed in a confined volume of oxygen does not change. The oxygen, therefore, is not made active by the metal, whilst saturated with hydrogen and brought into oxygen, not only quickly forms water, but likewise is in a condition adequate to bring to pass the most energetic processes of oxidation." As proof, he instances the oxidation of indigo by these means, the decomposition of potassium iodide, the conversion of ammonia into ammonium nitrite, and the production of phenol from benzol.

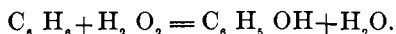
Further on, he describes the products of oxidation of petroleum-ether by sodium in contact with moist air, but does not decide whether these oxidation-processes are due to oxygen rendered atomic by direct action of the sodium, or by the hydrogen first set free and afterwards decomposing the oxygen molecule.

In this publication no mention is made of the formation of hydrogen peroxide, nor is the antecedent probability of its formation on hypothetical grounds alluded to.

On meeting with this research of Hoppe-Seyler, it appeared to me that there was no reason why the atomation of oxygen by palladium-hydrogen should not be in obedience to the same law, as its atomation by phosphorus. Nor any reason why the same secondary products should not be necessarily formed, as resultants of the recombination of this atomic oxygen with itself or with oxygen to form ozone, with water to form hydrogen peroxide, and with nitrogen and the elements of water to form ammonium nitrite and nitrate. The probability was rendered stronger, because I had performed the experiment, before encountering these results detailed by Hoppe-Seyler, of submitting benzol to oxygen in presence of moist phosphorus, and found that, under these circumstances, the benzol was converted into phenol.

On trying the experiment with hydrogenized palladium in pres-

ence of air and water, the formation of hydrogen peroxide was demonstrated (Ber. Bericht. XIV., 976). Furthermore, since the formation of phenol from benzol could not be accounted for by direct oxidation with atomic oxygen, and since I had shown that ozone decomposes benzol entirely into oxalic, formic and acetic acids, together with a small amount of some black, amorphous substance (ib. p. 975), the formation of phenol in Hoppe-Seyler's experiments could be explained only on the supposition of the intermediate production of hydrogen peroxide. This supposition proved correct, and an experiment in which benzol was heated directly with hydrogen peroxide, yielded phenol according to the equation :—



Of the two other by-products (ozone and ammonium nitrite) I looked for the former only, because I was satisfied with the demonstration of the production of ammonium nitrite given by Hoppe-Seyler (loc. cit.) This last point, however, has been emphatically denied by Traube (Ber. Bericht. XVI., 1206) on the strength of obtaining a negative result, thereby inciting Hoppe-Seyler to bring forward the following experiments (Ib. 1923.)

“All the glass apparatus and caoutchouc tubing, just previous to the beginning of the experiment, together with the hydrogenized palladium, were cleansed with water, which had been distilled with pure sulphuric acid and afterwards with a little pure soda. From the glass vessel, in which was the wet foil (91 square centimetres in area and 13.2 gm. in weight), the air went through a wash-bottle with some pure water, then through caustic soda, and finally through sulphuric acid. The foil was allowed to remain for three days in the vessel, and a small fresh portion of air was drawn through the apparatus very two or three hours. At the close of the experiment the foil and the interior of the vessel were washed out with a couple of cubic centimetres of pure water, two or three drops of pure caustic soda added and the mixture evaporated with boiling to a small volume. After cooling, it was acidulated with pure sulphuric acid, and tested with (1) potassium iodide starch paste; (2) with sulphanic acid and naphthylamine sulphate; (3) with metadiamidobenzole; (4) with sulphindigotic acid; (5) with ferrous sulphate and sulphuric acid. In like manner, the water in the wash-bottles through which the air after passing from the glass vessel was drawn, was tested.” In both liquids, the sulphindigotic acid

and the ferrous sulphate with sulphuric acid did **not** give reactions, the other three test-liquids did.

