XXIX.—*Lines of Discovery in the History of Ozone, with an Index of its Literature, and an Appendix upon the Literature of Peroxide of Hydrogen.*

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LINES OF DISCOVERY IN THE HISTORY OF OZONE.

I.—ITS ORIGINAL DISCOVERY, SOURCES AND PROPERTIES.

The history of ozone begins with the clear apprehension, in the year 1840; by Schönbein, that in the odor given off in the electrolysis of water, and accompanying discharges of frictional electricity in air, he had to deal with a distinct and important phenomenon. Schönbein's discovery did not consist in noting the odor; that had been done by Van Marum, more than half a century before, but in first appreciating the importance and true meaning of the phenomenon. For while Van Marum, Cavallo, and others who followed them, connected the odor with the electricity, calling it the "electrical odor," or "aura electrica," and thus made it the property of an imponderable agent, Schönbein ascribed it to the peculiar form of matter operated upon.

The hypothesis of Van Marum necessarily remained barren of fruits; that of Schönbein speedily enriched chemical science with a host of acquisitions.

Clinging tenaciously to the doctrine that there could not be a variety of origin for one and the same odor, and that the kind of matter producing it in every case must be identical, Schönbein fixed his discovery by giving to that one and certain kind of matter, the name of Ozone. By adhering to this guiding clue, he added as a third source of ozone, the action of moist phosphorus upon air (1840-1843); and since that time, besides electrolysis, electrical influence, and the action of air upon moist phosphorus, no other sources of ozone of practical utility have been discovered.

The fact that Schönbein so stoutly insisted, and eventually so triumphantly established, the identity of the ozone from whatever

source derived, must not be lost sight of in any estimate of his merits as a discoverer. The earliest attack came from De la Rive, who attributed the odor to metallic oxides set free from the metals used as electrodes, or as terminals in electric discharges. But Schönbein pointed out, that besides the improbability of an odor arising from solid bodies, this hypothesis required that solid bodies should have the property of indefinite suspension in the atmosphere, instead of being deposited, or washed down by water (1840-1843).

The next attacks came from Fischer, who regarded Schönbein's ozone as probably peroxide of hydrogen, and from Williamson, who thought there were two kinds of ozone, one the ozone given off in electrolysis, and which he regarded as a higher oxide of hydrogen, differing from the previously well-known peroxide, and the other formed by the action of phosphorus on moist air. But Schönbein disposed of both objections;—of the first, by showing that the chemical and physical properties of ozone are not the properties of peroxide of hydrogen; and of the second, by demonstrating that, whatever might be the true nature of ozone, the gaseous matter obtained in the electrolysis of water, was in all respects identical with that formed by the action upon air of moist phosphorus (1844-1845).

During these first five years, Schönbein was busily engaged in ascertaining the properties of ozone. Since no peculiar methods were employed in the furtherance of these discoveries, they need not detain us here, further than briefly to summarize them, and to point out what corrections have been rendered necessary by the labors of subsequent investigators.

They are:—1st. Its eminent oxidizing powers, as shown by its ability to transform most metals into their higher oxides, and to raise the lower oxides into the condition of peroxides. Certain of the non-metals—phosphorus, chlorine, bromine, and iodine—are similarly oxidized. Schönbein's statement that it does not unite with nitrogen under ordinary circumstances, but enters into combination when alkali is present, has been abundantly disproved; among others, by Berthelot (1877), who has shown that no combination occurs, even when alkali is present. It oxidizes sulphites and nitrites into sulphates and nitrates,

and many sulphides into their corresponding sulphates. It destroys (as has since been more elaborately demonstrated by Houzeau, 1872) many gaseous compounds of hydrogen, like those with sulphur, selenium, phosphorus, iodine, arsenic, and antimony. It discharges vegetable colors and powerfully attacks many organic bodies. The nature of its action in the latter case has been more extensively studied by Gornp-Besanez (1863), and he has described the products of the reactions which occur when ozone is allowed to act upon organic substances, alone or in presence of alkali.

2d. According to Schönbein, ozone is insoluble in water. The observations of subsequent experimenters conflict on this point, but there appears to be much evidence to show that it is soluble in water, though only in small degree.

3d. Schönbein pointed out that atmospheric air strongly charged with ozone, acts powerfully on the mucous membranes, and produces symptoms of catarrh. This, and his analogous statement that ozone is present in the atmosphere and plays there a very important role, attracted to the subject not only great popular attention, but enlisted as observers a multitude of students of medicine the world over, who hailed the newly discovered body as an invaluable therapeutic agent, and rushed forward to establish, by sufficiently numerous observations, the relations between its presence or absence in the atmosphere, and the kind and prevalence of disease. Thirty years have passed away, and neither anticipation has been realized. Indeed, at the present hour, the possible value of ozone as a therapeutic agent, is obscured by its having fallen into the hands of empirics; and the multiplication of inexact observations, and the crude and hasty generalizations therefrom, have covered with a sort of scientific opprobrium the whole subject of Atmospheric Ozone.

