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**BULLETIN FOR THE HISTORY OF CHEMISTRY**  
**VOLUME 26, CONTENTS**  
**NUMBER 1**

<b>DEXTER AWARD 2001</b>	1
<b>CUTTING-EDGE CHEMISTRY: SOME 19TH-CENTURY RUSSIAN CONTRIBUTIONS</b> <i>Richard E. Rice, James Madison University</i>	2
<b>D. I. MENDELEEV'S CONCEPT OF CHEMICAL ELEMENTS AND <i>THE PRINCIPLES OF CHEMISTRY</i></b> <i>Masanori Kaji, Tokyo Institute of Technology</i>	4
<b>HYDRATING IONS IN ST. PETERSBURG AND MOSCOW; IGNORING THEM IN LEIPZIG AND BALTIMORE</b> <i>Richard E. Rice, James Madison University</i>	17
<b>NIKOLAI ZININ AND SYNTHETIC DYES: THE ROAD NOT TAKEN</b> <i>Nathan M. Brooks, New Mexico State University</i>	26
<b>THE BEGINNINGS OF SYNTHETIC ORGANIC CHEMISTRY: ZINC ALKYLs AND THE KAZAN' SCHOOL</b> <i>David E. Lewis, University of Wisconsin-Eau Claire</i>	37
<b>CUTTING-EDGE CHEMISTRY: SOME 19TH-CENTURY RUSSIAN CONTRIBUTIONS. A COMMENTARY</b> <i>Seymour H. Mausekopf, Duke University</i>	43
<b>OPPOSITION TO THE FORMATION OF THE AMERICAN CHEMICAL SOCIETY: NOTED ADDED IN PROOF</b> <i>James J. Bohning, Lehigh University</i>	46
<b>FOUR GIANTS IN A COLLEGE CHEMISTRY DEPARTMENT: OBERLIN COLLEGE, 1880-1966</b> <i>Norman C. Craig, Oberlin College</i>	48
<b>EDGAR BUCKINGHAM: FLUORESCENCE OF QUININE SALTS</b> <i>John T. Stock, University of Connecticut</i>	57
<b>DULONG AND PETIT: A CASE OF DATA FABRICATION?</b> <i>Carmen J. Giunta, Le Moyne College</i>	62
<b>BOOK REVIEWS</b>	72

**NUMBER 2**

<b>THE HISTORY OF OZONE. II. 1869-1899 (1)</b> <i>Mordecai B. Rubin, Technion-Israel Institute of Technology</i>	81
<b>FRANCIS HOME AND JOSEPH BLACK: THE CHEMISTRY AND TESTING OF ALKALINE SALTS IN THE EARLY BLEACHING AND ALKALI TRADE</b> <i>Frederick G. Page, University of Leicester</i>	107
<b>THE OSTWALD-GIBBS CORRESPONDENCE: AN INTERESTING COMPONENT IN THE HISTORY OF THE ENERGY CONCEPT</b> <i>Carl E. Moore, Alfred von Smolinski, and Bruno Jaselskis, Loyola University, Chicago</i>	114
<b>THE NATURAL DEFENSE OF A SCIENTIFIC PEOPLE: THE PUBLIC DEBATE OVER CHEMICAL WARFARE IN POST-WWI AMERICA</b> <i>Andrew Ede, University of Alberta</i>	128
<b>CHEMISTRY AT RICE, 1912 to 1998</b> <i>Edward S. Lewis, Rice University</i>	136
<b>BOOK REVIEWS</b>	145

***The Cover...*** W. Ostwald and J. S. Gibbs, correspondents

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

*Mordecai B. Rubin, Technion-Israel Institute of Technology*

### 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

*Bull. Hist. Chem.*, 2001, 26, 48.

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

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

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 discus-

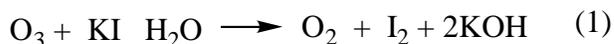
sion on methods for ozone detection followed this lecture with the majority agreeing that Schönbein's procedure was of limited value but that no satisfactory substitute was available. Like the weather, everyone complained but went on using the Schönbein method. Levy, who was responsible for ozonometric 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 tournesol 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',N'-tetramethyl-*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:



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:



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:



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), Hauteville 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

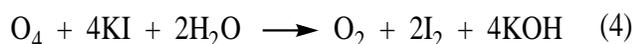
Soret (40) had determined that the molecular formula of ozone was  $\text{O}_3$  in 1865 by a study of volumetric relationships and confirmed this in 1867 by diffusion studies (41). An objection by Wolffenstein (42) to the effect that turpentine reacts with both oxygen and ozone was dismissed by Soret (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  $O_3$  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  $O_3$  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  $O_3$  in the experiment designed to prove that it is  $O_3$ . However, if one assumes that ozone is  $O_4$ , one can write reaction 4 with KI:



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  $O_4$ . The goodness of the fit is simply evidence of the skill of the experimentalist. The same argument applies to Otto's work mentioned above.

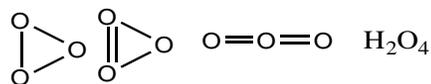
A testy reply from Ladenburg (50) followed rapidly. He argued that a number of workers (cf. section

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  $O_4$  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  $O_3$  in 1865 and remains that way although the allotrope  $O_4$  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 dioxides. He also considered that ozone might be the anhydride of an acid  $H_2O_4$  related to potassium tetroxide,  $K_2O_4$ . In 1870, Clausius (57) accepted the formulation  $O_3$  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 Cailletet, 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 ( $-102.5^{\circ}\text{C}$ ) 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 observed that the liquid was stable when cooled by liquid ethylene at  $-140^{\circ}\text{C}$ . By slow warming of such a system, the boiling point of ozone was determined to be around  $-106^{\circ}\text{C}$ . 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 into 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  $-119^{\circ}\text{C}$ . The present handbook value is  $-111.35^{\circ}\text{C}$ , halfway between Troost's and Olszewski's values. Troost used an oxygen-ozone mixture generated by operating a Berthelot (silent discharge) tube at  $-79^{\circ}\text{C}$  (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  $-125^{\circ}\text{C}$ .

### 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 Schöne (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. Schöne 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, Hautefille and Chappuis (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.

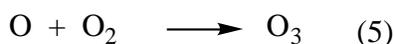
#### 5. Effect of Ultrasound

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.



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.
3. Photochemical Formation of Ozone.
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 to -23° C and Beill (34) 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 with 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 6° 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 O<sub>2</sub>. 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 (137h) 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 CO<sub>2</sub>. A bimolecular alternative, also proposed by Debus (150), was suggested as a possibility for the thermal reaction.

Hauteville 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 O<sub>3</sub> 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.

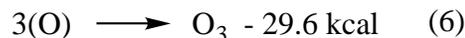
Quantitative thermochemical studies were first performed by Hollmann (152) in 1868 in response to a challenge issued in 1864 by the Society of Arts and Sciences in Utrecht. He determined the difference in the amount of heat evolved by flames (hydrogen, methane, ethylene and flames of a number of liquids) 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 ozonimeter based on the pressure change observed during the reaction.



### Inorganic Reactions

Schönbein's earliest work with ozone described oxidation of a variety of inorganic compounds including elements and compounds such as sulfites and nitrites. 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:



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. On the one hand, Remsen and Southworth (168) showed that when electrically generated ozonized oxygen was mixed with

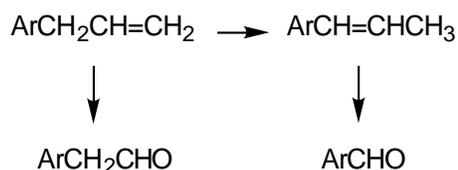
carbon monoxide in the presence of moisture, no carbon dioxide was formed after long standing either in the dark or in sunlight; this result was confirmed by Baumann (86) with ozone generated from phosphorus. On the other hand, the result obtained when carbon monoxide and air were passed together over 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 CO<sub>2</sub> 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

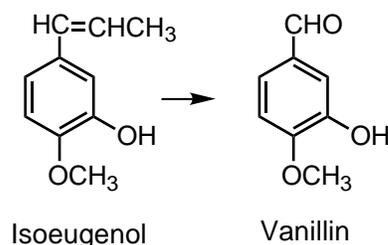


Other reactions investigated by Otto (171) and others include the following:

- Methane reacted to give formaldehyde in low yield (171). Also Maquenne (173).
- Ethylene (171), Houzeau and Renard (174). Tetrachloroethylene, Besson (175).
- Acetylene gave a violent reaction with ozone, products were not identified (171).
- 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).
- 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,  $\text{C}_8\text{H}_{20}\text{O}_3$ . Hydrogen peroxide and ethyl alcohol were obtained after

isomerization of their naturally occurring allylic isomers. These were apparently converted to the corresponding substituted acetaldehydes by ozonolysis (172).



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  $8^\circ$  they obtained, in addition to formic and acetic acids, a gelatinous, explosive product, which they called ozobenzine (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  $0^\circ$ ; ozotoluene exploded at  $8^\circ$ . 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  $15^\circ$  and at  $50^\circ$ . Dieckhoff (184) is cited by Harries (185) as having obtained ozobenzene as a crystalline material which exploded at  $50^\circ$  on rapid heating and decomposed without explosion upon slow heating. Harries later established the correct molecular formula of this material, the triozone 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  $C_6H_6O_7$  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 min-

utes 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

(215). 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 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. Fröhlich (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, Fröhlich 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 Wolffhügel (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 Marengo et al. (231) have shown



Ozone

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.



Antozone

### Conclusion

By the end of the 19th century, ozone had been obtained as a pure liquid, its boiling point established, its composition as O<sub>3</sub> 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

- Part 1. M. B. Rubin, "The History of Ozone. The Schönbein Period, 1839-68," *Bull. Hist. Chem.*, **2001**, *26*, 40-56.
- Christian Friedrich Schönbein, 1799-1868. Professor at the University of Basel from 1828. For biographical information see R. E. Oesper, *J. Chem. Educ.* **1929**, *6*, 432-40. This author has also given an overview of Schönbein's research work, *J. Chem. Educ.*, **1929**, *6*, 677-85. A much more extensive early source is the book by E. Hagenbach, *Christian Friedrich Schönbein, Programm für die Rectoratsfeier der Universität, Basel*, 1868. A biography of Schönbein has appeared recently in honor of the 200th anniversary of his birth: P. Nolte, *Christian Friedrich Schönbein. Ein Leben für die Chemie 1799-1868*, Arbeitskreis Stadtgeschichte der Volkshochschule Metzingen-Ermstal e.V., 1999. ISBN 3-9802924-6-0. The Basler Magazine of the *Basler Zeitung* dated Saturday, October 16, 1999, also has a cover photo of Schönbein and a long article with photographs on the man and his work.
- G. C. F. Meissner, *Neue Untersuchungen über den elektrisierten Sauerstoff*, Göttingen, bei Diederich, 1869; *Untersuch über die elektr. Ozon erzeugung, etc.* Reprinted from *Abhandl. der K. Gesell. der Wissenschaften zu Göttingen*, Göttingen, 1871; *Untersuchungen ueber die elektrische Ozonerzeugung und ueber die Influenz-Elektrizitaet auf Nicht-Leiter*, Göttingen, 1871. Georg C. F. Meissner, 1829-1905. Prof. Physiology and Zoology in Freiburg 1857-60. From 1860 Prof. Physiology, Göttingen. Discovered the existence of touch centers in human skin. His interest in ozone undoubtedly derives from contact with Schönbein during the short period (1855-57) he spent as Prof. Anatomy and Physiology in Basel. He also played a role in hygienic aspects of drinking water in Göttingen.
- C. B. Fox, *Ozone and Antozone. 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.
- C. Engler, "Historisch-kritische Studien über das Ozon," *Leopoldina*, **1879**, *15*, 124-7; 141-4; **1880**, *16*, 91-4; 104-112; 125-8; 134-42; 156-60; 170-6. Carl Oswald Viktor Engler, 1842-1925. From 1876 Professor in Halle, moved to Karlsruhe in 1887, Curator of the Lebensmittel-Prüfungscommission. Member of the Reichstage, 1887-90.
- A. R. Leeds, "Lines of Discovery in the History of Ozone with an Index of its Literature," *Ann. N.Y. Acad. Sci.*, **1879**, *1*, 363-404. A supplemental discussion and bibliography for the period 1879-1883 appeared in *Ann. N.Y. Acad. Sci.*, **1883-5**, *3*, 137-152. 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. Vice President of the American Chemical Society.

7. A. R. Leeds, "The History of Antozone and Peroxide of Hydrogen," *Ann. N.Y. Acad. Sci.*, **1879**, *1*, 405-425.
8. A. R. Leeds, "Recent Progress in Sanitary Science," *Ann. Lyceum Nat. Hist. N.Y.*, **1876**, *11*, 266-288.
9. A. R. Leeds, "Ozone and the Atmosphere," *Ann. N.Y. Acad. Sci.*, **1879**, *1*, 193-219.
10. 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.
11. T. Andrews, "Ozone, Part 1," *Nature*, **1874**, *9*, 347-9; "Part 2," 364-6. From a lecture presented to the Royal Society of Edinburgh Dec 22, 1873. A German translation: "Ueber das Ozon," *Ann. Phys.*, **1874**, *152*, 311-31. Thomas Andrews, 1813-1885. Professor of Chemistry and Vice-President, Queen's College, Belfast, Member of the Royal Society, London. Discovered the phenomenon of critical pressure and did important work in thermochemistry.
12. 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.
13. 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.
14. G. S. Newth, "An Apparatus showing Experiments with Ozone," *J. Chem. Soc.*, **1896**, *69*, 1298-9.
15. W. A. Shenstone and J. T. Cundall, "The Volumetric Relations of Ozone and Oxygen. A Lecture Experiment," *J. Chem. Soc.*, **1887**, *52*, 625-6. William Ashwelll Shenstone, 1850-1908. Pharmacy degree, London School of Pharmacy, 1878. Clifton College, Bristol, 1880-1908; fellow Roy. Soc. London, 1898. James Tudor Cundall, 1865-. From 1890 Senior Science Master, Edinburgh Academy.
16. 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 alkaloid chemistry and worked on the structure of benzene ("Ladenburg benzene").
17. Schönbein's ozonometric kit was marketed by Buchbinder Burgy of Basel. Another supplier was Krebs, Kroll and Cp. who marketed an ozonometric paper with a scale of 0-15.
18. T. Moffatt, as reported in *Ber.*, **1872**, *5*, 814
19. A. Levy, "Sur la recherche de l'ozone dans l'air atmosphérique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1878**, *86*, 1263-65. Cf also "Sur le dosage en poids de l'ozone atmosphérique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1877**, *85*, 42-3.
20. A. Houzeau, "Sur l'ozone atmosphérique," *Ann. Chim. Phys.* [4], **1872**, *27*, 5-68. Jean August Houzeau, 1829-1911. Prof. Chem. at École supérieure des science et des lettres à Rouen and at the École d'agriculture de Dept. de la Seine inferieure (both from 1858). Active for many years in ozone research.
21. C. Giannetti and A. Volta, "Sulla produzione dell'ozono a mezzo delle scariche elettroforiche," *Gazz. Chim. Ital.*, **1874**, *4*, 471-8.
22. C. Wurster, "Ueber einige empfindliche Reagentien zum Nachweise minimaler Mengen activen Sauerstoffs," *Ber.*, **1886**, *19*, 3195-3205. Casimir Wurster, 1854-1913. Active in paper technology and physiology.
23. G. Erlwein and Th. Weil, "Die Unterscheidung von Ozon, salpetriger Säure und Wasserstoffsperoxyd," *Ber.*, **1898**, *31*, 3158-9. Theodor Weyl, 1851-1913. Worked under Baumann in Berlin, Habilitation 1895 at Tech. Hochschule, Charlottenburg, Prof. Physiological Chem., wrote several textbooks for medical students.
24. On the importance of the purity of the potassium iodide used, see for example, G. Papasogli, "Einwirkung der Kohlensäure auf Jodkalium und auf ozonempfindliches Papier," *Gazz. Chim. Ital.*, **1881**, 277-282.
25. P. Behrend and H. Kast, "Titration geringer Gasmengen in Gasgemischen," *Dingl. Polytech. J.*, **1890**, *270*, 423-431.
26. B. C. Brodie, "An Experimental Inquiry on the Action of Electricity on Gases. I. On the Action of Electricity on Oxygen," *Philos. Trans. R. Soc. London*, **1872**, *162*, 435-84. Preliminary report: "On the Action of Electricity on Gases," *Proc. R. Soc. London*, **1871-2**, *20*, 472-5. Sir Benjamin Collins Brodie, 1817-1880. Studied under Liebig, had a private laboratory in London. Prof. Chem. in Oxford 1855-1873. Member Royal Society, President of the Chemical Society.
27. A. R. Leeds, "Wasserstoffsperoxyd und Ozon," *Ber.*, **1880**, *13*, 1132; *Chem. News*, **1880**, *41*, 163-5.
28. H. McLeod, "On the Electrolysis of Aqueous Solutions of Sulphuric Acid, with special Reference to the Forms of Oxygen Obtained," *J. Chem. Soc.*, **1886**, *49*, 591-609. Herbert McLeod, 1841-1923. From 1871-1901 Prof. Chem. and Physics at Royal Indian Engin. College, Coopers Hill, Staines, England. Since 1901 Dir. of Roy. Soc. Cat. of Scientific Papers. Hon LLD, St. Andrews.
29. D. Tommasi, reported in *Ber.*, **1874**, *7*, 1026.
30. J. L. Soret, "Note sur la production de l'ozone par la décomposition de l'eau à de basses temperatures," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1853**, *38*, 445-8. Also *J. Prakt. Chem.*, **1854**, *62*, 40. Jacques Louis Soret, 1827-1890. Editor in chief of Archives des sciences phy-

- siques et naturelles. From 1876 Prof. of medicin physique at the Univ of Geneva.
31. P. Thenard, "Sur un nouveau procédé de dosage de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 174-7. *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 351. Baron Arnould Paul Edmond Thenard, 1819-1884. Son of L. J. Thenard, the discoverer of hydrogen peroxide. 1864, Member of the Paris Academy.
  32. e.g., M. Berthelot, "Fixation de l'azote sur les matières organiques et formation de l'ozone sous influences des faibles tensions électriques," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1877**, 85, 173-8; *Ann. Chim. Phys.* [5], **1877**, 12, 453-66. Pierre Eugène Marcellin Berthelot, 1827-1907. D.Sc. 1854. 1850-9, Preparateur de chimie at College de France. From 1859-76 Prof. Chem., Ecole sup. de pharm., from 1864 also Prof. Organic Chem., College de France. Member Paris Academy and academies of London, Munich, Stockholm, St. Petersburg, etc. Inspector of Higher Education in 1876, Senator in 1881, Minister of Public Instruction 1886-7, Foreign Minister 1895-6. One of the most prolific French chemists of all time with many books and over 1,000 publications.
  33. A. Thenard and P. Thenard, "Mémoire sur l'action comparée de l'ozone sur le sulfate d'indigo et l'acide arsenieux," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 458-65.
  34. A. Beill, "Über den Einfluss der Temperatur auf die Ozonbildung," *Monatsh. Chem.*, **1893**, 14, 71-80.
  35. H. N. Warren, "Eine verbesserte Form des Ozonisierungsapparates," *Ber.*, **1894**, 27, R762; *Chem. News*, 70, 41.
  36. a. P. Hautefille and J. Chappuis, "Sur la rétrogradation produite par l'effluve électrique dans la transformation de l'oxygène en ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1882**, 94, 646-9. b. "Recherches sur l'effluve électrique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1880**, 91, 281-3. c. "Recherches sur l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1880**, 91, 228-30. Paul Gabriel Hautefille, 1836-1902. From 1876 Maitre de Conférences at the Ecole norm. superieure. Also from 1871 assistant (sous directeur) under Henri St. Claire Deville of Lab. of Ecole d'hautes études Paris. James Chappuis, 1854 -1943. Prof. Physics; 1877 in Montauban, 1878 in Poitiers, 1879-92 at Ecole norm. sup. in Paris, from 1881 Ecole centr. d. arts and manufacture in Paris.
  37. W. A. Shenstone and J. T. Cundall, "Ozone from Pure Oxygen: Its Action on Mercury, with a Note on the Silent Discharge of Electricity," *J. Chem. Soc.*, **1887**, 51, 610-624; *Chem. News*, **1893**, 68, 151-2.
  38. W. A. Shenstone and M. Priest, "Studies on the Formation of Ozone from Oxygen. Part II," *J. Chem. Soc.*, **1893**, 63, 938-61; *Chem. News*, **1893**, 67, 284-5.
  39. M. Otto, "Colorimeter, More Especially Applicable for use as an Ozonometer; an Improvement," *J. Soc. Chem. Ind.*, **1898**, 17, 1073. Eng. Pat. 17524, Aug 13, 1898. Marius-Paul Otto, 1870-1939. His doctorate on ozone (thesis "Recherches sur l'ozone", 1897, Faculty des Sciences de Paris pour obtenir le grade de docteur és sciences physiques, Gauthier-Villars et fils) was done at the Sorbonne under Friedel and represents the first rational exploration of the reactions of ozone with organic compounds. He later became involved in the design and development of commercial ozone generating equipment and was instrumental in the ozonation of the water supply of his birthplace, Nice. President of the Compagnie des Eaux et de l'Ozone and a Commander of the Legion of Honor.
  40. J. L. Soret, "Recherches sur la densité de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1865**, 61, 941.
  41. J. L. Soret, "Recherches sur la densité de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1867**, 64, 904-8. *Ann. Chim. Phys.* [4], **1868**, 13, 257.
  42. O. Wolffenstein, "Beitrag zur Ozonfrage," *Ann. Phys.*, **1870**, 139, 320-329.
  43. J. L. Soret, "Bemerkungen über eine Abhandlung des Hrn. O. Wolffenstein, die Dichtigkeit des Ozons betreffend," *Ann. Phys.*, **1870**, 141, 294-99.
  44. Dubrunfaut, "Sur la nature de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1870**, 70, 159-62.
  45. Ref. 26, p 465.
  46. M. Otto, "Sur la densité de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1897**, 124, 78-81.
  47. A. Ladenburg, "Ueber Dichte und Molekulargewicht des Ozons," *Ber.*, **1898**, 31, 2830-1.
  48. W. Staedel, "Dichte und Molekulargewicht des Ozons," *Ber.*, **1898**, 31, 3143-4. Wilhelm Staedel, 1843-1919. Ph.D. 1865 Tübingen. In 1876 extraordinarius, 1881 Prof. ordinarius in Polytech. of Darmstadt.
  49. M. Gröger, "Ueber Dichte und Molekulargewicht des Ozons," *Ber.*, **1898**, 31, 3174-6.
  50. A. Ladenburg, "Ueber Dichte und Molekulargewicht des Ozons," *Ber.*, **1899**, 32, 221-2.
  51. A. Ladenburg, "Eine neue Methode zur Molekulargewichtbestimmung des Ozons," *Ber.*, **1901**, 34, 631-5.
  52. H. Kolbe, "Ueber die chemische Constitution der elementaren Moleküle," *J. Prakt. Chem. N.F.*, **1873**, 7, 119-126.
  53. M. Traube, "Ueber die Constitution des Wasserstoffhyperoxyds und Ozons," *Ber.*, **1893**, 26, 1476-81. Moritz Traube, 1826-94.
  54. J. W. Brühl, "Ueber das Wasserstoffhyperoxyd," *Ber.*, **1895**, 28, 2847-66. See p 2864 for a triangular structure for ozone. Julius W. Bruhl, 1850-1911. Ph.D. Göttingen 1875. From 1879 Prof. Tech. Chem. at Lemberg. From 1888 Prof. hon. at Heidelberg.
  55. O. Brunck, "Ueber Ozonbildung," *Z. anorg. Chem.*, **1895**, 10, 222-47. Otto Brunck, 1866-1911. Ph.D. Erlangen, studied in Munich 1884-89. From 1893 at Bergakademie Freiberg i.S. Prof. from 1896.
  56. A. Wolkowicz, "Ozon im Sinne des periodischen Systems," *Z. anorg. Chem.*, **1894**, 5, 264-5.