I have been thus particular to quote these elaborate experiments, because the establishment of the fact of the production of nitrous acid under the conditions studied, is of so great theoretical importance, and because the cumulative evidence of the certainty of this fact, can best be appreciated by a critical examination of the above detailed account of Hoppe-Seyler's labors.

The discovery of the formation of hydrogen peroxide has not only been admitted on all hands, but apparently has three claimants. For whilst Traube brought it forward as a new observation of his own (Ber. Bericht. XVI. 222), and placed great stress upon it in support of his hypothesis, later on he calls attention to his mistake, and credits me with the observation (*ib.* 2429). In the same way, he states that Hoppe-Seyler had overlooked the production of hydrogen peroxide in his article upon the activation of oxygen, written in 1879 (Ber. Bericht. XII. 1551). But Baumann states (Ber. Bericht. XVI., 2149) that Hoppe-Seyler first noted the phenomenon (Zeitschr. f. physiol. Chem. II., 25), and that, therefore, when he himself observed it in the contact of hydrogenized palladium with water and air, he regarded it as no new thing. (Zeitschrift, f. physiol. Chem., V., 248). Not having access to the Zeitschrift referred to, I am unable to form an opinion as to whether Traube or Baumann is right in this particular. [See Appendix to this article.]

The third body; the ozone, which, according to my interpretation of these phenomena, is always to be looked for, was sought in my own experiment in the atmosphere in the bottle over the hydrogenized palladium. But although only a negative result was obtained, as, in fact, I anticipated, in view of the very small amount of oxidation possible by a small piece of hydrogenized palladium (Bericht. XIV., 978), yet I see no more *a priori* reason militating against the probability of the formation of ozone by the hydrogenized palladium, than for the production of hydrogen peroxide or ammonium nitrite.

Subsequent to the work above alluded to, a long series of articles upon the "Activation of Oxygen" has been published by M. Traube. In the earliest of these (Ber. Bericht. XV., 222), Traube lays down the following propositions:

I.—"Palladium-hydrogen gives, when shaken with water and air, immediately and in large quantity hydrogen peroxide. The forma-

tion of hydrogen peroxide under these circumstances has been hitherto overlooked."

It has been already mentioned that Traube himself corrects the latter part of the statement, and credits me with having first noted the reaction. I do not know where Traube has shown by quantitative determination that hydrogen peroxide is formed in notable amount. In one of my own experiments with a piece of hydrogen palladium weighing 10 grammes, 0.67 mgrm. of hydrogen peroxide was obtained. Hoppe-Seyler, in a recent publication (*Bericht. XVI.*, p. 1920), obtains a similar result. He states that with palladium, hydrogenized to its maximum, whether the contact with water and air is continued only a few minutes or many hours, the percentage of  $H_2O_2$  does not increase beyond 2 mgrm. in a liter. The highest percentage obtained was 6 mgrm. per liter."

II.—"The oxidations effected by palladium-hydrogen, in presence of air and water, do not proceed from it directly, but entirely from the resultant hydrogen peroxide."

III.—"There is one case only, so far as my present experience goes, in which the oxidation-processes effected by palladium-hydrogen, in presence of air and water, are different from those of hydrogen peroxide. Whilst the last does not turn potassium-iodide-starch blue, rapid bluing occurs by palladium-hydrogen and oxygen. This action is due to the palladium playing the part of a carrier of oxygen from the hydrogen peroxide to the potassium iodide."

IV. "In opposition to the view of Hoppe-Seyler, my investigations have shown that nascent hydrogen is not able to activate oxygen by splitting of its molecule."

V. "The frequent production of  $H_2O_2$  by oxidation-processes, is not proof of the contemporaneous presence of active oxygen, since this  $H_2O_2$ , as I have show by direct experiments and contrary to former assumption, never arises by oxidation of water by means of active oxygen. In these oxidation-processes it is formed by a mode of reduction."

These four last propositions, have provoked a controversy, which has run through many numbers of the *Berichte*, and has become so involved and so voluminous that I fancy but few chemists have found leisure and inclination to follow it.

