THE HISTORY OF OZONE. II. 1869-1899 (1)

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Introduction

By the time of C. F. Schönbein’s death in 1868 (2), ozone had become an accepted fact of chemistry. Its molecular formula had been determined by Soret in 1865 and it was recognized to be a substance of unusual properties which had never been isolated in the pure state. The contrast between O_2 and O_3 aroused a great deal of interest. Some of ozone’s inorganic chemistry had been clarified but its reactions with organic compounds had not undergone any sort of systematic investigation. Analytical methods had been developed and used for investigations of ozone’s role in the atmosphere. In spite of considerable progress since its discovery in 1839, there were still large gaps in the knowledge of its properties. The period 1869-99 was mainly one of consolidation in which some of these gaps were filled but much progress remained for the next century. Great hopes were held for ozone.

A number of books on ozone appeared during the period 1869-99. These include three by Meissner (3) in which he collected his efforts on ozone rather than publishing individual articles in journals of the time; this may have had its convenience for Meissner but his books are available in very few libraries today. An 1873 book by Fox (4) was mainly concerned with the extensive investigations of atmospheric ozone pursued all over the world. Review articles were not lacking. An excellent critical, annotated review by Engler (5) appeared in sections in 1879 and 80. A review by Leeds (6) with an extensive bibliography appeared at the same time. Leeds, who seems to have set himself up as an arbiter of ozone work, also reviewed the history of antozone (7), included considerable material on ozone in a long article on Sanitary Science (8), and provided a review on atmospheric ozone (9). A more superficial summary

CORRECTION


In Rubin’s paper, “The History of Ozone. The Schönbein Period, 1839-1868,” the symbols for ozone and antozone were written incorrectly. Following is a corrected version of the last six lines of page 48:

“He gave ozone the symbol $\Theta$ , implying that it is a negatively charged species, and its complement, antozone, the symbol $\Xi$ . Thus lead dioxide, a compound containing ozone according to Schönbein, was written PbO $\Theta$ .

Barium peroxide, on the other hand, supposedly contained antozone and was written Ba $\Theta$ .”

Dr. Alfred Bader has pointed out that in addition to Hunt (1848) and Odling (1861) Loschmidt suggested in 1861 that ozone was O_3 (J. Loschmidt, Chemische Studien I. Konstitutions-Formeln der organischen Chemie in graphischer Darstellung, Carl Gerold’s Sohn, Vienna, 1861, 29).
was given by Hammerschmied (10). Thomas Andrews (11), the author with Tait, of key work in the elucidation of the composition of ozone, published a two-part summary of his work, complete with diagrams of apparatus, in Nature in 1874; a German translation also appeared.

Ozone also appeared in textbooks of the time, certainly a criterion of respectability. For example, the 1877 chemistry text edited by Wislicenus (12) included a diagram with instructions for construction of an ozone generator followed by sections on preparation and reactions of ozone as does the textbook by Kolbe (13). Even lecture demonstrations appeared. Newth (14) described an apparatus with projection equipment for demonstrating to an audience the volume changes when ozone is formed from oxygen, heated, or allowed to react with turpentine as Shenstone and Cundall (15) had done earlier without the projection. Another lecture demonstration was reported by Ladenburg (16) who used the low temperatures which became available in the 1890s to obtain liquid ozone and demonstrate that it is blue (no safety precautions mentioned).

Analysis

Although Schönbein’s original discovery of ozone was based on his sense of smell, many workers appear to have been led astray by odors which they identified incorrectly as being due to ozone. We begin with a discussion of analytical methods for ozone because of a serious problem with much of the quantitative data reported during the period covered by this article. As discussed below, many of the values for ozone concentration were too high, sometimes by as much as 50%.

1. Qualitative Analysis

The liberation of iodine by reaction of ozone with potassium iodide solution was discovered by Schönbein at a very early stage of ozone research (1). He developed the use of starch-iodide paper for the detection of ozone together with a color scale (0-10) for giving a measure of its relative concentration. His “ozonometric” paper was available commercially (17) and was used by investigators all over the world for studies of atmospheric ozone. The fact that other substances (e.g. nitrites, hydrogen peroxide) could also give positive tests was common knowledge; and, despite a number of efforts, Schönbein and others were not successful in finding a satisfactory substitute. Chemists’ dissatisfaction is illustrated in a lecture by Moffatt (18) to the Chemical Society of London on an ozonometer. A lively discussion on methods for ozone detection followed this lecture with the majority agreeing that Schönbein’s procedure was of limited value but that no satisfactory substitute was available. Like the weather, everyone complained but went on using the Schönbein method. Levy, who was responsible for ozonometric measurements at the Montsouris observatory, emphasized (19) that ozonometric papers do not provide a numerical concentration of ozone but are useful nonetheless.

Houzeau (20) continued to champion his method based on the change in color of a tourneosol indicator as a result of the formation of potassium hydroxide in the reaction of ozone with potassium iodide (see below). Except for support by Giannetti and Volta (21), who found this method to their liking, it never achieved much acceptance. Other methods developed included the use of paper impregnated with $N,N',N'-tetracetyl-p$-phenylenediamine which turned blue upon exposure to a variety of oxidizing agents as developed by Wurster (22). A method due to Erlwein and Weil (23) employed alkaline solutions of $m$-phenylenediamine which gave a burgundy color with ozone but no color at all with hydrogen peroxide or nitrites.

The color change on reaction of ozone with silver foil to black peroxide was also used as a qualitative test for ozone. This method was not particularly sensitive and a positive result appeared to require the presence of moisture (see section on inorganic reactions).

2. Quantitative Analysis

The reaction of ozone-enriched air or oxygen with potassium iodide solution was shown by a number of workers, beginning with Andrews and Tait in 1860, to involve no change in the volume of the gas. This required the following stoichiometry (reaction 1) in which one molecule of oxygen is formed for every molecule of ozone reacting:

$$\text{O}_3 + \text{KI} \rightarrow \text{H}_2\text{O} \quad \text{O}_2 + \text{I}_2 + 2\text{KOH} \quad (1)$$

A standard iodimetric procedure, with all the usual precautions (24) could then be used for the quantitative analysis of ozone. A procedure for analysis of small volumes of gas (ca 100 cc, 0.3-8 volume percent of ozone) was described by Behrend and Kast (25). The practice of these and most other workers was to bubble ozone-containing gas into acidified KI solution and then to titrate with sodium thiosulfate using a starch indicator.
Brodie (26) and Leeds (27) demonstrated that the correct procedure is reaction of ozone with neutral potassium iodide solution, followed by acidification after the flow of gas has been interrupted, and finally titration with standardized thiosulfate. Results obtained from reaction of ozone with acidified KI solutions were shown to be unreliable and to give values higher than correct by as much as 50%. With the exception of McLeod (28), who discarded the results of 27 experiments after learning of this problem, most workers continued to use acidified KI solutions until the beginning of the 20th century. This leaves us today in the unsatisfactory situation of having to treat most of the quantitative results obtained with a degree of suspicion. Qualitative trends are probably reliable but precise measurements may not be so.

Tommasi (29) described a procedure for analysis of mixtures of ozone and chlorine (assuming the ozone survived in the presence of chlorine) in which one sample of gas mixture was titrated with standardized potassium ferrocyanide and a second sample analyzed in the same way after passage through a tube containing platinum black (see section on thermal decomposition).

An alternative titration procedure for ozone was reaction with excess standardized arsenious acid, presumably according to reaction 2:

$$3O_2 \rightarrow 2O_3$$

followed by titration of the unchanged acid with permanganate. This method was used as early as 1853 by Soret (30); a detailed procedure was described by Thenard père (31) who found that arsenite did not react with hydrogen peroxide or nitrites but that the permanganate used for back titration of arsenite did react with these substances, resulting in low values for ozone. Here again, there is room for doubt of accuracy, particularly with ozone generated from air. This method achieved considerable acceptance (19, 32). The differences in reaction between ozone and various substrates, such as arsenite and indigo, created difficulties for the Thenards, father and son (33).