57. R. Clausius, "Zur Geschichte des Ozon," *Ann. Phys.*, **1870**, *136*, 102-105.
58. E. Schöne, "Ueber das Verhalten von Ozon und Wasser zu Einander," *Ber.*, **1873**, *6*, 1224 -29; *Liebigs Ann. Chem.*, **1874**, *171*, 87-109. Herman Emil Schöne, 1838-1896. Ph.D. Göttingen, from 1860 assistant in Berlin. From 1875 Prof. at Land und Forstwirtschaft Akad. zu Petrowskoje Rasumowskoje in Moscow.
59. L. Carius, "Ueber Absorption von Ozon in Wasser," *Ber.*, **1872**, *5*, 520-6. "Ueber Absorption von Ozon in Wasser," *Ber.*, **1873**, *6*, 806-9. "Verhalten des Ozons gegen Wasser und Stickstoff," *Liebigs Ann. Chem.*, **1874**, *173*, 1-30. Ludwig Carius, 1829-1875. Studied 1850-2 with Wöhler in Göttingen, assistant to Bunsen in Heidelberg for 6 years. From 1861 extraordinarius, from 1865 Prof. ordinarius in Marburg.
60. M. Berthelot, "Sur la formation de l'eau oxgénée, de l'ozone et de l'acide persulfurique pendant l'électrolyse," *Ann. Chim. Phys.* [5], **1878**, *14*, 354-61; *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1878**, *86*, 71-6.
61. C. Rammelsberg, "Ueber das Verhalten des Ozons zum Wasser," *Ber.*, **1873**, *6*, 603-5. This reference cites a letter from Carius to Rammelsberg concerning the problems involved in ozone solubility studies. Carl Friedrich Rammelsberg, 1813-1899.
62. A. R. Leeds, "Solubility of Ozone in Water," *J. Am. Chem. Soc.*, **1879**, *1*, 220-28.
63. L'abbé Mailfert, "Sur la solubilité de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1894**, *119*, 951-3.
64. A. Ladenburg, "Ueber das Ozon," *Ber.*, **1898**, *31*, 2508-13.
65. P. Hautefille and J. Chappuis, "Sur la liquéfaction de l'ozone et sur la couleur à l'état gazeux," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1880**, *91*, 522-5; *Ber.*, **1880**, *13*, 2408.
66. P. Hautefille and J. Chappuis, "Sur la liquéfaction de l'ozone en présence de l'acide carbonique et sur sa couleur à l'état liquide," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1880**, *91*, 815-7.
67. P. Hautefille and J. Chappuis, "Sur la liquéfaction de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1882**, *94*, 1249-51.
68. K. Olszewski, "Bestimmung des Siedepunktes des Ozons und der Erstarrungstemperatur des Äthylens," *Monatsh. Chem.*, **1887**, *8*, 69-72. Karol Stanislaw Olszewski, 1846-1915. Ph.D. Heidelberg 1872. From 1876 extraordinarius, 1891 Prof. ordinarius Univ. of Cracow. Together with Sigmund Florenty Wroblewsky he developed large scale liquefaction of gases in 1883 simultaneously with James Dewar (London).
69. L. Troost, "Sur la température d'ébullition de l'ozone liquide," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1898**, *126*, 1751-3. Louis Joseph Troost, 1825-1911. From 1874 Prof. Chem. at Sorbonne and from 1879 Directeur des Laboratoriums d. Ecole d'hautes etudes. Prof. honor. at Sorbonne. Member Paris academy.
70. J. Chappuis, "Sur le spectre d'absorption de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1880**, *91*, 985-6.
71. J. Chappuis, "Sur le spectre d'absorption de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1882**, *94*, 858-60. For a detailed report see J. Chappuis, "Étude spectroscopique sur l'ozone," *Ann. sci. de l'École Norm. Sup.* [2], **1882**, *11*, 137-86.
72. E. Schoene (Schöne), "Spectrum of Ozone and the Presence of Ozone in the Atmosphere," *J. Chem. Soc.*, **1885**, *48*, 713. From *J. Russ. Chem. Soc.*, **1884** [2], 250-2.
73. G. D. Liveing and J. Dewar, "Note on the Absorption-Spectra of Oxygen and some of its Compounds," *Proc. R. Soc. London*, **1889**, *46*, 222-30. Sir James Dewar, 1842-1923, Studied with Kekulé, was assistant in Edinburgh and became Prof. in Cambridge in 1875 until he moved to the Royal Institution in 1877. A pioneer in low-temperature work, he invented the flask that bears his name.
74. K. Olszewski, "Ueber das Absorptionsspectrum des flüssigen Sauerstoffs und der verflüssigten Luft," *Ann. Phys. N.F.*, **1888**, *33*, 570-75.
75. J. Dewar, "Optical Properties of Oxygen and Ozone," *Proc. R. Inst.*, **1889**, *12*, 468-78.
76. P. Hautefille and J. Chappuis, "Quelques faits pour servir à l'histoire de la nitrification," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1881**, *92*, 134-7.
77. W. N. Hartley, "On the Absorption Spectrum of Ozone," *J. Chem. Soc.*, **1881**, *39*, 57-60; "On the Absorption of Solar Rays by Atmospheric Ozone," *J. Chem. Soc.*, **1881**, *39*, 111-128; *Chem. News.*, **1881**, *43*, 142. Sir Walter Noel Hartley, 1846-1913, D.Sc. Dublin, studied in Edinburgh and in Marburg. In 1867 asst. in Bartholomew's Hospital London and the Royal Institution. 1871 demonstrator at Kings College, London. From 1879 Prof. Chem. Royal College of Science in Dublin. Received the Longstaff Medal of the Chemical Society.
78. M. Otto, "Sur l'ozone et les phénomènes de phosphorescence," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1896**, *123*, 1005-7.
79. J. Chappuis, "Quelques faits pur servir à l'histoire de la phosphorescence," *Bull. Soc. Chim. Fr.*, **1881**, *35*, 419-20.
80. E. Sarasin, "De la phosphorescence des gaz raréfiés après le passage de la décharge Électrique," *Ann. Chim. Phys.* [4], **1870**, *19*, 180-90.
81. A. de la Rive, "Observations sur la notice de M. Sarasin relative a la phosphorescence des gaz Raréfiés," *Ann. Chim. Phys.* [4], **1870**, *19*, 191-2.
82. J. Dewar, "Phosphorescence and Ozone," *Proc. R. Inst.*, **1889**, *12*, 557-60.
83. H. Becquerel, "Recherches sur le magnétisme spécifique de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1881**, *92*, 348-50.
84. M. Berthelot, "Stabilité chimique de la matière en vibration sonore," *Ann. Chim. Phys.* [5], **1880**, *20*, 265-70.

85. C. Than, "Ueber die bildung des Ozons bei raschen Verbrennungen," *J. Prakt. Chem.*, **1870**, 109, 415-420.
86. E. Baumann, "Zur Kenntnis des aktiven Sauerstoffs," *Z. Physiol. Chem.*, **1881**, 5, 244-56. Eugen Baumann, 1846-1896. M.D. 1879. Privatdozent, then extraordinarius in Physiological Chem. at Univ. of Berlin and then Prof. Chem. at Freiburg i/Br.
87. a. A. R. Leeds, "The Atomation of Oxygen," *J. Am. Chem. Soc.*, **1883**, 5, 205-15. b. "Atomation (2d Paper). Atomation of Oxygen at Elevated Temperatures, and the Production of Hydrogen Peroxide and Ammonium Nitrite, and the Non-isolation of Ozone in the Burning of Purified Hydrogen and Hydrocarbons, in Purified Air," *J. Am. Chem. Soc.*, **1884**, 6, 17-23.
88. J. J. Thomson and R. Threlfall, "Some Experiments on the Production of Ozone," *Proc. R. Soc. London*, **1886**, 40, 340-42. Sir Joseph John Thomson, 1856-1940. D.Sc. Dublin. In 1880 Fellow Trinity Coll. Cambridge. In 1883 lecturer, from 1884 Cavendish Prof. of exptl physics. 1894 President Cambridge Philosophical Society. 1884 FRS. Nobel Prize in physics 1906. Many honorary doctorates including Oxford, Dublin, Columbia. Sir Richard Threlfall, 1861-1932. M.A. 1887 Cambridge. 1884 assistant demonstrator. 1886-98 Prof. physics, Univ of Sydney. From 1898 director of Chem. Fabrik in Oldenburg at Birmingham. FRS 1899. Hon. degrees Victoria, Manchester.
89. E. Bichat and A. Guntz, "Sur la production de l'ozone par des décharges électrique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1888**, 107, 334-6; *Ber.*, **1890**, 23, 730c; *Ann. Chim. Phys.* [6], 19, 131-44. Ernst Adolphe Bichat, 1845-1905. From 1874 Prof. at Lyceum of Versailles, then Prof. at Lyceum Henri IV in Paris. Prof. physics in Fac. of Science of Univ of Nancy.
90. See L. I. Smith, F. L. Greenwood, and O. Hudrlik, "Ozone", *Org. Synth.*, Coll. Vol. 3, John Wiley and Sons, New York, 1955, 673-685.
91. M. Berthelot, "Appareils destinés a faire agir l'effluve électrique sur les gaz," *Ann. Chim. Phys.* [5], **1877** 10, 75-82. "Nouvelle recherches sur les phénomènes chimiques produits par l'électricité de tension," *Ann. Chim. Phys.* [5], **1877**, 12, 446-52. "Appareil pour soumettre a l'effluve électrique un volume limité de gaz," *Ann. Chim. Phys.* [5], **1877**, 12, 463-6. "Appareil pour faire passer l'etincelle électrique dans les gaz," *Ann. Chim. Phys.* [5], **1877**, 12, 467-8. "Appareil pour soumettre a l'effluve électrique un volume limité de gaz," *Ann. Chim. Phys.* [5], **1877**, 12, 463-6. Engler claims (C. Engler, ref. 5, **1880**, p. 142) that this apparatus was copied from an earlier design by Kolbe (ref. 13) although the textbook he cites was published in 1877, the same year as the first Berthelot publication.
92. M. Berthelot, "Recherches sur l'ozone et sur l'effluve électrique," *Ann. Chim. Phys.* [5], **1879**, 17, 142-4; *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1879**, 88, 50-2.
93. N. Teclu, "Neue Ozon-Apparate," *J. Prakt. Chem. N.F.*, **1899**, 60, 402-3. Nicolae Teclu, 1839-1916. Prof. Chem. at Handelsakademie, Vienna.
94. M. Otto, "Recherches sur l'ozone. I. Preparation de l'ozone," *Ann. Chim. Phys.* [7], **1898**, 13, 77-106. Anon., "Otto's ozonapparat," *Z. elektrochem.*, **1895**, 2, 11. Eng. pat. no 748, 1895. M. Otto, "Ozone, Production of," *J. Soc. Chem. Ind.*, **1897**, 16, 931.
95. P. Hautefille and J. Chappuis, "Recherches sur la transformation de l'oxygène en ozone par l'effluves électrique, en présence d'un gaz étranger," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1880**, 91, 762-5.
96. A. M. Villon, "L'ozonisation Industrielle," *Bull. Soc. Chim. Fr.*, [3], **1893**, 9, 730-31.
97. A. R. Leeds, "Comparative Results Obtained with Previous Electrical Ozonisers, with Description of a Modified and More Powerful Form," *J. Am. Chem. Soc.*, **1879**, 1, 431-452.
98. L. v. Babo and A. Claus, "Über das Volum des Ozons," *Ann. Chem. Pharm., II Supp.*, **1863**, 297-305.
99. A. Houzeau "Experiences sur l'électrolisation de l'air ou de l'oxygène comme moyen de production de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1870**, 70, 1286-7; *Ann. Chim. Phys.* [4], **1871**, 22, 150-71. "Sur la préparation de l'ozone à l'état concentré," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 74, 256.
100. A. W. Wright, "On a Simple Apparatus for the Production of Ozone with Electricity of High Tension," *Am. J. Sci.*, **1872**, 104, 26-29. Arthur William Wright, 1836-1915. Ph.D. Yale 1861. From 1869 Prof. Physics and Chem. at Williams College. In 1872 Prof. Molecular Physics and Chem. at Yale University.
101. A. Boillot, "Préparation de l'ozone au moyen d'un nouveau mode de production des effluves électrique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 214-5. "Sur un nouveau mode de production de l'ozone, au moyen du charbon (deuxième Note)," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 1712-3. "Action des effluves électrique sur l'air atmosphérique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1873**, 76, 869-71.
102. T. Wills, "On an Improved Form of Ozone Generator," *Nature*, **1873**, 8, 146. Thomas Wills, 1850-1879 (!). Demonstrator for chemistry at Royal Naval College. Member London Chem Soc.
103. F. Richarz, "Die Bildung von Ozon, Wasserstoffsperoxyd und Ueberschwefelsäure bei der Elektrolyse verdünnter Schwefelsäure," *Ann. Phys. Chem. N.F.*, **1885**, 24, 183-209. Franz Richarz, 1860-1920. Privatdozent 1883 Univ. of Bonn. From 1885 Prof. Physics at Univ. Greifswald and from 1901 in Marburg.
104. M. Berthelot, "Sur l'acide persulfurique, nouvel acide oxygéné du soufre," *Ann. Chim. Phys.*, [5], **1878**, 14, 345-363. "Nouvelles observations sur les réactions chimiques de l'effluve et sur l'acide persulfurique," *Ann. Chim. Phys.* [5], **1878**, 14, 363-6.
105. F. Le Blanc, "Sur l'ozone et l'eau oxygénée," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 537-8.

106. G. Targetti, "Sulla Produzione Dell'ozono per Via Elettrolitica," *Nuov. Cim.* [4], **1899**, 10, 360-5. Summary in *Z. Phys. Chem.*, **1900**, 35, 372.
107. P. Lenard, "Ueber Wirkungen des ultravioletten Lichtes auf gasförmiger Körper," *Ann. Phys.* [4], **1900**, 1, 486-507.
108. A. R. Leeds, "Relation between the Temperature and Volume in the Generation of Ozone, with Description of a New Form of Ozonator," *J. Am. Chem. Soc.*, **1879**, 1, 8-18; *Liebigs Ann. Chem.*, **1879**, 198, 30-42.
109. R. Böttger, *Ber.*, **1879**, 12, 2187. Rudolph Böttger, 1806-1881, Prof. Physics in Frankfurt/Main.
110. R. Engel, "Notes de laboratoire. D. Expérience de cours sur la production de l'ozone dans l'oxydation lente du phosphore," *Bull. Soc. Chim. Fr.*, **1886**, 44, 426-7. Rodolphe Charles Engel, 1850-1916. Prof of Chem. and Medicine at Montpellier. Then Prof. of Chem. Ecole centrale, Paris.
111. C. T. Kingzett, "Report on the Atmospheric Oxidation of Phosphorus and some Reactions of Ozone and Hydric Peroxide" *J. Chem. Soc.*, **1880**, 37, 792-807. "Is Ozone Produced during the Atmospheric Oxidation of Phosphorus?" *Chem. News*, 40, 96. Charles Thomas Kingzett, 1852-1935. Founder and chemist at the Sanitas Company, London. Inventor of the Sanitas product resulting from his investigations concerning ozone and the essential oils. Member Chem. Soc. London. One of the founders of the Inst. of Chem., founder of The Chemical Encyclopedia.
112. A. R. Leeds, "Peroxide of Hydrogen and Ozone. First Paper," *J. Am. Chem. Soc.*, **1880**, 2, 34-41. "On Peroxide of Hydrogen and Ozone. Second Paper," *J. Am. Chem. Soc.*, **1880**, 2, 147-60. "Ueber die Bildung von Wasserstoffhyperoxyd und Ozon bei Einwirkung von feuchtem Phosphor auf Luft," *Ber.*, **1880**, 13, 1066-70.
113. H. McLeod, "Note on the Formation of Ozone during the Slow Oxidation of Phosphorus," *J. Chem. Soc.*, **1880**, 37, 118-20.
114. J. Elster and H. Geitel, "Ueber Ozonbildung an glühenden Platinflächen und das elektrische Leitungsvermögen der durch Phosphor ozonisirten Luft," *Ann. Phys. N.F.*, **1890**, 39, 321-31.
115. T. Ewan, "Ueber die Oxydationsgeschwindigkeit von Phosphor, Schwefel und Aldehyd" *Z. Phys. Chem.*, **1895**, 16, 315-43; also *Philos. Mag.*, **38**, 505-536. Thomas Ewan, 1868-1955. M.Sc. Manchester, Ph.D. 1890 Munich; from 1894 demonstrator in Leeds.
116. J. H. van't Hoff, "Über die Menge und die Natur des sogen. Ozons, das sich bei langsamer Oxydation des Phosphors bildet," *Z. Phys. Chem.*, **1895**, 16, 411-16. Jacobus Henricus van't Hoff, 1852-1911, Ph.D. Utrecht in 1874, also studied with Kekulé and Wurtz. Nobel Prize in Chemistry in 1901. His neighbor in Wurtz' lab. was A. Le Bel; the two independently proposed the tetrahedral carbon atom in 1874. Assistant in the Veterinary College in Utrecht 1876-78, Prof. in Amsterdam 1878-96, then moved to Berlin. The triumvirate of Arrhenius, Ostwald, and van't Hoff dominated physical chemistry during the latter part of the 19th century.
117. F. Molnar, "Ueber die Einfluss einiger Gase und Dampfe auf die Entzündungstemperatur des Phosphors, und auf die langsame Verbrennung desselben," *Ber.*, **1889**, 22c, 170.
118. H. Moissan, "Production d'ozone par la décomposition de l'eau au moyen du fluor," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1899**, 129, 570-3. Henri Moissan, 1852-1907. Prof., École supérieure de pharmacie in Paris. Prof. of Chem. Univ of Paris. Nobel Prize 1906 for his contributions to fluorine chemistry.
119. A. Valentini, "Apparecchio, per la preparazione dell'ozono secondo il metodo di Schönbein," *Gazz. Chim. Ital.*, **1884**, 14, 215.
120. C. C. Frye, "On the Nature of an Oxidizing Substance Produced by Distilling Aqueous Solutions of Potassium Permanganate and Sulphuric Acid *in Vacuo*," *Chem. News*, **1896**, 73, 122.
121. L. Ilosva, "Il n'y a pas d'ozone dans l'oxygène préparé avec l'acide sulfurique concentré et le permanganate de potassium," *Bull Soc. Chim. Fr.*, [3], **1889**, 2, 734-6. Ludwig Ilosvay de Nagy-Ilosva, 1851-1936. Ph.D. Budapest 1875, pupil of K. v. Than. Tech Hochschule Budapest from 1876. From 1882 Prof. Gen. Chem., 1886-92 Dean of Chemistry, 1893-98 Dean of Arch. and Eng, 1900-02 Rector.
122. C. Winkler, "Ein Vorlesungsversuch," *Z. anorg Chem.*, **1892**, 1, 82. Clemens Alexander Winkler, 1838-1904. From 1873 Prof. Chem. at Bergakademie, Freiberg.
123. H. Croft, "Anomalous Production of Ozone," *Am. J. Sci.*, **1872**, 103, 466.
124. G. Bellucci, "Sulla produzione dell'ozono durante la nebulizzazione dell'acqua," *Gazz. Chim. Ital.*, **1876**, 6, 88-97; report in *Ber.*, **1876**, 9, 581.
125. E. F. C. von Gorup-Besanez, "Ozone Reactions of the Air in the Neighbourhood of Graduation-houses for Salt Evaporation (Gradirhäusern)," *Ann. Chem. Pharm.*, **1872**, 161, 232-51; abstract *J. Chem. Soc.*, **1872**, 25, 384-5. Eugen Franz Cajetan von Gorup-Besanez, 1817-1878. M.D. 1843 Munich. Studied 1836-8 in Vienna, 1839-42 in Padua and München, 1843 in Chem Lab of Buchner. From 1846 in Erlangen, from 1855 Prof. ordinarius. Wrote two textbooks.
126. J. Bellucci, "Sur la prétendu dégagement de l'ozone des plantes," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1874**, 78, 362-5.
127. O. Brunck, "Ueber 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

- Peroxide. (Second Note)," *J. Chem. Soc.*, **1896**, 69, 1015-21.
129. O. Brunck, "Ueber Ozonbildung," *Z. Anorg. Chem.*, **1895**, 10, 222-47.
130. A. R. Leeds, "On the Production of Ozone by Heating Substances containing Oxygen," *J. Am. Chem. Soc.*, **1880**, 2, 411-5; *Ber.*, **1880**, 13, 2351-3.
131. S. Kappel, "Ueber die Bildung von Ozon und Wasserstoffhyperoxyd," *Arch. Pharm.* [3], **1882**, 17, 574-7.
132. e.g., G. Bellucci, as reported in *Ber.*, **1879**, 12, 1699-70. A. Besson, "Sur quelques propriétés oxydantes de l'oxygène ozoné et de l'oxygène irradié," *Compt. rend.*, **1895**, 121, 125-8. J. Schiel, "Ueber Ozonbildung durch Kohlenwasserstoffe," *Ber.*, **1879**, 12, 507-8, *Bull. Soc. Chim. Fr.*, **1880**, 33, 176-7.
133. M. Berthelot, "Sur les propriétés oxydantes de l'essence de térébenthine," *Ann. Chim. Phys.* [3], **1860**, 58, 426-46.
134. C. T. Kingzett, "On Ozone as a Concomitant of the Oxidation of the Essential Oils. Part I.," *J. Chem. Soc.*, **1874**, 27, 511-24; "Report on the Atmospheric Oxidation of Phosphorus and some Reactions of Ozone and Hydric Peroxide," *J. Chem. Soc.*, **1880**, 37, 792-807.
135. C. Engler and J. Weissberg, "Ueber Activierung des Sauerstoffs, 2 Mittheilung. Der active Sauerstoff des Terpentinsöls," *Ber.*, **1898**, 31, 3046-55.
136. J. B. A. Dumas, "Recherches sur la fermentation alcoolique," *Ann. Chim. Phys.* [5], **1874**, 3, 57-108. See pages 80-81.
137. (a). C. Than, "Ueber die Bildung des Ozons bei raschen Verbrennungen," *J. Prakt. Chem.*, **1870**, 109, 415-420. (b). Pincus, "Ungewöhnliche Ozonbildung," *Ann. Phys.*, **1871**, 144, 480. (c). H. Struve, "Studien über Ozon, Wasserstoffhyperoxyd und salpetrigsäures Ammoniak," *Z. Anal. Chem.*, **1871**, 10, 292-8. (d). R. Blochmann, "Ueber die Vorgänge in Innern der nichtleuchtenden Flamme des Bunsen'schen Brenners," *Liebigs Ann. Chem.*, **1873**, 168, 295-358. (e). R. Böttger, "Formation of Ozone by combustion of hydrogen in Oxygen," *J. Chem. Soc.*, **1874**, 27, 653. (f). W. Raduloicitch as cited by N. Menshutkin, *Ber.*, **1877**, 10, 2059. (g). F. Jeremin, "Ueber den Einfluss der Temperatur des Volta'schen Bogen auf die schwefelsäuren Salze des Bariums und Cadmiums," *Ber.*, **1881**, 14, 1704-5. From *J. Russ. chem. Gesellsch.*, **1881**, 244. (h). J. T. Cundall, "Note on the production of ozone by flames," *Proc. Chem. Soc. London*, **1890**, 6, 26-7; (i). O. Brunck, "Ueber Ozonbildung bei hohen Temperaturen," *Ber.*, **1893**, 26, 1790-94.
138. J. Dewar, "Phosphorescence and Ozone," *Proc. R. Inst.*, **1889**, 12, 557-60.
139. E. Bichat and A. Guntz, "Sur la production de l'ozone par des décharges électrique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1888**, 107, 334-6. *Ber.*, **1890**, 23, 730c; *Ann. Phys. Chim.* [6], 19, 131-44.
140. L. Ilosva, "Se forme-t-il de l'ozone ou du peroxyde d'hydrogène pendant la combustion vive, ou bien sont-ce les oxydes superieurs de l'azote qui de forment alors qu'on peut constater avec les réactions de l'acide azoteux et azotique (IV)," *Bull. Soc. Chim. Fr.*, [3], **1889**, 2, 360-377. "Peut-il se former de l'ozone en abaissant la température de la flamme? Y a-t-il de l'ozone près de la flamme?," *Bull. Soc. Chim. Fr.*, [3], **1890**, 4, 707-14. The negative claim of Ilosva's earlier paper was partly retracted in 1890.
141. see H. Struve, "Studien über Ozon, Wasserstoffhyperoxyd und salpetrigsäures Ammoniak," *Z. Anal. Chem.*, **1871**, 10, 292-8. Heinrich Wilhelm Struve, 1822-1908. 1849-67 älterer Laborant and Bergprobirer am Labor. d. Berg-Departem in St. Petersburg. From 1869 expert for gerichtl. chem at Civil-Medic. Verwalt Kaukasiens in Tiflis.
142. Pincus, "Ungewöhnliche Ozonbildung," *Ann. Phys.*, **1871**, 144, 480.
143. Ref. 5, 1880, 16, 139.
144. M. Berthelot, "Sur la stabilité de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1878**, 86, 76-7; *Ann. Chim. Phys.* [5], **1878**, 14, 361-3.
145. E. Mulder, "Sur un ozonomètre à effluve et sur la vitesse de décomposition de l'ozone," *Recl. Trav. Chim. Pays-Bas*, **1884**, 3, 137-57; **1885**, 4, 139-46. Eduard Mulder, 1832-1924. Prof. Chem., Univ of Utrecht 1868-1902.
146. R. von Helmholtz and Franz Richarz, "Ueber die Einwirkung chemischer und elektrischer Processe auf den Dampfstrahl und über die Dissociation der Gase, insbesondere des Sauerstoffs," *Ann. Phys. N.F.*, **1890**, 40, 161-202. This paper was dedicated to Richarz' deceased teacher Helmholtz.
147. E. Mulder and H. G. L. van der Meulen, "L'ozone en présence du noir de platine," *Recl. trav. chim. Pays-Bas*, **1882**, 1, 167-72.
148. I. Remsen, "On the Transformation of Ozone into Oxygen by Heat," *Am. Chem. J.*, **1882-3**, 4, 50-53. Ira Remsen, 1846-1927. Assistant in Tübingen 1870 (also studied in Munich and New York). Prof. Chem. and Physics Williams College 1872; from 1876-1912 Prof. at Johns Hopkins Univ. Editor (1879-1913) and founder *American Chemical Journal*. President Am. Chem. Soc. 1902. LLD Columbia 1893, Princeton 96, also Yale, Harvard, Toronto, etc.
149. See section on inorganic reactions, also cf. A. R. Leeds, "The Conversion of Carbon Monoxide to Carbon Dioxide by Active (i.e. Nascent) Oxygen," *J. Am. Chem. Soc.*, **1883**, 5, 78-91. H. B. Dixon, "The Mode of Formation of Carbonic Acid in the Burning of Carbon Compounds," *J. Chem. Soc.*, **1896**, 69, 774-89.
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

