THE HISTORY OF OZONE.  THE SCHÖNBEIN PERIOD, 1839-1868

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Introduction

Ozone has been known as an accompaniment to electrical storms during all the history of mankind. Its first identification as a distinct chemical compound was due to Christian Friedrich Schönbein (1) (Fig. 1), Professor of Chemistry at the University of Basel from 1828. To a considerable extent he dominated the study of ozone chemistry until his death in 1868. The molecular formula of ozone was determined in 1865 by Soret and confirmed by him in 1867, shortly before Schönbein’s death. The year 1999 marks the 200th anniversary of Schönbein’s birth and is a fitting time for a presentation of the early history of ozone from the time of his first report through the rest of his lifetime. It is interesting to note that at least 13 citations of Schönbein’s work on ozone have appeared in the chemical literature during the period 1988-98.

Discovery

On March 13, 1839, Schönbein reported to the local Naturforschung Gesellschaft in Basel that the electrolysis of water produced an odor at the positive electrode which was the same as the odor produced by an arc between electrodes (2):


This odor had, of course existed since the occurrence of lightning in the presence of an oxygen atmosphere on earth. Much later, when static electricity machines were developed, van Marum (3, 4) attributed the odor accompanying operation of the machine in air or oxygen to the electricity itself and it became known as the odor of electricity. His results were largely ignored except for the term “odor of electricity.”

Schönbein had acquired a Grove cell, paid for by popular subscription in Basel, after attending a conference in Manchester during the preceding summer. This cell provided a much more powerful current than the equipment he had used previously in his studies of passivation of metals and van Marum’s “odor of electricity” was very
pronounced in his poorly ventilated laboratory. The suggestion that the odor was due to a distinct chemical substance was formally proposed in 1840 in a lecture to the Bavarian Academy of Science and to a wider audience when a letter to Faraday was read before the Royal Society (5) and one to Arago (6) before the French Academy of Science. In this latter paper Schönbein proposed the name ozone (7) for the new substance. A detailed 1840 report to the British Association for the Advancement of Science which appeared in 1841 included the following points (8):

1. The peculiar smell makes its appearance as soon as the electrolysis of water begins and continues to be perceived for some time after stopping the flow of electricity.
2. The phosphorus smell (sic) is produced at the positive electrode only, and under no circumstances whatsoever at the negative one: when the gases resulting from electrolysis of water are collected in separate vessels, the smell is perceived only in that which contains oxygen.
3. The odoriferous principle can be preserved in well-cleaned vessels for a great length of time.
4. Formation of the odoriferous substance depends upon:
   a. The nature of the positive electrode. Only well cleaned gold and platinum give the odor.
   b. The chemical constitution of the electrolytic fluid. The odor is obtained from water when mixed with sulfuric acid, phosphoric acid, nitric acid, potash and a series of oxides. It is not obtained with solutions of halides, HCl, HBr, HI, HF, ferrous sulfate, nitrous acid, or stannous chloride. Dilute sulfuric acid is best.
   c. The temperature. A strong odor develops at comparatively low temperatures, no odor when the electrolysis solution is near its boiling point.
5. Addition of powdered charcoal, iron, tin, zinc or lead filings, antimony, bismuth, arsenic, or mercury to the odoriferous gas results in almost instantaneous disappearance of the odor. Likewise small quantities of nitrous acid, and solutions of ferrous chloride, ferrous sulfate, and stannous chloride cause disappearance of the odor.
6. Clean gold or platinum plates exposed to the odoriferous principle become negatively polarized. The odor must be due to some gaseous substance disengaged (conjointly with oxygen) from the fluid due to the decomposing power of the current. But what is the nature of that substance? Is it elementary or compound? It has some resemblance to chlorine or bromine, maybe part of the family of halogenia. We can hardly help drawing from the facts the conclusion, that the odoriferous substance is a body very like chlorine or bromine. However it may be nothing but a secondary result of the electrolytic action.

In his 1840 paper (6) Schönbein remarked that the odor of ozone is very similar to that of phosphorus when exposed to air. In 1844 (13) he added the reaction of white phosphorus with moist air to the list of ozone-forming reactions, a procedure confirmed (14) by Marignac (15) and by Rivier and Fellenberg (16). Schönbein allowed pieces of phosphorus to stand with air (or air and a small amount of added water) in a closed vessel at room temperature. When the luminescence had ceased, the gas was washed with water to remove phosphoric acid and found to have the characteristic odor of ozone. A variety of tests, particularly oxidations of metals and various dyes, showed the product to have properties identical with those of electrically produced ozone, not to mention the identity of odors. One of these reactions was the oxidation of potassium iodide to give elementary iodine. This led to the starch-iodine reaction as a test for ozone, although Schönbein continued to place strong reliance on odor as a diagnostic test for ozone. The formation of ozone was shown to parallel the luminescence of the phosphorus. Later it was shown (17) that the formation of ozone is limited to white phosphorus, another example of allotropism.

A. Becquerel (18) visited Basel in 1850 and gave a detailed report of his observations to the French Academy (19). Later, an effort (20) by Fremy (21) and Becquerel to give ozone the name “electrified oxygen” was countered strenuously (22) by Schönbein, who pointed out that ozone produced by reaction of white phosphorus should then be called phosphorized oxygen and so on; the name ozone prevailed and is with us to the present day. Houzeau (23) apparently had problems with the term ozone and used the incorrect name “na-
scent oxygen” or “oxygéne odorant” until about 1870 (24), long after ozone had achieved world-wide acceptance. He did confirm the earlier results on formation and reactions of ozone.