The relation between ozone and oxygen involves the reactions 3a and 3b below in which the number of molecules in the system changes as reaction 3 proceeds in either direction:

$$3O_2 \rightarrow 2O_3$$

$$2O_3 \rightarrow 3O_2$$

Some reactions of ozone, such as the KI reaction, do not involve any change in the concentration of gas molecules. Others involve complete consumption of the gas with concomitant changes in volume and/or pressure. These facts provided the basis for an alternative approach to analysis of ozone in closed systems. This was pioneered by Andrews and Tait and used by Soret in his 1865 determination of the molecular formula of ozone. Both volume change at constant pressure and pressure change at constant volume were applied, generally using sulfuric acid manometers (mercury was avoided because of possible reaction with ozone). A complication in such measurements is the thermal decomposition of ozone which has a slow but appreciable rate even at room temperature (see section on thermal decomposition). Among those using this method were Beill (34), Warren (35), Hautefille and Chappuis (36), Shenstone and Cundall (37), and Shenstone and Priest (38).

The first analytical apparatus based on the light absorption properties of ozone in the visible region of the spectrum was developed by Otto (39) at the end of the century.

Molecular Formula and Structure of Ozone

Soret (40) had determined that the molecular formula of ozone was $O_3$ in 1865 by a study of volumetric relationships and confirmed this in 1867 by diffusion studies (41). An objection by Wolfenstein (42) to the effect that turpentine reacts with both oxygen and ozone was dismissed by Soret (43) who showed that this was not correct on the time scale of his experiments. Soret’s conclusion was generally accepted although Dubrunfaut (44) maintained that the evidence that ozone was an allotrope of oxygen was not convincing; he claimed that a pure substance should have only a single line in its spectrum. A number of confirmations of Soret’s work appeared in subsequent years. The first of these was due to Brodie (26) who, labeling Schönbein as a dabbler, indicating that some work of Andrews was incorrect (it was correct), impugning unscientific motives and behavior to Soret, and characterizing Meissner with the statement (45) “this chemist has the art of singularly misinterpreting his results,” went on to conclude that
ozone was indeed \( \text{O}_3 \) by methods very similar to those used by Soret.

More than 20 years later, there was another flurry of activity in this area. Otto (46) determined, by weighing, the density of a known volume of an ozone-oxygen mixture (ca 5% ozone) and, by iodimetric titration, the weight of ozone contained in this volume. His values for the density of ozone were 1.6546 and 1.6623; the value calculated for \( \text{O}_3 \) is 1.6584. This work is valueless since it suffers from the circular reasoning mentioned below in connection with the work of Ladenburg.

While Otto provided no justification for reopening the question of the molecular formula of ozone, one year later Ladenburg (47) introduced his work by noting that all of the earlier determinations involved dilute solutions of ozone in oxygen. With the development of cryoscopic methods, it was possible to liquefy ozone and obtain mixtures in which ozone was the major component. This would greatly reduce the errors of measurement and provide a value of much higher precision for the density of ozone. He proceeded, like Otto, to determine the density of a known volume of an ozone-oxygen gas mixture and showed, by iodimetric titration of a known volume of the gas, that the mixture was 86% ozone. He was then able to calculate the density of ozone and found that it was 1.456 times greater than that of oxygen.

Ladenburg’s method was attacked within a very short time by Staedel (48) and by Gröger (49). Both pointed out that the method involved circular reasoning. In order to calculate the amount of ozone by iodimetric titration, it is necessary to know the stoichiometry of the reaction. Ladenburg assumed the reaction (1) for his calculation. In other words, he assumed that ozone is \( \text{O}_3 \) in the experiment designed to prove that it is \( \text{O}_3 \). However, if one assumes that ozone is \( \text{O}_4 \), one can write reaction 4 with \( \text{KI} \):

\[
\text{O}_4 + 4\text{KI} + 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{I}_2 + 4\text{KOH}
\]

from which the ozone concentration of Ladenburg’s gas mixture can be calculated to have been 43% and the density calculated fits equally precisely with the value expected for \( \text{O}_3 \). The goodness of the fit is simply evidence of the skill of the experimentalist. The same argument applies to Otto’s work mentioned above.

A testy reply from Ladenburg (50) followed rapidly. He argued that a number of workers (cf. section on liquid ozone) had shown that the method he used to obtain highly purified ozone gave compositions much higher than 43% and therefore the calculation for \( \text{O}_4 \) is not reasonable. Nonetheless, he returned to the laboratory bench (51) and modified his method by going back to Soret’s original approach but determining the amount of ozone present in the gas mixture from the loss of weight (Soret had determined the volume change) when a known volume of gas was allowed to react with turpentine (contains a high concentration of pinenes). Amusingly, this last effort was performed with a gas mixture containing 8% or less ozone in oxygen, not very different from the composition of the ozone-oxygen mixtures used by Soret.

We note that neither of Soret’s methods nor the method of Brodie for determining the molecular formula are subject to the criticism above. Soret’s first method was based on volumetric relationships without the use of iodimetric titration at all, and his second method involved ratios of titration values so that they are independent of any assumed stoichiometry. Ozone was \( \text{O}_3 \) in 1865 and remains that way although the allotrope \( \text{O}_4 \) was later suggested to exist.

Speculations about the structure of ozone began to appear; both linear and cyclic structures were suggested. The first of these was due to Kolbe (52) who, in a paper in which he expressed his doubts of a ring structure for benzene, considered the possibility that ozone had a 3-membered ring structure and wondered why four-, five-, etc. membered ring allotropes could not exist. Traube (53), Brühl (54), and Brunck (55) also suggested ring structures for ozone including a 3-membered ring containing one double bond in order to account for the fact that only one atom of oxygen was available for many reactions.

A linear structure was proposed by Wolkowicz (56) who considered ozone to be a combustion product of oxygen analogous to sulfur and selenium dioxide. He also considered that ozone might be the anhydride of an acid \( \text{H}_2\text{O}_4 \) related to potassium tetroxide, \( \text{K}_2\text{O}_4 \). In 1870, Clausius (57) accepted the formulation \( \text{O}_3 \) for ozone but maintained that his original idea that ozone was atomic oxygen need only be modified by assuming that the third atom of oxygen was in a special state.
Physical Properties of Ozone

1. Ozone in Water

Although he reported in 1847 obtaining a positive starch-iodide test for ozone in ground-water after an electrical storm, Schönbein (1) considered that ozone was insoluble in water. Ozone, particularly from the phosphorus reaction, was washed by bubbling through water. When volumetric measurements began, ozone volumes were routinely measured over water because of ozone’s facile reaction with mercury. It was claimed by many workers to be “insoluble” although there were dissenters. This conclusion was based mainly on the fact that qualitative tests showed that ozone could be stored over water without disappearance of the odor.

Questions arose, however, when Andrews and Tait, the first workers to use quantitative volumetric measurements, reported that samples of ozone stored over water underwent decomposition as shown by an increase in the volume of the gas on standing. These results were confirmed by Schöne (58) who monitored the volume change when an ozone-oxygen mixture was allowed to stand at ordinary temperature over water. A slow volume increase due to the conversion of ozone into oxygen was observed with a half life of about 3 days. Schöne attributed his results to slow thermal decomposition of ozone (reaction 3b) and not to dissolution of ozone in water. He confirmed earlier results of Carius (59) that there was no reaction between ozone and water except for the thermal decomposition; in particular tests for hydrogen peroxide were completely negative. This result was reconfirmed by Berthelot (60) and refuted various suggestions that the hydrogen peroxide often accompanying ozone was formed by reaction of the ozone with water.

Detailed studies of ozone solubility were performed beginning in 1872. They were complicated by the fact that, at best, concentrations of only a few percent of ozone in oxygen were available. As pointed out by Carius (61), the partial pressure of ozone in any single experiment was small and the concentration of dissolved ozone could be so small as to avoid detection. Furthermore, the concentration of ozone in oxygen or air might well be variable from experiment to experiment or even within a given experiment. A further complication was due to the fact that nitrogen free oxygen had to be used in electrical experiments, otherwise the product contained oxides of nitrogen which reacted with ozone. It was not difficult to obtain qualitative evidence for the presence of ozone in water but quantitative measurements were of limited value. Carius (59) bubbled ozone, generated electrochemically or electrically, through water for times ranging up to several hours and found that the resulting aqueous solution gave a variety of positive tests for ozone except for difficulties in the reaction with silver metal. His results were confirmed by Rammelsberg (61). Later Leeds (62), using ozone generated by the phosphorus reaction, succeeded in obtaining a positive silver reaction. Carius measured the amount of dissolved ozone by iodimetric titration. He obtained a considerable range of values, the maximum solubility observed corresponded to a concentration of 8.81 cc (STP, 0.0189 g) of ozone per liter of water at 18.2° and 741.5 mm using 3.29 volume percent (4.93 weight %) of ozone in oxygen.