- chemistry and medicine at Guy's Hospital, London. Prof. Chem. Royal Naval College. From 1873-88 Prof. Chem. at Marine Academy, Greenwich, after 1888 in Kassel.
151. T. Woods, "On the Nature of Ozone," *Philos. Mag.* [4], **1864**, 28, 106.
152. P. J. Hollmann, "Sur l'équivalent calorifique de l'ozone," *Arch. Néerland.*, **1868**, 3, 260-72.
153. T. Fairley, "Study of Hydrogen Dioxide and Certain Peroxides, including Experiments to Determine the Heat of Formation of the Oxygen-molecule," *J. Chem. Soc.*, **1877**, 31, 1-19. He reported being unable to consult Hollmann's original paper.
154. M. Berthelot, "Sur la formation thermique de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1876**, 82, 1281-3; *Ann. chim. Phys.* [5], **1877**, 10, 162-9.
155. E. Mulder and H. G. L. van der Meulen, "Expériences thermochimiques sur l'ozone," *Recl. Trav. Chim. Pays-Bas*, **1882**, 1, 65-7, *Ber.*, **1882**, 15, 511-13; E. Mulder and H. G. L. van der Meulen, "Recherches thermochimiques sur l'ozone," *Recl. Trav. Chim. Pays-Bas*, **1882**, 1, 73-90; H. G. L. van der Meulen, "Sur la détermination directe et indirecte de la chaleur de décomposition de l'ozone," *Recl. Trav. Chim. Pays-Bas*, **1883**, 2, 69-90.
156. E. Mulder, "Sur un ozonometre à effluve et sur la vitesse de décomposition de l'ozone," *Recl. Trav. Chim. Pays-Bas*, **1884**, 3, 137-57.
157. A. Volta, "L'ozono sopra alcuni metalli nobili," *Gazz. Chim. Ital.*, **1879**, 9, 521-32.
158. J. Ogier, Formation de l'acide iodeux par l'action de l'ozone sure l'iode," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1877**, 85, 957-9. Jules Francois Ogier, 1853-1913. From 1875 Préparateur de chimie at College de France.
159. (a). l'Abbé Mailfert, "Recherches sur l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1882**, 94, 860-3. (b). *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1882**, 94, 1186-7.
160. L. Maquenne, "Action de l'ozone sur les sels de manganèse," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1882**, 94, 795-7. Leon Gervaise Marie Maquenne, 1853-1925. DSc 1880 Paris. Prof. Chem. in Coll. Chaptal in Paris, then Prof. Plant Physiology at Museum of Natural History in Jardin d. Planaetes in Paris. Director Lab physiol. veget., Ecole pract d. hautes Et., Paris
161. M. Berthelot, "Sur l'incompatibilité entre l'acid azoteux, l'ozone et l'oxygène humide," *Ann. Chim.* [5], **1878**, 14, 367-8.
162. E. Schöne, "Experimentaluntersuchungen über das Wasserstoffhyperoxyd. Funfte Abhandlung. Ueber das Verhalten des Wasserstoffhyperoxyds zum Ozon und Chlor," *Liebigs Ann. Chem.*, **1879**, 196, 239-258.
163. M. Berthelot, "L'ozone se combine-t-il avec l'azote libre en présence des alcalis, pour former des composés nitreux et des nitrates?," *Ann. Chim. Phys.* [5], **1877**, 12, 440-45; *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1877**, 84, 61-4.
164. A. Boillot, "Action des effluves électriques sur l'air atmosphérique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1873**, 76, 869-71.
165. W. A. Shenstone and W. T. Evans, "Observations on the Influence of the Silent Discharge on Atmospheric Air," *J. Chem. Soc.*, **1898**, 73, 246-54.
166. A. R. Leeds, "Upon Ammonium Nitrite, and Upon the By-products Obtained in the Ozonisation of Air by Moist Phosphorus," *J. Am. Chem. Soc.*, **1879**, 1, 145-57; *Liebigs Ann. Chem.*, **1879**, 200, 286-301; *Chem. News.*, **1881**, 97-100.
167. L. Carius, "Oxydation des Ammoniaks durch Ozon," *Ber.*, **1874**, 7, 1481-5; "Ueber Bildung von salpetriger Säure, Salpetersäure und Wasserstoffsuperoxyd in der Natur," *Liebigs Ann. Chem.*, **1874**, 173, 31-55. Cf. also L. Ilosva, "Von den bei der Aufeinanderwirkung von Ozon und Ammoniak sich bildenden Nebenproducten," *Ber.*, **1894**, 27, 3500-3.
168. I. Remsen and M. S. Southworth, "On the Action of Ozone on Carbon Monoxide," *Am. J. Sci.*, **1876**, 111, 136-9; *Ber.*, **1875**, 8, 1414-17.
169. I. Remsen and E. H. Keiser, "On the Conduct of Moist Phosphorus and Air towards Carbon Monoxide," *Am. Chem. J.*, **1882-3**, 4, 454-8. Remsen later established that ordinary white phosphorus may contain traces of a carbon impurity which could be responsible for the carbon dioxide observed, I. Remsen, "Historical Note Concerning the Presence of Carbon in Phosphorus," *Am. Chem. J.*, **1884**, 6, 72.
170. A. R. Leeds, "Oxidation of Carbonic Oxide by Air over Phosphorus at Ordinary Temperatures," *J. Am. Chem. Soc.*, **1879**, 1, 232.
171. M. Otto, "Recherches sur l'ozone. II. Propriétés chimiques de l'ozone," *Ann. Chim. Phys.* [7], **1898**, 13, 106-144.
172. M. Otto, (No title), Ass. franç. pour l'avanc. des Sciences, C. rendus du Congrès de Bordeaux, **1895**, 236.
173. L. Maquenne, "Action de l'ozone sur les carbures," *Bull. Soc. Chim. Fr.*, **1882**, 37, 298-300.
174. A. Houzeau and A. Renard, "Application de l'ozone concentré à l'étude de la Chimie organiques: ozobenzine," *Bull. Soc. Chim. Fr.*, **1873**, 19, 407-8; *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1873**, 76, 572. Guillaume Adolphe Renard, 1846-1919. D.Sc. 1879 Paris, Prof. at Ec. sup. des sci. in Rouen.
175. A. Besson, "Sur la préparation de l'éthylène perchloré et l'action de l'oxygène ozonisé sur ce corps," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1894**, 118, 1347-50. cf. also A. Besson, Sur quelques propriétés oxydantes de l'oxygène ozoné et de l'oxygène irradié," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1895**, 121, 125-8. Jules Adolphe Besson, 1861-. Prof. adj. of Chem., Univ. Caen
176. A. Houzeau, "Sur l'oxydation instantanée de l'alcool," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 142-3.
177. A. W. Wright, "On the Oxidation of Alcohol and Ether by Ozone," *Am. J. Sci.*, **1874**, 107, 184-9.

178. A. Boillot, "Action de l'ozone sur l'alcool absolu; combinaison du cyanogène avec l'hydrogène, sous l'influence des effluves électriques," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1873**, 76, 1132.
179. W. R. Dunstan and T. S. Dymond, "An Investigation of the Conditions under which Hydrogen Peroxide is Formed from Ether," *J. Chem. Soc.*, **1890**, 57, 574-87.
180. M. Berthelot, "Sur le peroxyde d'éthyle," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1881**, 92, 895-7.
181. A. Houzeau, "Sur le pouvoir décolorant de l'ozone concentré," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 349-51. Comment by P. Thenard follows.
182. A. Renard, "Sur l'ozobenzène," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1895**, 120, 1177-79; "Sur l'ozotoluène," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1895**, 121, 651-2.
183. A. R. Leeds, "Ueber die Einwirkung von Ozon, nascirendem Sauerstoff und Wasserstoffhyperoxyd auf Benzol," *Ber.*, **1881**, 14, 975-7.
184. Dieckhoff, Habilitationsschrift, Karlsruhe, 1891.
185. C. D. Harries, "Ueber die Einwirkung des Ozons auf organische Verbindungen. (Erste Abhandlung)," *Liebigs Ann. Chem.*, **1905**, 343, 311-375.
186. Jouglet, "L'action de l'ozone sur la nitroglycérine, la dynamite, et différents autres composés explosifs," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1870**, 70, 539-40.
187. J. B. A. Dumas, "Recherches sur la fermentation alcoolique," *Ann. Chim. Phys.* [5], **1874**, 3, 57-108. See page 81.
188. A. Boillot, "Note concernant l'action de l'ozone sur les substances animales," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1875**, 81, 1258. Fresh meat and milk exposed to ozone; "Note sur la propriété décolorante de l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1875**, 80, 1167-8.
189. E. J. Maumené, "Action de l'ozone sur les jus sucrés," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1875**, 81, 107.
190. A. R. Leeds, "Action of ozone upon the coloring matter of plants," *J. Am. Chem. Soc.*, **1879**, 1, 228-29. "Bleaching of sugar syrups by ozone," *J. Am. Chem. Soc.*, **1879**, 1, 229-30.
191. N. Fradiss, "Die Ozonisation der Zuckersäfte," *Chem. Zentralbl.*, **1899** I, 1301. From *Zeit. Zucke.-Ind. Böhm.*, 23, 364-9.
192. W. Stelzer, "Über Ozon," *Pharm. Centr.-H.*, **1897**, 38, 453-4; *Chem. Zentralbl.*, **1897** II, 406.
193. A. Wagner, "Ueber einige Ozonwirkungen," *Z. Anal. Chem.*, **1883**, 22, 316-18.
194. A. W. Wright, "On the Action of Ozone upon Vulcanized Caoutchouc," *Am. J. Sci.*, **1872**, 104, 29-31.
195. J. D. Boeke, "Einwirkung von Ozon auf Pyrogallol," *Ber.*, **1873**, 6, 486-88.
196. M. Nencki, "Zur Geschichte der Oxydationen im Thierkörper," *J. Prakt. Chem.* (N.F.), **1881**, 23, 87-96. C. Binz, "Die Verhalten von Blut und Ozon zu einander", *Ber.*, **1883**, 16, 92. *Centralbl. med. Wissensch.*, **1882**, 72, 1-5. E. Bourquelot, "Bemerkungen über die oxydierenden Stoff, welche man bei Lebewesen antreffen kann." *Chem. Zentralbl.*, **1897** II, 45-6. Cf also ref. 86.
197. H. Day, M.D., *Ozone in Relation to Health and Disease*, J. Churchill & Sons, London, 1878. Originally presented as an address delivered before the Congress of the Sanitary Institute of Great Britain in 1878.
198. J. Dewar and M'Kendrick, "On the Physiological Action of Ozone," *Nature*, **1874**, 9, 104-5.
199. M. Filipow, "Zur therapeutischen Bedeutung von Sauerstoff und Ozon," *Ber.*, **1885**, 18, 31. From *Arch. f. d. ges. Physiol.*, 34, 335-61.
200. H. Schulz, "Über chronische Ozonvergiftung," *Chem. Zentralbl.*, **1892** I, 996. from *Arch. Pathol.*, 29, 365-85.
201. E. Renzi, "Ueber das Ozon," *Arch. Pathol. Anat.*, **1886**, 104, 203-40.
202. D. Labbé and Oudin, "Sur l'ozone considéré au point de vue physiologique et thérapeutique," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1891**, 113, 141-4.
203. J. N. Hearder, "Physiological Effects of Ozone," *Nature*, **1874**, 9, 182-3.
204. E. Chappuis, "Action de l'ozone sur les germes contenus dans l'air," *Bull. Soc. Chim. Fr.*, **1881**, 35, 290-1.
205. Ohlmüller, "Über die Einwirkung des Ozons auf Bakterien," *Arbeiten a. d. Kaiserl. Gesundheitsamt*, **1891**, 8, 229-51.
206. E. van Ermengen, "De la stérilisation des eaux par l'ozone," *Ann. de l'inst. Pasteur*, **1895**, 9, 673-709.
207. A. Calmette, "Rapport sur la stérilisation industrielle des eaux potables par l'ozone," *Ann. de l'inst. Pasteur*, **1899**, 13, 344-357.
208. L. Marmier and H. Abraham, "Sur la stérilisation industrielle des eaux potables par l'ozone," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1899**, 128, 1034-5. Henri Azariah Abraham, 1868-1943. Maître de conférence, Ecole normale, Paris. Prof. Physics, Univ. of Paris.
209. Behrens, *Vierteljahresschrift f. pr. Pharmacie von Wittstein*, **1873**, 22, 230.
210. G. Vulpius, "Ueber Ozonwasser," *Arch. Pharm.* [3], 22, 268-78.
211. Dr. Graf and Comp., "Darstellung eines haltbaren Ozonwassers," *Ber.*, **1891**, 24, 174c. Ger. Pat. 52452, 28 Sept 1889.
212. F. Jeremin, *Ber.*, **1878**, 11, 988-9, as reported by Beilstein from an unnamed Russian journal.
213. Widemann, "Emploi industriel de l'ozone en Amérique; destruction du goût empyreumatique du whisky; fabrication du vinaigre," *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1872**, 75, 538.
214. E. Andréoli, "Ozone, its Commercial Production and Applications," *J. Soc. Chem. Ind.*, **1897**, 16, 89-96.
215. E. Andréoli, *Ozone: its Commercial Production, its Applications.* H. Alabaster, Gatehouse and Co., London, 1893. A mixed review appeared in *Chem. News*, **1893**, 68, 72.
216. E. Andréoli, "Elektrischer Apparat zur gleichzeitigen Erzeugung von Ozon und Licht," *Ber.*, **1895**, R 122. Ger. Pat. 77925, 16 Nov, 1893.

217. Fröhlich, no title, *Bericht über die erste Hauptversammlung der Deutschen elektrochemischen Gesellschaft*, **1894**, p 30.
218. A. M. Villon, "Neue Anwendungen des Ozons," *Chem. Zentralbl.*, **1893** I, 105.
219. W. J. Engledue, "Ozone and its Commercial Applications," *J. Soc. Chem. Ind.*, **1898**, 17, 1101-6.
220. J. B. C. Kershaw, "Ozone, Production of, and Cost, as compared with other Ordinary agents," *J. Soc. Chem. Ind.*, **1898**, 17, 1173.
221. M. Krüger, Das Ozon, seine Darstellung und Verwendung," *Chem. Zentralbl.*, **1895** I, 451. from *Elektrochem. Z.*, 1, 60-2.
222. de Carvalho, C. R. *Hebd. Séances Acad. Sci., Ser. C*, **1876**, 82, 157.
223. P. Thenard, no title. *C. R. Hebd. Séances Acad. Sci., Ser. C*, **1876**, 82, 157-9.
224. E. Schöne, "Über die Beweise, welche man für die Anwesenheit des Ozons in der atmosphärischen Luft angeführt hat," *Ber.*, **1880**, 13, 1503-8.
225. L. Ilosva, "Y a-t-il de l'ozone et du peroxyde d'hydrogène dans l'air," *Bull. Soc. Chim. Fr.*, [3], **1889**, 2, 377-88.
226. C. Engler and W. Wild, "Ueber die Trennung des Ozons von Wasserstoffsperoxyd und den Nachweis von Ozon in der Atmosphäre," *Ber.*, **1896**, 29, 1940-2.
227. E. Schoene (Schöne), "Spectrum of Ozone and the Presence of Ozone in the Atmosphere," abstracted in *J. Chem. Soc.*, **1885**, 48, 713. From *J. Russ. Chem. Soc.*, **1884** [2], 250-2.
228. A. Houzeau, "Sur l'ozone atmosphérique," *Ann. Chim. Phys.* [4], **1872**, 27, 5-68.
229. G. Wolffhügel, "Ueber den sanitären Werth des atmosphärischen Ozons," *Zeit. f. Biologie*, **1875**, 11, 408-58.
230. S. Sandroni, D. Anfossi, and S. Viarengo, "Surface Ozone Levels at the End of the Nineteenth Century in South America," *J. Geophys. Res.*, **1992**, 97, 2535-9.
231. A. Marengo, H. Gouget, P. Nedelec, J.-P. Pages, J. Karcher, "Evidence of a Long-term Increase in Tropospheric Ozone from Pic du Midi Data Series: Consequences: Positive Radiative Forcing," *J. Geophys. Res.*, **1994**, 99, 16617-16632.
232. [www.giub.unibe.ch/~evi/cabo/cabomonts.html](http://www.giub.unibe.ch/~evi/cabo/cabomonts.html). Accessed Feb. 2001.
233. W. Sutherland, "The Spontaneous Change of Oxygen into Ozone and a Remarkable Type of Dissociation," *Phil. Mag.* [5], **1897**, 43, 201-14. William Sutherland, 1859-1912. B.A. 1879 Melbourne, B.Sc. 1881 London. MA 1883 Melbourne. Physicist in Melbourne.
234. C. Engler and O. Nasse, "Ozon und Antozon," *Ann. Chem. Pharm.*, **1870**, 154, 215-237; also C. Engler and W. Wild, "Mittheilungen über Ozon," *Ber.*, **1896**, 29, 1929-1940.
235. A. R. Leeds, "The History of Antozone and Peroxide of Hydrogen," *Ann. N.Y. Acad. Sci.*, **1879**, 1, 405-425.
236. e.g., The title of the 1873 Fox book (Ref. 2) was "Ozone and Antozone."

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## FRANCIS HOME AND JOSEPH BLACK: THE CHEMISTRY AND TESTING OF ALKALINE SALTS IN THE EARLY BLEACHING AND ALKALI TRADE

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*Frederick G. Page, University of Leicester*

This paper considers the analytical work of two chemists in Scotland during the second half of the 18<sup>th</sup> century. It examines their efforts to understand and determine the strength of alkaline salts at a time when quantitative analytical measurement was beginning to be made in a form recognizable by present day chemists. In this period atomic weights and chemical formulae, which we now regard as essential aids in analysis, had not come into being. There is therefore a temptation for present day chemists to regard the period as one in which quantitative chemical analysis seemed almost impossible. It will be shown however that the analytical methods and chemical thinking of Francis Home (1719-1813) and Joseph Black (1728-1799) were adequate for the needs of the early alkali trade and the use of these alkaline materials in bleaching.

*The Chemical Revolution* of Archibald Clow and Nan Clow is of particular value to historians for its account of the early Scottish kelp industry as a source of natural alkali (1). These authors made little reference to analytical chemistry associated with this industry, although Tennant's method of estimating barilla (impure alkali) was given as an example of volumetric analysis (2). A full critical review of this book was made by F. W. Gibbs, who confirmed the Clows' view that the growth of 18<sup>th</sup>-century chemistry was paralleled by a corresponding growth of chemical manufacturing (3).

The early bleaching industry depended upon the cleansing properties of alkali solutions, and before the

synthetic alkali of Leblanc became available the industry used natural alkali from kelp and other plant origins. Since chemical analysis was regarded as of limited value to the manufacture of Leblanc alkali (4), it is not surprising that earlier analytical requirements remained of secondary importance.

### **The Early Bleaching Industry in Scotland**

The empirically based art of bleaching had origins in Hellenistic technology but by what route the methods became common in Britain is uncertain (5). The Netherlands and Germany appear to have been the first in Europe in this field (6), and it was to these countries that Britain sent linen from its expanding textile industry to be bleached and then returned, thus establishing a seasonal export-import business. Such trade, known to have occurred within the first few decades of the 1700s, diminished when satisfactory bleaching operations were established in Britain; but the process remained slow and complicated. For example, a typical "bucking" (alkaline wash) solution might be made thus (7):

*The Concentrate:* Blue ashes (30 lb); White pearl ashes (30 lb); Marcoft ashes (200 lb) or Cashub ashes (300 lb); and Muscovy ashes (300 lb) placed in water to make up to 170 gallons.

*Bucking Liquid:* 2 gallons of the above slurry were combined with 2 lb of soap, and the whole was then made up to 40 gallons.

The linen would be steeped in this kind of alkaline solution for some hours, followed by several washes in wa-

ter and repeated buckings, finally being “soured” in buttermilk residues (lactic acid), washed and exposed to sunlight until some satisfactory degree of bleaching had been achieved.

This was a typical bleaching operation at the time Home and Black were considering the topic. Clearly, a cursory glance at the bucking solution formula above, with its puzzling admixture of similar materials, suggests it was the outcome of an empirically based development. These empirical activities lacked chemical understanding we now have. It was Dr. Francis Home who changed this situation, and his influence was recognized in an early history of this industry by Higgins (8). In 1952 Clow and Clow considered the importance of Joseph Black’s analysis of various kelps but gave no description of any contemporary chemical methods (9). There is a similar absence of practical analytical procedure in the work by Musson and Robinson although they clearly showed the work of Home and Black in the wider context of the association of science with industry (10).

Home suggested the use of sulfuric acid instead of milk sours, and this may have been one reason why John Roebuck (1718-1794) and Samuel Garbett (1717-1807) set up their acid works at Prestonpans near Edinburgh in 1749 (11). Whether Roebuck foresaw the potential market in this new industry is not known; but according to Jardine (1796) (12), several of Roebuck’s chemical friends knew that he (Roebuck) had tried out the “bleaching” effect of sulfuric acid even before the publication of Home’s *Experiments on Bleaching* in 1756. Durie (13) has suggested that it was Roebuck’s partner, Samuel Garbett, who initiated early tests with acid. The availability and low cost of acid from the Prestonpans works may have stimulated interest in the use of that product in the bleaching process.

## Francis Home and Joseph Black

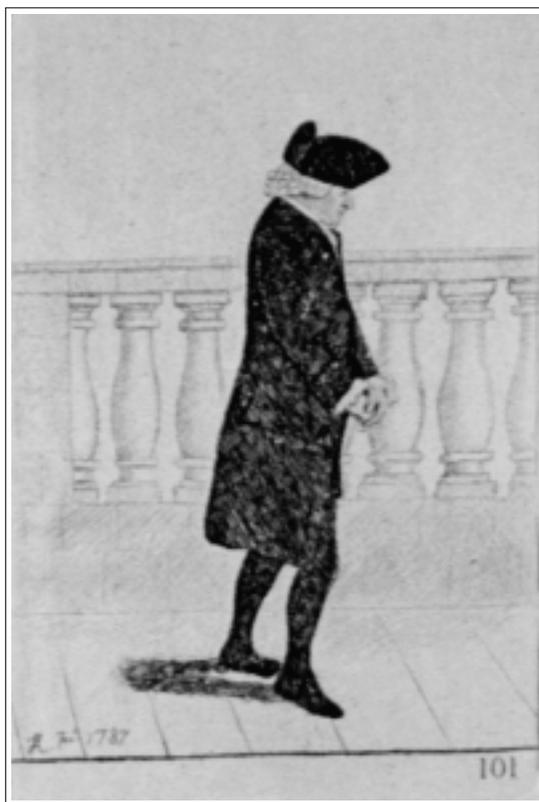
Home’s publication of 1756, *Experiments on Bleaching* (7), was followed by a second Dublin edition in 1771 (14). In this second edition there is an appendix written by Black (Fig. 1 and 2) entitled “An Explanation of the

Effect of Lime upon Alkaline Salts: and a Method pointed out whereby it may be used with Safety and Advantage in Bleaching” (15). Also included are “An Experimental Essay on the Use of Leys and Sours in Bleaching” by James Ferguson (16), and “An Abstract of the foregoing Essays, containing, Practical Rules and Plain Directions for the Preparation and Use of the Sours made of Oil of Vitriol, and of the Leys made of Bleaching-ashes with the addition of Quicklime.” The title page (opposite page 282) names David Macbride as author.

In 1768 Francis Home became the first Professor of *Materia Medica* at the University of Edinburgh (17). He had been born almost 50 years earlier at Eccles in Berwickshire and after taking his M.D., at Edinburgh in 1750, he practiced in that city.

His professorship (1768-1798) was contemporaneous with that of Joseph Black’s (1766-1799), and both were Fellows of the Royal College of Physicians for 30 years; clearly, they knew each other well.

At that time the scale of bleaching operations was expanding and efforts were being made to improve the treatment of cotton and linen, particularly in the final stages of finishing. If this expansion were to continue, then a faster and more efficient method of bleaching would be necessary. The time saved by using sulfuric acid was its main advantage and this accounts for its use by the industry. It can be argued that the innovations involving the use of chemicals in bleaching during the 18<sup>th</sup> century arose, not from rising costs caused



Francis Home, courtesy of the Wellcome Trust

by the uncertain availability of raw materials and shortage of land for bleach fields, but by the slowness of the field bleaching method itself (18). The Board of Trustees for Fisheries, Manufactures and Improvements in Scotland (hereafter referred to as the Board of Trustees) concerned itself with the protection of the quality of manufactured cloth and in particular with the nature of prevailing bleaching processes. To this end Francis Home was invited to provide a course of lectures on the subject, and by these means his recommendation to use sulfuric acid instead of milk sours became known. The use of acid (19):

..will answer to all the purposes of milk and bran sours; nay, in several respects, be much preferable to them. I am of the opinion that five hours will do as much with this sour, as five days with the common sort.