And yet to chemists in general it should have great interest, because the discussion involves the endeavor to demonstrate, by critical experiments, the nature of those obscure chemical reactions involved in the so-called nascent state, catalysis, oxygen-carrying, etc.

To physiological chemists its interest should be no less. On the one hand, Hoppe-Seyler thinks that he has demonstrated that it is hydrogen which possesses in the nascent state the power of producing in contact with ordinary oxygen, the most energetic oxidations, water at the same time being formed. "These facts, he remarks, are of the greatest importance in physiology, because for the first time it has been shown from the properties of chemical substances that the energetic oxidations stand in well ascertained dependence upon other processes, by which bodies are formed that act upon oxygen in the same way as hydrogen when in the nascent state." Traube, on the other hand, ascribes the activation of oxygen in the organism to oxygen-carriers. By oxygen-carriers he means bodies like platinum, which, according to the explanation of De la Rive, have the property of readily yielding the oxygen which they have taken up to other bodies, and then forthwith as quickly taking up new oxygen again.

I propose to consider these several propositions and present the arguments and experiments which have been brought forward both pro and con. Inasmuch, however, as besides the contradictory results obtained by the contending parties in the performance of the same experiments, there is a different mode of interpreting the significance of these results, there will be no use in weighing the value of the experimental evidence until some mode of interpretation is agreed upon which will be impartially applied in every case.

#### INTERPRETATION OF RESULTS.

And 1st. It must be agreed I think on all hands, that the existence of atomic oxygen, as a substance distinct from, and antecedent to the production of ozone, is a demonstrated fact. The demonstration consists in the proof that this atomic oxygen will effect oxidations which ozone will not, as in the oxidation of carbon monoxide to dioxide, at common temperatures. And the converse of this proposition is likewise true, which is, that when ordinary oxygen is brought into a condition to effect the oxidation of carbon monoxide to carbon dioxide atomic oxygen must be present, and the substance which is capable by its presence of effecting this oxidation must have the power of splitting the oxygen molecule, that is, of setting free its constituent atoms.

The original experiment upon which the first proposition was founded was that of the oxidation of carbon monoxide in the passage of air over moist phosphorus. Although both ozone and hydro-

gen peroxide are formed in the course of this experiment, yet as neither of these bodies will oxidize the monoxide, the necessity of the existence of atomic oxygen to account for the fact, is admitted. Subsequent to this observation, Baumann noted that palladium-hydrogen had the same property as phosphorus, and that in its presence moist air could raise the monoxide to dioxide (quoted in Ber. Bericht., XVI. 123). This result prompted Traube to ascertain whether or no ignited palladium placed in dilute hydrogen peroxide and agitated in contact with carbon monoxide out of contact with air, would produce carbon dioxide (Bericht, XVI. 126). He obtained an affirmative result, and this result is confirmed by Baumann (*ib.* 2150). But their modes of interpretation are different. Traube reasons that inasmuch as air was absent no atomic oxygen could have been formed, but that the palladium by catalytic action caused the hydrogen peroxide to effect an oxidation which alone it could not have effected.

Whilst admitting and confirming Traube's result, for Baumann agrees with Traube in finding that ignited palladium in contact with  $H_2O_2$  and CO produces much more  $CO_2$  than palladium-hydrogen when agitated with CO and water, Baumann's explanation is different. There appears to have been a tacit admission on his part that the formation of  $H_2O_2$  must occur as an intermediate step when the palladium-hydrogen is agitated in contact with water and CO out of contact with air. Further; that it is possible that this  $H_2O_2$  is then decomposed by the palladium, ozone being formed. (He might have added, atomic oxygen is likewise formed.) And although this formation of ozone by decomposition of  $H_2O_2$  with palladium has not been observed, yet he regards it as eminently probable, inasmuch as when  $H_2O_2$  is decomposed by sulphuric acid (this fact was originally noted by Riche (Bull. Soc. Chem., 1860, 178), ozone is given off. Having repeated this experiment of Riche (J. Amer. Chem. Soc., I, 442), I can confirm his statement, the liberated ozone being so powerful as to blacken silver foil. But Baumann appears to have gone further and to have subjected carbon monoxide to the action of the evolved gas, since he states (without giving the particulars of the experiment) that the carbon monoxide was more powerfully oxidized by this gas than by any of the other methods. This being the case, as Baumann justly observes, the decomposition of the  $H_2O_2$  by sulphuric acid must be attended by the evolution of atomic oxygen as well as ozone.