The best determinations were those of Mailfert (63) who allowed ozone (from air or oxygen, not stated) to stand over water and determined the concentrations of ozone both in solution and in the headspace. He measured these concentrations at 12 temperatures between 0 and 60° by titration with arsenious acid (method of Thenard) so that his results are ratios and not subject to the problem of iodimetric analysis. The coefficients of solubility (ratio of g/l of ozone in solution to g/l in the gas phase ranged from 0.64 at 0° to 0.03 at 55°. Ladenburg’s results (64), determined in an unspecified manner, were not in agreement.

Thus, by 1900 it was clear that ozone had significant, but low solubility in water and that, when stored over water, it decomposed slowly at room temperature, presumably via a thermal reaction. These facts acquired considerable importance with the use of ozone for purification of water (see section on practical applications of ozone).

2. Liquid Ozone

The desirability of obtaining ozone in the pure state rather than as a minor component of air or oxygen was appreciated from the beginning of ozone research. Andrews attempted without success to achieve this by cooling with solid carbon dioxide (dry ice); the temperature was not sufficiently low. Progress in cryoscopic techniques made this possible.

Shortly after Cailletet and Pictet succeeded (1877) in liquefying nitrogen and oxygen by adiabatic expansion of pressurized gas, Hautefille and Chappuis (65) reported obtaining concentrated ozone as a deep blue gas using the new technique and starting from ozone-
oxygen mixtures produced by silent discharge at low temperature; they stressed that the gas must be maintained at low temperature to avoid explosion. Later the same year (66) they repeated their experiments with a mixture of ozonized oxygen and carbon dioxide. The result was a mixture of colorless carbon dioxide and a blue liquid, presumed to be ozone. Two years later (67), with the apparatus of Caillletet, ozone itself was obtained as a deep blue liquid which was stable at low temperature. Except for the color which stimulated subsequent work of Chappuis on spectra of ozone, the only additional information from this work was the observation that the mercury used for pressurization was not attacked at low temperatures. Explosions were encountered in the work with gaseous ozone due to ethylene coolant coming in contact with ozone and have plagued workers using high concentrations of ozone ever since.

Attempts by Olszewski (68) to obtain liquid ozone using boiling ethylene (-102.5° C) as coolant were not successful, but he did obtain larger quantities of deep blue, liquid ozone (from ozone-oxygen mixtures generated by silent discharge) using liquid oxygen as coolant. He did not succeed in obtaining ozone as a solid by pumping on the liquid although this method was successful in converting liquid ethylene to the solid. He did not succeed in obtaining ozone as a solid by pumping on the liquid although this method was successful, but he did obtain larger quantities of deep blue, liquid ozone. He emphasized by the complete destruction of his glass apparatus to a powder when a sample of ozone came in contact with ethylene at the boiling point of ozone. He observed that the liquid was stable when cooled by liquid ethylene at -140° C. By slow warming of such a system, the boiling point of ozone was determined to be around -106° C. The care required in these experiments was emphasized by the complete destruction of his glass apparatus to a powder when a sample of ozone came in contact with ethylene at the boiling point of ozone. Samples of ozone alone did not explode. A sample sealed in an ampoule gave a blue gas at room temperature.

Using a similar procedure, Troost (69) determined the boiling point of ozone to be -119° C. The present handbook value is -111.35° C, halfway between Troost’s and Olszewski’s values. Troost used an oxygen-ozone mixture generated by operating a Berthelot (silent discharge) tube at -79° C (dry ice-methylene chloride); liquefaction was achieved by cooling with liquid oxygen. Ladenburg (64) also attempted to determine the boiling point of ozone but surrendered after a violent explosion occurred upon warming a sample of liquid ozone to -125° C.

3. Absorption and Emission Spectra

Very shortly after the observation that ozone gas was blue, Chappuis (with Hautefille’s blessing) studied the absorption spectrum of ozone in the visible region of the spectrum. A preliminary report (70) was published in 1880 followed by a second paper (71) in 1882 on the spectrum of gaseous ozonized oxygen measured in a 4 meter tube. The most intense band was observed between 5935 and 6095 Å, an additional ten bands were observed between 4440 and 5770 Å. Chappuis’ results were confirmed by Schöné (72) and later by Liveing and Dewar (73). Olszewski (74) observed some of the ozone bands in spectra of liquid oxygen and liquid air and Dewar (75) obtained similar results in spectra of oxygen gas at pressures of about 80 atm. Schöné also reported that the spectrum of ozone could be detected in the atmosphere, particularly during the Russian winter when the concentration of water vapor in the atmosphere was minimal. He suggested that spectroscopy could be used for quantitative analysis of ozone. In fact, Chappuis and Schöné (76) had used spectroscopy in 1881 for qualitative analysis of the products formed in silent discharge of moist air; Otto’s colorimetric apparatus for ozone analysis was mentioned earlier.

The absorption spectrum in the ultraviolet region was reported by Hartley (77) one year after Chappuis’ first paper. He used ozonized oxygen in a 91-cm tube with quartz ends and, correcting for the absorption spectrum of oxygen, found a broad absorption in the ultraviolet with its mean at 2560 Å.

It should be noted that extinction coefficients were not determined in any of this work. However, the views of these workers were, in part, remarkably modern. They considered it very likely that ozone existed in the upper atmosphere and in higher concentration than at ground level. Hartley, as well as Dewar and Liveing, suggested that the short wave length limit of solar radiation at the surface of the earth was due to light absorption by atmospheric ozone. How right they were! The suggestion by Hartley that light absorption by ozone is responsible for the blue color of the sky was less fruitful.

Otto (78) reported that shaking gaseous ozone with a variety of organic liquids resulted in phosphorescence which could also be observed with highly purified water but not with ordinary water. He suggested that this was due to the highly exothermic decomposition of ozone as did Chappuis (79) in experiments on the reaction between ozone and phosphorus. The effect of impurities was attributed to destruction of ozone by chemical reaction.

Sarasin (80) arced (platinum, silver, or brass electrodes) pure oxygen at low pressure (e.g. 3 mm) and
observed a whitish light emission for a number of seconds after interrupting the current. The presence of powdered silver resulted in reaction typical of ozone and partly quenched the emission. Hydrogen, nitrogen, chlorine, and iodine gases did not give such a result. Sarasin’s technique was to close his eyes and only open them when he interrupted the current. De la Rive’s comments (81) followed. Dewar (82) observed a similar phenomenon and showed that the region of phosphorescence gave a positive starch-iodide test.

4. Specific Magnetism

Becquerel (83) studied magnetic properties of a number of gases. Continuing work of his father who had found (1850) that oxygen presented remarkable anomalies, he investigated the ozone-oxygen mixture obtained by silent discharge on oxygen. He was unable to determine precise numerical values because of decomposition of ozone, but stated that ozone is more magnetic than oxygen by an amount which is much greater than the density effect of ozone.

5. Effect of Ultrasound

In a paper on the effect of ultrasound on various substances, Berthelot (84) reported that there was no effect of ultrasonic radiation on ozone after one and one-half hours exposure at 7200 Hz.

Formation and Practical Preparation of Ozone

Investigations on the formation of ozone and practical methods for its preparation were a major effort in ozone chemistry during this period. By the end of the 19th century, the silent discharge method had supplanted other procedures and became the method of choice. Siemens and Halske as well as other companies supplied laboratory and industrial apparatus for generating ozone and the Berthelot tube had become the device of choice in such instruments. We note that odor and/or positive starch-iodide tests were often taken as establishing the presence of ozone. While these are indicative, they are hardly conclusive and a number of workers were led astray by such tests.

The idea that ozone was formed by combination of an atom of oxygen with a neutral molecule (reaction 5) seems to have been first expressed by Than (85) in 1870 and gained wide acceptance.

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]  (5)

For example, both the Engler (5) and Leeds (6) reviews included it as accepted fact although direct evidence was absent. Baumann (86), referred to atomic oxygen as a fact without feeling the need for justification and Leeds published two papers (87a,b) entitled “The Atomation of Oxygen.” Shenstone and Priest (38) proposed in 1893 that the function of the silent discharge was formation of oxygen atoms.