His suggestion, slow to gain interest initially, was by the 1770s ultimately adopted in the Scottish bleach fields and was supported by the Board of Trustees, who in 1756 had awarded a premium of £100 to Home “for ingenious and useful experiments in the Art of Bleaching” (20). At that time sulfuric acid was becoming more readily available from the new lead chamber method of manufacture. In the same year (1756) William Cullen (1710-1790) was appointed Professor of Chemistry at Glasgow University after having submitted to the Board of Trustees his experimental results regarding chemical aspects of the bleaching industry and the use of timber and sea weed as sources of ashes (21).

It seems reasonable to suppose that alkaline bucking solutions were used in the bleaching process because of their cleansing and detergent value (22). The use of soda in some form has for these reasons been retained to this day. Nevertheless it is difficult to account for the apparent complexity of these early alkaline washes (their composition is discussed later). Of course, empirically influenced adjustments would be made from time to time, and the reasons for these would no doubt have become obscure with the passage of time. At some time in the past, lime was included in these formulations and found to give a better result; but because lime was known to degrade linen fibers, government control interceded to protect the standard of workmanship. Indeed, “the use of lime in bleaching was forbidden by law, although Francis Home in 1756 said it was used in Manchester and in Scotland” (23). Clearly there were divergent opinions and misunderstandings about the use of lime; with this background and in the knowledge of its prohibition Home applied his chemical knowledge to improve

the bleaching process. His realization of the scant understanding within the industry, and perhaps also government, probably motivated his researches. Working without the advantages given by chemical formulae, he analyzed materials used in bucking solutions, particularly the expensively imported Muscovy ashes, and showed that these were significantly different from others such as common pearl ashes and blue ashes.

Steeped in modern terminology, we may no longer have the ability to appreciate a reaction without benefit of composition and a balanced chemical equation. This however, can be misleading since our modern language of chemistry incorporates the solutions to the very problems that so troubled the 18th-century chemists. Nevertheless, it will be shown that Black’s study of the decomposition of magnesium and calcium carbonates played an important part in chemical enlightenment, particularly in Scotland, and this, together with Home’s work, influenced chemical understanding and analysis concerned with bleaching.

In the absence of archival evidence it is difficult to assess with any certainty the personal familiarity and communication between Francis Home and Joseph Black. One important biographer of Black, Sir William Ramsay, listed Black’s colleagues and friends but made no mention of Francis Home (24). It seems inconceivable that there was no regular communication between them in view of their parallel academic positions (25). However, the results of their individual chemical researches overlapped and reinforced each other to the advantage of established bleaching processes. Black’s chemical theory reinforced Home’s practical contribution as seen in the 1771 edition of *Experiments on Bleaching*, and it is important to note that their work opened the way and encouraged further analytical progress.

### Home’s *Experiments on Bleaching* 1771

From this second edition we find that:

1. Home, analyzed various alkaline salts including pearl ashes and blue ashes (26):

In order to discover what effect acids would have on these ashes, and what quantity of the former the latter would destroy; from which I might be able to form some judgement of the quantity and strength of the salt they contained; I took a drachm [ *one-sixteenth of an ounce, assuming Avoirdupois*] of blue pearl ashes, and poured on it a mixture of one part spirit of nitre, and six parts water; which I shall always after-

wards use, and call the *acid mixture*. An effervescence arose, and, before it was finished, 12 tea-spoonfuls of the mixture were required. This effervescence with each spoonful of the acid mixture was violent, but did not last long.

This was Home's method of measuring the strength of the alkali salt by neutralizing a weighed amount with a measured quantity of acid of known strength. He warned however that this measurement is not the entire truth "...as there are other bodies beside alkaline salts, that effervesce with acids" (27). In a later experiment the importance of purity was shown and the process of crystallization was described (28).

2. In experiment number 27 he showed Muscovy ashes to be different from pearl ashes and blue ashes in that the more expensive imported material contained an alkaline salt (potassium hydroxide) and lime, "and the latter in much greater proportion than the former" (29).

3. Having developed a method of testing alkaline salts that bleachers could carry out for themselves, he constantly recommended experimentation as the best means to improve bleaching operations.

4. He emphasized that it was unnecessary to buy Muscovy ashes, as the same result could be achieved by mixing pearl ashes with quicklime (CaO).

5. He showed that lime degrades cloth but, if mixed with ordinary pearl ashes or blue ashes, the bleaching action (cleansing) was accelerated without damage to the cloth. This he proved by trials in the bleach fields.

6. He confirmed that Muscovy ashes on their own gave good whiteness but some degradation of the cloth fibers. Home then established the reasons for the composition of bucking solutions and the use of Muscovy ashes, provided they were mixed with a certain amount of pearl ash or blue ash. In this he showed the impor-

tance and value of chemists and of chemical knowledge in bringing about technical improvements in industrial processes.

Although early bleachers had learned, by their trial and error methods, the value of including Muscovy ashes in their bucking solutions, they were unaware, prior to

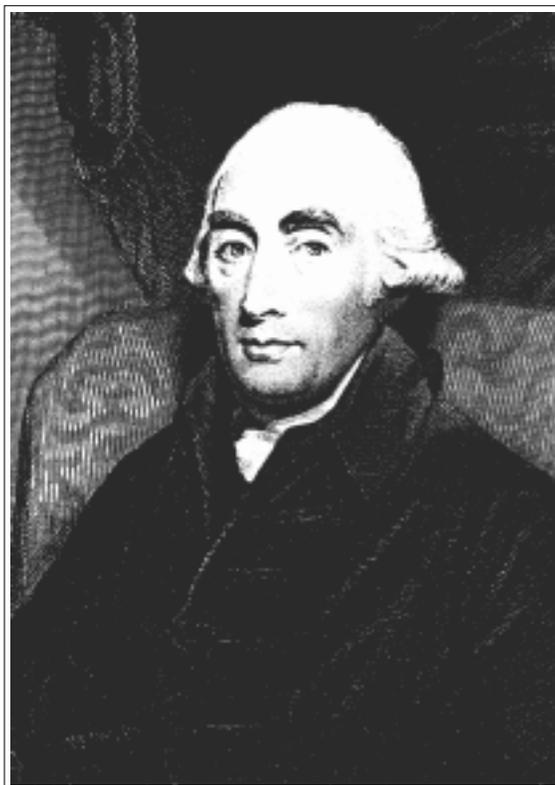
Home's work, that this arose from the lime content, and that addition of lime itself to blue ashes and pearl ashes therefore provided a much cheaper means of achieving the same result. Home found the explanation in terms of chemistry and analysis although, according to Edelstein (30), he employed empirical means in determining the optimum ratio of alkaline salts (blue and pearl ashes) to added lime. He certainly had a good empirical appreciation of the practical value of the admixture of ashes with lime in bucking solutions whereby mild alkali was converted to caustic alkali, while the lime was precipitated as chalk. He appears however to have had only limited theoretical insight into the underlying chemistry. What he did not understand, however, and

what Black added, was the exact interpretation of this reaction, as involving the transfer of fixed air.

### Joseph Black's Contribution

Black had established the chemical nature of lime and fixed air (carbon dioxide) through his now well known work on magnesia alba (magnesium carbonate) and quicklime, which involved accurate quantitative analysis. His experiments showed that caustic alkalis were merely alkali salts deprived of their carbon dioxide or fixed air (31):

..the lime is found to have attracted and detained a considerable part of the salts of the ley, or more properly to have attracted and detained a substance which before was attached to the salts.



Joseph Black (1728-1799)

It was this new insight which, while adding greatly to the current chemical knowledge, was also relevant to the bleaching industry.

Limestone had for many centuries provided lime, and it seems natural that the early bleaching artisans should see this material as a possible helpful additive to their process. Modern elementary chemistry shows that by “burning” limestone and dissolving the quicklime in water, lime water (a saturated solution of calcium hydroxide) is formed. Slaked lime (calcium hydroxide), being only slightly soluble, persisted as undissolved, suspended solid in bleachers’ solutions. It was this material that was so detrimental to the cloth and caused yellowing and fiber degradation. For these reasons the use of lime in bleaching was forbidden by law (32). This legislation was proved to be in error by Home and Black although confusion and misunderstanding of the processes continued, even into recent biographical accounts (33). Limewater in itself had no harmful effect but undissolved slaked lime did. However, this latter constituent would have been absent so long as an excess of ashes remained (34). Black showed that the reaction of lime-water, or undissolved slaked lime (calcium hydroxide) with ashes, i.e., causticization, removed the potentially harmful lime, producing very desirable strong caustic and innocuous chalk (calcium carbonate).

Furthermore, Black noted (35):

..that if we free the bleaching salts entirely of this air [the carbon dioxide], they will be so much the more active and powerful, and that a smaller quantity of them will serve the purpose, than when used in their present state.

Appreciating the technical advantage of the expensive Russian imported ashes, in that “the whole, or very near the whole of the air [carbon dioxide] has been separated already” (36), Black made the case for using lime with the much cheaper ashes made from kelp, in order to achieve a similar degree of bleaching. There were clear hints here about the value of quality control and the purity of the lime and nature of the ashes. More importantly perhaps for future chemistry, he noted explicitly “that lime and Mephitic air [carbon dioxide] are capable of uniting together in one certain proportion only” (37). He described a simple observation to determine the required amount of lime but added (38):

..a bleacher however, who generally uses the same kind of lime and the same kind of ashes, will soon learn by the help of these trials to hit the due proportion so nearly as to need no amendment.

## Conclusions

With Black’s theory and Home’s *Experiments on Bleaching*, the ill-founded laws forbidding the use of lime could be questioned. Whatever reasons had initiated this legislation, it was the work of Home and Black that showed it to be unnecessary. Black in particular had provided chemical principles that found application in bleaching; he brought a new chemical understanding, made available through laboratory based chemical experiment and analysis.

Of course, sunlight continued to play an important part in the bleaching process and some seasonal limitations continued. The increasing use of sulfuric acid instead of milk sours sped up the process whereby mineral deposits on the cloth were removed, which otherwise might act as mordants at a later stage of dyeing. Nevertheless the process remained slow and cumbersome. Fears of the consequences of mistakes when using this acid lingered despite the fact that Home had shown its safe use by experiment (39). A Manchester physician, Dr A. Eason, having industrial chemical interests, advocated the use of muriatic acid (hydrochloric) instead of vitriol, but there is little evidence the former gained common use in the industry (40).

Black’s correspondence with James Ferguson of Belfast, another contributor to the *Appendix* in the 1771 Dublin edition of Home’s *Experiments on Bleaching*, is seen in Ramsey’s (1918) biography of Black as documentary evidence of Black’s involvement in the bleaching industry (41). Indeed, the wording in these letters closely resembles that used by Black in the *Appendix*. It is to Ferguson, according to Edelstein (42), that credit should be given for promoting the work of both Black and Home, whose chemical and analytical work no doubt influenced the relaxation and later repeals of the existing laws regarding the use of lime (43). Black reported in his paper that by chemical analysis and practical testing, those ashes containing “a salt that is most free from the above-mentioned aerial matter” [fixed air], can be shown to be the most effective (44). This was shown by the analysis and use of Muscovy ashes, which contained free or caustic alkali. Black argued that there was no reason for distrusting and avoiding lime in bleaching if it was used in the presence of excess ashes. The process of causticization was not new but Black was the first to provide its chemical understanding.

It is not certain what motivated Black and Home in their work related to the bleaching industry. We know

that their chemical achievements occurred in a period now described as the Scottish Enlightenment, when anticipations concerning the usefulness of chemistry were running high and were reinforced by accumulated knowledge (45). It seems reasonable that Black and Home, if motivated by this growth of chemical knowledge, would seek to establish its practical application in the already expanding industrial processes.

The Board of Trustees saw the need for a low-cost alkali without the restraints of imported material. Thus, the opportunity for chemistry and the application of scientific knowledge became apparent and a part, albeit small, of the early industrial revolution in Britain.

The role of chemical analysis at that time was not clearly defined or obvious, and those active in this practice were singularly few when one considers the growing interest in chemistry. Furthermore, where analytical results were obtained, could these have been realistically employed by early chemical plant artisans? Bleaching processes were already established when legal intervention (perhaps based on ill-judged chemistry) prohibited the use of cheap lime, but it was chemistry that influenced its future repeal. The analytical chemistry of Home and Black was unlikely to have been seen as an immediate impetus to greater production in the textile industry. However, their work provided the theoretical basis on which the processes and materials used in the industry could be understood and measured. The relatively simple observation by Home that sulfuric acid allowed rapid bleaching probably affected the overall industry more than any advantages gained from chemical analyses of already empirically understood bucking solutions or alkali samples. Certainly the discovery of acid washes released the production stranglehold caused by inordinately lengthy bleaching processes.

More importantly, it was from Home's quantitative method of determining the strength of blue ash and pearl ash by neutralization or "saturation," in which he used a teaspoon measure, that a branch of analysis had its origins. This was developed by William Lewis (46) and became known as titrimetry, so important in the future chemical industry.

## REFERENCES AND NOTES

1. A. Clow and N. L. Clow, *The Chemical Revolution. A Contribution to Social Technology*, Batchworth Press, London, 1952, Ch. III, IV, and IX.
2. Ref. 1, p 80. Charles Tennant (1768-1838) was a prominent Scottish bleacher. His method appeared in "A Table showing the Quantity of Soda (either free or combined with Sulphur or Carbonic Acid) contained in the Specimen under Trial with Sulphuric Acid containing 10 per Cent. real Acid..." *Ann. Philos.* (London), **1817**, *10*, 114 - 115. Barilla was the ash obtained by burning certain plants that grew freely along the Mediterranean shores.
3. F. W. Gibbs, "Prelude to Chemistry in Industry," *Ann Sci.*, **1952**, *8*, 271-281; a review of the Clows' *The Chemical Revolution* (1952).
4. See W. A. Campbell, "Analytical Chemistry of the Leblanc Soda Trade," *Proc. Anal. Div. Chem. Soc.*, **1978**, *15*, 208-210, (208). John Mascarene of Cambridge, New England, was one notable exception; see F. G. Page, "The Birth of Titrimetry: William Lewis and the Analysis of American Potashes," *Bull. Hist. Chem.*, **2001**, *26*, 66-72, footnote 7.
5. S. H. Higgins, *A History of Bleaching*, Longmans, Green & Co., London, 1924, 17.
6. S. Parkes, *Chemical Essays Principally Relating to the Arts and Manufactures of the British Dominions*, printed for the author and published by Baldwin, Craddock and Joy, London, 1815, Vol. 4, 23-26. Parkes gives a detailed technical and commercial account of bleaching practice in Holland and in the same volume refers to the work of Home. See also J. Horner, *The Linen Trade of Europe during the Spinning-Wheel Period*, M'Caw, Stevenson & Orr Ltd., The Linenhall Press, Belfast, 1920.
7. F. Home, *Experiments on Bleaching*, printed by Sands, Donaldson, Murray & Cochran for A. Kincaid & A. Donaldson, Edinburgh, 1756; 2nd ed. (containing the *Appendix* by Joseph Black), T. Ewing, Dublin, 1771, 16. The work by J. Dunbar, *Smegmatologia, or The Art of Making Potashes, Soap, and Bleaching of Linen*, Edinburgh, 1736, is probably the first publication on bleaching. See also J. R. Partington, *A History of Chemistry*, Macmillan, London, 1962, Vol. 3, 141.
8. Ref. 5, pp 23-26.
9. Ref. 1, p 79.
10. E. Musson and E. Robinson, *Science and Technology in the Industrial Revolution*, Manchester University Press, Manchester, 1969, Ch. III, section XII.
11. See Ref. 3, p 279.
12. G. Jardine, "Account of John Roebuck," *Philos. Trans.* (Edinburgh), **1796**, *4*, 65-87 (79).
13. J. Durie, *The Scottish Linen Industry in the Eighteenth Century*, John Donald, Edinburgh, 1979, 84.
14. Ref. 7, (1771).
15. Ref. 7, Black in Home, (1771), pp 267-282.
16. James Ferguson of Belfast, with whom Black discussed the use of lime in bleaching long before Black's paper appeared in Home's *Experiments on Bleaching*, (1771). See 'Ferguson to Black,' September 27, 1763, Edinburgh

- University Library (EUL), Gen. 873/1/13,14 and 'Black to Ferguson' (replying) October 14, 1763, EUL, Gen. 873/1/9-11.
17. L. Stephen and S. Lee, Ed., *Dictionary of National Biography*, Smith, Elder, London, 1908, Vol. IX, 1122-1123.
  18. L. Gittins, "Innovations in Textile Bleaching in Britain in the Eighteenth Century," *Business Hist. Rev.*, **1979**, 53, 194-201, (201).
  19. Ref. 7, (1771), pp 83-4.
  20. Ref. 1, p 136.
  21. J. Thomson, *Account of the Life, Lectures, and Writings of William Cullen, M.D.*, Blackwood, Edinburgh, 1832, Vol. 1, 76-9, in which the author reported on Cullen's "Remarks on Bleaching," written in 1755 for the Board of Trustees but not published. Located in the Scottish Record Office (Archives of the Board). Not seen.
  22. Bucking: to soak or steep in alkaline solution; see A. Rees, *Manufacturing Industry*, David and Charles, Trowbridge, 1972, Vol. 1, 178; originally published as *The Cyclopaedia; or Universal Dictionary of Arts, Science and Literature*, 39 vol., 1802-1819.
  23. Ref. 7, (Partington), p 141.
  24. W. Ramsay, *The Life and Letters of Joseph Black, M.D.*, Constable, London, 1918.
  25. S. M. Edelstein, "Two Scottish Physicians and the Bleaching Industry, The Contributions of Home and Black," Part IX in "Historical Notes on the Wet Processing Industry," *American Dyestuff Reporter*, **Sept. 26, 1955**, 681-684 (682). Reprinted in *Historical Notes on the Wet-Processing Industry*, Dexter Chemical Corporation, 1972, 35-38. The absence of documented evidence regarding communications between Home and Black is discussed on pp 35-36.
  26. Ref. 7, (1771), pt. 3, section 1, p 64. The 1756 and 1771 account by Home is word for word identical. For convenience in referring to Black's contribution the 1771 edition has been used here.
  27. Ref. 7, (1771), p 64.
  28. Ref. 7, (1771), p 64, Exp. No. 14.
  29. Ref. 7, (1771), p 82, and Exp. No. 27-34
  30. Ref. 25, (1955), p 683.
  31. Ref. 7, Black in Home (1771), p 268, "An Explanation of the Effect of Lime upon Alkaline Salts..."
  32. Ref. 5, p 13.
  33. L. Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, Edinburgh University Press, Edinburgh, 1975, 79.
  34. Ref. 7, Black, in Home (1771), par. 2, p 268, 278
  35. Ref. 7, Black in Home (1771), p 277.
  36. Ref. 7, Black in Home (1771), p 277.
  37. Ref. 7, Black in Home (1771), p 277.
  38. Ref. 7, Black in Home (1771), p 281.
  39. Ref. 7, Home (1771), pp 55-6.
  40. Dr. Eason, "Observations on the Use of Acids in Bleaching of Linen," *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, **1785**, 1, 240-2. Ref. 24, pp 52-54.
  41. Ref. 25, (1955), p 684.
  42. The earliest mention that bleachers were to be prohibited from using lime occurred in 1633 and is recorded in *The Acts of the Parliaments of Scotland* (1625-1641). This and other similar acts of prohibition were first repealed in 1823. Higgins, Ref. 5, pp 13-16, cites a prosecution for using lime in 1815. See also Partington, Ref. 7, p 141.
  43. Ref. 7, Black in Home (1771), p 271.
  44. J. R. R. Christie, "The Origins and Development of the Scottish Scientific Community, 1680-1760", *Hist. Sci.*, **1974**, 12, 122-141; also Donovan, Ref. 33; and M. P. Crosland, 'Rise and Fall of Scottish Science' in *Emergence of Science in Western Europe*, Macmillan, London, 1975.
  45. Ref. 4, (Page).

## ABOUT THE AUTHOR

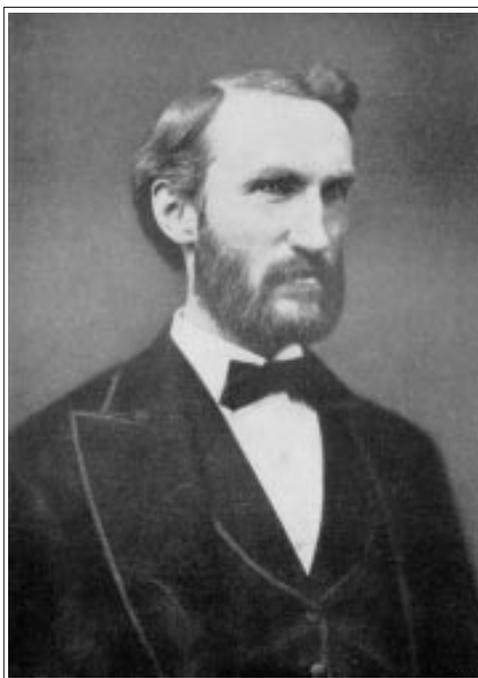
The author retired from the chemical industry in 1989 and then pursued an interest in history of science, gaining an M.Sc. at the Oliver Lodge Laboratory of the University of Liverpool. His studies of early industrial analytical chemistry under the supervision of Professor W. H. Brock resulted in his earning a doctorate from the University of Leicester in 1999. He is currently engaged as Research Consultant for the Open University's A. R. Wallace Project.

## THE OSTWALD-GIBBS CORRESPONDENCE: AN INTERESTING COMPONENT IN THE HISTORY OF THE ENERGY CONCEPT

*Carl E. Moore, Alfred von Smolinski, and Bruno Jaselskis, Loyola University, Chicago*

In the late 1800s and early 1900s, one of the premier figures in German chemistry and physics was the eminent natural philosopher and scientist Wilhelm Ostwald. Early in his career Ostwald developed a strong interest in the concept of energy from both the perspective of the philosopher and the outlook of what was later to be called the physical chemist. He became a leader in a community of scientists with somewhat similar leanings who called themselves energeticists (1). They supported and promoted what they hoped would become a universally accepted cosmological construct based on the unifying concept of energy (2). This energy-based paradigm embraced thermodynamics as an integral part of its structure.

As a consequence of this view, for a time Ostwald did not subscribe to matter-based atomic models and even declared that the concept of matter itself was superfluous and that the intrinsic phenomena experienced in physics and chemistry could be accounted for satisfactorily by analyzing energy transformations (3).



Josiah Willard Gibbs

In support of the energy cosmological model, in 1892 he wrote (4):

Thatsächlich ist die Energie das einzige Reale in der Welt und die Materie nicht etwa ein Träger, sondern eine Erscheinungsform derselben. (Actually energy is the unique real entity (das einzige Reale) in the world, and matter is not a transporter (Träger) [of energy] but rather a state of the former.) (5)

This energy-mass equivalence concept was later stated by Einstein and by G. N. Lewis (6, 7).

Ostwald's deep and abiding interests in energetics most likely were the motivating forces that caused him forcefully and tenaciously to approach Josiah Willard Gibbs (who was to become a prominent figure in American science) with the proposal that Gibbs rewrite and republish his masterpieces on thermodynamics. In addition, Ostwald went so far as to advise Gibbs that he should republish those in an easily accessible and widely distributed journal. He also suggested to Gibbs that he could make these tracts still more generally avail-

able if he would have them translated into the German language (8).

However, history has shown that to convince the obdurate Gibbs to republish would take not only the prestige of the distinguished scientist and scholar, Ostwald, but also his considerable diplomatic skills as the editor-manager of a new journal (9). Yet even the talented and gracious Ostwald was never able to induce Gibbs to do a rewrite.

The correspondence between Ostwald and Gibbs — a total of twenty letters written between 1887 and 1895 — was initiated by Ostwald by way of a letter dated April 26, 1887. In this inaugural letter (No. 88) Ostwald stated his purposes for contacting Gibbs were, first, to invite Gibbs personally to contribute to the new journal *Zeitschrift für physikalische Chemie* and, second, to request and encourage Gibbs to revise and reprint his thermodynamic treatises — which he had published in the “Transactions of the Connecticut Academy of Art & Sciences” — in a place where they would be more easily accessible (10). At the time of his first letter to

Gibbs, Ostwald was near the zenith of his career as a scientist. This productive period (~1887) was marked by the following: appearance of his landmark textbook *Lehrbuch der allgemeinen Chemie*, which came to be called *Der grosse Ostwald*; his establishment, with Jacobus Henricus van't Hoff, of the *Zeitschrift für physikalische Chemie*; his ascent to the Chair of Physical Chemistry at Leipzig; and his acquisition of Walther Nernst and Svante Arrhenius to add to his outstanding group of assistants.