Furthermore, Baumann tried the experiment of passing moist air

over palladium-hydrogen to see whether the water condensed after its passage contained  $H_2O_2$ . The result was negative. But inasmuch as moist air and CO passed over dry palladium-hydrogen had yielded  $CO_2$ , Baumann thinks that the negative result might be accounted for on the ground that the atomic oxygen could have produced  $CO_2$  under circumstances, under which the oxidation of water to  $H_2O_2$  was not demonstrable. Since, later on, Baumann says that he agrees with me in the interpretation I have given of these phenomena, I think he would further assent to the following as a more explicit formulation of his own remarks and observations, viz. :--

That inasmuch as carbon monoxide is oxidized under the conditions stated, the palladium must have effected the atomation of the oxygen molecule. The oxygen set free from the  $H_2O_2$ , which, when spontaneously liberated will not oxidize CO to  $CO_2$ , will bring about this oxidation in the presence of palladium. In other words, the so-called catalytic actions of palladium, platinum, and metals of that group are due to atomation.

Since these metals do not combine with the oxygen under the conditions named, they are in no proper sense *carriers of oxygen*. They do not carry oxygen, but, on the contrary, decompose it, bringing it into the atomic condition, and thus effect their so-called catalytic actions.

#### EXPERIMENTAL PROOFS.

In his first paper (Bericht. XV., 664) Traube brought forward the deportment of zinc when shaken in contact with water and air, both in neutral and acid solution, in support of his hypothesis; also that of copper in presence of sulphuric acid.

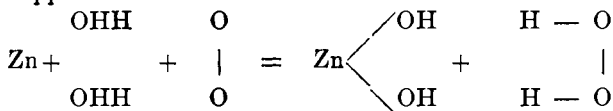
But in the mode of statement, the actual conduct of the experiments and the inductions based thereon, these proofs are of the most inconclusive character.

Traube begins by stating that in case the oxidation of zinc, by shaking with air and water, produces atomic oxygen, then an oxidizable body present at the same time must be rapidly oxidized. But he finds that whether pure zinc or very dilute sulphuric acid is employed, such oxidation is not produced, although in both cases abundance of  $H_2O_2$  is formed.

Traube places great emphasis on the fact that pure zinc out of contact with air does not decompose water and set free its hydrogen. Therefore, that what the affinity of the zinc alone for the oxygen of the water will not effect, this affinity, aided by the affinity of a whole molecule of atmospheric oxygen, will succeed in



doing ; that is, the two together will split up the molecule of water. The supposed reaction is as follows :—



According to Bonsdorff and Boutigny (Gmelin-Kraut, 3d vol., 1st part, p. 5), when zinc is inclosed in glass tubes with water from which the air has been expelled by boiling, it remains unaffected for years. According to J. Davy (*ibid.*) it does not decompose pure water even on boiling, and even in contact with copper it does not appreciably decompose pure water.