The discussion on formation and preparation of ozone is divided into the following sections:

1. Electrical Discharge for Ozone Production.
2. Electrolysis of Aqueous Solutions.
4. Miscellaneous Chemical Methods, Real and Unreal.
5. Thermal Formation of Ozone.

1. Electrical Discharge for Ozone Production

As noted above, the silent discharge method for preparing ozone became the method of choice for laboratory and subsequent industrial preparation of ozone. Houzeau became so enamored of this method that he predicted that it would be possible in the future to prepare pure ozone, a result which has never (fortunately, in view of the hazards) been achieved. A large number of papers as well as numerous patents appeared (an undoubtedly incomplete list of such patents is available from the author) describing variations in the design and operation of such equipment. Thomson and Threlfall (88) established, as did Bichat and Guntz (89), that a high potential was not sufficient, there had to be an actual discharge for ozone to form. Meissner (3) also addressed considerable attention to this question.

The heart of any ozone generator is the silent discharge tube through which oxygen or air flows with application of high voltage alternating current. Interestingly, such tubes have been described even in more modern times (90) as “Berthelot tubes”. In 1877 Berthelot (91) reported details of an apparatus for producing ozone by silent discharge which included detailed drawings and instructions for construction and operation. Undoubtedly its wide acceptance and the credit it received were due, at least in part, to the fact that it worked well and that so much detailed information was provided. He also reported (92) that combination of oxygen with hydrogen does not occur when a mixture of the two is subjected to the silent discharge.

The use of oxygen rather than air was preferred. Not only was a higher yield of ozone obtained, but the
formation of oxides of nitrogen could be avoided. Both dry and moist oxygen could be used as shown by a number of workers (37,38,88,93) but best results were obtained using pure, dry oxygen (94). Temperature was shown to play an important role in determining the yield. Among others, Hautefille and Chappuis (36,95) showed that the yield of ozone doubled when the temperature of operation was reduced from +20° C to -73° C. Otto (94), reported that the yield increased from 5.2 volume percent of ozone at 20° C to 10.4% at -73° C. Otto (94), using a variation of the Siemens apparatus at a potential of 6000 volts, found that the yield of ozone improved fairly regularly with increasing frequency of alternating current, obtaining 175 mg ozone/liter (ca 9%) at the highest frequency (83.5 Hz). Villon (96) reported use of voltages on the order of 100,000 volts and high (unspecified) frequencies for industrial preparation of ozone. Ozone formation also proceeded at reduced oxygen pressure. Hautefille and Chappuis (36a,c) found an interesting effect, presumably thermal in origin, when operating below 50 mm oxygen pressure. Using pressure change to measure formation of ozone, they found the expected decrease in pressure until the discharge was interrupted, at which point the system returned to its original state in a short time.

Leeds (97) made a study of the ozonizers of von Babo and Claus (98), Houzeau (99), Wright (100), Boillot (101), Wills (102), and Siemens (1). He concluded that the Siemens version was much superior both in terms of yield of ozone and reliability of operation and described his own version of the Siemens apparatus.

2. Electrolysis of Aqueous Solutions

The electrolysis of aqueous, acidic solutions led to Schönbein’s discovery of ozone (1) and was used preparatively by some of the early workers in the field. It has the potential for giving higher concentrations of ozone than any of the other conventional methods, as demonstrated by McLeod (28) who claimed concentrations of ozone as high as 16 volume percent under certain conditions. Electrolysis was rarely used, however, probably due to lack of familiarity with design of electrodes and operation of such equipment as well as to the convenience of the silent discharge method. Leeds (9) stated that “electrolysis was not found a convenient method of preparing ozone in considerable quantities.”

The new work done on electrolysis during this period was mainly concerned with the composition of the aqueous solution from which ozone and oxygen had been liberated and which had considerable oxidizing power on its own. Berthelot (60) and later Richarz (103) studied the effect of temperature, current density, and acid concentration on the formation of persulfuric acid and hydrogen peroxide, both of which were found in the aqueous solution after electrolysis. The formation of hydrogen peroxide was attributed to reaction of oxygen atoms with water. Persulfuric acid was also formed by silent discharge on a mixture of sulfur dioxide or trioxide and oxygen (104). Le Blanc (105) claimed to have observed hydrogen peroxide formation in electrolysis much earlier (1854) but only communicated this result in 1872. He suggested, incorrectly, that hydrogen peroxide was formed by the reaction of ozone with water. McLeod (28) also noted the presence of additional oxidizing material in the aqueous electrolyte. The importance of various parameters in electrolysis was also studied by Targetti (106).

3. Photochemical Formation of Ozone

The first report of photochemical formation of ozone appeared in 1900. Lenard (107), after commenting that cathode rays were known to cause ozone formation in air, described his experiments on the effect of ultraviolet light on a number of gases using a zinc arc as light source. While no reaction was observed if a piece of window glass were placed between the light source and a sample of air or oxygen (wet or dry), a very strong ozone odor and immediate coloration of starch-iodide paper were observed using a quartz window. He commented, “The gas was not breathable.” Much work followed in later years.

4. Miscellaneous Chemical Methods, Real and Unreal

a. The Reaction of Phosphorus with Oxygen

The reaction of white phosphorus with oxygen, usually in the presence of water, was a popular method in the early days of ozone chemistry because of its simplicity and the low investment required. It became less and less important for preparation of ozone after the passage of time since it suffered from low yields and variable results although Leeds (108) described a modified procedure, also cited by Böttger (109), by using solutions of potassium dichromate and sulfuric acid instead of water for reaction with phosphorus, and claimed to achieve ozone concentrations of up to 2.5 mg/liter in air. The apparatus he developed could be purchased for $30 from his institution (Stevens Institute of Technology, Hoboken, NJ/USA). It does not seem to have attracted much interest. Interestingly, he (97) published work on an improved electrical ozonator a few months
after describing his phosphorus apparatus. Leeds confirmed earlier reports that the amount of ozone produced in the phosphorus reaction is a function of temperature, requiring a minimum of 60° and increasing up to about 25°; Engel (110) confirmed that the lower temperature limit does not apply at reduced pressure.

Kingzett (111) questioned whether ozone was formed at all in the reaction of phosphorus but later retracted this view after a strong protest from Schöne who, together with others (112,113), confirmed that both ozone and hydrogen peroxide are formed in the phosphorus reaction.

No progress whatsoever was made in understanding the process by which ozone is formed in this reaction except to claim that atomic oxygen was formed somehow and reacted with O2. Earlier workers had shown that the luminescence of phosphorus was a necessary condition for ozone formation. This was confirmed by Chappuis (79), who also suggested that decomposition of ozone may be accompanied by phosphorescence. Elster and Geitel (114) reported that air in the vicinity of reacting phosphorus developed enhanced electrical conductivity. The first study of the kinetics of the phosphorus-oxygen reaction appeared from van’t Hoff’s laboratory in 1895; Ewan (115) found a square root dependence on oxygen pressure for the rate of reaction of phosphorus with dry oxygen (reaction was more rapid in presence of moisture) and suggested that the kinetics supported the idea that oxygen molecules were cleaved into two oxygen atoms. He did not go further to suggest that these were responsible for formation of ozone in a subsequent reaction with molecular oxygen. His work was followed by a paper of van’t Hoff himself (116) suggesting that the cleavage of oxygen might involve formation of one negatively and one positively charged oxygen atom and that only one of these was effective in producing ozone.

Molnar (117) investigated various factors, such as moisture content and atmospheric components, affecting the ignition temperature of phosphorus. He reported that turpentine combines with oxygen in the presence of phosphorus.

b. Reaction of Elemental Fluorine with Water

One procedure which does appear free of doubt is the work of Moissan (118) on the exothermic reaction of elemental fluorine with water. He reported concentrations of ozone as high as 14.4 volume percent (using titration of acidified KI solutions for analysis, correct values were probably lower) by bubbling fluorine gas through water at 0° in a copper vessel. The gas was blue at these relatively high ozone concentrations.

c. Chemical Reactions that do not Produce Ozone.

A number of reports of ozone formation, some dating to earlier times (1), were shown to be the result of impurities in the reagents; the odors and positive starch-iodide tests observed were apparently due to chlorine containing impurities. Purification of reagents resulted in disappearance of the supposed positive ozone tests.