Gibbs, fourteen years older than Ostwald, was perhaps past the summit of his career at the time of the first letter from Ostwald. Following his masterpieces on thermodynamics, as well as the rest of his career, Gibbs seems principally to have concerned himself with his teaching and his very productive research in pure mathematics and statistical mechanics. These latter works did not bring him the renown among chemists he had been accorded by his earlier fundamental publications on thermodynamics. Relying heavily on the language of mathematics, Gibbs employed a very condensed style

Letter No. 88 (14, 15)  
Ostwald to Gibbs  
Riga Polytechnic Institute  
Laboratory of Chemistry  
26, April [18] 87

My dear Colleague:

Since the beginning of this year, I have been publishing in collaboration with J. H. van't Hoff a journal of physical chemistry, stoichiometry, and chemical affinity. Supported at the beginning by association of a number of prominent peers, I now have the honor to count as collaborators to the journal nearly all the researchers of importance in this branch of science. This encourages me to approach you also and to ask that you participate in the journal by contributing papers as well as by allowing me to quote your name among the contributors. If you are not comfortable in expressing yourself in German, I shall gladly provide for the translation from English.

I should like to take this occasion to express a desire that many professional colleagues share with me. Your comprehensive treatise in **Vol. III** of the “Connecticut Transactions,” which is fundamental for the application of thermodynamics to chemical problems, is not readily accessible; couldn't you decide to reprint it in a revised form that is expanded and illustrated with examples of which there is now no lack? I cannot deny that at present the study of your work is pretty difficult, particularly for the chemist, who is usually not at home in a mathematical treatment. I would be most happy if you would decide on a German edition; the provision of a publisher and the execution of the translation I will gladly take care of. Thereby, the study of these areas, particularly in Germany, would gain wider distribution than is presently the case.

Please excuse me for writing in German. I understand enough English to be able to read it, but I am not sure that I am expressing correctly what I mean when I write in English.

Yours respectfully,  
Professor Dr. Wilh. Ostwald  
Chemical Laboratory, Riga Polytechnic Institute, Russia

of writing. It did not endear him to his readers, who found that his parsimonious use of words and his lack of examples and graphics made his original and fundamental treatments of thermodynamics very difficult to understand.

Josiah Willard Gibbs (1839 - 1903) was the only son in the family of five children born to Josiah Willard Gibbs, Professor of Sacred Literature at Yale, and Mary Anne Van Cleve. He attended Yale College and obtained an undergraduate degree with honors in both Latin and mathematics. Later he wrote a thesis on a mathematical treatment of gears, for which he was awarded Yale's first doctorate in engineering. In 1863 Gibbs, having completed the doctorate, received a three-year faculty appointment as a tutor at his alma mater. He taught Latin the first two years and natural philosophy (physics) the third year. Then he and his two sisters rented their house and departed for Europe to study abroad. He studied mathematics and physics in one-year stints at Paris, Heidelberg, and Berlin (11). When he returned to New Haven, three years later, he accepted a nonpaying appointment at Yale as Professor of Math-

ematics and Physics, a position he held for nine years. Finally he became a salaried professor when Johns Hopkins tried to lure him away from Yale (12). He held the Yale faculty position until his death in 1903.

In his introductory letter Ostwald presented Gibbs with several items that would require a substantial amount of work (13). The first was couched in a very warm and friendly invitation to become a contributor to the new journal *Zeitschrift für physikalische Chemie*. The second, almost an entreaty, was to republish his thermodynamic works in an accessible journal. The third was a request to do a rewrite of his treatises. At this third point Ostwald lapsed into the role of editor and critiqued the treatises, pointing out to Gibbs that he thought the works should be expanded, that there should be more examples, and that now ample examples were available. He made the point that the work was perhaps excessively mathematical and that chemists, who often were lacking in mathematics preparation, would certainly have difficulty with it. In addition he suggested he would be most happy if Gibbs would decide to publish a German edition.

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Gibbs, not surprisingly, laid the Ostwald letter aside for about three months, finally replying on August 3,

1887 (No. 89). In this handwritten communication he indicated no interest in following up on any of Ostwald's suggestions or requests.

**Letter No. 89 (16)**

Gibbs to Ostwald  
New Haven Conn.  
Aug 3 1887

Dr. W. Ostwald  
My dear Sir:

Please accept my apologies for my delay in replying to your very kind letter. Some points required a certain consideration (the more, as at that time I had not yet seen your valuable Journal), & when I had laid your letter aside, the pressure of other engagements prevented me from returning to it.

I am very glad that you have undertaken a Journal of this character, for which there seems to be an abundant opening. The subject is one in which I have felt a lively interest, & to which although my time for the last years has been given almost exclusively to other subjects I have always hoped to be able to return.

Nevertheless I am not able to make any engagements, but can only assure you of my good wishes for your undertaking & my grateful appreciation of your kind interest in my own work.

I remain  
Yours very respectfully,  
J. Willard Gibbs

Despite this reply, Ostwald, who considered energy and energy transformations fundamental to all phenomena and processes, was assiduous in his pursuit of information relating to energy and consequently pressed Gibbs for his cooperation. As further exemplified a few years later, he proposed with characteristic zeal what amounted to a secular religion based on energy (17), which may have further alienated him from the Leipzig humanities faculty and contributed to his retirement from Leipzig in 1906.

Ostwald, in addition to writing Gibbs, enlisted the aid of a former student, Morris Loeb, to try to procure a copy of Gibbs' treatise. Loeb's response is described in a German language footnote appended by a previous investigator to the information on letter 90. **Our translation follows:**

Since you had already asked me in June to get you a copy of Willard Gibbs' Treatise, you probably are astonished not to have it yet in October. When I arrived in New York 8 days ago, my first errand was to my book dealer, who let me know that the book doesn't exist at all at book dealers, since the Conn. Academy prints only for members, etc. And there is

**Letter No. 90. (18, 19)**

Gibbs to Ostwald  
New Haven Oct 26 1888

My dear Sir:

I hear through Mr. Loeb (now I believe in Newport R I) that you are desirous of obtaining a copy of my "Equilibrium of Heterogeneous Substances." My extra copies have been long since exhausted, it can only be obtained by purchasing Vol. III of the "Transactions of the Connecticut Academy," of which it constitutes a large part (325 pp). This will be sent to any address by the secretary Mr. Addison Van Name (New Haven, Connecticut) on receipt of the price \$6.00 by International Post Office money order or otherwise.

I send by book-post a few minor papers on kindred subjects, of which I beg your kind acceptance.

I remain  
Yours very truly,  
J. Willard Gibbs

no hope to get it by chance as second hand. This is why I immediately talked to Professor Wolcott Gibbs, whose assistant I have become, and induced him to write to Willard Gibbs and ask him to directly forward you a copy of the desired. I hope that this will soon occur, and thus I will be able, even though late, to fulfill your wish.

Gibbs responded to the request of the treatise through Mr. Loeb in a letter (No. 90) dated October 26, 1888. Gibbs also included a few of what he described as minor papers for consideration for publication in Ostwald's and van't Hoff's new journal.

Ostwald repeated his request for permission to publish a German translation of Gibbs' treatises (No. 91). It is worth noting that when Gibbs finally reluctantly gave his permission for Ostwald to publish a German translation, Ostwald was about half finished with the translation.

**Letter No. 91 (20)**

Ostwald to Gibbs  
Editorial Staff of the  
Zeitschrift für physikalische Chemie  
Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig, 14. Nov. 1888

My Dear Sir:

Please accept my warmest thanks for the gracious notification about the manner by which I can acquire a copy of your large treatise; I have just written Mr. Addison van Name and forwarded him a money order for 6 dollars. Likewise, I thank you very much for the courtesy of sending the separate copies of the forwarded papers; I hope soon to be able to reciprocate the kindness.

Would you object if I would publish a German translation of your fundamental work? It is accessible with such great difficulty and contains so much important material that such an attempt appears to be very useful. If you generally agree, I will make you some suggestions about the form.

Respectfully,  
Yours truly,  
W. Ostwald

Gibbs wondered whether the utility of a German edition justified the cost of translation and publication (No. 92).

Letter No. 92 (21)  
Gibbs to Ostwald

New Haven 1888 Dec 7 1888  
Professor W. Ostwald

My dear Sir:

I should be very glad to have my essays in Thermodynamics made accessible to a larger circle of readers. Yet I should have feared that the call for a German edition would hardly justify the labor & expense of the translator & publisher. If, however, you think differently, I should be glad to hear from you more definitely in regard to what you think practicable.

With thanks for your kind interest in my work,

I remain,  
Yours truly,  
J. W. Gibbs

On Christmas Day 1888 Ostwald wrote Gibbs a post card (No. 93) and described to him his idea of publishing the series of small volumes which became known as *Ostwalds Klassiker der exakten Wissenschaften*.

**Letter [Post Card] No. 93 (22)**  
Ostwald to Gibbs  
Leipzig, Dec. 25, 88

Most Distinguished Colleague:

I am planning next year to prepare an edition of classical essays from the fields of physics and chemistry which will be issued as individual bound publications and will have the purpose of making easily accessible the knowledge and use of the original works which have brought about the development of science (23). I would like to publish your work in this form. Whenever the plan has developed sufficiently, I will give you the details.

Respectfully yours,  
W. Ostwald

The establishment and publication of this famous collection belongs among the important achievements of W. Ostwald in the field of the organization of science.

At this point Gibbs informed Ostwald that Veit & Company of Leipzig had shown an interest in publishing his treatises, even to the extent of doing a German translation. Gibbs gave Ostwald a quote from a Veit & Company letter (No. 94). Then he wrote, "I shall be glad to hear in regard to the maturing of your plans as soon as may be."

**Letter No. 94 (24)**

Gibbs to Ostwald  
New Haven Jan 17 1889  
Professor Wm Ostwald

My dear Sir,

I have received a letter from Veit & Comp. (Leipzig [Leipzig]) offering to republish my papers on Thermodynamics in English or German. With reference to a translation they say:

"In the last case (if I should prefer a translation) we would get support from the very distinguished Professor Felix Klein at Göttingen—who became friendly with us—in preparing the edition in the best way, that is to say by helping us to find a suitable translator and supervising the translation." (25, 26)

I have replied that I had already received a proposition of a similar nature from you, & that I was waiting to have the details of your plan. Of course I said nothing in regard to your farther purposes wh[ic]h you mentioned in your postal card.

I shall be glad to hear in regard to the maturing of your plans as soon as may be.

Very truly yours,  
J. Willard Gibbs

In the letter that follows (No. 95) one sees Ostwald the organizer and facilitator at his very best. It is possible that this gift of the ability to organize may have obscured another facet of Ostwald — *i.e.*, Ostwald the thinker.

**Letter No. 95 (27)**

Ostwald to Gibbs

Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig, 30. Jan. 1889

Dear Colleague,

The plan, which I recently suggested to you, will consist of publication of a series entitled *Classiker der exacten Wissenschaften*, [Classics of the exact Sciences] which will contain, in separate volumes, the reprint of a word for word text of papers which have had or will have an important influence on the development of science. I will be able in the very near future to send you a prospectus. The first issue, Helmholtz's "*Erhaltung der Kraft*" [Preservation of Energy], will soon reach the bookstores.

In this series of classics I was planning to print your large treatise, but in a German translation, that I will either take care of personally or at least have done under my supervision (28).

It is evident that you will have complete freedom of decision under which form [language] you will prefer to issue that in any case, very desired new publication of your works. I can only add that it will bring me great pleasure if I can contribute something to help to get your researches the circulation they deserve.

Whatever the costs of the translation, etc. amounts to will be underwritten by the publisher. Of course I cannot offer you an honorarium or only a very small sum since the publication should be brought on the market as cheaply as possible and already the costs of the translation are coming into question.

Respectfully yours,  
W. Ostwald

On February 16, 1889, Gibbs wrote to Ostwald (No. 96) that Veit and Company had made him a better offer. He proposed to publish with them if they could find someone to do the translation. He indicated that he had no doubt that Veit and Company could find a suitable

translator. He thanked Ostwald for his kind interest in the matter and seemingly terminated the discussion of publication. One is free to speculate as to how Ostwald, a power in the fields of physics and physical chemistry, may have reacted privately to Gibbs' rejection of his generous offer.

**Letter No. 96 (29)**

Gibbs to Ostwald  
New Haven Febr 16 1889

My dear Professor Ostwald:

Your very kind letter of Jan. 30 is rec[eiv]e[d]. It would be very gratifying to me to have my paper appear in such a Collection as you propose to publish & of course I highly appreciate the advantage of having the translation made by yourself or under your supervision. Under any other circumstances, I should most gladly accept your offer. In one point, however, Veit & Co have made a more comprehensive proposal, in that they include *all* my papers on Thermodynamics, i.e., three minor papers with the long one ('Equil. Het. Sub.'). These other papers are doubtless of minor importance, yet I naturally feel a certain pleasure in having them included (30). Of course I see that such a publication of *all* the papers could be quite out of place in your collection.

If therefore Veit & Co can give satisfactory guarantees of a creditable translation, as I have no doubt from their letter that they can, I shall feel that it is best for me to accept their proposal, but I shall not the less appreciate the very kind interest wh[ic]h you have shown in the matter.

Yours very sincerely,  
J. Willard Gibbs

Ostwald, without Gibbs' permission, then published a letter from Gibbs to Professor Oliver J. Lodge in the *Zeitschrift für physikalische Chemie*. The letter (No. 97) dealt with the relationship between chemical and electrical energy.



Wilhelm Ostwald

**Letter No. 97 (31)**

Ostwald to Gibbs

Editorial Staff of the  
*Zeitschrift für physikalische Chemie*  
Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig  
March 31, 1889  
My dear Colleague,

As you will learn from the enclosed copy, I took the liberty to translate your letter mailed to Prof. Lodge, about the relationship between chemical and electrical energy, and to publish it in the journal, which I am editing (32).

I hope you won't be offended that I have taken this action without first consulting you, but the letter appeared to me to be so interesting, that I didn't want to deprive my readers of its contents, by just waiting for the time consuming letter exchange to America and back.

Should you so desire, I shall gladly provide you with several copies of the German reprints.

Yours truly,  
W. Ostwald

Ostwald negotiated a transaction with Veit & Co., which would lead to a transfer of the copyrights to the German translation of Gibbs' treatise on thermodynamics (No. 98). He now was in a strong position from which to ask Gibbs again to consider updating the treatises by writing some notes. He even added a monetary incentive by offering Gibbs a "reasonable honorarium."

**Letter No. 98 (33)**

Ostwald to Gibbs

Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig  
3 March [18] 91

Very honorable Colleague:

Some time ago, at my request for the copyrights to a German edition of your fundamental work, you wrote me that you had transferred them to the publisher, Veit & Co, Mr. Credner (34). Mr. Credner, with whom I have a friendly relation, recently said that he has not been able to find a suitable translator, and he is ready to cede these rights to me. Now I would like to propose to you that the German translation of the work *On the Equil. of Hetero. Subst. and, possibly in addition, the work On the Geometr. Repr. by Surfaces* be issued together, as a separate volume (35). Please tell me whether you possibly could write some notes to the earlier work that would reflect the present point of view of science.

The importance of your work is so great that I would like to do all that I can to procure for it an appropriate dissemination.

As the situation is, I can hardly promise you a pecuniary return of significance, but for the notes a reasonable honorarium could be made available.

Yours very truly,  
W. Ostwald

Gibbs gave Ostwald verbal permission to publish the German edition, but he did not agree to write explanatory notes, although he promised to take the note writing under consideration (No. 99).

**Letter No. 99 (36)**

Gibbs to Ostwald

New Haven, Mch 27 1891

Dear Professor Ostwald:

If Veit & Co (not finding a suitable translator) are disposed to give up the matter to you, & you are still disposed to undertake it, I think that you had better do so, & should be very glad to have you.

I think that your proposal to include the paper on the "Geom. Rep. by Surfaces" is a judicious one. That is doubtless the most important of the minor papers. It contains, I believe, the first solution of a problem of considerable importance, viz: the additional condition (besides equality of temperature & pressure) with [*sic*] is necessary in order that two states of a substance shall be in equilibrium in contact with each other. The matter seems simple enough now, yet it appears to have given considerable difficulty to physicists. (See Clausius, *Wied. Ann.* IX, p. 355, 1880, where he gives the solution in a somewhat different form (37).) I suppose that Maxwell referred especially to this question when he said (*Nature* XI, p. 359) that by means of this model, problems which had long resisted the efforts of himself & others, could be solved at once (38). In the 4th Edition of his "*Theory of Heat*" he gives several pages to this geometrical representation.

Moreover, the treatment of a homogeneous body in this paper is really identical in spirit, with my treatment of heterogeneous bodies in the longer paper, (except that the latter does not admit of the simple geometrical representation), & I think that its previous perusal is very well adapted to diminish the difficulties which students may feel in reading the latter.

In regard to notes, I cannot make any engagement at present, but I will think about it, & write you again, at least if I hear that the matter has been definitely arranged between you & Veit & Co.

Yours faithfully,  
J. Willard Gibbs

Ostwald moved rapidly ahead. The problem of copyrights having been settled, he was about halfway through the translation into German. Then he made an-

other appeal for the notes, reminding Gibbs that he still had time to complete the task (No. 100).

## Letter No. 100 (39)

Ostwald to Gibbs

Editorial Staff of the  
Zeitschrift für physikalische Chemie  
Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig, April 12, 1891

Dear Sir,

The agreement between Veit & Co. and myself is already completely settled since Herr Credner, the owner of the firm, with whom I am on friendly terms, completely agrees to transfer to me all rights that he would have, for the publication of a German translation of your work. Since I already have it about half translated, as soon as I am finished, I intend to start the printing so that the German edition could be finished by autumn.

While I thank you very much for your kind consent, I mention that in case you decide to write annotations for the German edition, these would be needed at the completion of the printing of the text (40). Thus, you still have perhaps some 6-8 months' time, and then the annotations would be put in an appendix.

Yours very truly,  
W. Ostwald

Ostwald expressed his very high regard for Gibbs' treatises (No. 101). He also lapsed into the role of editor and chided Gibbs a bit about publishing a huge vol-

ume in a virtually inaccessible journal. He used the occasion to inquire once again about the subject of notes.

Letter No. 101 (41)  
Ostwald to Gibbs

Editorial Staff  
Zeitschrift für physikalische Chemie  
Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig, Aug. 9, 1891

Very honorable Colleague,

Since in the next few days the first galley proofs of the German translation of your highly important works will reach you, I take the liberty to ask that you look over these and the sheets to follow to determine whether I have assessed and properly rendered the not always easy to understand meaning of your presentations.

If you also would take a glance at the formulas, that would be helpful to the German edition. Please disregard the many typographical errors committed by the typesetter, who is not yet accustomed to my handwriting; I am going to read two revisions and shall make the utmost effort to eliminate them.

The translation of your main work is nearly completed; I cannot forgo in this place to express repeatedly my admiration to you. If, over a long span of time, you would have submitted this work in single papers to an accessible journal, you presently would be not only known in the narrow circle of discriminating judges, but also would be considered everywhere not only the greatest thermodynamics expert since Clausius, but also one who far surpasses him in many cases with respect to rigor and versatility of judgment. I hopefully the German translation will lead more promptly to the recognition you have earned.

Meanwhile, have you considered the question of some notes?

With special high regard,  
Very respectfully yours,  
W. Ostwald

Letter No. 102 (42)  
Gibbs to Ostwald  
Goshen, Mass.  
Aug 16/ [18] 91

My dear Dr Ostwald:

I am much obliged to you for the elegant typographical form which the printer has given to my "Thermodynamic Studies" & for the care with which the translation has been made.

I have corrected such typographical errors as I have noticed, although I have not been able to compare with the original. In one or two places a word seems to have slipped out. In the second sentence (page 1) is not a verb wanted after Flüssigkeit, meaning to "indicate" or "represent?"

In the first note on page 3 after the parenthesis do we not want "can be derived" or something like it? I see that the formulae are printed entirely in *Roman* type. The usual & I think the best practice is to use *Italics* (except perhaps for Capitals) for letters and algebraically.

I suppose the printer set it up without thinking anything about it. It seems a pity to commence on a long work, without commencing in the best way. But if it is too late to change in this article, I would suggest that the change be made in the next. I give my printer a standing order to put such things in *Italics*, except  $\log \sin \tan$  & *c*. But this is a purely typographical matter, which you will of course arrange with the printer as you think best.

It is very hard for a printer to set up formulae correctly from manuscript. As soon as I return to New Haven (in two weeks), I will send you an *imperfect copy* of my longer paper which you can use to cut out formulae for the printer (or give it to him whole). You may also find it useful in preparing the figures. — On page 8 we have  $W^c$   $H^c$   $\sum^c$  and  $W^8$   $H^8$ . The indexes ought to be of the same size both large or both small. — I think I would put the date on the first page. I have it not with me, but you must have it.

Very truly Yours,  
J. W. Gibbs

Letter No. 103 (43)

Ostwald to Gibbs

[After Aug. 16, 1891] (44)

Dear Sir,

Today I received sheets 2-4 with your corrections, which, I am sorry to say, convince me how necessary it is for you to look it over. Please accept my warmest thanks.

I have talked with the publisher about the "italics;" they will be used throughout instead of the commonly used typeface. Even if the first sheet is already printed, the use of Italics in the formulas in the main publication will certainly be carried out. An issue of the original is now in the hands of the typesetter, so that in the future also fewer errors in the formulas will occur.

I cannot find the dates of your works on the publications; I plan to publish these and a few historical notes in a short foreword. Also, I would like very much to put your picture in front, and would be much obliged if you would agree to send me a good, if possible, fairly large picture of you; even better would be a negative (octavo format).

With best regards,  
W. Ostwald

Letter No. 104 (45)

Ostwald to Gibbs

Editorial Staff

Zeitschrift für physikalische Chemie

Prof. Dr. W. Ostwald

Brüderstr. 34

Leipzig, Nov. 23, 1891

Dear Colleague,

Your errata, as you desire, will be appended to the text; the table of contents shall, as customary in German publications, go to the front and be enlarged to include the first two papers. Since, unfortunately, you cannot write any notes for it, I ask you please to write at least a foreword for the translation that would in particular contain the dates of publication of your works.

I would like again to repeat my desire to include your picture; should you send a negative, the reproduction expenses would be minimal, and since I confidentially hope that through the translation the recognition of your work will make a great advance, I find the inclusion of a picture quite suitable. I will gladly mention in my foreword that this has happened at *my* explicit desire.

Sheet 15, of which I sent you yesterday a new copy, has meanwhile arrived. You do not need to send a new correction.

With best regards  
Yours very truly,  
W. Ostwald

Letter No. 105 (46)  
Gibbs to Ostwald  
New Haven Dec 11/[18]91  
My dear Professor:

With regard to the preface, I think that such an one as you may write will be amply sufficient.

The dates of which you speak are as follows:

Vol II Part 2 of Trans. Conn. Acad. containing my two first papers was published in Dec 1873.

Vol III Pt. 1 containing the first part of *Equil. Het. Sub.* was published in June 1876.

Vol III Pt. 2 containing the remainder was published in July 1878.

You will see that the printer has put his date on each folio, as it was "closed" for printing.

My private edition of "Graphical Methods" was distributed six months before the volume of which it formed a part.

I also distributed a few advance sheets from the *Equil. Het. Sub.*, so that Maxwell noticed the same in the South Kensington Science Conferences in May 1876 (See *Conferences & c* p. 145).

I give these details because you have asked for them. But I think it quite sufficient to say in the *Inhaltverzeichnis* under Graph. Methods & c (from the "Transactions of the Connecticut Academy of Arts & Sciences," Vol II, 1873); under Method of Geom. Representation (same as before); under *Equil. Het. Subs.* (from & c Vol III, 1876-8).

I may add that the American Academy of Arts & Sciences (Boston) awarded to me in 1880 their Rumford gold medal for these papers. If you mention this fact you should do it in such a way that it will not be confused with Rumford medal of the Royal Society of London. (Count R. founded a medal in each Society.) (See *Proceedings Amer. Acad.* Vol XVI, p 407 & 417, May 25, 1880 and Jan. 12, 1881.) (This journal you will doubtless find in the Library of the Royal Saxon Academy if not in other libraries.)

I thank you very heartily for the interest which you have expressed in the matter of the portrait, but I think as before that it would be hardly worth while.

I think that you should refer to my paper "On the Vapor-Densities of Peroxyde of Nitrogen & c" in the *American Journal of Science*, Vol XVIII, 1879, wh[ic]h is in fact a continuation of the subject discussed under the head "Gas-mixtures with convertible Components", pp 234 - 248 of *Equil. H. S.* It does not I believe add anything to the *theory*, but it gives a more detailed comparison with experiment.

Very truly Yours,  
J. W. Gibbs

P. S. Possibly you may think it worthwhile to refer to my letters on the electromotion force of galvanic cells in the *British Assoc. Reports* for 1886 & 1888, one of which you translated in your Journal. They relate to the last subject treated in the *Equil. Het. Subs.*

J. W. G.

Letter No. 106 (47)  
Ostwald to Gibbs

[Leipzig,] Apr. 18, (18) 95

My dear Colleague,

I have the urgent wish to dress up this set of volumes of my journal with your picture and use the occasion that a former student, Dr. Coggeshall, is traveling through New Haven, and through him to relay this request to you. A negative (Cabinet-Format, approximately 12 x 16 cm) would be the most desirable for me.