Fremy and Becquerel’s 43-page paper (20) confirmed much of the work of Schönbein and of Marignac (see later). In addition, an important contribution was the demonstration that the very low concentrations of ozone formed by arcing oxygen must be due to the oxygen itself and not to impurities present. They repeatedly arced a sample of oxygen contained in a tube with electrodes at the closed end and immersed at its open end in potassium iodide solution. The volume of the gas decreased steadily as the arcing was continued until the volume was so small that the experiment had to be interrupted. Since the stoichiometry, as shown below, involves formation of two molecules of ozone from three of oxygen and the two molecules of ozone react with potassium iodide to form two molecules of oxygen, the volume of gas decreases steadily. This result was confirmed (25) by Andrews (26) and Tait (27).

$$3O_2 \xrightarrow{\text{spark}} 2O_3$$

$$2O_3 + 4KI + 2H_2O \rightarrow 2O_2 + 4KOH + 2I_2$$

Schönbein’s conclusions did not remain unchallenged. N. W. Fischer (28) argued in 1845 (29) that the three methods gave three different substances: the odor from arcing air was the odor of electricity as van Marum had suggested, the odor from electrolysis was due to hydrogen peroxide, and the odor from reaction of phosphorus was simply phosphoric acid. A brief polemic between the two ensued (29, 30), Schönbein arguing that Fischer did not know how to perform the starch-iodide test properly (31). About 10 years later Andrews (32) addressed this question and showed that the products of arcing and of electrolysis were both decomposed very rapidly to oxygen by heating at 235-240°C or by boiling water.

Another dissent (33) came from A. W. Williamson (34), working in Liebig’s laboratory in Giessen. He obtained the ozone odor from electrolysis of aqueous sulfuric acid solutions but failed to obtain anything similar from the reaction of moist air with phosphorus. This was later explained by others to be due to the fact that he used finely divided phosphorus so that the ozone formed was destroyed by reaction with phosphorus. Williamson’s paper brought forth a testy reply from Schönbein (35), who reiterated the identity of a long list of properties (eleven in all) of the electrolysis and phosphorus reaction products and went on to chide the young man for his lack of faith in his elders, “Does Herr W. not believe him and Marignac?”

Objections aside, ozone was quickly accepted by the chemical world of the mid-19th century. It presented a number of fascinating challenges: 1) determination of its composition, 2) its isolation as a pure substance, 3) the study of its chemistry, and 4) understanding the contrast between its behavior and that of ordinary oxygen. When the allotropic nature of ozone became established (see below), these questions became more acute. How could two such closely related substances as dioxygen and ozone be so different in their properties? In an 1847 letter to Schönbein, Berzelius (36) commented that Schönbein’s discovery of ozone was one of the most important discoveries in chemistry. Likewise, Liebig, in a footnote to Schönbein’s invited review in Annalen (37), commented in superlatives on the importance of his contribution. Schönbein continued to work on various aspects of ozone chemistry for the remainder of his life with about 200 papers on the subject, and many other chemists joined him. Reviews (inter alia: 11, 37, 38, 39, 40, 41, 42, 43) and books (44, 45) appeared with increasing frequency and by 1846 the topic had crossed the Atlantic (46). Ozone was off to a running start and has never slowed since. First it was a chemical curiosity of great interest, then a reagent for organic synthesis and an extremely useful tool for structure determination of natural products, and more recently a component of smog and a key ingredient of the upper atmosphere.

Analysis for Ozone

The first analytical instrument for ozone analysis was Schönbein’s nose, and smell continued to be an important diagnostic for the presence of ozone, one of the most sensitive of all methods. A variety of other qualitative methods were developed (47), the most important being the starch-iodide test properly (31). About 10 years later Andrews (32) addressed this question and showed that the products of arcing and of electrolysis were both decomposed very rapidly to oxygen by heating at 235-240°C or by boiling water.

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Among other qualitative tests used were conversion of silver to its peroxide and a variety of color tests including the decoloration of colored substances such as indigo and litmus, the blue coloration of guaiacum and of pyrogallol, etc. (50).

Quantitative analysis for ozone was delayed until the determination of its molecular weight and the stoichiometry of its various reactions, discoveries that occurred at later stages of ozone research. A number of quantitative methods, useful for determining relative concentrations, were developed in spite of this limitation. Schönbein (51) used solutions containing known weights of indigo with the change to colorless serving as an end point. He concluded that a mixture from the reaction of phosphorus with moist air contained 1/1300 part ozone in air. After Bunsen developed a titrimetric method for iodine analysis, titration of the iodine liberated from potassium iodide solution became a standard method for ozone analysis. Houzeau (52) developed a variation on this procedure based on the fact that KI and ozone react to give elemental iodine and potassium hydroxide (see above). Acid-base titrimetry with tournesol as indicator was used after reaction of KI with ozone, but this method never gained wide acceptance. Here again, the stoichiometry of the KI-ozone reaction was not known. Another useful titrimetric method involved the oxidation of arsenious acid (53); this was used by Soret (54), although he later used the iodimetric method.

Preparation of Ozone

The three methods described by Schönbein, arcing air or oxygen, electrolyzing aqueous acid solutions, and exposing phosphorus to moist air, were all used by investigators in the early days of ozone research. The most convenient of these for many investigators was the phosphorus reaction. Marignac described (14) a simple apparatus in which air was passed through a long tube filled with pieces of white phosphorus. The resulting gas could be washed with water and dried before use. Erdmann (55) described (56) an even simpler arrangement in his work on the reaction of ozone with indigo. Two flasks were connected by glass tubing; one contained water to which were added pieces of white phosphorus and the second contained an aqueous suspension of indigo; additional phosphorus could be added as required.

The phosphorus reaction was the subject of considerable investigation. Schönbein showed (17) that only white phosphorus produced ozone and investigated various aspects of the reaction (57, 58, 59). Marchand (60) also studied the reaction in detail (61) and concluded that many of Schönbein’s observations were correct but limited to the conditions under which he performed his experiments. For example, Marchand obtained ozone from phosphorus and dry oxygen without the presence of water, another proof of the allotropic nature of ozone. Schönbein also reported a number of oxidations using the slow reaction of phosphorus in the presence of vapors of various compounds (see below). At best the phosphorus reaction produced ozone concentrations of much less than 1% and its use for preparation of ozone was gradually abandoned.