These include the reaction of concentrated sulfuric acid with potassium permanganate or dichromate reported once again by Valentini (119) and shown by Rammelsberg (61), Leeds (97), Frye (120), and Ilosva (121) to be incorrect. A patent even appeared describing the use of this method for preparation of ozone and Winkler (122) based a lecture demonstration on the supposed ozone formed. Leeds (97) reexamined earlier qualitative reports that the action of sulfuric acid on barium peroxide, a known method for preparation of hydrogen peroxide, produced ozone. He reacted 20 g of barium peroxide with sulfuric acid, passed the gas through a series of water-containing wash bottles to remove hydrogen peroxide and determined that 14 mg (!) of ozone were formed. It should be noted that aerosols of hydrogen peroxide can pass unchanged through water washes.

Croft’s report (123) that crystallization of iodic acid results in formation of ozone, detected by odor and starch-iodide test, was shown by Leeds (97) to be due to impurities, purified iodic acid did not show this behavior. There were also reports of an ozone odor associated with waterfalls (124) and with salt evaporation installations (125). Bellucci (126) confirmed earlier work by Cloez that ozone is not produced together with the oxygen of growing plants. Brunck’s claim (127) that heating a mixture of potassium chlorate and manganese dioxide produced ozone was refuted by McLeod (128). Brunck also claimed (129) that heating a number of metal oxides ((Mn, Co, Ni, Ag, Hg, Pb, Cr, U) resulted in ozone formation based on positive starch-iodide tests given by the evolved gases—in spite of a report by Leeds (130) 15 years earlier that washing the gases formed by heating metal oxides (Hg, Mn, Pt, Ag, also periodic acid) with small volumes of water gave aqueous solutions testing positively for chloride and gases testing negatively for ozone. Color tests alone were also the basis for Kappel’s report (131) that pas-
sage of air over copper metal covered with aqueous alkali resulted in oxidation of the copper and formation of ozone and hydrogen peroxide.

As noted in reference 1, confusion arose between ozone and the peroxidic products formed by the action of light and oxygen (photo-oxygenation) on a variety of compounds. This continued (132) although considerable evidence was provided that the products of these reactions were derived by combination of oxygen with the organic substrate. In particular, Berthelot (133) concluded that the oxidizing action in such cases was due to an oxidizing substance formed by reaction of the substrate with oxygen and not to ozone, other workers agreed including Kingzett (134) and Engler and Weissberg (135). Dumas (136) established that ozone is not formed in alcoholic fermentation.

5. Thermal Formation of Ozone

Thermal instability was one of the first properties of ozone described by Schönbein and was repeatedly confirmed by other workers (see section on thermal decomposition): juxtaposition of the words thermal and formation sounds like an oxymoron. Nonetheless, a number of disputed claims of thermal formation of ozone were mentioned in ref. 1 and continued to appear. Many of these were reports (137) of formation of ozone in flames. The first of these was due to Than (137a) in 1870 who claimed to have detected the odor of ozone after holding a cool, inverted beaker over a flame. Cundall’s report (137b) is similar: “air aspirated through a tube fixed about 5 mm from the flame of a Bunsen burner both tastes (!) and smells strongly of ozone.” The quantities of ozone, if formed at all, were insufficient for other methods of identification. Leeds (87b) carried out combustion of purified hydrogen in purified air and identified hydrogen peroxide and ammonium nitrite, he found no evidence for ozone. The best experiment, still unsatisfactory, was performed by Dewar (138) who designed an apparatus in which air was drawn over platinum heated to about 1600° and then rapidly quenched to normal temperature by contact with flowing water as it left the hot area. He stated that the aqueous product of this rapid quenching contained ozone but unfortunately gave no evidence at all in support of this statement. Bichat and Guntz (139) carried thermal formation of ozone to the extreme of proposing that the formation of ozone by electrical discharge was due to the heat developed in such equipment and was not an electrical phenomenon at all.

Critics (140) of the thermal formation of ozone emphasized that the positive tests observed were hardly conclusive proof of the presence of ozone. One explanation for the effects observed was formation of nitrogen oxides (141) although Pincus (142) reported that the ozone odor was observed from combustions with pure oxygen. The most reasonable position was probably that of Engler (143), who argued that oxygen atoms were probably formed in combustion or thermal reactions and could react with oxygen molecules to form transient ozone. Resolution of this question required the future development of appropriate methods of analysis and received considerable attention during the first part of the 20th century.

Thermal Decomposition of Ozone

The thermal instability of ozone was one of the first properties established by Schönbein and was observed by many other workers. It was eventually shown to involve reaction 3b, which accounts for the increase in volume of the gas upon heating or standing as first reported by Andrews and Tait in 1857. Qualitative studies on the rate of decomposition were made by Berthelot (144) who studied the decomposition of ozone at 12° in glass vessels using iodimetric titration for analysis and found that the concentration was reduced to 55% of its original value after five days, independent of the presence or absence of water. He also found that the presence of platinum foil had no appreciable effect. Brodie (26) also made a brief study of decomposition at various temperatures. Mulder (145) determined that the rate of thermal decomposition depended on concentration of ozone, on pressure, and on temperature. Richarz (146) examined the decomposition of ozone in a water vapor stream and found that hydrogen peroxide was formed.

This decomposition of ozone to oxygen requires that stored samples of ozone, even at room temperature, be analyzed immediately before use. The reaction is catalyzed by platinum black as found by Mulder and van der Meulen (147) who observed rapid decomposition at room temperature and exploited this behavior in thermochemical studies as described in the section below on thermochemistry.

The first attempt to determine the mechanism of the thermal decomposition was due to Remsen (148), who suggested that the decomposition products of a molecule of ozone would be one molecule and one atom of oxygen. He and others (149) had previously established that carbon monoxide is not oxidized by ozone.
but is converted to carbon dioxide by supposed atomic oxygen (from reaction of palladium-hydrogen with oxygen). The Remsen experiment involved thermal decomposition of ozone in the presence of carbon monoxide; if oxygen atoms were involved, CO should be oxidized. The experimental result was absolutely no formation of CO₂. A bimolecular alternative, also proposed by Debus (150), was suggested as a possibility for the thermal reaction.

Hautefille and Chappuis (36) studied the formation of ozone by electrical discharge using the pressure change of the system as analytical tool. At low oxygen pressure (below about 50 mm), they found that interruption of the discharge was followed by rapid decomposition of ozone until the pressure was restored to the original value before discharge. The pressure could be made to oscillate by repeated interruption of the discharge. They attributed this behavior to thermal decomposition of ozone, apparently because dissipation of heat was inefficient at the low pressures of gas used.

Thermochemical Studies

The first attempt to study the thermochemistry of ozone was due to Woods (151), who was interested in distinguishing between the atomic proposal of Clausius and the O₃ composition for ozone. He found that reaction of ozone with nitrous oxide or with oxygen resulted in identical temperature increases and was not able to go further.

Quantitative thermochemical studies were first performed by Hollmann (152) in 1868 in response to a challenge issued in 1864 by the Society of Arts and Sciences in Utrecht. He determined the difference in the amount of heat evolved by flames (hydrogen, methane, ethylene and flames of a number of liquids) in pure oxygen and in ozonized oxygen. The amount of ozone present was determined by the iodimetric method but it is not clear what stoichiometry he employed. All of the measurements gave values in good agreement and corresponded to about 355.5 cal/g for the thermal decomposition of ozone. For the decomposition of two ozone molecules (reaction 3b) this corresponds to 34.1 kcal/mol, much lower than later values. Fairley (153) considered a bimolecular mechanism for thermal decomposition of ozone.

Berthelot (154), apparently unaware of the work of Hollman, used a different method. He determined the heat of the oxidation of arsenious to arsenic acid by ozone (oxygen does not react with arsenious acid) presumably according to reaction 2. Ozonized oxygen (generated by silent discharge on pure oxygen) was bubbled through a standardized solution of arsenious acid in a calorimeter and the amount of unreacted arsenious acid determined. The oxidation liberated 4.3 kcal/g of ozone reacted, correcting for the heat of oxidation of arsenious acid (using earlier values), he obtained for reaction 6:

Further work was done by Mulder and van der Meulen (155) using a modification of the Berthelot method, they obtained slightly higher values; they used equation 3b so that their numbers (63.3 and 66.7 kcal/mol) are approximately twice those of Berthelot. van der Meulen went on to do a direct determination of the heat of decomposition of ozone using the platinum black catalyzed decomposition. He found a value of 71.8 ± 1.3 kcal (average of three experiments) for reaction 3b.