In the hope of a favorable answer I remain

Yours very truly,  
W. Ostwald

Letter 107 (48)  
Ostwald to Gibbs

Prof. Dr. W. Ostwald  
Brüderstr. 34  
Leipzig  
November 14, 1895

Dear Colleague,

Today I received the negative. My heartiest thanks! I am very pleased through the publication of the picture to express additional witness to the respect all of us owe you. The reimbursement for the negative will soon be sent to you by the publisher; should you desire some reprints made by the photogravure, it will be a pleasure to provide them for you.

Yours very truly,  
W. Ostwald

Letter No. 109 (50)

Gibbs to Ostwald

New Haven, 16 March, 1896.

(This communication consisted of a letter of recommendation from Gibbs to Ostwald for an American chemist, B. B. Boltwood, who wished to work for a semester with Ostwald in Leipzig.)

Letter No. 108 (49)  
Gibbs to Ostwald

New Haven Dec 7 [18]95

My dear Professor Ostwald:

I am glad that the negative have [*sic*] reached you safely.—I should be pleased to have half a dozen copies of the reproduction.

Yours faithfully,  
J. Willard Gibbs

P.S. I have received from your publisher the \$3.00 wh[ich] I expended.  
J. W. G.

### Conclusion

Wilhelm Ostwald, with dogged persistence, clever negotiating, and good management skills, buttressed the energy concept by making readily available to the science community the hitherto virtually inaccessible thermodynamic treatises of J. Willard Gibbs. The closure of the Ostwald-Gibbs' correspondence occurred harmoniously with Gibbs seeking to place a student in Ostwald's laboratory at Leipzig.

The opinion is sometimes expressed that Wilhelm Ostwald was one of the supremely effective organizers

of science, but that his creativity in the matters of science was no match to that of some of his assistants such as Svante Arrhenius and Walther Nernst. There is no question as to the potency of his organizational and administrative abilities, as is shown by his effective dissemination of Gibbs' contributions to thermodynamics.

But the question of level of intellectual creativity warrants further consideration. A monistic concept of energy was central to the theme of Ostwald's research. His enormous academic effort along this research pathway produced major textbooks, ninety Ph.Ds, and a number of other creative scholars; and his research laboratory turned out significant scientific achievements stemming from his energy paradigm. In 1909 he was awarded the Nobel Prize for his contributions to reaction kinetics.

### REFERENCES AND NOTES

1. R. J. Deltete, *The Energetics Controversy in the Late Nineteenth-Century Germany: Helm, Ostwald and their Critics*, Ph.D. Thesis, Yale University, 1983, Vol. I, 120.
2. Ostwald later in his career devoted much of his study to monism, any doctrine based on the assumption of a single underlying principle. Ostwald believed in the mass-energy equivalency principle which was later formulated as  $E = mc^2$ .
3. W. Ostwald, "Referat über W. Wien, 'Über den Begriff der Lokalisierung der Energie,'" *Wied. Ann.* **1892**, 45, 685-728," *Z. physik. Chem.*, **1892**, 9, 770-771.
4. Ostwald visualized energy as one would a substance, such as water, which may exist in more than one state.
5. The translations from German are ours throughout.
6. A. Einstein, "Ist die Trägheit einer Körpers von seinem Energieinheit abhängig?" *Ann. Physik.*, **1905**, 18, 639-41.
7. G. N. Lewis, "The Fundamental Laws of Matter and

- Energy," *Science*, **1909**, 30, 84. Also see G. N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923, 50, footnotes 1, 2.
8. H. G. Körber and G. Ostwald, *Aus dem wissenschaftlichen Briefwechsel Wilhelm Ostwalds, I. Teil, Briefwechsel mit Ludwig Boltzman, Max Planck, Georg Helm, und Josiah Willard Gibbs, Herausgegeben von Hans-Gunther Körber unter Mitwirkung von Grete Ostwald*, Akademie-Verlag, Berlin, 1961.
  9. The *Zeitschrift für physikalische Chemie* was founded and published by Wilhelm Ostwald and Jacobus Henricus van't Hoff. The journal appeared for awhile as a Leipzig edition (**1959**, 210) and a Frankfurt edition (**1959**, New Series, 19) because of the 1949 partition of Germany. In 1990 the Leipzig version was discontinued and the Frankfurt publication continued
  10. The Connecticut Academy's Transactions were published in only a limited quantity whose number was set to be just sufficient to serve the membership of the academy. Hence, its volumes did not get into the hands of the book-sellers.
  11. The estate left to the Gibbs' children—Josiah Willard, Anna, and Julia—was inventoried in 1870 at \$23,500, which included the equity in the Gibbs' home. To estimate the size of this estate in US dollars of the year 2000, one must take into account the rate of inflation, which is an arbitrary choice based on estimated property values, costs of food, labor, etc. We have chosen an inflation rate of roughly 3% per annum. From the equation  $F_n = P(1+r)^n$  where F is the value of one dollar, P is one 1870 dollar and n is (2000 - 1870 = 130), the number of years. This calculation gives a value for F of around 50. Thus the Gibbs' estate would probably be worth about fifty times its 1870 value or about \$1.2 million in U. S. dollars of the year 2000. Another author, using a 2% inflation rate, estimates a P value of 13. We feel the use of a 3% rate of inflation yields a more realistic estimate.
  12. L. P. Wheeler, *Josiah Willard Gibbs, The History of a Great Mind*, Yale University Press, New Haven, CT, 1951, 91. President Gilman of Johns Hopkins made Gibbs an offer of \$3,000 per annum. Yale countered the offer by offering \$2,000.
  13. About ten years had elapsed since the publication of Gibbs' treatises. New developments had occurred that would justify a revised edition.
  14. Bibliographic Citation to Letter No. 88: microfilm, handwritten in German, letterhead printed, *Gibbs Correspondence*, No.15, Yale University Library.
  15. W. R. Longley and R. G. Van Name, *The Collected Works of J. Willard Gibbs, I, Thermodynamics*, Yale University Press, New Haven, CT, 1928; J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances." *Trans. Conn. Acad. Art Sci.*, **1876**, 3, 108-248 and **1878**, 3, 343-524.
  16. Letter No. 89, *Gibbs Correspondence*, No. 151.
  17. C. Hakfoort, "Science Deified: Wilhelm Ostwald's Energeticist World-View and the History of Scientism," *Annals Sci.*, **1992**, 49, 525-544.
  18. Details about Letter No. 90 contain a letter in German by Morris Loeb, a student of Ostwald, to whom he wrote on October 12, 1888, from Newport, RI.
  19. Letter No. 90, *Wilhelm Ostwald Archives*, No. 42/1, Grossbothen, Saxony.
  20. Letter No. 91, *Gibbs Correspondence*, No. 153.
  21. Letter No. 92, *Wilhelm Ostwald Archives*, No. 42/2.
  22. Post Card No. 93, *Wilhelm Ostwald Archives*, No. 42/2.
  23. The establishment and publication of the famous collection, *Ostwalds Klassiker der exakten Wissenschaften*, belongs among the important achievements of W. Ostwald in the field of the organization of science. (See also H. G. Körber, "Einige Gedanken Wilhelm Ostwalds zur Organisation der Wissenschaft," *Forsch. u. Fortschr.* **1957**, 31, 97-103.) Ostwald disclosed some details about the creation of the "Klassiker" in his *Lebenslinien* 2, pp 55-56. His contemporaries approved of the publication of such a collection of authoritative papers.
  24. Letter No. 94, *Gibbs Correspondence*, No. 174a.
  25. Veit & Co. to Gibbs on December 30, 1888; see Letter No. 110.
  26. Gibbs gives Ostwald a direct quote from the Veit & Co. letter.
  27. Letter No. 95, *Gibbs Correspondence*, No. 156.
  28. See Veit & Co. letter to Gibbs on March 5, 1889. See Letter No. 113.
  29. Letter No. 96, *Gibbs Correspondence*, No. 156.
  30. The three small papers mentioned by Gibbs were "Graphical methods....," "A Method of geometrical representation....," and "On the vapor-densities...". (Refer to Letter No. 112.)
  31. Letter No. 97, *Gibbs Correspondence*, No. 160.
  32. There was an interesting letter from Gibbs to Oliver Lodge dated November 21, 1887, "Electrochemical Thermo-Dynamics," *Report of Brit. Assoc. Adv. Sci.*, **1888**, 58, 343-346, and after that also published as Prof. Willard Gibbs, "Zur elektrochemische Thermodynamik," *Z. physik. Chem.* **1889**, 3, 159-163.
  33. Letter No. 98, *Gibbs Correspondence*, No. 151.
  34. Refer to Letters 110-114.
  35. Ref. 16 (W. R. Longley and R. G. Van Name); J. W. Gibbs, "A Method of Geometrical Representation of Thermodynamical Properties of Substances by Means of Surfaces," *Trans. Conn. Acad. Art Sci.*, **1873**, 2, 382-404.
  36. Letter No. 99, *Wilhelm Ostwald Archives*, No. 42/3.
  37. R. J. Clausius, "On the Behavior of Carbon Dioxide with Respect to Pressure, Volume and Temperature," *Wied. Ann.*, **1880**, 9, 337-357.
  38. J. Clerk-Maxwell, "On the Dynamical Evidence of the Molecular Constitution of Bodies." *Nature* **II**, **1874-1875**) 357-359 (March 4) and 374-377 (March 11). This two-part paper was a lecture delivered at the Chemical

- Society on February 18, .
39. Letter No. 100, *Gibbs Correspondence*, No. 161.
  40. In Letter No. 100 Ostwald suggested that Gibbs expand the text and provide some illustrations.
  41. Letter No.101, *Gibbs Correspondence*, No. 163.
  42. Letter No. 102, *Wilhelm Ostwald Archives* No. 42/4.
  43. Letter No. 103, *Gibbs Correspondence*, No.162; presumably written in September 1891 as an answer to letter No.102.
  44. The German publisher added brackets and dating.
  45. Letter No. 104, *Gibbs Correspondence*, No. 164.
  46. Letter No. 105, *Wilhelm Ostwald Archives*, No. 42/5.
  47. Letter No. 106, *Gibbs Correspondence*, No. 166.
  48. Letter No.107, *Gibbs Correspondence*, No.167.
  49. Letter No. 108, *Wilhelm Ostwald Archives*, No. 42-46.
  50. Letter No. 109, *Wilhelm Ostwald Archives*, No. 42-47.

### FUTURE ACS MEETINGS

- March 23-27, **2003**—New Orleans, LA  
September 7-11, **2003**—New York, NY  
March 28-April 1, **2004**—Anaheim, CA  
August 22-26, **2004**—Philadelphia, PA  
March 13-17, **2005**—San Diego, CA  
August 28-September 1, **2005**—Washington, DC  
March 26-30, **2006**—Atlanta, GA  
September 10-14, **2006**—San Francisco, CA  
March 25-29, **2007**—Chicago, IL  
August 19-23, **2007**—Boston, MA  
April 6-10, **2008**—San Antonio, TX  
August 17-22, **2008**—Philadelphia, PA  
March 22-26, **2009**—Salt Lake City, UT  
August 16-21, **2009**—Washington, DC  
March 21-26, **2010**—San Francisco, CA  
August 22-27, **2010**—New York, NY  
March 27-31, **2011**—Anaheim, CA  
August 28-September 1, **2011**—Chicago, IL  
March 25-29, **2012**—San Diego, CA  
August 19-23, **2012**—Boston, MA

## THE NATURAL DEFENSE OF A SCIENTIFIC PEOPLE: THE PUBLIC DEBATE OVER CHEMICAL WARFARE IN POST-WWI AMERICA

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*Andrew Ede, University of Alberta*

On April 22, 1915 the German army released 168 tons of chlorine gas from 5,730 cylinders that had been laboriously transported to the front at Ypres (1). There were 15,000 injuries and 5,000 deaths. The German army pushed through a wide hole created in the front line, only to have their attack falter because of heroic resistance and a lack of reserves (2). The attack set off a race on all sides to produce protective measures and more potent chemical agents. This search drew in large numbers of chemists and other scientifically trained men to the war effort. In an editorial as early as May 1915 it was stated, "...that we of old heard of 'soldier's battles' and 'general's battles' but it remains for the present war to produce a new sort, the 'chemist's battle'.(3)" The 'chemists' war' was the first conflict in which it was popularly believed that science would have a significant effect on the outcome of the struggle.

On June 25, 1918 President Wilson authorized the creation of the Chemical Warfare Service (CWS), and the Service came into being as an independent branch of the military by War Department General Order 82, on June 28, 1918 (4). Major General William L. Sibert was appointed the first Director of the CWS (5). Sibert began an aggressive enlistment drive among chemists and by the end of the year some 1,294 scientists and engineers were officers in the CWS (6). These men were granted significant resources for research and development of both defensive and offensive equipment, tactics and training.

The late entry of America into the war limited actual CWS participation in combat. Despite limited mili-

tary operations, by war's end, the US had the largest chemical warfare research establishment in the world, a complete production infrastructure, and a significant stockpile of chemical weapons. By the end of the war, the CWS had produced some 6,215 tons of war gases and used 1,812 tons (7). The CWS produced or oversaw the production of the largest supply of war chemicals of any of the combatants, on the order of 100 tons per day. The comparable figures for German production are uncertain, but the likely peak in German production was between 30 and 50 tons per day (8).

The activity of the CWS was extremely expensive, and from its inception to April 1919, the CWS had expended just over \$83 million. While this represented only 0.6% of the total expenditure for the war, the CWS represented less than 0.1% of the military force of the National Army (9). For the chemists at the American University Research Station, the CWS offered the biggest, best funded and best staffed laboratories in North America, which were comparable to or better than most European facilities. With the end of hostilities there was strong pressure to reduce the US military and to close facilities like the Research Station, but the scientists were not willing to see the dissolution of the CWS without a protest.

Peyton March, Chief of Staff of the Army from 1918 to 1921, who was opposed to chemical warfare on humanitarian grounds, acted to disband the CWS, advocating the demobilization of the Service and the transfer of its remaining elements to the Corps of Engineers

(10). John J. Pershing, Douglas MacArthur, and Malin Craig, who succeeded March, all objected to chemical warfare to a greater or lesser degree. This led to a major dispute between the CWS and the other sectors of the military, particularly the various Chiefs of Staff and the Army. Brigadier-General Amos A. Fries, who returned from command of the European forces of the CWS to replace General Sibert after the war, quickly realized that to save the CWS he would have to go outside the military. He did not hesitate to recruit anyone he could to the cause.

Fries organized a two-tiered campaign to preserve the CWS. His first concern was to directly lobby members of Congress in 1919, when the government was considering the post-war role of the military. After the war, pride in the American military and the residue of war mentality carried the CWS along, but the American people were opposed to a large military and the expense that such an organization required. Demobilization and reduction of the war effort, combined with an increasingly isolationist policy, made supporters of the CWS look like spendthrifts and war mongers.

The efforts of Fries and the enthusiasts for the CWS were partially successful. The March-Baker Bill (Senate Bill 2715) to disband the CWS was defeated, but the National Defense Act (June 1920) limited the CWS to 100 officers and 1,200 other ranks (11). Despite the reduced resources, the CWS remained responsible for research, manufacturing, training of the military, and organizing special gas troops. This was an impossible task, especially when the budget was slashed from its wartime annual level of over \$40 million to \$2 million in 1920-21 (12). Nevertheless, Fries triumphantly managed to maintain the CWS as a continuing part of the military in the face of serious opposition at the highest levels.

It was clear that without public support the opponents of the CWS would eventually prevail. Thus, the second tier of Fries' offensive was a publicity campaign to convince the public that chemical warfare was the way of the future in warfare and that any further curtailment of the CWS would leave America unprepared for future conflicts. Fries hired Thomas R. Shipp, Inc., a professional Washington publicist, to aid in this work (13). Fries began speaking publicly at every opportunity and co-authored a book with Clarence J. West in 1921 (14). *Chemical Warfare* was both a handbook for chemical warfare and a promotional piece aimed at a popular audience. They state in the preface, "The present

work was undertaken by both authors as a labor of patriotism and because of their interest in the Service (15)" and conclude, "It is hoped that the facts here presented may further increase interest in Chemical Warfare, for there is no question but that it must be recognized as a permanent and very vital branch of the Army of every country (16)."

Fries was aided in his efforts to publicize the CWS by many of its former members and by chemists from the large industrial base that had supplied the Service. The role call of the officer corps of the CWS reads like a who's who of American chemistry, and many scientists who were not in the Service had worked on war projects sponsored by the CWS or the Military Committee of the National Research Council. A number of these chemists formed the National Chemical Defense Association as part of the lobbying effort. The board of directors represented some of the most important chemists of the day. Notable among this group were J.F. Norris, President of the American Chemical Society; Wilder Bancroft, owner and editor of the *Journal of Physical Chemistry*; and William J. Hale, head of the chemical branch of the National Research Council.

While certain members of Congress were persuaded by Fries, convincing the public on chemical warfare was a more difficult task. The public was generally horrified by the thought of gas attacks. The press, both in newspapers and popular magazines, had run many stories on the horror of gas warfare, including a number of detailed personal accounts by survivors. After the war there were numerous articles about the future of warfare, some by important military leaders such as General Eugene Debenet, Commander of the French First Army. Debenet argued that poison gas was already superior to explosives, and that new and more powerful gases would be discovered, some of which could be fired onto the battlefield by machine gun (17).

In order to shape public opinion, the public had to hear about the importance of the CWS, particularly from those people with technical or scientific training. Fries' initial strategy was to spread a positive message about the CWS as widely as possible. One of the most important positive arguments presented to defend chemical warfare was that chemical warfare was a humane weapon. Supporters argued that it killed very few people and that those wounded by gas frequently made a complete recovery, as opposed to the injuries caused by projectiles and explosives. This argument was frequently supported by references to the relative levels of destruc-

tion and death caused by various weapons. As was pointed out in a short article in *Scientific American*, the “humanity of gas warfare” is (18):

...tied up with that of the preparedness of the enemy against this form of attack; but the statistics of the war, contrary to general belief, have shown that the casualties and permanent injuries due to gas attack against troops that are adequately prepared against it, are far less than those suffered from shrapnel and high explosive shell.

The low rate of mortality appeared in the public debate as early as 1922 when Rear Admiral William S. Sims argued in a *New York Times* letter to the editor that gas resulted in 27.3% of American casualties, but only 1.87% died of their exposure (19). The issue of casualties was initially confused in the post-war period by the variety of figures presented to the public. The figure of 88,980 gas casualties, of which 38,396 were by mustard gas, as presented in the *New York Times*, was based on admissions to hospitals (20). In 1937 August Prentiss listed admissions as being 70,552 of which only 27,711 were caused by mustard gas (21). In the end, the initial claim of 1.87% mortality was rounded out to 2%; and this figure was repeated continually by both supporters of the CWS and other commentators (22).

Prentiss provided the most comprehensive analysis of the effects of gas attack, compiling tables that showed that gas was not particularly deadly. For example, 26.8% of American casualties were caused by gas, but only 2% died from their exposure, while 25.8% of non-gas wounded died of their injuries (23). Prentiss gave similar figures for French, English, and German forces, but notably the Russians were not included. This comes in part from a lack of information, but it also demphasizes the effect of gas on an unprepared enemy. In one attack at Barnowitschi on September 7, 1916 the Russians suffered an estimated 6,000 injuries and 3,000 deaths (24), producing about a 33% mortality rate. This was close to the level of mortality (25%) suffered at Ypres in 1915. The far higher death rate for the unprepared forces at Ypres and the mortality rate for the ill-equipped and untrained Russians seem closer to what a civilian population might experience.

In addition to lobbying efforts, the supporters of the CWS were aided in their efforts to keep chemical warfare in the news by the international situation. First, there was a series of disarmament conferences and the ongoing discussions of the League of Nations; and second, regular reports of continued gas research and production by the European powers kept the issue alive.

In 1921, the Washington Conference on Disarmament began to create a treaty to outlaw chemical warfare. The American delegation was in favor of the treaty, as was stated in a typical editorial (25):

The only way to make sure that war will not again be ruthless is to make it certain in advance that ruthless war will not pay, and that those guilty of it will be condemned to fearful punishment.

The response to this was swift. J. E. Zanetti, Professor of Chemistry at Columbia University and former Lieutenant Colonel in the CWS, wrote to the editor to say that there was no way of controlling gas warfare short of outlawing all of the chemical industry, so international treaties were useless (26). In the same edition a speech by Fries before the American Institute of Chemical Engineers was reported. Defending the CWS, he argued that “Warfare by chemicals is the natural means of defense of a scientific people (27).” Fries closed by calling upon the members of the Institute to write to Congress opposing the abolition of the CWS.

Despite the efforts of the pro-CWS side, in 1921 the Washington Conference formulated the Five Powers Treaty, which was a “Treaty between the United States of America, the British Empire, France, Italy, and Japan, to protect neutrals and noncombatants at sea in time of war and to prevent the use in war of noxious gases and chemicals. (28)” The treaty mirrored popular feeling. In a *New York Times* poll, 366,795 respondents voted for the abolishment of gas warfare, while only 19 supported it (29). The ratification of the Five Powers Treaty by Congress was a serious setback for the CWS. Using the spirit of the Treaty as a guide, the War Department (following General Pershing’s directive), modified the terms of CWS so that it was to work on only defensive aspects of chemical warfare (30). As it happened fate took out some of the sting of the Treaty. France, despite being a signatory at the conference, later refused to ratify the treaty; lacking this ratification, the Treaty never officially came into force.

With the French failure to ratify, the battle for public opinion became even more important. In addition to the effort to portray chemical warfare as humane, the pro-CWS faction used two other strategies to shape public opinion. The first was continued reporting of the manufacturing and research on chemicals by foreign powers. As early as 1922 Fries had told reporters that Britain and France were continuing to research war gases (31). The other strategy was to present the positive and peacetime uses of war chemicals. The most frequent idea was to use war gas as a pesticide, particularly against

the boll weevil (32). War gases were also suggested for use against diseases such as grip, influenza, and pneumonia; but the most novel application (33) was to cure paresis, a form of partial paralysis that was often diagnosed in 'insane hospitals.'

At the Conference on the Supervision of the International Trade in Arms in 1925 the issue of chemical warfare was again introduced. As with the earlier disarmament conference, the American delegation was instrumental in negotiating an agreement. This agreement was the Geneva Protocol, which prohibited the use of chemical and biological weapons. The Protocol was signed by the United States and then sent to Congress for ratification. Fries quickly organized an anti-Geneva Protocol campaign directed at members of Congress. Leading the antiratification faction was Senator James W. Wadsworth, who argued the CWS line that gas was a humane weapon and that the United States should not limit its military options (34). However, what led to the failure to ratify was a letter and telegram campaign organized by Fries through the National Chemical Defense Association. John Thomas Taylor, the secretary to the NCDA, was also vice-chairman of the national legislative committee of the American Legion (35). He introduced a motion at the annual national convention of the Legion condemning the Geneva treaty, which the Legion passed. A flood of letters against the treaty followed from Legionnaires and Legion posts to government members and officials. In addition to the Legion, letters and telegrams came from the Veterans of Foreign Wars, the Association of Medical Surgeons, the American Chemical Society, and the American Institute of Chemical Engineers. In the face of this protest, and despite personally approving of the treaty, Senator Borah, Chairman of the Senate Foreign Relations Committee, withdrew it from Senate consideration (36).

While some Americans regarded the failure to ratify and the Legion's role in this as a moral victory, it was decried by others. The Legion's position was satirized

in a cartoon in *The Nation*, and Representative Hamilton Fish, Jr., who was the chairman of the committee that created the preamble to the Legion constitution commented (37):

I deplore the fact that the last American Legion should have permitted itself to be rushed into the adoption of a hasty and ill-considered resolution...The Legion is a civilian organization composed of veterans to make right the master over might and to "promote peace and good-will on earth." It was not organized for purposes of war and trying to prevent humane agreements among nations to mitigate the horrors of war.



The international impact of the efforts to outlaw chemical and biological warfare did not stop. The Geneva Gas Protocol as formulated in 1921 was slowly ratified, so that by 1936 39 nations had agreed to its conditions. A significant number of nations did not sign on, including the United States, Brazil, Czechoslovakia, and Japan. The failure to ratify created a tension both between the supporters of the CWS and the public and the CWS and the military. Rejecting the Geneva Protocol was defended as militarily pragmatic by the supporters of the CWS, since many believed that chemical and biological weapons would

be used in any future war. However, given the public outcry against gas, the dislike of chemical warfare by various Presidents and the objection of the central military command to the very existence of the CWS, failure to ratify did not signal support for 'scientific war' but a reluctance to submit American military policy to international control. In essence, the US followed the Protocol but did not ratify it, while other nations ratified it but did not abide by its restrictions (38).

Even among the signatories, there was a constant stream of reports and accusations about violations. France and Germany accused each other of producing war gases in the interwar period, probably with justification. Italy used chemical weapons against the Ethiopians in 1935. Japan, not having ratified the Protocol, became the most active developer of chemical and biological weapons starting in 1932. Although it was kept

secret at the time, Japan began human tests and used chemical and biological weapons in China starting in 1933, with much of the work being carried out by Unit 731 (39). Chemical and biological weapons continued to be an area of research in many countries. With weak support for the Geneva Protocol and lack of surveillance, international control was ineffective. Rather it was traditional military reluctance and tactical and strategic limitations that controlled their use. In all cases in the period, chemical weapons were used only on people who could not defend themselves or retaliate in kind.