The electrochemical method could be improved by use of low temperatures (53). Much later it was shown that electrolysis provided much higher concentrations of ozone in oxygen than any other method by using specially constructed equipment and carefully controlled conditions.

The breakthrough in ozone preparation was achieved by Siemens (62), who exploited Rühmkorff’s development of a high voltage transformer (63). In a long paper on electrostatic induction, Siemens described (64) in detail a silent discharge apparatus for preparing ozone from air or oxygen. It became routinely possible to achieve ozone concentrations in oxygen on the order of 5%, and commercial equipment for generating ozone utilizing Siemens’ discovery eventually became available. A modification of this apparatus was described (65) by Babo (66), who also studied the effect of various experimental parameters on the yield of ozone.

A number of dubious methods for forming ozone by chemical reaction also appeared. Böttger (67) reported (68) that the reaction of sulfuric acid with permanganates formed ozone, and Weltzien (69) claimed (70) a similar result for reaction of dichromate with sulfuric acid. Both of these results were later (71) shown to be due to impurities in the oxidizing agents, purified potassium permanganate or potassium dichromate giving no oxidizing gas. Leeds (72) suggested that chloride impurities were responsible in both cases. Schönbein reported (73) that ozone was formed when barium peroxide was added in small amounts to a permanganate-sulfuric acid mixture. The reaction of barium peroxide with acids to produce hydrogen peroxide had been reported in 1818 by Thenard (74), so that Schönbein’s system can be assumed to have contained this peroxide. He and Houzeau (24) claimed at various times that the action of sulfuric acid on barium peroxide (or other metal peroxides) produced ozone (via hy-
drogen peroxide?) but later confirmation of such chemistry is lacking. In fact, Schönbein used Thenard’s method to prepare hydrogen peroxide for comparison with ozone.

Formation of ozone by passage of air over hot platinum wire was claimed by van der Willigen (75) and by Le Roux (76, 77), based on odor and starch-iodide tests; but St. Edme (78) attributed these results to nitrogen oxides.

Reactions of Ozone

1. Inorganic Reactions

In his very first papers on ozone, Schönbein (5, 6, 8) described its reactions with metals to give peroxides. The product of reaction with silver was shown to decompose thermally to give an 87% yield of silver metal and an odorless gas, which was oxygen. It was given the formula AgO₂ (Schönbein used 8 for the atomic weight of oxygen). Other metals that gave peroxides included lead, tin, iron, manganese, antimony, and bismuth; also (79) cobalt and nickel were transformed to oxides. Arsenic was converted to arsenic acid, phosphorus to phosphoric acid, nitrous acid to nitric acid, nitrites to nitrates, sulfurous acid to sulfuric, sulfides to sulfates, selenides to selenates, iodine to iodate, and so on (80). Schönbein also reported in his first papers (5, 6, 8) that ozone was not formed in the presence of hydrogen halides and attributed this to the destruction of ozone by the halides. van den Broek (83) studied the reaction of ozone with hydrochloric acid in the gas phase at water aspirator pressure in the presence of metallic gold and concluded that chlorine gas (plus water) was formed as evidenced by the formation of gold chloride. The reaction of ozone with iodide to produce iodine has been noted above.

2. Organic Reactions

Progress in the investigation of reactions of ozone with organic compounds was much slower. Early work was of a purely qualitative nature. In spite of an avowed fear (84) of the complexity of organic chemistry, Schönbein reported (85) in 1845 that the ozone odor disappeared in the presence of straw, humus, humus-containing earth, sawdust, flour, potato starch, egg white, etc. One year later he added (79) wood alcohol, guaiacum, and ethylene gas to the list and later the reactions of mushrooms (84) and cyanine dye (86), and in 1868 additional natural materials (87). He noted (88) the important fact that organic substances were not converted to the highest oxidation state of carbon (CO₂) but instead to aldehydes, and carboxylic acids. In this paper he also commented that the product(s) of reaction of ethylene are similar to those obtained upon slow oxidation of diethyl ether in the presence of phosphorus (88, 89) without going into detail. These products were identified only much later (90) as formic and acetic acids and formaldehyde. A noteworthy sidelight of this work is the fact that he also observed a peroxidic material from the ethylene reaction.

Gorup-Besanez (91) explored a variety of organic reactions (92) and reported that uric acid is converted rapidly into allantoin, urea, and CO₂; amyl alcohol to valeraldehyde and valeric acid; tannic acid to oxalic acid and CO₂; potassium cyanide to potassium cyanate; albumin and casein undergo complex reactions, and tyrosine was rapidly converted to a red-brown product. He reported that urea, creatin, alloxan, allantoin, leucine, inositol, starch, fibrin, a number of acids (hippuric, acetic, butyric, palmitic, lactic, and tartaric), and glycerol failed to react. In all the above, ozone was generated by the phosphorus reaction, the gas being collected in glass vessels and washed with water before addition of the substrate.

Schönbein attempted to determine whether the oxidations proceeded in a stepwise manner via the lower oxides by exposing silver to a limited amount of ozone (82). In all cases he obtained only the peroxide, so that no firm conclusion could be drawn. He also performed competition reactions by exposing a number of metals simultaneously to an ozone atmosphere. Silver reacted most rapidly; zinc required a day for appreciable reaction. He was not able to evaluate the importance of surface condition in these reactions and the stoichiometry was not determined. In particular, the fact that reaction involved the formation of oxygen in addition to the metal peroxide was not appreciated and caused considerable difficulty in studies of the composition of ozone (see later).