Mulder (156) also reported the first studies of the rate of decomposition of ozone using an ozonometer based on the pressure change observed during the reaction.

\[
3(O) \rightarrow O_3 - 29.6 \text{ kcal} \quad (6)
\]

Inorganic Reactions

Schönbein’s earliest work with ozone described oxidation of a variety of inorganic compounds including elements and compounds such as sulfites and nitrates. The general result was oxidation to the highest oxidation state. Many, but not all, of these reactions resulted in formation of molecular oxygen in addition to the oxidation product. Considerable repetition and extension of such experiments was reported later including work by Brodie (26), Volta (157), Ogier (158), Mailfert (159a,b), and Maquenne (160). Aluminum, copper, gold, palladium, and platinum were found not to react with ozone. Volta also showed that hydrogen was not oxidized by ozone except when the hydrogen was adsorbed on platinum or palladium.

The presence of water was suggested to be essential in some cases, such as the reaction with mercury (158) and with silver metal, and the reaction of ozone with lower oxides of nitrogen (161). The reaction with mercury was investigated in detail by Shenstone and Cundall (37) who prepared ozone by silent discharge on highly purified, carefully dried oxygen and reported that the resulting ozone decomposed without reacting appreciably with mercury in contrast to the results of
Volta (157) and other reports that mercury could not be used in volumetric apparatus because of its reaction with ozone.

In contrast to earlier reports, Schöne (162) found that ozone decomposed rapidly in the presence of dilute aqueous hydrogen peroxide. Correcting for the thermal decomposition of ozone, he was able to show that both reactants lost one atom of oxygen so that the overall process was given by reaction 7:

$$\text{H}_2\text{O}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O} + 2\text{O}_2$$ (7)

McLeod (113) confirmed this and added the observation that reaction occurred in neutral or basic but not in acidic medium.

The reaction between nitrogen and ozone acquired special interest in connection with the possibility that electrical storms might provide a mechanism for fixation of atmospheric nitrogen. While Carius (59) showed that there was no reaction between nitrogen and ozone, both he and Berthelot (163) established that reaction did occur in the presence of alkali. Many workers including Boillot (164), Hautefille and Chappuis (76), and Shenstone and Evans (165) noted the formation of nitrogen oxides in preparation of ozone by silent discharge on air; reaction occurs in the discharge tube. Similar results were obtained in phosphorus generation of ozone from air by Berthelot (163) and by Leeds (166) where ammonium nitrate and lower oxides of nitrogen were detected among the reaction products. Leeds attributed the result to formation of oxygen atoms in the phosphorus reaction. It might be noted that Hautefille and Chappuis detected hyponitrous acid spectroscopically. The reaction of ammonia with ozone was shown by Carius (167) to result in formation of ammonium nitrate and hydrogen peroxide. Thus the possibility of nitrogen fixation as an adjunct to electrical storms was established although no evidence of its reality was obtained.

Hautefille and Chappuis (95) also suggested that the apparent quenching of ozone formation in the presence of chlorine was the result of reaction of ozone with chlorine. The reaction of ozone with HCl had been established earlier (Ref. 1).

The technical difficulties involved in working with ozone at this time can be seen from investigations of the reaction of ozone with carbon monoxide in the presence of moisture, no carbon dioxide was formed after long standing either in the dark or in sunlight; this result was confirmed by Baumann (86) with ozone generated from phosphorus. On the other hand, the result obtained when carbon monoxide and air were passed together over moist phosphorus was controversial. Remsen and Keiser (169) reported that no carbon dioxide was formed using mercury seals and special precautions to avoid contact of the gas mixtures with corks and rubber at all times during the experiments. Blank runs (no carbon monoxide) without these precautions invariably gave positive tests for carbon dioxide. Leeds (170) and Baumann (86) both maintained the opposite and Leeds strenuously resisted the claim that contact of ozone with cotton (used to remove traces of phosphorus or other solids), cork, or rubber was responsible for his positive result. Eventually, it was established that traces of carbon impurity in phosphorus were responsible for the CO₂ observed (169).

**Organic Reactions**

Schönbein (1) had noted in 1847 that ozone does not oxidize organic compounds to carbon dioxide, the highest oxidation state of carbon. Oxidation does occur with a variety of compounds but only to intermediate states in contrast to most inorganic reactions which afford the highest possible oxidation state. Reactions of a random collection of substances were examined before 1869 and this characterized much of the state of affairs during the period covered by this article, with a few exceptions. The most significant work on reactions of ozone with organic compounds appeared almost at the end of the century from the laboratory of Otto (171), who examined reactions of ozone with a variety of organic compounds using defined experimental conditions followed by isolation and characterization of products. His work can be described as the first reasonably rigorous examination of the application of ozone in organic chemistry and the first recognition of the behavior of certain functional groups. It preceded the exhaustive investigations of Harries by nearly a decade (cf. Ref. 185).

The best example of Otto’s work is the synthesis of vanillin which was performed by bubbling ozonized air (5 mg ozone per liter of gas) for 24 hours into a hot (water bath) acetic acid solution of isoeugenol (100 g) followed by distillation of the acetic acid, conversion to the bisulfite adduct, liberation of the aldehyde, and purification. The crystalline product, obtained in “high yield” was characterized by its melting point and com-
bustion analysis. Anisaldehyde and piperonal were obtained similarly from anethole and isosafrole. The three starting materials were obtained by base-catalyzed isomerization of their naturally occurring allylic isomers. These were apparently converted to the corresponding substituted acetaldehyes by ozonolysis (172).

Other reactions investigated by Otto (171) and others include the following:

a. Methane reacted to give formaldehyde in low yield (171). Also Maquenne (173).

b. Ethylene (171), Houzeau and Renard (174). Tetrachloroethylene, Besson (175).

c. Acetylene gave a violent reaction with ozone, products were not identified (171).

d. Alcohols were oxidized to aldehydes and carboxylic acids. Methanol and ethanol were investigated by Otto (171), Houzeau (176), Wright (177), and Boillot (178); ethylene glycol and glycerol by Otto (171).

e. Phenol and the dihydric phenols gave some dark material but were largely recovered unchanged while low yields of the corresponding azo compounds were obtained from phenylamine and \( p \)-toluidine (171).

The case of diethyl ether is of special interest since it provided the first real example of the importance of the medium in ozonolysis reactions and showed that an intermediate product was formed. The usual procedure in early organic ozonolysis experiments, continuing into the 20th century, involved heating and treatment with water before attempted isolation of products. Under such conditions, Wright (177) observed the formation of hydrogen peroxide from the reaction of diethyl ether with ozone as did Dunstan and Dymond (179). However, Berthelot (180) showed that the reaction of anhydrous ether with ozone generated from dry oxygen yielded an explosive material which he named “peroxyd d’éthyle” and to which he assigned the formula, \( \text{C}_8\text{H}_{18}\text{O}_3 \). Hydrogen peroxide and ethyl alcohol were obtained after this product was treated with water. Houzeau (181) claimed that hydrogen peroxide was produced in the reaction of indigo with ozone to give isatin.

The reaction of ozone with benzene, first reported in 1873 by Houzeau and Renard (174), attracted considerable attention and again suggested formation of a peroxidic substance as the initial product of ozonolysis of organic compounds. Using purified benzene at 8° they obtained, in addition to formic and acetic acids, a gelatinous, explosive product, which they called ozobenzene (later ozobenzene). Analysis of this material gave the (incorrect) molecular formula \( \text{C}_6\text{H}_6\text{O}_6 \). Renard (182) confirmed this result more than 20 years later after Leeds (183) had reported failure to obtain the explosive product; Renard also reported similar formation of explosive ozotoluene and ozo-o-xylene upon reaction at 0°; ozotoluene exploded at 8°. Renard attributed Leeds’ failure to repeat the earlier results to the use of impure benzene. Leeds did observe formation of oxalic, formic and acetic acids. Otto (171) also observed oxalic acid and did obtain the explosive material using ozonized air or ozonized oxygen at 15° and at 50°. Dieckhoff (184) is cited by Harries (185) as having obtained ozobenzene as a crystalline material which exploded at 50° on rapid heating and decomposed without explosion upon slow heating. Harries later established the correct molecular formula of this material, the triozonide of benzene.