The supporters of chemical warfare, rather than benefiting from the success of the antiratification campaign, were being placed more and more on the defensive. In the face of the popular image of gas warfare, there were increasing efforts by supporters of the CWS to convince the public that gas was not as dangerous as it was portrayed. An example is a 1928 article by Dr. Harry N. Holmes, a board member of the NCDA and a former member of the CWS. Holmes argued that the public would be less afraid of chemical warfare if it could be demonstrated scientifically that defense against attack was an easy matter. He suggested that tear gas be dropped on a small city to test the effectiveness of gas defense training (40):

Every citizen should have first been provided with a gas mask supplied by the War Department and he should have been educated in methods of quickly adjusting the mask and in a knowledge of the very great protection obtained in a house with closed windows and doors. It would be most interesting to see how quickly a population of ten thousand, for example, could protect itself from the tear gas....From such experiments on a large scale we might arrange for a thoroughly tested conclusion as to the real merits of gas warfare. In the meantime, the public bases its opinions upon prejudice and unreasoning fears.

Dr. Holmes found no volunteers to undertake his experiment, and such suggestions did little to reassure the public as to the humanity of the supporters of the CWS. The ease with which Holmes argued that gas warfare was not a serious threat can be directly contrasted with a 1919 article about Lewisite (41):

...Now the latest American gas, produced in commercial quantities although not used at the front, was a great many more times as toxic as mustard gas and belonged to the same class of poison gas [causing injury by contact as well as inhalation]...We have reason to believe that American scientists developed superior skill in gas warfare which should be a comforting thought in view of the possibility that in another war gas will be the important weapon.

Anyone reading about the triumphs of American gas warfare in 1919 might well find Holmes' argument difficult to accept. A gas mask and a bit of training could not effectively protect the public in the face of the new chemical weapons which would challenge even well prepared soldiers on the battlefield.

Although material promoting chemical warfare continued to be published, in particular Haldane's 1925 piece "Chemistry and Peace" (42) published in both *Atlantic* and *Current Opinion* and subsequently expanded into a book *Callinicus: A Defense of Chemical Warfare* (1925), the debate was more frequently spurred on by the publication of antiwar pieces. Nicholas Murray Butler, the President of Columbia University, published *The Path to Peace* (1930), in which he made predictions of what a future war would be like. Bertrand Russell's *Which Way to Peace* (1936) was even more specific (43):

Take, for example, mustard gas, which was used in the Great War. This has the advantage of poisoning the ground, which remains dangerous for days. At first it produces no noticeable effects, but within a few hours symptoms appear. If the exposure is slight, the patient usually recovers; if severe, after some days of intolerable agony the patient dies — if he is fortunate.

A far wider audience learned about chemical warfare from popular fiction. A number of novels appeared after the war in which the devastation caused by gas warfare was a major element, usually as part of some future war. Will Irwin's *The Next War* (1921) described 'Lewisite bombs.' Charlotte Haldane wrote *Man's World* (1926), M. S. Southwold *The Gas War of 1940* (1931); and M. Dalton *The Black Death* (1934). All shared the conviction that gas would play a major and devastating part in any future war, especially for civilians.

The best known of the fictional accounts of gas war was H.G. Wells' *The Shape of Things to Come* and the later hit movie "Things to Come." In a particularly lurid passage a flock of goats was exposed to an unnamed future gas as a test (44):

All succumbed to the effect of the gas except three, which dashed their brains out against the enclosure.

James Kendall, Professor of Chemistry in the University of Edinburgh and former Lieutenant-Commander in the United States Naval Reserve and the Liaison Officer with the Allied Services on Chemical Warfare, wrote a book attacking the antichemical side and arguing that chemical warfare was both humane and neces-

sary. In *Breathe Freely!* (1938) he specifically targeted Russell and Wells for attack, calling Russell an ultrapacifist, whose inaccurate pronouncements fostered panic, while Wells was not only inaccurate but "...lets his imagination fairly run riot...(45)" Kendall argues that (46):

One who misinterprets the past and the present of chemical warfare in such an obvious way is scarcely a reliable guide to its future, and it is to be feared that Mr. Wells has allowed what we may call his 'uncritical humanitarianism' to lead him temporarily into the ranks of the sensationalist.

Of the two, Wells is the more significant offender, but Kendall seemed unaware of the irony of accusing a writer of science fiction of being a sensationalist.

Despite the staunch defense of chemical warfare by Kendall, Haldane and most of all Fries, by the mid-1930s, the issue was largely moot. The first serious blow to the CWS had been Pershing's new Standing Order in 1922 that removed the offensive element of the CWS mandate. No gas shells had been filled since 1922. By 1930 the CWS was conducting little research and training no one in chemical offense or defense (47).

In practical terms, the combined effect of long term objections to the CWS within the military, popular opposition, and the Depression damaged the Service so badly it had no chance of returning to the status and stature of the war years. In 1934 the CWS submitted a budget request for \$1,255,000 (plus \$275,000 carried over from the previous year), but was granted only \$448,000. Lobbying efforts restored some funding so that the budget was settled at \$748,378. Further lobbying of Congress resulted in a restoration of the CWS budget to \$1.2 million in 1935. However, this was enacted by the Military Subcommittee of the House Appropriations Committee, not by the War Department (48). Once again, the CWS had gone outside the military to lobby Congress. In the tight budget times of this era this was not appreciated.

In 1937, the War Department tried to change the name of the Chemical Warfare Service to the Chemical Corps. The CWS favored this change, and the War Department felt that it might lead to a decrease in interservice tension. However, President Roosevelt vetoed the bill, stating (49):

It is my thought that the major functions of the Chemical Warfare Service are those of a "Service" rather than a "Corps." It is desirable to designate as a Corps only those supply branches of the Army which are

included in the line of the Army...I am doing everything in my power to discourage the use of gases and other chemicals in any war between nations. While, unfortunately, the defensive necessities of the United States call for study of the use of chemicals in warfare, I do not want to aggrandize or make permanent any special bureau of the Army or the Navy engaged in these studies. I hope the time will come when the Chemical Warfare Service can be entirely abolished.

The CWS was able to survive through the postwar years in large part because of the lobbying efforts organized by Fries among professional chemists and engineers, especially from the National Research Council and the American Chemical Society. The opinions of these scientists were taken seriously by the decision makers in Congress, but they largely failed to win public support. The CWS was transferred to the War Department General Staff as a technical staff division in 1939, and then later placed under the control of Services of Supply in 1942. Essentially nothing of the original organization remained by the end of World War II, and the CWS was officially abolished in 1962 (50).

A further problem for the pro-CWS side was the paradoxical argument that they were forced to make for the public. Within the military, the effectiveness of chemical warfare was discussed in terms of the ability of various substances to incapacitate or kill the enemy, and conversely how to protect friendly forces. Reflections of these discussions can be seen in the books by Fries and West, and Prentiss, with their tables and descriptions of toxicity and applications. Supporters ended up arguing in public that chemical warfare was necessary and useful but at the same time not a threat to civilians because it could be easily defended. This was an impossible conflict. If the chemicals were effective, then worries about civilian exposure seemed justified, and gas warfare could be as much of a threat to humanity as people like Wells suggested. If chemicals were not a serious threat, then why spend money supporting the CWS and an ineffective weapon? While the pro-CWS faction frequently characterized detractors as uninformed, misguided, or even hysterical, the actual tone of most published objections was similar to those expressed in "Fair Square:" "Let us keep faith [with disarmament treaties] and incidentally save the tax payers millions of dollars by abolishing the Chemical Warfare Service (51)."

For the scientists, the reason to continue the work of the CWS was partly a patriotic belief in readiness, but there was also direct benefit. Chemistry was the premier research area for American scientists in the in-

terwar years, so the CWS represented a major investment in basic and applied research. That science should be a part of a strong national defense was not a new idea, but it had rarely been put into practice. Even after the war, the pared down CWS represented one of the largest concentrations of scientists in a single organization. More scientists worked for the CWS Research Division than in the French, German, or British counterparts. For most of the scientists involved, the size of the projects and the funding available were on a scale never imagined in the prewar years. Those involved in the Service were not willing to let such a significant organization collapse.

The CWS established networks of scientists and showed what a large organization could produce. Those scientists had experienced the potential of large-scale work; and even with the CWS incapacitated, they continued to envisage the potential of science on a grand scale. After the war, the lobbying efforts brought scientists out of the laboratory and onto the political stage. In particular, the campaign to block the ratification of the Geneva Treaty demonstrated the power of collective action by scientists and their professional organizations. In general, the scientists lost the public debate over the fate of the CWS; but in a larger sense, they succeeded in making science a national issue. The CWS would serve as a template for the military use of scientific talent in the atomic era, when many chemists, in addition to the more conspicuous physicists, would again be called upon to bring science to war. Many of the same philosophical issues were placed before scientists and the public at the end of World War II, but the decision of the military and government was radically different.

## REFERENCES AND NOTES

1. A. M. Prentiss, *Chemicals in War*, McGraw-Hill, New York, 1937, 663.
2. Ref. 1, p 663.
3. —, "Suffocating the Enemy," *Literary Digest*, **1915**, 50, 1066.
4. Ref. 3, p35.
5. —, "The Chemical Warfare Service," *Science*, **1918**, 48, 133-4.
6. A. A. Fries and C. J. West, *Chemical Warfare*, McGraw-Hill, New York, 1921, 33.
7. Ref. 1, p661.
8. —, "United States Chemical Warfare Service-I," *Scientific American*, **1919**, 120, 318.
9. L. P. Ayres, *The War With Germany, A Statistical Summary*, Government Printing Office, Washington DC, 1919.
10. F. J. Brown, *Chemical Warfare. A Study in Restraints*, Princeton University Press, Princeton, NJ, 1968, 76-7.
11. L. F. Haber, *The Poisonous Cloud*, Clarendon Press, Oxford, 1986, 301.
12. Ref. 11, p302.
13. R. S. Allen, "Chemical Warfare, a New Industry," *The Nation*, **1927**, 124, 33.
14. Ref. 6, pv-vii.
15. Ref. 6, pvii.
16. Ref. 6, pvii.
17. *New York Times*, Sept. 25, 1921, VII, 1.
18. —, "The Humanity of Poison Gas," *Scientific American*, **1919**, 120, 310.
19. W. S. Sims, "Gas is Humane Weapon," *New York Times*, July 22, **1922**, 6.
20. Editorial, "A Chemists' War," *New York Times*, Sept. 20, **1920**, 14.
21. Ref. 1, p 675
22. For example, Kendall, *Breathe Freely*, Appleton-Century, New York, 1938, 51; C. L. Parsons, quoted in W. S. Mullett, "Humane Chemical Warfare," *Literary Digest*, Sept. 19, 1931; and H. S. Villard, "Poison Gas, 1915-1926," *The Nation*, Jan. 12, 1927, 124, 32.
23. Ref. 1, p 671.
24. Ref. 1. P 664.
25. Editorial, "To Control Ruthlessness," *New York Times*, Dec. 5, 1921, 16.
26. J. E. Zanetti, "Chemical Warfare," *New York Times*, Dec. 8, 1921, 18.
27. —, "Defends Chemical Service," *New York Times*, Dec. 8, 1921, 19.
28. Washington Conference. *Protocol*. Sessional Paper No. 47, **1921-22**, 188.
29. Editorial, "Preventing a Chemists' War," *New York Times*, Mar. 31, 1922, 16.
30. General Orders 24, War Department, **1922**, Sections 1-5, replacing General Orders 54, **1920**.
31. —, *New York Times*, May 25, 1922, 20.
32. —, "To Use Poison Gas on Boll-Weevil," *New York Times*, Sept. 13, 1922, 31.
33. —, "Army Chemists Use Poison Gases on Disease; Grip, Pneumonia, Paresis Said to be Cured," *New York Times*, May 2, 1923, 1.
34. United States Senate, *Congressional Record*, 69th Congress, **1926**, (LCVIII), 152.
35. R. S. Allen, "Chemical Warfare, a New Industry," *The Nation*, Jan. 12, 1927, 124, 33.
36. E. M. Spiers, *Chemical Warfare*, MacMillan, Houndsmills, 1986, 46.
37. H. Fish, Jr., quoted in R. S. Allen, "Chemical Warfare, a New Industry," *The Nation*, Jan. 12, 1927, 124, 33.
38. The United States did not ratify the Geneva Protocol until 1974.

39. For information on the Japanese chemical and biological program, see P. Williams and D. Wallace, *Unit 731: The Japanese Army's Secret of Secrets*, Hodder & Stoughton, London, 1989. The issue of Japan's use of biological and chemical weapons in China has not been resolved to date as stockpiles of materials may still exist and claims for compensation have been made.
40. —, quote of H. H. Holmes, "A Test of Chemical Warfare," *Scientific American*, May, 1928, 130, 464.
41. H. E. Howe, "The Competition in Poison Gas," *Scientific American*, May 17, 1919, 120, 518.
42. J. B. S. Haldane, "Chemistry and Peace," *Atlantic*, 1925, 135, 1-18; *Current Opinion*, 1925, 78, 333-40.
43. B. Russell, *Which Way to Peace?* Michael Joseph, London, 1936, 31.
44. H. G. Wells, *The Shape of Things to Come*, Hutchinson, London, 1935, 132-3. Emphasis in Wells.
45. Ref. 44, p18-19.
46. Ref. 44, p15.
47. L. F. Haber, *The Poisonous Cloud*, Clarendon Press, Oxford, 1986, 303.
48. F. J. Brown, *Chemical Warfare*, Princeton University Press, Princeton, NJ, 1968, 141-2.
49. President F. D. Roosevelt, Ref. 47, p.125.
50. General Orders 44, Department of the Army, 1962.
51. "Fair Square." Letters to the editor, *New York Times*, Nov. 16, 1923, 6.

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### CALL FOR NOMINATIONS FOR THE 2003 EDELSTEIN AWARD

The Division of the History of Chemistry (HIST) of the American Chemical Society (ACS) solicits nominations for the 2003 Sidney M. Edelstein Award for Outstanding Achievement in the History of Chemistry. This award, first given to Dr. John Parascandola in 2002, honors the memory of the late Sidney M. Edelstein, who established the Dexter Award in 1956, and it also continues the outstanding tradition of the Dexter Award, which ended in 2001.

The Edelstein Award is sponsored by Ruth Edelstein Barish and Family and is administered by HIST. In recognition of receiving the Edelstein Award, the winner is presented with an engraved plaque and the sum of \$3500, usually at a symposium honoring the winner at the Fall National Meeting of the ACS, which for 2003 will be held in New York City, September 7-11. The award is international in scope, and nominations are welcome from anywhere in the world. Previous winners of the Dexter and Edelstein awards have included chemists and historians from the U.S., Canada, Germany, France, Holland, Hungary, and Great Britain.

Each nomination should consist of

- a complete curriculum vitae for the nominee, including biographical data, educational background, awards, honors, publications, presentations, and other service to the profession;
- a letter of nomination, which summarizes the nominee's achievements in the field of the history of chemistry and cites his/her unique contributions that merit a major award; and
- at least two seconding letters.

Copies of no more than three publications may also be included if they are available.

All nomination material should be sent *in triplicate* to Professor Roald Hoffmann, Chair of the Edelstein Award Committee, Department of Chemistry and Chemical Biology, Cornell University, Baker Laboratory, Ithaca, NY 14853-1301 (e-mail: rh34@cornell.edu), by December 31, 2002.

## CHEMISTRY AT RICE, 1912 to 1998

*Edward S. Lewis, Rice University*

### Early period up to 1925. An Auspicious Opening

Twenty-one years after the charter of the William Rice Institute in 1891 the new institute admitted its first students in 1912.

The period up to 1925 not only included the start of all instruction including chemistry, but also World War I, which took faculty and students away for military service and governmental research. Before the war Rice Institute started with a celebration with visiting scholars from all over the world. This is commemorated in "The Book of the Opening (1)."

A number of departments started with a senior professor of international reputation, such as H. A. Wilson in physics, Julian Huxley in biology, and Griffith Evans in mathematics. This was not the case in chemistry. The faculty in chemistry started with W. F. Edwards, lecturer, in 1912, the year of the first classes at the Rice Institute. Edwards had a B.A. degree from the University of Michigan, and according to the catalog (2) he had been president of the University of Washington, an unconfirmed statement. He was joined briefly by several short-term appointments, and in 1916 by Harry Boyer Weiser, who had a Ph.D. from Cornell with Wilder Bancroft. With the exception of Weiser, the earliest appointments before 1920 lasted an average of 1.8 years. Weiser stayed for 32. Appendix 1 lists all chemistry faculty with approximate dates.

Mention must be made of one extremely short appointment, that of the organic chemist Frank C.

Whitmore. He observed that the essential reference for this field, Beilstein's *Handbuch*, a multi-volume German compilation, was not in the library. Whitmore asked the president, E. O. Lovett, to purchase this for the library. Lovett refused on grounds of the great expense of this series; but after being told how essential it was for organic chemistry, he relented and offered to buy one volume. This ridiculous offer, equivalent to owning the A-C volume of an encyclopedia, insulted Whitmore, who then resigned immediately. He went to Pennsylvania State University, where he became established in a long career as one of the country's premier organic chemists. Notable was not only the loss for Rice of a potentially distinguished chemist, but also the practice of an assistant professor's going directly to the president with a request. Nowadays, the chain of command to access the president is much longer. The source of this story is vague. I have heard it from many sources both from Rice and Penn. State; an extremely short tenure is clear from the Rice catalog of that time. After 1920 many appointments lasted for years; some faculty of that period stayed on to retirement.

The earliest laboratories were located in the mechanical building, one of the original structures. A wooden annex was added somewhat later to accommodate some of the teaching and research needs. A catalog of this period describes the department as being "splendidly equipped" for modern research and teaching. A new chemistry building, started in 1923, was ready for occupancy in 1925. The cornerstone was laid by the distinguished chemist Edgar Fahs Smith, according to the 1923 yearbook (3).

A worldwide characteristic of the early period was an emphasis on analytical chemistry. The department had at least one and often two analytical chemists for many years. The early curriculum included general chemistry in the first year and analytical chemistry in the second year, and these two courses, with laboratories, were taken by all science-engineering students. Medical schools used the quantitative analysis and the organic course results as a screen for admission. Math 100, physics, English, and history were also taken in the first year, and science students took more mathematics, physics, and often a foreign language in the second year. With the exception of architecture students no one had a major until the junior year. Then the different majors had a variety of courses, but always five courses per year. All students, regardless of intended major, took the notorious Math 100 in the first year (and sometimes again and again). This rigorous program changed very little until the 1950s.

In the junior and senior years chemistry majors took additional courses in organic, analytical, and physical chemistry, all with laboratories, as well as physics and mathematics. These, together with various humanity courses, completed the program to the bachelor's degree. All courses were one-year offerings in the early period; later one-semester courses were allowed. The first recipients of the bachelor's degree graduated in 1916. The yearbook shows that Mary Willard Fox received the B.A. with honors in chemistry in 1916. The first Ph.D. in chemistry was awarded to Jacob Sherrick in 1919.

Senior and graduate courses were listed. It is not obvious how many were actually offered, but a catalog of about 1916 mentioned the availability of courses in inorganic, organic, physical, electro-, sanitary, and agricultural chemistry, as well as a chemistry seminar.

Virtually the entire research effort in chemistry was that of Weiser; the first two Ph.D.s and four out of five

later ones were his students. Thus, of the first 19 research papers published through 1920, 15 were Weiser's. The listing of research papers and Ph.D. students is derived from a complete, unpublished compilation of research papers and Ph.D. theses up to 1993 by the present author (4). These papers and theses covered a variety of subjects, mostly on inorganic precipitates and colloids; but there were also several on luminescence of inorganic solids.



Mechanical Engineering Building, 1916, Rice Institute  
courtesy of Rice Institute Library

### **Lovett Continues his Administration, 1925 to 1946**

The year 1925 marked the opening of the new chemistry building, adding greatly to the space available for the department. This is the motive for dividing President Lovett's term into two parts. Some space was also allocated to architecture, chemical engineering and psychology, and library space for all four departments. The building was ornamented by a cement sculpture caricature of H. B. Weiser as a dragon clutching a student, presumably a freshman, with his

claw. The building had an octagonal tower as a hood exhaust adorned with the symbol of an element of the first row of the periodic table on each of the eight sides.

From 1925 to 1946 there were only six additions to the faculty, and of these three preceded great depression of the early 1930s. Although the earliest faculty members had very short terms, those appointed after 1920 stayed on much longer, partly because of the deression. The faculty was nevertheless reasonably active in research, most contributing to the publications, even though Weiser still led in this count. Walter Kirner (an organic Ph.D. with Conant at Harvard) joined the faculty in 1925. Although a good chemist in his own right, he is remembered here as the mentor of George Holmes Richter, who earned his Ph.D. in 1929. Richter joined the faculty in 1931, after a post-doctoral year at Cornell (with Wilder at Weiser's suggestion) and in Germany, where he felt more at home among organic

chemists. Because he replaced Kirner, there was still only one organic chemist on the faculty of five members. They were Weiser, who remained until retirement in 1948; A. D. Garrison (retired in 1955); H. O. Nicholas (retired in 1957); Arthur Scott (a Harvard Ph.D. with T. W. Richards), who left for Reed College in 1936; and Richter (retired in 1974). Thus the thirties and early forties were a period of stability, but with a hint of stagnation. This was maintained until 1946 when a new president and new money for the institute started a post-World War II revival.

Research continued at a modest pace until World War II, with an average of over eight research papers and patents per year through 1943. Again Weiser contributed the most, but all the faculty published at least some in this period. There was about one Ph.D. per year from 1925 to 1944. In 1944 and 1945 there were no publications from the department, a reflection of the influence of unpublished war research, the absence of graduate students, and the increased teaching demands from special military training programs.

### **The Houston Administration, 1946 to 1959**

President Lovett had offered to resign earlier but had been persuaded to stay on until a successor could be found. In 1946 William V. Houston was selected as the second president of the Institute. Houston was from Cal Tech, where he had a reputation as an excellent physicist. At the same time a new source of funds was acquired by the purchase of the Rincon oil field. This added considerably to the annual income of the Institute, and the stagnant period ended.

Over the next five years six new appointments in chemistry brought the total in 1961 to 10 faculty, now consisting of four organic, four physical, and two analytical chemists. Weiser had retired in 1947 and Richter had become chairman and dean. W. O. Milligan, who was appointed a post-doctoral fellow with Weiser after completing his Ph.D. (also with Weiser) in 1934, was appointed to the faculty in 1946. Milligan maintained a productive research program in quantitative studies of gas adsorption on solids and the use of X-rays to characterize and provide some structural information about his favorite substances, the hydrous oxides. Milligan became the Director of Research of the Robert A. Welch foundation, a title he kept in later appointments at Texas Christian University and then Baylor University.

Other departments of the Institute also became stronger in this period with new additions to the faculty.

President Houston's efforts were helped by a completely new board of trustees under the chairmanship of George R. Brown. Brown's immense contributions to the entire institution are too large to describe here, but the name Brown is now found on three academic buildings, an undergraduate college, the school of engineering, and several teaching awards.

The leadership of President Houston and the foresight and ambition of Holmes Richter led to remarkable changes. In faculty recruitment Richter set a very high standard; most of his appointments had held nationally competitive post-doctoral fellowships. In this period only three of his eleven appointments lasted for less than five years. Later two (Turner and Curl) were elected to the National Academy of Sciences, and Curl received the Nobel Prize. The advances in research productivity grew from fewer than six papers per year through 1949 to more than 16 papers per year from 1950 through 1962. About four Ph.D.s per year were granted in this same period.

J. E. Kilpatrick joined the faculty in 1947; his research included the statistical mechanical consequences of some model systems, low-temperature calorimetry of organic substances, and contributions to the Rice computer, where he took advantage of his experience with the "Maniac" computer at Los Alamos. J. Waser, in single-crystal X-ray diffraction and E. S. Lewis in physical organic chemistry and reaction mechanisms, both arrived in 1948.

With the recruitment of R. B. Turner and M. G. Ettliger in 1951 there was a major change in the managing of research. Turner brought in substantial external funds. Joined by a number of post-doctoral fellows, he brought the Rice department into intimate contact with the rest of the world of academic chemistry. Turner's research involved the heats of hydrogenation of unsaturated hydrocarbons, which he measured with his own hands because the precise experiments were very difficult. Turner also had a synthetic program that occupied most of his graduate students. The heats of hydrogenation work was widely appreciated and quoted; it had a world-wide impact on the treatment of the energetics of organic molecules. Turner became the first department member to be elected to the National Academy of Sciences.

After a few years Richter placed Turner in charge of graduate student recruiting, at which he was very successful. The number of highly qualified graduate students increased markedly. This was also the beginning

of a series of building changes, made possible because the other occupants since 1925 had found other space. The first air-conditioning appeared in the building, and it soon spread throughout the campus. The wide corridors were narrowed, some small classrooms being lost to research. Turner succeeded Richter as chairman in 1961, while Richter continued as dean.

The description of Richter as dean and chemistry recruiter omits some other features. He was an effective and popular teacher, especially of the first organic course. He was a source of many stories, which he would tell at lunch in a very low voice, forcing quiet from his listeners. He was insistent on attendance at examinations; once a student, having been denied a postponement, was delivered by ambulance, swathed in bandages, on a stretcher. Richter administered the examination without comment. Many Houston doctors still remember his organic course.