The reaction with rubber was first reported by Soret in 1853 (53) and noted by a number of other workers.
Soret reported that when ozone was generated electrolytically at low temperature, the rubber connections of his apparatus were rapidly attacked but that this did not happen at room temperature. He correctly attributed the difference to the higher concentration of ozone formed at lower temperature. Much later this reaction became the basis of a simple method for determining when a solution bubbled with ozone had become saturated.

The only reaction of an organic compound with ozone which is clearly documented is the reaction with indigo. Schönbein described (93) the decoloration of indigo by ozone (from phosphorus) in 1851 and stated baldly that it is known that indigo is converted to isatin. However, Erdmann (56) reported full details of an experiment in which an aqueous suspension of indigo was treated with ozone from phosphorus and the product isatin was isolated and characterized by melting point.

**Composition, Molecular Formula**

What was this mysterious substance? The task of determining the composition of ozone was a formidable one in the 1840s, particularly because it was obtained as dilute solutions (<1% in the early work) in air or oxygen. Even today, the usual ozone generator produces a mixture of oxygen and ozone with concentrations on the order of 5%. This precluded the use of conventional methods, such as gas density, for determination of its relative molecular weight. A nontrivial technical problem was the extremely high reactivity of ozone towards rubber, most metals, etc., mentioned earlier. Much effort by Schönbein and others went into unsuccessful methods for producing pure ozone. As early as 1845 Schönbein (94) recognized that low-temperature methods might be successful. Later Andrews and Tait (25) tried to condense ozone at dry ice-ether temperature (-76°C) without success and many years passed before the necessary low-temperature techniques became available for obtaining pure ozone (and the hazards were realized). de la Rive (10) had proposed that the odor observed in electrolysis was due to particles of oxidized material disengaged from the positive electrode during electrolysis but abandoned this proposal (95) after Schönbein’s work appeared. Schönbein considered at an early stage (96) that ozone was oxygen in an unspecified “nascent state.”

The first question to be answered was whether ozone is composed of a single element or is a compound substance. Because the early methods for preparation of ozone involved air and moisture, Schönbein considered combinations of hydrogen, oxygen, and nitrogen. His first proposal was that nitrogen was not an element but was formed by decomposition of ozone. This met with many objections and was quickly discarded when Marignac (14) showed that electrolysis of water under air-free conditions readily produced ozone. This result was confirmed by a number of workers including Houzeau, and Fremy and Becquerel. Schönbein’s approach was mainly based on the preparation of substances that were possible candidates and comparison of their properties with those of ozone. He published papers reporting that ozone was not nitrous acid (97) and comparing ozone with chlorine (98) and was led to the conclusion that ozone was a compound of hydrogen and oxygen. Comparison with hydrogen peroxide, prepared by the Thenard procedure from reaction of barium peroxide with acid (74), showed that the two substances were different in spite of a number of similarities; his conclusion was that the ratio of oxygen to hydrogen in ozone differed from that in hydrogen peroxide. It was even suggested by Gentile (99) that ozone was CO₃₂⁻.

The first breakthrough in the elucidation of the composition of ozone came from Geneva. After demonstrating that ozone was formed by electrolysis under nitrogen-free condition as mentioned above, Marignac (14), acting on a suggestion of his colleague de la Rive, reported in 1845 that ozone was formed by arcing pure, dry oxygen. Curiously, he did not include this result in a second paper published at about the same time in *Compt. Rend.;* but it was published by de la Rive (100) as a postscript to a paper on another subject. These results were reproduced by Marchand (101), who demonstrated them to Berzelius and Erdmann. Further confirmation was provided by Fremy and Becquerel (20), by Houzeau (24b), and by Babo (102). Ozone was an allotrope of oxygen! The repeated experimental confirmations indicate how important this allotropy was in the eyes of chemists of the time. How was it possible that two allotropes of the same element could differ as markedly in their properties as oxygen and ozone? In the 1847 letter to Schönbein referred to earlier, Berzelius wrote (36) that the question of the allotropy of ozone was settled. Pleased as he may have been by the compliment included in that letter, Schönbein had already objected to the conclusion (103), arguing that allotropy was reserved for solid substances and that Marignac’s oxygen was not really dry. Since ozone was formed in very low yields, mere traces of moisture present would suffice for its formation. In the same paper he suggested
another experiment to settle the question, namely thermal decomposition of carefully dried ozone and measurement of the amount of water formed. Meanwhile he continued to maintain that ozone was a compound of hydrogen and oxygen until 1850 (see below).

The results of such thermal experiments were confusing. Williamson (104) and Baumert (105) reported independently that there was a significant gain in weight when thermally decomposed ozone was passed over a weighed amount of drying agent. Other workers, including Schönbein (42) himself in 1850, observed the opposite result. In one of the few quantitative experiments he performed, Schönbein prepared 300 liters of ozone by the phosphorus method, dried it by passing through sulfuric acid, and carried out its decomposition at 300°C. The gas was then passed over pumice coated with concentrated sulfuric acid. There was no gain in weight. This result was confirmed by Andrews (32), who obtained variable results using electrochemically generated ozone until he separated the electrodes in his apparatus by a diaphragm. Reproducible results were then obtained. The weight gain of the drying agent was less than 5% of the theoretical amount of water had ozone been a compound of hydrogen and oxygen. Andrews attributed the variability of results to the presence of traces of carbon dioxide in the ozone-oxygen mixture used, an argument which was disputed by Baumert (106). Soret (107) made the reasonable suggestion that the electrochemically generated ozone of Baumert contained traces of hydrogen. Using, like Andrews, a porous diaphragm to separate the electrodes in the electrolysis apparatus to ensure that no hydrogen was present in the oxygen-ozone mixture, he reproduced the Schönbein and Andrews results. The allotrope conception prevailed.