Investigations of minor importance were performed by Jouglet (186), Dumas (187), Boillot (188), Maumené (189), Leeds (190), Fradiss (191), Stelzer (192), and Wagner (193).

The first experiments relating to the structure of rubber also appeared. Wright (194) demonstrated that volatiles formed by passage of ozone through vulcanized
rubber tubing and collected in water gave an acid reaction, which he attributed to sulfuric acid. Leeds (9) also examined the reaction of rubber with ozone in connection with the storage of ozone. Serious investigation of the composition of rubbers using ozonolysis began in the 20th century.

The first attempt to establish the structure of an organic substance by ozonolysis appears to be due to Boeke (195), who tried unsuccessfully to determine the structure of pyrogallol by ozonolysis. He obtained, in very low yield, a product having the molecular formula C₆H₆O₇ but was not able to establish its structure.

**Biological Aspects**

The oxidizing power of ozone prompted speculation that it was involved in some biological oxidations (196), but no evidence in support of such ideas was obtained. The deleterious effects of ozone on the human respiratory system and on animals had been observed very early in the study of ozone chemistry, and additional results were published during the period of this review including a summary by Day. (197). These effects were confirmed by Dewar and M’Kendrick (198), Filipow (199), Schulz (200), and Renzi (201). Labbe and Oudin (202), on the other hand, claimed that animals were not affected by breathing air enriched in ozone and that hemoglobin counts increased slightly. Hearder (203) commented on the beneficial effects of ozone as well as its unpleasant character upon breathing and its negative effect on plants.

The action of ozone on bacteria and microorganisms became of considerable interest. Apparently, the first investigator to examine such behavior was Chappuis (204), who immersed cotton wads in aqueous solutions containing brewers yeast. Solutions containing wads pretreated with ozone remained clear for extended periods while solutions containing untreated wads rapidly became cloudy. The interpretation was that microorganisms on the cotton were destroyed by ozone. More extensive studies followed later, particularly in connection with the use of ozone for water purification. The first of these was due to Ohlmüller (205) in 1891, mentioning earlier work by Fröhlich, who tested the effect of ozone on typhus and anthrax bacteria. He found no effect when dried bacteria were exposed to dry ozonized air and a very slow reduction in bacterial count when either component was moist. Dramatic results were obtained when ozonized air was bubbled through aqueous suspensions of typhus, anthrax, or cholera bacteria. Bacterial counts were reduced to zero within a few minutes exposure. Ohlmüller also examined waters from various sources and studied the effect of addition of organic material where he found that ozone was less effective, presumably because of competing consumption of ozone. He concluded that treatment with ozone did not appear promising for purification of air but offered excellent prospects for water treatment provided that significant amounts of organic material were not present.

Similar results were reported by van Ermengen (206) four years later in a pilot study of water purification of the Vieux-Rhin River at Oudshoorn near Leiden. In another study, Calmette (207), reporting to the city of Lille on water purification apparatus designed by Marmier and Abraham (208) for treatment of water from the Emmerin River near Lille, also noted complete destruction of pathogenic organisms. The use of ozone for water purification was described as a triumph.

On a completely different note, a variety of commercial preparations of “Ozone Water” were marketed for therapeutic purposes at this time. Rammelsberg (61) tested the product of Krebs, Kroll, and Co. and found that it contained significant amounts of chloride ion. He concluded that such preparations contained, in fact, hypochlorite and not ozone. He cited work by Behrens (209) and a letter from Carius on the subject; both of these workers arrived at the same conclusion, as did Vulpius (210). Dr. Graf and Comp. (211) marketed a stable ozone water for medical purposes obtained by passing ozonized oxygen into water containing supposed stabilizers such as sodium chloride or magnesium chloride, and Jeremin (212) reported that ozone dissolves to a considerable extent in aqueous oxalic acid, that such solutions are stable, and that they can be used as a disinfectant particularly after aging. *Caveat emptor.*

**Practical Applications of Ozone**

Discussions of practical applications of ozone began to appear with increasing frequency as improved methods for its preparation were developed. The high reactivity of ozone combined with the fact that its decomposition product was harmless oxygen prompted numerous suggestions for its use. The first to appear was apparently a report by Widemann (213) who, during a trip to America, introduced the treatment of whiskey with ozone in Boston and the production of vinegar in White Plains, NY.

Andréoli (214) presented a long lecture to the London Industrial Chemical Society on production and applications of ozone in 1897 following his 1893 book.
He described the merits of the ozone-generating apparatus of his design (216), which could be operated continuously to produce 30 g of ozone per electrical horsepower hour from air, and went on to present his vision of present and future practical applications of ozone, giving credit to an earlier presentation on this subject by Fröhlich (217). Among the potential uses he described were the purification of water and air, the treatment of foods (improvement of molasses, upgrading of fish oils, bleaching of sugar syrups), and beverages (coffee, beer, wine, brandy). He noted that ozonized oxygen must be used in certain cases to avoid the presence of nitrogen compounds formed when air is ozonized. In conclusion, he called on industry to engage in more active research on the use of ozone. Villon (218) also reported in some of the above applications.

On the same note, Engledue (219) presented a lecture to the same body one year later on the work of the Commercial Ozone Syndicate in England, which was concerned with economic aspects of commercial applications of ozone. The apparatus used was capable of generating 175 g of ozone per electrical horsepower hour, significantly more than Andreoli’s equipment. The applications being studied were the cleaning of brewers casks, refining and bleaching of linseed oil, and preparation of a variety of other oils. An interesting discussion followed, the general point of view being that treatment with ozone was too expensive to be practical except for materials of high value used in small quantity; large-scale applications such as treating drinking water were considered to uneconomical. Kershaw (220) arrived at a similar opinion and concluded that bleaching powder is a much more economical agent than ozone. In connection with the use of ozone for purifying water and beverages, he noted that unforeseen difficulties might arise. Another summary of applications of ozone was due to Krüger (221).

In fact, investigations of the purification of municipal water supplies had already begun when the papers above were published. The efficacy of ozone in rapidly destroying bacteria present in water was established (previous section) and the fact that no undesirable products were produced was emphasized. Ohlmüller (205) reported in 1891 the use of an apparatus developed by O. Frölich (from Siemens and Halske) using water from the River Spree and canal water. The only caveat in his work was the observation that the presence of significant amounts of organic matter reduced the effect on bacteria. Similar positive results were obtained by van Ermengen (206) on water from the Vieux-Rhin river at Oudshoorn near Leyden at a facility of the Cie générale pour la fabrication de l’ozone founded by Baron Tindal. Again, Frölich from Siemens and Halske was responsible for the design of the ozone generating equipment. Marmier and Abraham (208) performed similar studies on water from the river Emmerin near Lille, using an ozone generator based on Berthelot tubes. As noted in the previous section, a municipal commission chaired by Calmette (207) reported that the results were a triumph. The bacterial populations were reduced to zero with the exception of a trace of B. subtilis, a harmless bacterium; the organoleptic properties of the water were much improved; and no harmful effects of the ozone treatment could be detected. The commission enthusiastically recommended that the municipality adopt ozone treatment for its water supply. In all of these cases ozone generated from dry air was bubbled through the water. Much activity in water purification followed in subsequent years.

The purification of air by treatment with ozone was also discussed by a number of workers during this period. However, Ohlmüller (205) showed that this was much less likely to be efficacious than water treatment. Unsupported claims that breathing low concentrations of ozone was beneficial were made. Carvalho’s (222) description of an ozone generator for home use was followed by critical comments of Thenard (223) on the hazards of exposure to ozone.