In repeating these experiments I have obtained different results. The purest zinc which I could procure contained lead, iron and carbon in minute amounts, and consequently the deportment of absolutely pure zinc with pure water is not determined by my own trial. Forty grammes of this zinc in extremely thin fine turnings were introduced into the upper portion of a eudiometer tube completely filled with redistilled water free from ammonia. The tube was surrounded by a water bath and maintained at a temperature of 70° for seven hours, during the whole of which time it was connected with an air-pump and a vacuum maintained. The open end of the eudiometer was then plunged into a vessel filled with mercury, and the apparatus allowed to stand from the middle of June to the middle of September. Between the upper surface of the mercury and the zinc in the eudiometer there intervened a space of 8 centimeters filled with water, so that contact between the two metals could not occur. During the whole of this long interval bubbles of gas came off slowly, and finally amounted to a volume of 15.95 cubic centimeters, reduced to 0° and 760 m.m. After the introduction of a suitable excess of oxygen and explosion by the electric spark, a reduction of the measurements showed that the 15.95 cubic centimeters of gas collected during the course of three months consisted of hydrogen. The zinc was very faintly tarnished, appearing somewhat less bright, and of a slightly different color from fresh surfaces of other portions of the same zinc, but no oxide was visible.

Now, it is a well-known fact that zinc, especially when in fine powder, may be employed to bleach a solution of indigo. In this case the indigo blue ( $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ ) is converted into reduced or white indigo ( $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$ ) by the fixation of nascent hydrogen.

Two interpretations of this phenomenon are possible:—1st.

That the hydrogen liberated from water by ordinary zinc in the manner above described, small in amount though it may be, is adequate in amount, when a large surface of zinc dust is employed, to reduce the indigo. 2d. That soluble indigo or sulphindigotic acid, being acid in its reaction, liberates the nascent hydrogen on contact with zinc, which brings about its reduction. The latter is the correct explanation. For when sulphindylate of potash is employed, the salt being made as nearly neutral as possible, it is found that zinc does not act as a reducing agent, but as a powerful oxidizing agent. Under these circumstances, the blue solution is bleached, it is true, but not by the reduction of the indigo, since the solution retains a yellow tint in contact with the air, and contains no white indigo, the indigo having undergone oxidation. When large amounts of indigo carmine are employed this complete oxidation and decoloration are somewhat difficult to obtain, because of the energy with which fine shavings of zinc are themselves oxidized and the great amounts of zinc hydrate which are formed. On shaking up a liter bottle containing a hundred grms. of zinc in fine shavings, with 100 cc. of indigo carmine solution, the contents of the flask become at once bluish-gray from admixture of suspended zinc hydrate. In this first bottle, which now contains oxidized zinc, complete decoloration is hard to effect, but on filtering off the solution into a bottle containing fresh zinc, bleaching occurs immediately.

My own observations, therefore, are directly opposed to those of Traube, who stated that zinc would not bleach solution of indigo. Moreover, inasmuch as the indigo in my experiments was oxidized and not reduced, they show that zinc shaken up in contact with water and air brings about phenomena of energetic oxidation.

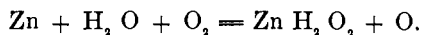
In the second place, hydrogen peroxide is formed under the same conditions. As stated by Traube, the reaction for the peroxide entirely disappears in case the water, after brisk agitation with the zinc, is allowed to remain in contact with it. And inasmuch as the reaction with potassium iodide or with potassium iodide and ferrous sulphate is affected by substances other than  $H_2O_2$ , the author did not rely upon these tests in proving qualitatively the presence of the latter body. Instead of so doing freshly-prepared cold malt extract was used. Upon this was floated freshly-made tincture of guaiacum, and it was noted whether any blue color was developed along the surface of contact of the two liquids. If not, the water decanted from the surface of the zinc was poured down the

side of the test-tubes, so as to flow under the guaiacum tincture and above the malt extract. Only when these precautions were observed was the development of a blue color regarded as a satisfactory indication of the formation of hydrogen peroxide.

The oxidation of indigo by zinc in neutral solution would lead us to anticipate the decomposition of potassium iodide under the same circumstances. This anticipation is verified by experiment in case starch is added to the potassium iodide and the mixture then shaken up with the zinc. Under these circumstances iodide of starch is formed, whilst it is not formed in case potassium iodide solution alone is agitated with zinc, the liquid poured off, and then starch added.