Speculation on the nature of ozone as an allotrope of oxygen was not lacking. As part of his contemplation of periodic relationships, Hunt (108) suggested (109) in 1848 that, by analogy with SO₂, there should exist a compound of oxygen having the formula O₃ and that this was probably the formula for Schönbein’s ozone. Odling (110) made a similar proposal in 1861; based on Andrews and Tait’s evidence that ozone was denser than oxygen, he suggested O₃ as the simplest candidate. In 1858 Clausius (111), having learned that the correct formula for oxygen is O₂, proposed (112) that ozone was atomic oxygen, O₁. In order to explain the known fact that ozone was stable for long periods, he suggested that the oxygen atoms were polarized and repelled one another. Schönbein’s response (113) to such speculation was to dissociate himself completely from “the dogmas of present-day atomists.” This was strange behavior from the man who did not hesitate to propose a new substance on the basis of odor alone! Nonetheless, he read a paper (114) before the Naturforschung Gesellschaft in Basel on the “atomic weight” of ozone; but this dealt with the composition of the peroxides obtained with various metals and with a correction indicating that Osann’s (115) supposed PbO₂ was, in fact, Pb₃O₄.

The approach that eventually led to the correct molecular formula for ozone was due to Andrews and Tait (25), who reported their results in a detailed paper including literature citations, drawings of the apparatus used, and a detailed experimental section (unlike many of the papers appearing in those years). The thermal instability of ozone had been noted by Schönbein and others in the earliest stages of its investigation. Andrews and Tait performed precise measurements of the volumetric relationships involved in thermal decomposition. They used a pair of identical vessels, each filled with pure oxygen and fitted with sulfuric acid manometers. One vessel served as a reference while the other contained electrodes that allowed generation of ozone either by arcing or by the silent discharge method. They reported that formation of ozone by either method resulted in a decrease in volume. Heating at 237°C resulted in reversal of the process with regeneration of the entire original volume. Ozone was denser than oxygen! These results were reproduced by Babo and Claus (116) and by Soret (117). It should be noted that Meidinger (118) had observed earlier that the volume of oxygen formed in electrolysis was appreciably less than one-half the volume of hydrogen obtained at the other electrode. He concluded that ozone must be denser than oxygen but did not go further. Andrews and Tait also found that the volume decrease was larger with silent discharge than with arcing, and that arcing the gas mixture from silent discharge resulted in an increase in the volume of the gas to the value obtained upon arcing oxygen directly.

Andrews and Tait realized that if a procedure could be found for completely converting the ozone formed into nonvolatile product(s), the ratio of the volume increase observed on thermal decomposition of an ozone-oxygen mixture to the volume decrease when ozone from a second sample of the same mixture reacted completely would provide the ratio of the density of ozone to that of oxygen. The problem was to find a suitable reaction for complete consumption of ozone. They attempted to use mercury or silver; the volume change was negli-
gible, leading to the conclusion that ozone consisted of many atoms of oxygen. The possibility that the reaction of mercury with ozone resulted in formation of an oxide of mercury together with a molecule of oxygen was rejected as being unlikely. This, the correct explanation, was suggested by Babo and Claus and by Soret. Reactions of ozone with metals afford one molecule of oxygen for each molecule of ozone consumed.

The solution to the problem was found by Soret, who first confirmed (107) Andrews and Tait’s results on volumetric relationships. He then found (119) a method for the complete consumption of ozone in the reaction of oils of turpentine (térébenthine) and of cinnamon (cannelle). Both of these naturally occurring materials contain considerable amounts of unsaturated compounds and react rapidly and quantitatively with ozone. An ozone-oxygen mixture was divided into two samples. One sample was heated and the volume increase was measured; the second was allowed to stand over one of the oils and the volume decrease measured. The results are summarized in Soret’s table above. The calculated dilatation (volume increase) is the value of 2 calculated for $O_3$ from the ratio (volume decrease by reaction/volume increase by heating).

The value of the ratio calculated for $O_3$ is unity (instead of 2 for $O_4$) and becomes increasingly smaller as the number of oxygen atoms increases, so that the conclusion that ozone is indeed $O_3$ is clear from the experiment. Later workers confirmed Soret’s conclusion.

Additional confirmation for the formula $O_3$ was provided by Soret’s studies, reported two years later (120) on the rate of diffusion of ozone through a small aperture (the use of porous materials for diffusion led to decomposition of ozone) using chlorine as a reference. The calculated value for the square root of the inverse ratio of diffusion rates is 0.82 for $O_3$ and 0.95 for $O_4$. Soret found 0.84. Nearly 30 years had passed since Schönbein’s initial suggestion that ozone is a distinct substance. His death in 1868 precluded comment by him on this result.

### Atmospheric Ozone

In his 1840 paper (6) Schönbein considered the possibility that ozone was found in the atmosphere and proposed testing for it by exposing platinum strips to air (121). This awareness derived in part from his experience (Ref. 11, p 251; Ref. 22, p 346) when lightning struck a church near his home in Basel, and the odor persisted long after the electrical storm was over; he had a similar experience earlier in life. He identified that odor with the one he later detected upon electrolysis of acidified water. The further knowledge that ozone had a variety of very unpleasant physiological effects (see

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<th>Corps absorbant</th>
<th>Diminution de Volume par l’essence</th>
<th>Calculée</th>
<th>Observée</th>
<th>Différence</th>
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<td>3,77</td>
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<td>2,85</td>
<td>2,72</td>
<td>-0,13</td>
</tr>
</tbody>
</table>
below) resulted in a concern with atmospheric ozone (122) which persisted to the very end of his work (49). Having shown that starch-iodide paper exposed to ordinary air developed the characteristic color due to iodine formed, he concluded that ozone was continuously present in the atmosphere. He also obtained a positive test for ozone in ground water after an electrical storm (123). The very low concentrations of ozone in the atmosphere were attributed to destruction of ozone because of its high reactivity. Schönbein developed a commercially available kit (124), based on starch-iodide paper, with a chromatic scale from 0-10 for ozone concentration. The dry paper strips, exposed to the atmosphere for a specified period of time, developed a brown color (iodine) and were then moistened to obtain a colored strip for comparison with the chromatic scale supplied. Berigny (125), who was largely responsible for introducing ozonometric measurements in France, later developed a similar system (with a chromatic scale of 0-21) as did Osann (126).