What causes have led to these lamentable results in the past? what prospects are there that both subjects can be reinstated in good scientific standing in the future?

And first, with regard to ozone as a therapeutic agent. Without considering at present the unsettled questions of a medical

The following table will, it is hoped, prove of some service as an aid to identification:—

Body less slender, sometimes quite robust, more convex, the pronotum generally not at all impressed, although sometimes exhibiting very feeble traces of the usual two impressions.

Prothorax widest at or near anterior third, the sides at this point more strongly rounded and evenly coarctate to the apex.

Eyes smaller, but very slightly prominent and not so coarsely faceted, the tempora very slightly visible behind them, broadly rounded and convergent posteriorly, and distinctly less prominent than the eye.....45 **pudicus**

Eyes very convex, prominent, more coarsely faceted as usual.

Form more robust; prothorax but slightly narrowed toward base, the sides parallel in the apical half and strongly arcuate; legs pale.....46 **robustulus**

Form more slender; prothorax strongly narrowed toward base, the sides strongly rounded in the anterior third.

Eyes smaller, scarcely longer than the first antennal joint.

47 **confinis**

Eyes much larger and more prominent, very coarsely faceted, distinctly longer than the first antennal joint.

48 **pauperculus**

Prothorax gradually and moderately narrowed from apex to base and broadly, evenly, and rather strongly arcuate; body rather slender and convex.

Pronotum with a distinct median impunctate line extending from the basal margin to the apex, gradually becoming broader throughout its length.....49 **languidus**

Pronotum without a median impunctate line, the punctures a little more sparsely distributed in the middle near the apex.

50 **blpuncticollis**

Prothorax widest at or near the middle, the sides at this point rather narrowly rounded and very obtuse, thence parallel or feebly convergent and more or less feebly arcuate to the apex, and more distinctly convergent and more nearly straight to the base.

Size larger, not less than 2 mm. in length; pronotal punctures distinctly separable, the interspaces shining; eyes normal for the group and without trace of tempora.

Prothorax large, as wide as the elytra.

Punctuation excessively fine and dense, lustre dull; median impunctate line of pronotum very narrow.

Piceous; sides of prothorax in anterior half parallel.

51 **simptarius**

Castaneous; abdomen piceous; sides distinctly convergent from behind the middle to the apex.....52 **pallidulus**

- Punctuation coarser and sparser; lustre shining; median impunctate line of pronotum wide and evident. .53 **convexus**
- Prothorax distinctly narrower than the elytra; color black, rarely slightly piceous.
- Antennæ less robust, much longer than the head and prothorax, the latter relatively much smaller.54 **debilis**
- Antennæ robust, never longer than the head and prothorax, the latter relatively larger.
- Elytra slightly longer than wide, with two small approximate impressions at the middle of the base; abdomen much narrower than the elytra, slender, linear, with the sides straight.55 **bidifidus**
- Elytra slightly but distinctly wider than long and but very slightly wider than the abdomen.
- Abdominal punctuation fine and very dense, with the surface alutaceous; punctuation and pubescence throughout very dense, the latter conspicuous.
- Elytra not at all impressed, rather convex . . .56 **fallax**
- Elytra distinctly impressed near the suture toward base, . . .57 **providus**
- Abdominal punctuation very minute and much sparser, the surface distinctly shining; pubescence extremely short and fine, and, although sometimes rather dense, never decidedly conspicuous.
- Legs pale flavate; prothorax narrowed very slightly behind, the base almost as wide as the apex.
- . . .58 **inquisitus**
- Legs black or piceous-black, the tarsi and sometimes the knees paler; prothorax strongly narrowed behind, the base being much narrower than the apex.
- Prothorax more strongly transverse, about one-fourth wider than long, the surface more finely and densely punctate and decidedly alutaceous, the median impunctate line very fine and slightly tumid.
- . . .59 **facetus**
- Prothorax more elongate, not more than one-fifth wider than long, more coarsely, sparsely punctate, shining or polished; median impunctate area not tumid.
- Punctuation denser, the punctures separated by about their own diameters.60 **confusus**
- Punctuation sparser, the punctures separated by about twice their own diameters. . .61 **scrupulus**
- Size smaller, 1.5 mm., slender; lustre dull, the punctures of the pronotum not distinct.62 **insolitus**