*Nitrous Acid.*—When redistilled ammonia-free water, which failed to give any coloration with sulphanilic acid, was agitated with zinc, the decanted liquid gave a decided reaction for nitrous acid. But when ordinary distilled water, which itself gave a faint coloration with sulphanilic acid, was shaken with zinc, the decanted liquid gave no reaction for nitrous acid, and remained entirely colorless. These reactions were explained by those occurring when a solution of potassium nitrite, standardized for purposes of water analysis, was treated with hydrogen peroxide. After forty-eight hours it failed any longer to give the nitrous reaction, the acid present having undergone oxidation to nitrate.

To summarize the results detailed above, it may be stated that there is the same evidence of the production of atomic oxygen, when zinc is agitated in contact with water and air, as there is of the production of atomic oxygen when moist air is passed over phosphorus. Moreover, that this atomic oxygen arises from the splitting of the oxygen molecule by the zinc directly, and not by means of hydrogen resulting from any intermediate process. In other words, zinc reduces the oxygen, being rapidly converted in presence of water into hydrate, and setting atomic oxygen free, the equations being



It is this atomic oxygen, which the author supposes to be the efficient agent in the subsequent formation of hydrogen peroxide and nitrous acid, and the origin of the energetic oxidation of the neutral indigo solution and of the decomposition of the potassium iodide in presence of starch.

[To be continued.]

## APPENDIX.

The principal portion of this First Memoir was read at the June meeting of the Society, but its publication was delayed by the pressure of other duties subsequently devolving on the author.

Since the article was written I have had the pleasure of receiving letters both from Prof. Hoppe-Seyler and from Prof. Baumann, the former dated November 17, 1883, and the latter, December 10th. Prof. Hoppe-Seyler has likewise kindly sent me reprints of his papers in the *Zeitsch. für Physiol. Chemie*, bearing upon the matter referred to, and these, together with an extract from his letter, which I shall take the liberty of quoting, will best illustrate the history of the subject. Prof. Hoppe-Seyler says, \* \* \* "Both of us nearly at the same time and quite independently of one another, have investigated the properties of active oxygen, and in general with the same results. But it would appear from a passage in your memoir, 'The conversion of carbon monoxide into carbon dioxide by active (*i. e.* nascent) oxygen,' that my earlier publications have remained unknown to me. You there remark, 'According to these views the oxidizing effect of palladium hydrogen, as noted by Hoppe-Seyler at a late period in the history of these researches,' etc.

"My earliest observations upon the activating agency of hydrogen when in *stat. nasc.* were published as far back as 1876, and in 1877 were further elucidated in my *Handb. der physiol. Chemie*. The powerfully oxidizing action of H in *stat. nasc.* in the presence of oxygen when palladium-hydrogen is employed, I had already intimated in a preliminary note dated February 31, 1878, and shortly after this it was fully described in the spring of 1878 in *Zeits. für physiol. Chemie*, Bd. II., p. 22. Some further observations caused me to publish a short summary of the results so far obtained, in the *Berichte*. The formation of  $H_2O_2$  in certain reactions I had already noted in the beginning of my investigations, but the oxidations which are effected by the agency of H in *stat. nasc.* are more energetic than those produced by  $H_2O_2$ ."

The statement alluded to by Prof. Hoppe-Seyler (*Zeitsch. für physiol. Chemie*, Bd. II., p. 22) is as follows: "By far the most interesting reduction which active hydrogen is capable of effecting, is that of free indifferent oxygen, attended with the formation of water, whether it results in this case that hereby — OH or a combination HO-O — or  $H_2O + -O-$  is formed. This is the

origin of powerful oxidations, which indifferent oxygen is not capable of effecting."