The only evidence, other than qualitative color tests and odor, that ozone was indeed present in ordinary air was provided by Andrews. Having established the conditions for thermal decomposition of ozone (25), he showed (127) that a sample of air which colored starch-iodide paper gave no such effect after passage through a tube heated to 237° C. This eliminated a variety of thermally stable possibilities such as halogens. There was wide acceptance of ozone as a constituent of the atmosphere. The availability of a simple and convenient procedure, using commercially available test kits, prompted many workers to undertake regular measurement of atmospheric ozone concentrations. A sampling from Compt. Rend. alone for the period 1854 to 1865 reveals such reports by Karlinsky (128), Berigny (129), Sylvestri (130), Pietra Santa (131), and Poey (132, 133). Long-term measurements were made by Boeckel (134). In the course of time, considerable criticism was leveled at the simple starch-iodide method (135). In addition to the known lack of selectivity of the starch-iodide test, results were found to depend on the quality of the paper and the reagents used, on exposure to light, on the relative humidity, etc. Defenders were not lacking (136). A partial solution to these problems was the design of special “ozone boxes” in which the test paper was placed (137). One of Schönbein’s last papers (49) was concerned with developing a more selective test for ozone. Huizinga (47) reported use of Schönbein’s thallium oxide paper (49), but this does not appear to have achieved much acceptance by other workers.

The period discussed in this article saw the beginnings of atmospheric ozone studies, with the pace accelerating rapidly during the latter part of the 19th century. Marenco et al. (138) have recently provided an overview of the early methods for atmospheric ozone analysis and a detailed evaluation of results obtained at a specific location. It would appear that systematic measurements at a given location over a long period of time do have merit and can be compared with current atmospheric ozone concentrations.

Numerous attempts were made to correlate atmospheric ozone concentration with public health (139, 140). Thus Schönbein (139), observing higher concentrations of ozone at a time of snowfall, attributed the increased frequency of catarrhal and other conditions in winter to the increased concentration of ozone.

**Physiological Effects**

A report by Schönbein (141) on the physiological effects of ozone appeared in 1851 and was summarized (37) in the 1854 review of ozone commissioned by Liebig. Ozone affected breathing and caused chest pains and irritation of the mucous membranes; these were reiterated (73) in 1863. Small animals, such as mice, died quickly in an ozone atmosphere. A fully-grown rabbit died after breathing ozonized air for one hour with symptoms similar to chlorine poisoning. As is well known, this subject acquired greater and greater interest with the passage of time.

**False Trails**

1. **Antozone**

In an 1858 letter to Faraday, Schönbein (142), an admitted lover of speculation, proposed the existence of another form of oxygen, which he called antozone. He commented that “I am far from believing that the above is correct but it is necessary to have a hypothesis on which to base further experiment.” The two species, ozone and antozone, purportedly reacted together to give oxygen. On the assumption that both were formed under ozone-producing conditions, the low yield of ozone obtained was explained by its destruction by antozone. He gave ozone the symbol Q, implying that it is a negatively charged species, and its complement, antozone, the symbol ≈. Thus lead dioxide, a compound containing ozone according to Schönbein, was written PbOQ. Barium peroxide, on the other hand, supposedly contained antozone and was written BaO≈. The distinction...
was based on the fact that, under similar reaction conditions, barium peroxide liberated chlorine from dilute hydrochloric acid while lead dioxide did not. This distinction was later shown to be a matter of proper choice of reaction conditions and to have no relevance to any fundamental difference between the two peroxides.

Antozone appeared frequently in subsequent papers of Schönbein (143) and consumed a considerable amount of his research effort. It was reportedly obtained by heating a certain fluorspar (144). This particular odorous material was eventually considered to have no relation to ozone. Antozone engaged the attention of a number of other workers, particularly Meissner (145), whose work appeared (146) as a 370-page book. He also coined the alternative term “atmizone.” The importance attached to antozone is emphasized by sympathetic reviews that appeared in the United States (147).

Antozone was identified by its supporters as the white cloud formed when ozone was generated either by electrolysis or by the phosphorus reaction. Since this cloud passed through water without change, it was concluded that it could not be hydrogen peroxide. As work continued, more and more convoluted explanations had to be suggested to account for the observed results. Babo (148) and Weltzien (149) both suggested that antozone was simply hydrogen peroxide. The whole matter was laid to rest in 1870 (150) by Engler (151) and Nasse (152), who showed that the material in the cloud could be condensed in cool traps and that it consisted of aqueous hydrogen peroxide. They also generated a cloud having the same properties by application of a vacuum to a solution of hydrogen peroxide.

Leeds, summarizing the purported chemistry of antozone in 1879 (153) wrote, “By far the most important fact in the long and perplexing history of antozone, is the recent discovery that there is no antozone.” The history of antozone has many of the attributes of pathological science as defined by Langmuir (154).

2. Photooxygenation Reactions.

Another confusion was introduced by the oxidizing properties resulting from exposure of various substrates to oxygen and sunlight. For example, Schönbein (155) exposed indigo to air and sunlight and inferred from the disappearance of color that ozone had been formed and reacted with indigo. In retrospect, these reactions undoubtedly are early examples of the reaction of alkenes with singlet oxygen, indigo acting as photosensitizer in this case. A number of reactions of oil of turpentine with oxygen (156) also do not involve ozone.