**Atmospheric Ozone**

Except for the odor associated with electrical storms and the experiments of Andrews (1), little direct evidence was obtained for the presence of ozone in the atmosphere until 1885. Schöne claimed (224) in 1880 that all of the supposed evidence, even including the odor associated with electrical storms, could be explained by assuming the presence of hydrogen peroxide and Ilosva (225) questioned if ozone or hydrogen peroxide were present in air. Engler and Wild (226) reported an unsuccessful attempt to develop a procedure for first removing other components of atmospheric air and then analyzing for ozone. Nonetheless, the majority of chemists accepted the existence of atmospheric ozone and ozonometric measurements continued unabated. The first direct evidence was provided in 1885 by Schöne himself (227), who measured the spectrum of the atmosphere during the Russian winter (when interference by water vapor was minimal) and found bands characteristic of ozone as mentioned earlier (see spectroscopy section).
The commercial availability of kits, based on Schönbein’s or related procedures, for measuring relative ozone concentration meant that gentleman scientists as well as professional researchers could perform atmospheric ozone measurements easily for a modest investment. The results of such measurements to 1873 were summarized in the book by Fox (4). In one table he lists 52 locations where ozone measurements were made over significant periods of time. Among the many factors mentioned (often without citation, most of the citations given were to local journals) which workers of that time attempted to evaluate were: the effect of barometric pressure, elevation (ranging from various positions on the cathedral at Metz to the Alps), location (country, seaside, different locations in cities, closed rooms, hospitals), time of day, time of year, weather conditions (barometric pressure, wind, cloud, rain, snow, sun, fog, thunderstorms), phases of the moon, eclipses, asteroids, earthquakes, sunspots, etc. ad nauseam. In some cases, thousands of observations were made over periods of years in a single location. Other summaries were provided by Leeds (8,9,) and Houzeau (228). Houzeau mentioned Wolfe at Bern (1845), Boekel at Strasbourg (1853), Grellois at Constantinople (1855), Cook at Bombay (1863,4) and above all Berigny at Versailles (1855-70) as active in use of starch-iodide papers.

Numerous suggestions were also made that ozone levels correlated with public health. For example, Day (197), while dismissing some such suggestions, was convinced that cholera epidemics were related to the concentration of ozone in the air. Other workers, such as Wolflhub gel (229) also proposed such correlations. The ozone measurements were performed by scores of investigators all over the world including Australia, North and South America and most countries of Europe. Proper use of Schönbein’s procedure requires attention to quality of the paper, purity of reagents, conditions of measurement, etc. As we have noted earlier, there was general dissatisfaction with the method, particularly because of its lack of selectivity. Conclusions reached were often contradictory and most of this work can only be consigned to history. However, recent investigations by Sandroni et al (230) and Marenco et al. (231) have shown that Schönbein results can be converted into numerical values for ozone concentration and that measurements made by expert personnel in locations free of man-made pollution provide reliable data. Results (1876-1910) from the Montsouris observatory near Paris are being reexamined (232).

An intriguing suggestion that oxygen should be converted largely or completely to ozone in the upper atmosphere was made by Sutherland (233). This was based on a number of anomalies observed in the behavior of oxygen gas including: (a) a discontinuity observed by Bohr in the Boyle’s law behavior for oxygen between 11.4 and 14°C at pressures of about 0.7 mm mercury, (b) anomalous phenomena in measurements of radiometer repulsions under similar conditions by Crookes, and (c) results of Baly and Ramsay on expansion of oxygen gas at low pressure. Sutherland’s explanation for these anomalies was the formation of ozone from oxygen or vice versa, thus changing the actual gas concentrations.

Antozone

This phenomenon, originally proposed by Schönbein, was discussed in Part 1 of this series (1). Considered to be a positive complement to negative ozone, it was identified by Meissner and others as the white cloud accompanying ozone formation until Engler and Nasse (234) demonstrated in 1870 that this was simply an aerosol suspension of aqueous hydrogen peroxide. Leeds wrote a scathing report in 1879 on the history of antozone (235). References to antozone continued to appear sporadically (236) but it rapidly faded into well-deserved obscurity and remains only a historical curiosity.

Conclusion

By the end of the 19th century, ozone had been obtained as a pure liquid, its boiling point established, its composition as O3 repeatedly confirmed, and its heat of formation from oxygen determined, as well as qualitative ultra-violet and visible absorption spectra. The first speculations on the structure of ozone also surfaced. No single
figure dominated the ozone scene to the extent that Schönbein had done in the period from 1839-68. Marcellin Berthelot, who published about 20 papers on ozone during the period of this review, is probably the most outstanding.

Reliable methods for preparation and analysis had been developed and commercial equipment for preparation of ozone became available. Photochemical formation of ozone was also discovered. The thermal decomposition of ozone began to be studied in detail. The beginnings of rational investigation of its reactions with organic compounds appeared and a variety of inorganic reactions were established. Practical application of ozone for water purification and other possible uses were developed.

An enormous number of measurements of ground level concentrations of ozone were performed with very little merit. The presence of ozone in the upper atmosphere and its function as a filter for short wavelength ultra-violet radiation were suggested.

Ozone was poised for the great increase in its importance which occurred during the 20th century.

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REFERENCES AND NOTES

4. C. B. Fox, Ozone and Antiozone. Their History and Nature, J. & A. Churchill, New Burlington Street, London, 1873. This book had the following dedication: “To the memory of the great and illustrious father of ozonometry C. F. Schönbein, Professor of Chemistry at Basle, whose brilliant scientific researches deserve the gratitude of the world, the following pages are dedicated.” Cornelius Benjamin Fox, M. D. Edinburgh. Member of the Royal College of Physicians, London. Fellow of the British Meteorological Society; Fellow of the Obstetrical Society; Member of the Scottish Meteorological Society, etc.


J. Hammerschmied, *Das Ozon vom chemischen, physiologischen und sanitären Standpunkte*, lecture delivered April 9, 1873, supplied by Gerold’s Sohn, Vienna, 1873, pp 395-525.


J. Wislicenus, Ed., *Regnault-Strecker’s Kurzes Lehrbuch der Chemie, Anorganische Chemie*, 9th ed., F. Vieweg, Braunschweig, 1877, 73ff. Johannes Wislicenus, 1835-1902. Studied in America and then Halle and Zürich. Professor in Zürich, Würzburg (from 1872), and finally Leipzig (from 1885); he made important contributions to the stereochemistry of organic compounds and methods of organic synthesis.

H. Kolbe, *Kurzes Lehrbuch der Anorganischen Chemie*, Braunschweig, 1877, pp 106ff. Adolf Wilhelm Hermann Kolbe, 1818-84. Studied with Wöhler, Bunsen, and Playfair. Prof. Chem. in Marburg from 1851, he moved to Leipzig in 1865. From 1869 editor of *J. Prakt. Chem.* A pioneer in theoretical and organic chemistry, he is best known today for his article ridiculing van’t Hoff’s proposal (he did not refer to LeBel) of the tetrahedral carbon atom.


A. Ladenburg, “Vorlesungsversuche mit flüssiger Luft,” *Ber.*, 1898, 31, 1968-9. Albert Ladenburg, 1842-1911. In 1870 Privatdozent in Heidelberg; from 1874 Prof. of Chem. at Univ. of Kiel, from 1889 at Univ. of Breslau. In addition to his work with ozone, he was active in alcaloid chemistry and worked on the structure of benzene (“Ladenburg benzene”).

Schönbein’s ozonometric kit was marketed by Buchbinder Burgoy of Basel. Another supplier was Krebs, Kroll and Cp, who marketed an ozonometric paper with a scale of 0-15.

T. Moffatt, as reported in *Ber.*, 1872, 5, 814.


D. Tommasi, reported in *Ber.*, 1874, 7, 1026.

siques et naturelles. From 1876 Prof. of medicin physique at the Univ of Geneva.


45. Ref. 26, p 465.


86. E. Baumann, “Zur Kenntnis des aktiven Sauerstoffs,” Z. Physiol. Chem., 1881, 5, 244-56. Eugen Baumann, 1846-1896. M.D. 1879. Privatdozent, then extraordinary in Physiological Chem. at Univ. of Berlin and then Prof. Chem. at Freiburg i/B.


127. O. Brunck, “Über Ozonbildung bei hohen Temperaturen,” Ber., 1893, 26, 1790-94. Sestini protested that this reaction had been reported 22 years earlier by G. Orosi; F. Sestini, Reklamation der Entdeckung der ozonbildung aus Kaliumchlorat,” Chem. Zentralbl., 1895 II, 149.

128. H. M. McLeod, “ Liberation of Chlorine during the Heating of a Mixture of Potassic Chlorate and Manganic


143. Ref. 5, 1880, 16, 139.


150. H. Debus, “Chemical Investigation of Wackenroder’s Solution, and Explanation of the Formation of its Constituents.” J. Chem. Soc., 1888, 53, 278-357. His argument was based on analogy with the behavior of certain sulfur compounds. Heinrich Debus, 1824-1916, taught


184. Dieckhoff, Habilitationsschrift, Karlsruhe, 1891.


236. e.g., The title of the 1873 Fox book (Ref. 2) was “Ozone and Antozone.”

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