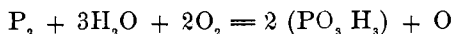
Pages 24 and 25, of the same article contains the statement alluded to by Baumann, as showing that I was anticipated by Hoppe-Seyler, in stating that  $H_2O_2$  is a product consequent upon the formation of atomic oxygen in presence of water. It is as follows:—

"Like the liberated hydrogen atom, so also the O-atom cannot remain free, but in case no other oxidizable substances are present it forms with water or indifferent oxygen, either  $H_2O_2$  or  $O_3$ ."

"The occurrence of nitrous acid in the combustion of hydrogen with air has given occasion to Bunsen (*Gasometr. Meth.* 1857, p. 65) to set forth appropriate precautions in gas analysis. Recently Zöller and Grete (*Ber. deutsch. Chem. Gesell.* X, 2144), have recognized the occurrence of small but clearly distinguishable quantities of  $NH_4NO_2$  in the combustion of pure hydrogen gas in pure atmospheric air."

"The action of hydrogen upon indifferent oxygen is the same therefore as the action of many other substances, which possess a very strong affinity to oxygen, such strongly reducing substances, for example, as phosphorus and magnesium."

"It has been lately found by Kämmerer (*Berichte* X, 1684) that in the combustion of magnesium in air, nitrous acid is formed. In the slow combustion of P at least one atom of oxygen becomes active for every molecule  $P_2$ ."



"The discovery of Schönbein that powdered zinc and iron, when shaken up with air and water, give rise to the formation of  $H_2O_2$ , can likewise be explained in hardly any other manner than as a result of a reduction of the indifferent oxygen."

"None of these processes, however, shows simply and clearly like the decomposition of palladium-hydrogen does, the reduction and oxidation effected by means of such decomposition."

I am very glad to yield to Prof. Hoppe-Seyler the merit of having investigated the phenomena consequent upon the evolution of atomic oxygen in a large number of cases, and more especially in that arising from the contact of palladium-hydrogen in contact with air and water. And the difference between his labors and my own appears to consist in the fact that whilst Hoppe-Seyler was engaged upon the demonstration of the formation of atomic

oxygen itself as the main topic of inquiry, I was more intent upon establishing the thesis that whensoever atomic oxygen is produced in the presence of air and water, ozone, hydrogen peroxide and ammonium nitrite are necessarily and simultaneously formed as secondary products. This hypothesis led me to anticipate, in entire ignorance of Hoppe-Seyler's labors, the formation of  $H_2O_2$  when palladium-hydrogen is agitated in contact with water and air, to establish the fact of its formation by experimental proof, and to determine quantitatively its amount. I think it not invidious, nor an undue detraction from the merits of Hoppe-Seyler's discoveries, to claim for myself priority in the two latter points.

STEVENS INSTITUTE OF TECHNOLOGY,

December 15, 1883.

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## ON A NEW OVERFLOW PIPETTE.

GEO. S. EYSTER, PH.D.

The well known Overflow Pipettes of Gay-Lussac and Stas, whilst adapted for the accurate measurement and delicacy of a given volume of a solution, are not so fit for the use of corrosive fluids, and are not easily extemporized from materials commonly found in a laboratory.

The following pipette is especially adapted for use in alkalimetry, and for the employment of such corrosive solutions as are used in the "copper" method of estimating sugar (Fehling's, &c.)

An ordinary pipette, graduated to deliver a definite volume, is clamped in a *reverse* position; that is with the mark *down*, and the jet *up*. A short piece of rubber tube connects the end that is now the lowest end with one arm of a glass T tube, the other arm of which is provided with the usual Mohr burette tip; or with a glass bead cock.

This glass bead cock is simply a short piece of glass rod, somewhat larger than the bore of the rubber tube, fused into a bead. This bead inserted into the rubber tube effectually stops the flow. When it is desired to open the cock, a slight pinch of the tube over the place where the bead is concealed, will open a channel for the passage of the solution. The flow can be regulated with the greatest nicety. This piece of apparatus is *old*, but does not seem to be as generally known as it should be.