3. Ozon-Wasserstoff.

Amid confusion as to whether ozone was a nascent state of oxygen, Osann (157) reported in 1855 (158) that electrochemically generated hydrogen could effect reductions of substances present in the neighborhood of the electrode which chemically generated hydrogen gas did not effect. Much of his work involved the reduction of silver oxide to silver. He proposed that there was a hydrogen analog of ozone which formed at the negative electrode during electrolysis and gave this the name ozone-hydrogen (Ozon-Wasserstoff) as distinguished from ozone-oxygen. A number of additional papers (159) on this subject followed. His results were disputed by other workers (160). An interesting summary of this and related work on the nascent state has been given by Jensen (161).

Conclusion

By the time of Schönbein’s death in 1868 ozone was an accepted fact of chemistry, while his proposal of the existence of antozone had fallen by the wayside. The variety of early methods for preparation of ozone was largely superseded by Siemens’ invention of the silent discharge apparatus. The isolation of pure ozone and determination of its properties remained for the future. At the end of this period, ozone had been identified as O₃, an allotrope of ordinary oxygen, and provided a fascinating puzzle for chemical theory, which required the passage of many decades before an understanding of ozone’s structure and reactivity was achieved.

Many oxidations of inorganic compounds to their highest oxidation states had been described, although the stoichiometry of these reactions was not known. Oxidations of a few organic compounds had also been reported without very much information on the products of reaction; Schönbein emphasized, however, that these oxidations did not proceed all the way to carbon dioxide and water. Systematic knowledge of ozone’s behavior with organic compounds materialized at the beginning of the 20th century.

Interest in atmospheric ozone dated from the very beginning of Schönbein’s discovery of ozone. Development of semiquantitative methods for analysis of atmospheric ozone prompted many workers to undertake regular studies of concentrations of atmospheric ozone.
at ground level. Quantitative methods for determination of ozone were also developed.

In view of the state of chemistry at the end of Schönbein’s lifetime, it is fair to say that a remarkable amount of progress was made between 1839 and 1868 in spite of a great deal of waste motion.

ACKNOWLEDGMENTS

Thanks are due to librarians and colleagues at a number of institutions for assistance in the literature searches involved in preparation of this article, particularly to Professor F. Gerson at the University of Basel, Professor R. Gleiter at the University of Heidelberg, Dr. E. Zass at the ETH, Zurich, and to Ms. Isabel Stirling, librarian at the Science Library, University of Oregon. We are grateful to Mr. W. Gorgé of the Swiss National Bank for a short history of Swiss currency.

REFERENCES AND NOTES

The journal cited here as Annalen der Physik und Chemie, now called Annalen der Physik, was commonly referred to during the period covered by this article by the name of its editor as Poggendorff’s Annalen. Likewise, the Journal für Praktische Chemie was referred to as Erdmann Journal.

It was accepted practice in the mid-nineteenth century, in the absence of abstract journals and facile communication, to publish the same work, often in word-for-word translation, in journals of various countries. Some journals also included detailed summaries of significant work appearing in other journals. Where more than one report of specific work appears, we have chosen one for detailed citation and added the other references at the end of the citation.


2. C. F. Schönbein, Ber. Verh. Nat. Ges. Basel, 1838-40, 4, 58, from a lecture on March 13, 1839. Author’s translation: Prof. S. calls the Society’s attention to the noteworthy new observation that a smell develops at the positive electrode during electrolysis of water which is strikingly similar to that obtained by the flow of electricity across electrodes.

3. Martin van Marum, 1750-1837. Dr. of Philosophy and Medicine, at first a practicing physician in Haarlem. In 1776 he began to give natural history lectures and in 1777 became Director of the Naturalienkabinets in Haarlem and, in addition, in 1784 of the physical and natural history Museums of the Teyler’schen Museum. He published a multi-volume work (French and German translations were published in 1775) on the researches he performed using the museum’s static electricity generator.

4. After sparking air and noting the odor formed, van Marum studied the behavior of oxygen as pure as could be obtained at that time. He observed diminution of the volume of oxygen upon sparking; the mercury was strongly calcined at its surface, and the glass was covered with a film of mercury, so that one could not see through the tube. “It is evident that the oxygen has united with mercury.” Van Marum also investigated sparking of ammonia, nitrous acid, gaz olefiant, etc. In a long paper on his investigations of electrochemical phenomena, W. Cruickshank noted the odor accompanying electrolysis of aqueous acidic solutions (Ann. Phys. [Gilberts Annalen], 1801, 7, 107).


7. From the Greek ozein, to smell, as suggested by his colleague, W. Vischer, Professor of Greek in Basel. Mohr has collected a number of early Greek references to the odor of ozone: “Aelteste Nachricht über Ozon und seine Benennung,” Ann. Phys. Chem., 1854, 91, 625-627.


9. Auguste Arthur de la Rive, 1801-1873. Professor of physics, Academy of Geneva. Member of the Paris
A. de la Rive, "Quelques Observations sur le Memoire..."

J. C. Marignac, "Sur la nature et la production de l'ozone,..."

C. F. Schönbein, "Ueber die Natur des eigenthümlichen Geruches,..."

A. de la Rive, "Neue Untersuchungen über die Eigenschaften der discontinuirlichen elektrischen Ströme von abwechselnd entgegengesetzter Richtung,..."


Jean Charles Galissard de Marignac, 1817-1894. Professor of Chemistry at École d’agriculture de Départ. de la Seine inférieure (both from 1858).


Thomas Andrews, 1813-1885. Professor of Chemistry, Queen’s College Belfast, Member of the Royal Society, London; discoverer of critical temperature of gases.

Peter Guthrie Tait, 1831-1901. Professor of Mathematics at Queens University, Belfast. From 1860 Professor of Physics at the University of Edinburgh and secretary of the Edinburgh Royal Society.

Nicolaus Wolfgang Fischer, M.D., 1782-1850. From 1842 Professor of Chemistry at the Academy of Geneva from 1842. Discovered gadolinium and purified terbium. From 1866 correspondent of the Paris Academy, 1881 member of the Royal Society, London. Received the Davy Medal of the Royal Society in 1886.


Antoine Cesar Becquerel, 1788-1878. Professor of Physics at Musée d’histoire naturelle, from 1829 member of Paris Academy. Received the Copley Medal of the Royal Society.


Edmond Fremy, 1814-1894. In 1846 Professor at the École Polytechnique in Paris and, from 1850, at the Musée d’histoire naturelle; director of the museum in 1879. Member of the Paris Academy and numerous other societies.


Jean August Houzeau. Professor of Chemistry at École superieure des science et des lettres à Rouen and at the École d’agriculture de Dept. de la Seine inférieure (both from 1858).


Thomas Andrews, 1813-1885. Professor of Chemistry, Queen’s College Belfast, Member of the Royal Society, London; discoverer of critical temperature of gases.

Peter Guthrie Tait, 1831-1901. Professor of Mathematics at Queens University, Belfast. From 1860 Professor of Physics at the University of Edinburgh and secretary of the Edinburgh Royal Society.

Nicolaus Wolfgang Fischer, M.D., 1782-1850. From 1814 Professor at the University of Breslau.


31. Schönbein emphasized that the iodide must be free from iodate and claimed that Fischer did not take proper precautions in his tests.


34. Alexander W. Williamson, 1824-1904. Studied in Heidelberg and Giessen (Dr. under Liebig, 1845). Professor of pure and practical chemistry at University College, London. Member Royal Society, London, corresponding member of the Academies of Paris and Berlin.


43. Ozon, in Handwörterbuch der Chemie, Band 5, p 835, Braunschweig, 1853.


45. G. Dachauer, Ozon, Gummi, München, 1864.


55. Otto Linné Erdmann, 1804-1869. Professor from 1830 at the University of Leipzig. Editor of the Journal für Praktische Chemie for many years.


60. Richard Felix Marchand, 1813-1850. Professor of Chemistry, University of Halle from 1843. Editor, with Erdmann, of J. Prakt. Chem. until his untimely death.


62. Ernst Werner von Siemens, 1816-1892. Electrical genius, founder of Siemens & Halske, predecessor of the present Siemens AG.

63. Heinrich Daniel Rühmkorff, 1803-1877. In 1840 he set up his own mechanical works in Paris; known for his induction apparatus. In 1864 he received a prize of 50,000 francs from the French government for this invention.


66. Clemens Heinrich Lambert von Babo, 1818-1899, Professor in Freiburg im Breisgau.
67. Rudolph Böttger, 1806-1881, Professor of Physics in Frankfurt/Main.
69. Carl Weltzien, M.D., 1813-1870, Professor of Chemistry in the Technical Institute of Karlsruhe; local chairman of the 1860 Karlsruhe Conference.
72. Albert Ripley Leeds, 1843-1902, Professor of Chemistry at Haverford College from 1867 to 1871; from 1871 Professor at Stevens Institute of Technology, Hoboken, NJ/USA.
77. François Pierre Le Roux, 1832-1907. Professor at the Conservatoire des arts et metiers, then Professor of Physics in Ecole Superieure de pharmacie, Paris.
84. C. F. Schönbein, “On Ozone and Ozonic Actions in Mushrooms,” Philos. Mag. IV, 1856, 11, 137. A letter to M. Faraday that includes the statement, “You know that I entertain a sort of innate dislike to touch anything in the slightest way connected with organic chemistry, knowing too well the difficulty of the subject and the weakness of my power to grapple with it.” See also Ann. Phys. Chem., 1856, 67, 496.
108. Thomas Sperry Hunt, 1826-1882. From 1847-72 chemist and mineralogist in the Geological Survey of Canada, simultaneously from 1856-62 Professor of Chemistry at the University of Quebec and from 1862-67 at the University of Montreal. From 1872-78 Professor of Geology at the Technical Institute, Boston, then in 1878 back to Montreal. From 1859 member of the Royal Society, London.
111. Rudolph Julius Emanuel Clausius, 1822-1888. Professor of Physics at the Polytechnic Institute of Zürich from 1855 and the University of Zürich from 1857; in 1867 he moved to Würzburg and in 1869 to Bonn.
121. Apparently nothing ever came of these experiments, since no further reference was made to them.
124. Supplied by Buchbinder Burg in Basel, cost 1 florin, 12 kroner. This sum was approximately equal to sFr 1.8 in the mid-19th century.
129. A. de Berigny, “Observations faites a l’observatoire meteorologique de Versailles avec le papier dit


133. André Poey. Founder and director of physical-meteorological Observatory in Havana; later lived in Paris.


145. Georg C. F. Meissner, Professor of Physiology, Göttingen.

146. G. Meissner, Untersuchungen über den Sauерstoff, bei Hahn, Hannover, 1863.


151. Carl Oswald Viktor Engler, 1842-1925. From 1876 Professor in Halle, in 1887 moved to Karlsruhe; Curator of the Lebensmittel-Prüfungscommission; Member of the Reichstag, 1887-90.

152. Otto Johann Friedrich Nasse, M.D., Marburg, 1839-1903. In Halle until 1880, then Professor of Pharmacology and Physiological Chemistry at Rostock.


157. Gottfried Wilhelm Osann, 1797-1866. Professor of Chemistry and Pharmacy at Dorpat and then Professor of Physics and Chemistry at Würzburg.


**ABOUT THE AUTHOR**

Mordecai B. Rubin is Emeritus Professor of Chemistry in the Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel 32000. Retirement is like a permanent sabbatical. A major interest for many years has been organic photochemistry. As a young man, many years ago, he developed an apparatus for small-scale ozonolysis, which was dubbed the Rubin ozonator.

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