The establishment of the Welch Foundation for the support of research in chemistry in the early 1960s had a real impact. Most of the faculty received awards (at that time about \$12,000 to \$15,000 per year), which then could support several graduate students or post-doctoral fellows, as well as providing equipment and faculty summer stipends. This stimulated the search for other external research funds, which was mostly successful.

There were some notable additions to the faculty in the late fifties. One was Zevi W. Salsburg, a Ph.D. from Kirkwood at Yale, who became in a short period an international authority on statistical mechanics. Another was Robert F. Curl, a Ph.D. from Pitzer at Berkeley, who started doing microwave spectroscopy and continued into all branches of molecular spectroscopy, and who contributed greatly to the C60 problem, including participating in the discovery of that molecule and in an inspired assignment of its structure. R. L. Sass (Ph.D.

University of Southern California) started out as a crystallographer but recently has established an international reputation on atmospheric methane and global warming as a member of another department.

Concern in the later 1950s over computational facilities culminated in the construction of a modern vacuum tube digital computer at Rice. Professors Salsburg and Kilpatrick provided many ideas, and the actual construction was supervised by Prof. Martin Graham of electrical engineering, who contributed great technical skill. These efforts led to a physically large and powerful state-of-the-art computer with highly original features both in circuitry and in logic. Unfortunately, the development of the transistor made the Rice computer obsolete very shortly after its completion; but it was the start of a thrust in computational work that still continues.

Houston resigned for health reasons in the late 1950s, and an interim acting president, Cary

Croneis, was in charge. A search at this time produced the name of Kenneth S. Pitzer, at the time professor of chemistry and dean of the College of Chemistry at the University of California at Berkeley. The department felt at home with this selection, in part because two of his Ph.D.s, Kilpatrick and Curl, were on the faculty, and the present author had known him while an undergraduate at Berkeley.

### The Pitzer Administration, 1961-1968

When Pitzer arrived on campus he had an immediate impact on chemistry as well as the rest of the Institute. He backed a change in the charter to allow the admission of nonwhite students, to allow the charging of tuition, and to change the name to the "William Marsh Rice University." Tenure was introduced to stimulate the activity of junior faculty. In chemistry he recog-



Groundbreaking ceremonies for Chemistry Building,  
Rice Institute, June 4, 1923  
courtesy of Rice Institute Library  
(LR) William M. Rice, Jr., Joseph L. Gillman, Jr., Edgar  
Fahs Smith, E. O. Lovett, William Ward Watkin, Dr.  
Weiser, Bishop Quinn

nized a lack in inorganic chemistry, so he persuaded J. L. Margrave to come as a full professor. He also arranged to fill the newly created Robert A. Welch chair with J. L. Franklin.

John Margrave had already established a reputation at Wisconsin in high-temperature chemistry. He also began a study of the chemistry of elemental fluorine and learned how to control its great reactivity so that direct fluorination was possible. In the course of his Rice career Margrave has won practically every national award in inorganic and fluorine chemistry and was the second man elected from the chemistry faculty to the National Academy of Sciences.

Franklin came from The Humble Oil Company (now ExxonMobil), where he had been employed for many years after earning a Ph.D. at the University of Texas. He had become a world expert on the energetics of gas phase ions as revealed by mass spectrometry. As occupant of the Robert A. Welch chair, Franklin not only added to the department by his research and contacts with chemists outside of Rice, but he inspired an appreciation of fine food. He was a gourmet cook as many of us remember, and he knew and patronized the world's best restaurants.

The appointment in 1973 of G. J. Schroepfer, Jr. as professor of chemistry and chairman of the newly created biochemistry department solved an urgent problem of the biology-chemistry interface. Pitzer did not stay to make this appointment, but he had realized the need. The biochemistry department has thrived since, and is now about as large as chemistry.

Faculty salaries rose under Pitzer and became nationally competitive. The amount of externally funded research grew far more than it had been earlier, and research not only in chemistry but in other sciences did very well. In spite of this effort directed toward the sciences and to engineering, Pitzer was very well liked in the humanities and social sciences. He contributed much effort to these fields as well, and they also prospered.

In Pitzer's eight years at Rice the department produced 43 Ph.D.s, and well over 300 research publications. Much of this number could be attributed to the extraordinary productivity of the Margrave group, but all members of the faculty contributed. It was indeed a fruitful and exciting period.

Some appointments in this period were, in addition to Margrave and Franklin, P. R. Brooks (Ph.D. UC Ber-

keley, Herschbach) who designed and performed some very difficult experiments on the reactions of oriented molecules in the gas phase; and R. V. Stevens (Ph.D. Indiana, Wenkert) who initiated an ingenious synthetic program for complex natural products. Stevens was rapidly promoted to professor, but could not resist an offer from UCLA. Two physical chemists, Graham Glass, in combustion and gas kinetics, and Edward Hayes, a theoretician, were later promoted. Four others did not stay more than five years. When Pitzer resigned in 1968 there were about 14 members of the chemistry faculty.

Pitzer resigned to accept the presidency of Stanford. Because of student problems of a serious nature related to the Viet Nam war, Pitzer had a difficult and unpleasant time at Stanford and might have wished he had stayed at Rice. However, the Rice board was believed to feel that the university had taken on too much of a challenge and apparently was glad to see Pitzer go, an attitude not shared by the faculty.

### **The Hackerman Administration, 1970-1985**

A two-year interim period under an acting president was unhappy for all. After much delay the board announced the selection of Norman Hackerman to assume the presidency. Hackerman, a physical chemist with a Ph.D. from Johns Hopkins, was at the time of this selection the president of the University of Texas at Austin. Hackerman was apparently charged with improving Rice's financial position. As a consequence there was a period of several years in which budgets were quite tight, but then advances continued.

The beginning of this period was a difficult time for the chemistry department. In the spring of 1970, Richard Turner died after a long illness. Then, less than a year later, Zevi Salsburg died suddenly in Los Angeles. Thus the loss of a premier organic chemist was followed by the loss of a very promising and distinguished physical chemist. The effect of these two premature deaths was difficult to overcome.

There were 18 new appointments in chemistry in this period; half remained on the faculty for an extended time. Those who earned tenure include, in chronological order, W. E. Billups and P. S. Engel in organic chemistry; L. J. Wilson in inorganic chemistry; R. E. Smalley in physical chemistry; T. Fukuyama and R. J. Parry in organic chemistry; R. B. Weisman and J. S. Hutchinson in physical chemistry; and K. H. Whitmire in inorganic chemistry. Whitmire came to Rice after a long sequence

of junior inorganic chemists who failed to achieve tenure, and later he became chairman of the department. In this same period Ernest Wenkert was brought in as professor and Michael Berry came to succeed Franklin as Welch professor; neither is still here.

Billups started a program of synthesis. He made a component of the boll weevil sex attractant, which had an impact on the cotton industry. The synthesis and reactions of some novel, very strained molecules including benzocyclopropene and methylenecyclopropene has kept his group occupied. He is now concerned with the organic chemistry of fullerenes. Engel initiated a study of organic photochemistry, which, together with studies of transient free radicals and their precursors the azo compounds, still continues.

Wenkert, an organic chemist most recently from Indiana with a Woodward Ph.D., was brought in as a possible replacement for Turner. Although this did not turn out to be the case, he did have a strong synthetic group, and got us well started in higher field NMR (high field was then 100Mhz), an area which he exploited in a number of publications. He was chairman of the department briefly before accepting a position at the University of California at San Diego.

During Wenkert's chairmanship the appointment of Fukuyama (a Kishi Ph.D. from Harvard) as assistant professor added immensely to the synthetic organic capability of the department. Fukuyama was a genius at very complex organic synthesis. He accomplished one major antibiotic synthesis after another, rapidly establishing an international reputation. Although he was rapidly promoted, he left in 1996 to accept a prestigious professorship at the University of Tokyo.

The appointment of Ronald Parry as associate professor (from Brandeis University) was the department's first in the biology-chemistry interface except for Schroepfer in biochemistry. His first work established the biosynthetic pathways of a number of natural products containing sulfur, and many other biosynthetic pathways have since been studied by using increasingly sophisticated techniques.

The acquisition of Rick Smalley was a great coup. He started doing innovative work on spectroscopy of substances in expanding helium jets at very low temperatures and continued this technique to make clusters of metals in the gas phase, and later clusters of carbon, leading to the discovery of the sixty carbon allotrope. He, along with Curl and Harry Kroto (visiting from Southampton), discovered this molecule, which they

named Buckminsterfullerene, as soon as the structure was proposed. They accomplished the feat of assigning the "Buckyball" structure, based only on mass spectral evidence. It was generally felt that this would be worthy of the Nobel prize, which in fact was awarded to all three in 1996.

President Hackerman resigned in 1985 and was succeeded by George Rupp. Although he had been selected by a very capable search committee, there was considerable concern over this choice. Rupp was the first nonscientist president; having previously been dean of the Harvard Divinity School. This concern turned out to be groundless. Not only did the humanities do well, but it was a very good period for the sciences.

### **The Rupp Period, 1985-1993**

George Rupp became president in 1985, an appointment lasting only eight years until he accepted the presidency of Columbia University. Rupp provided a strong sense of direction for every department including the sciences and was well recognized for his success. Among the arrivals in his period was a new dean of sciences, J. L. Kinsey from Massachusetts Institute of Technology. Kinsey had been a Rice undergraduate and earned a Ph.D. under Curl. He is an active department member as well as dean. M. A. Ciufolini was appointed in organic chemistry but left after several successful years to accept a position at the university of Lyon. Also in this period came the appointment of G. E. Scuseria, who has proven to be expert in using modern computational methods of quantum mechanics to calculate properties and stabilities of some fairly complicated molecules.

Several buildings were completed in Rupp's time, including George R. Brown Biosciences. This accommodated most of the organic chemical research as well as much biochemistry and bioengineering, vacating some of the 1925 chemistry building. Much of the physical chemistry research had already been transferred to the Space Science building, including the research groups of Curl, Kinsey, Smalley, and Weisman. All the teaching laboratories remained in the chemistry building along with some of the physical chemistry research and all the inorganic and some organic research, until the completion of the new Butcher Hall.

### **The Gillis Period, 1993-**

Malcolm Gillis, an economist from Duke, is the current president. After a period of uncertainty, he is

now well accepted. He has planned a number of additions to the Rice campus, and has witnessed the completion of a building for nanotechnology, a new field arising at Rice from the fullerene work. This building, now called Butcher Hall, accommodates not only research in nanotechnology, but also most of the undergraduate chemistry laboratories and all the inorganic chemistry from the former chemistry building. There are also related areas of physics and engineering research in the building. The chemistry department office has been moved to the adjacent Space Science building, which also contains physical chemistry research and one teaching laboratory. Nothing is left of chemistry in the "old chemistry building," now called Keck Hall.

Several new department members have come in the Gillis period: Andy Barron, an inorganic chemist from England *via* Harvard, as professor; James Tour, also as professor, an organic chemist with interests in organic molecules as computer components; Vicky Colvin, in nanochemistry; Seiichi Matsuda and Scott Singleton, both in bio-organic chemistry; Victor Behar in organic synthesis; and Anatoly Kolomeisky, a theoretician, all as assistant professors.

### Research Accomplishments

In the early years of the department H. B. Weiser was the principal contributor to research. He worked mostly on adsorption by precipitates, luminescence of inorganic materials and colloids. Later, Arthur Scott worked on atomic weights, including that of carbon which was adopted until the mass spectrometric method became more widespread. A. D. Garrison was mostly interested in petroleum processing and production; he had close relations with the petroleum industry. There was not very much exciting research until after World War II, when a new group of faculty selected in part for research promise started their work.

Kilpatrick started a program of heat capacities of hydrocarbons at liquid hydrogen temperatures and above and thus allowed for the calculation of entropies. He also did some theoretical work. Later, Turner measured the heats of hydrogenation in solution of a wide variety of unsaturated hydrocarbons, both open chain and cyclic, to clarify the effect of structure on energies, including consideration of steric and conformational effects. This work had a wide impact on quantitative organic chemistry. The new appearance of nuclear magnetic resonance (NMR) spectroscopy included a memorable application by Ettliger, who used it to establish

the structure of Feist's acid (5), the first time NMR had been used to prove an organic structure. In a long series of papers the substituent effects on rates and equilibrium constants of diazonium ion reactions and the discovery of a hitherto unsuspected rearrangement were described.

However, no research at Rice has had the impact of the Buckminsterfullerene discovery. This new carbon allotrope and the related fullerenes have had a world wide impact. Thus, in a review published in 1993, edited by Billups and Ciufolini (6), the 13 authors cited 892 references, including duplication and also references with several papers cited. There has been no diminution in the rate of publication since then. Also about half of the current Rice chemistry faculty, as well as some in other departments, have published papers on the fullerenes. In 1995 *Science* selected Buckminsterfullerene as the molecule of the year. It was therefore no great surprise that Curl, Kroto, and Smalley were awarded the Nobel Prize in chemistry in 1996. This distinction is a first for Rice in any field.

The past years have seen an enormous increase in the accomplishments of the Institute become University, not the least of these those of the Chemistry Department. We look forward with confidence and enthusiasm to the future (7).

### REFERENCES AND NOTES

1. "The Book of the Opening, Rice Institute, Houston, TX, 1914; an account of the distinguished visitors and the papers presented by some of them in celebration of the opening of the institute.
2. "General Announcements," a publication by the institute and later by Rice University containing course offerings and faculty lists. It was published annually except for a short period when it appeared in alternate years. It is called here the "Catalog."
3. The yearbook is an undergraduate student annual publication containing useful data of usually reliable nature. It has been called the *Campanile* for many years.
4. An unpublished compilation of departmental research publications and Ph.D.s and their thesis titles was assembled several years ago by the author. Based on faculty publication lists, *Chemical Abstracts*, and commencement programs, it was complete through 1993.
5. M. G. Ettliger and F. Kennedy, "The Structure of Feist's Acid and Esters," *Chem. Ind. (London)*, **1956**, 166.
6. W. E. Billups and M. A. Ciufolini, Ed., *Buckminsterfullerenes*, VCH Publishers, Inc., New York, 1993.

7. Much of the matter in this article is based on the author's memory, whose time at Rice covers more than half of the life of the Institute and the University together. Two appendices follow, the first lists the entire faculty from the beginning of classes to the present, the second lists department chairs from the first faculty member known to have this title of unknown starting date to the present.

## ABOUT THE AUTHOR

Edward S. Lewis, son of G. N. Lewis, received his undergraduate education at the University of California, Berkeley, and then earned his Ph.D. at Harvard under the supervision of Paul D. Bartlett. He joined the chemistry faculty at Rice in 1947, where he remained until his retirement in 1990. Professor Lewis spent a year at Oxford as a Guggenheim fellow in 1967-1968.

### Appendix 1

#### FACULTY MEMBERS OF THE RICE CHEMISTRY DEPARTMENT<sup>1</sup>

<u>NAME</u>	<u>DATES</u>		
W. F. Edwards	1912-1914	R. V. Stevens	1967-1973
A. R. Hitch	1915-1917	G. P. Glass	1968-
W. J. van Sicklen	1915-1916	E. F. Hayes	1968-1978, 1987-1992 <sup>5</sup>
H. B. Weiser	1916-1948	O. Gansow	1969-1973
G. L. Wendt	1917-1918	P. Haug	1969-1971
J. L. Sherrick	1918-1920	N. Hackerman	1970-1989
C. H. Classen	1918-1919	W. E. Billups	1970-
F. C. Whitmore	1919-1919	P. S. Engel	1970-
H. D. Draper	1919-1920	F. D. Rossini	1971-1975
H. O. Nicholas	1921-1971	J. J. Havel	1972-1975
W. M. Craig	1923-1926	F. T. Wall	1972-1979
A. J. Hartsook <sup>2</sup>	1923-1926	E. Wenkert	1973-1980
A. D. Garrison <sup>3</sup>	1925-1953	L. J. Wilson	1973-
W. R. Kirner	1925-1930	G. J. Schroepfer	1972-1996 <sup>6</sup>
A. F. Scott	1926-1937	R. E. Smalley	1976-
G. H. Richter	1931-1974	T. Fukuyama	1988-1996
F. H. Hurley, Jr.	1937-1942	S. Mukamel	1978-1981
W. O. Milligan	1946-1964	R. J. Parry	1978-
J. T. Smith	1946-1951	B. A. Sosinsky	1978-1982
J. E. Kilpatrick	1947-1985	M. J. Berry	1981-1992
E. S. Lewis	1948-1990	D. M. Stanbury	1981-1986
J. Waser	1948-1958	R. B. Weisman	1981-
R. B. Turner	1951-1971	J. S. Hutchinson	1983-
M. G. Ettlinger	1951-1964	K. H. Whitmire	1981-
G. R. Bird	1954-1959	M. A. Ciufolini	1985-1998
Z. W. Salsburg	1956-1970	M. P. D'Evelyn	1987-1993
T. E. Brackett	1958-1963	K. Burgess	1986-1992
R. F. Curl	1958-	J. L. Kinsey	1987-
R. L. Sass	1958- <sup>4</sup>	S.-J. Hwu	1988-1993
K. S. Pitzer	1961-1968	G. E. Scuseria	1989-
J. L. Margrave	1963-	A. R. Barron	1995-
J. L. Franklin	1964-1975	S. P. T. Matsuda	1995-
P. R. Brooks	1965-	V. L. Colvin	1996-
R. M. Magid	1965-1970	S. Singleton	1996-
T.S. Cantrell	1966-1970	V. Behar	1998-
		A. B. Kolomeisky	2000-
		N. J. Halas	2000- <sup>7</sup>

<sup>1</sup>Until 1940 the initial appointment was with the title “instructor;” after this instructor was used for very short-term appointments, and those are not included in this list. Visiting professors are also not included. <sup>2</sup>In 1926, Hartsook left to join the new Chemical Engineering Department. <sup>3</sup>Garrison was intermittently in Chemi-

cal Engineering. <sup>4</sup>Sass became more active in the Department of Ecology and Evolutionary Biology. <sup>5</sup>Hayes left in 1978 and returned in 1987 as professor of chemistry and vice president. <sup>6</sup>Schroepfer was primarily in Biochemistry. <sup>7</sup>Halas is primarily in the Department of Electrical and Computer Engineering.

## Appendix 2

### CHEMISTRY DEPARTMENT CHAIRS

H. B. Weiser	-1947 <sup>1</sup>
G. H. Richter	1947-1961
R. B. Turner	1961-1964
E. S. Lewis	1965-1968
J. L. Margrave	1968-1973
J. L. Franklin	1973-1978
E. Wenkert	1978-1980
E. S. Lewis	1980-1985
W. E. Billups	1985-1990
R. F. Curl	1990-1995
G. P. Glass	1995-2000
K. H. Whitmire	2000-

<sup>1</sup> The institute did not use the title “chairman” in the early years. The professor was the department head since there was then only one professor per department.

It is not clear whether Weiser was department head at his initial appointment in 1916.

### COMING EVENTS

October 3-5, 2002

“Industrial-Academic Relationships in the Chemical and Molecular Sciences”

Chemical Heritage Foundation

315 Chestnut Street

Philadelphia, PA 19106

Contact Todd Waters, Tel: 215-925-2222

[toddw@chemheritage.org](mailto:toddw@chemheritage.org)

May 3, 2003

Kanawha Valley Chemical Heritage Symposium

Charleston Marriott

Charleston, WV/USA

Contact: Lee Maddex ([lmaddex@wvu.edu](mailto:lmaddex@wvu.edu)) or

Michael Workman ([mworkma2@wvu.edu](mailto:mworkma2@wvu.edu))

## BOOK REVIEWS

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*Chemistry and Medical Debate: van Helmont to Boerhaave.* Allen G. Debus, Science History Publications/USA, Nantucket, MA, 2001. 296 pp, ISBN 0-88135-292-6, \$52.

For many years now Allan G. Debus has been a tireless worker in the history of chemistry. As he points out in this volume, when he first began to study the history of chemistry, it was unfashionable; and attention was mainly lavished on the physical sciences. His own choice of research was particularly obscure in those days. He studied Paracelsus and more significantly the legacy of Paracelsus in its European context. This was a topic familiar to German historians but was virtually unknown in North America. Debus made us alive to the fact that in the sixteenth and seventeenth centuries Paracelsian chemistry flourished in the courts of Europe and had strong associations with natural magic. It became clear from Debus' work and those that followed him that this tradition, obscure and strange though it may seem, played a very important part in the scientific revolution. Debus' studies also drew attention to the strong connections between early modern chemistry and medicine. Until recently Debus' scholarship has largely remained confined to the period in which he began his work. In this book he pushes the boat out and, building on his earlier studies, writes about chemistry and medicine from Paracelsus to Boerhaave. As usual, Debus' approach is to elucidate primary texts, and any reader looking for useful accounts of the chemistry of various figures in the era covered by this book can expect to find first-hand reporting rather than derivative repetition from secondary sources.

The first three chapters of the current work largely draw on Debus' earlier books, notably *The English Paracelsians* of 1965 and *Man and Nature in the Renaissance* of 1978. In these chapters he describes the chemistry and physiological concepts of Paracelsus and those of his defenders such as Peter Severinus. Debus

takes great pains to stress the medical dimensions of Paracelsus' work; quite rightly too, since it was doctors rather than those with a commercial or industrial (if that is the word) interest in chemistry who found his concepts most valuable. As usual Debus is wide ranging, describing the diffusion of Paracelsus' texts in continental Europe and England. Chapter 2 is mainly devoted to Jean Baptiste van Helmont and the new chemical medicine. Consistent with Debus' approach, he not only outlines Helmont's ideas but details responses to them, many of them by scholars who thought his work worthless. Eschewing strict nationalist approaches, he deals in Chapter 3 with Sylvius and then a number of English chemists, including Thomas Willis and Robert Boyle. Much of this chapter is given to the controversy over the place of chemistry at the Royal College of Physicians, a debate that is now fairly well known from the work of Harold Cook and others. From here, in Chapter 4, Debus goes on to take up an intriguing subject that has also been the center of recent attention; that is the uses to which the ancient Hippocratic texts were put during the scientific revolution. Hippocrates is usually considered an empiric, little bothered by theory; but Debus discovers in the writings of the German-born Otto Tachenius a figure who found in the books attributed to the Greek physician the philosophy of what was then modern chemistry. After this Debus enters relatively new territory for him. He takes on the early eighteenth-century controversies between the iatrochemists and the iatromechanists, in particular looking at debates over digestion. Displaying his customary catholic interests, he draws attention to the writings of a number of Spanish Paracelsians who until now can only have been known to a very few modern scholars. Chapter 6 deals with chemistry and medicine in the early Enlightenment and again spans a European canvas, taking in Hermann Boerhaave and Georg Ernst Stahl. This book is not simply an eclectic compilation of writings from early chemistry. Its principal theme is to show that there was a

continuous chemical tradition fuelled by Paracelsian origins even after they had been repudiated. This tradition, he rightly insists, had particularly strong links to medicine. As usual Debus writes clearly and punctuates his texts with numerous quotes from primary sources. No doubt scholars will disagree with many of

his interpretations, but this will remain a most useful contribution of an understanding of chemistry in this period. For many it could form a valuable introduction to the subject. *Professor Christopher Lawrence, Wellcome Trust Centre for the History of Medicine at UCL, London.*

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*Nationalizing Science: Adolphe Wurtz and the Battle for French Chemistry.* Alan J. Rocke, MIT Press, Cambridge, MA, 2001. xi + 443pp, Cloth, ISBN 0-262-18204-1. \$42.95.

“Adolphe Wurtz [(1817-84)] lived a modest life and died a modest death,” (p. 376), but he was perhaps best known for his immodest and controversial claim: “La chimie est une science française” which is inscribed on Wurtz’s statue outside the church of Saint-Pierre-le-Jeune in Strasbourg, in whose parsonage he was born. What could Wurtz have meant by this claim? How did he view the relationship between French and German chemistry and how did his contributions to chemistry reflect the ‘dialectics’ between different national styles?

This is the third and most recent book from the pen of Alan J. Rocke, the 2000 Dexter Award winner, and one of the premier historians of 19<sup>th</sup>-century chemistry. Whereas his first book, *Chemical Atomism in the Nineteenth Century*, Ohio State University Press, Columbus, OH, 1984, gave us the history of a particular scientific concept, chemical atomism, this book, as well as his earlier one entitled, *The Quiet Revolution: Herman Kolbe and the Science of Organic Chemistry*, University of California Press, Berkeley, CA, 1993, are written in the genre of scientific biography. Rocke is convinced that it is not enough for someone to make a scientific discovery or promote a particular scientific theory such as the chemical structural theory of organic chemistry advanced by Wurtz. One must also make the world take note of them. Wurtz’s world is that of Parisian science: a complex social-political-scientific network.

Rocke endeavors to take commonplace notions and repeated truisms about the state of 19<sup>th</sup>-century French chemistry and give them new life by ‘contextualizing’ the questions. To take one example: not only were laboratory facilities meager, a common reading of the state

of French chemistry, but Rocke gives reasons why this may be so, and further shows how this fact had a debilitating effect on French organic chemistry in contrast to the laboratory support for German chemistry. This comparative advantage of German chemistry gave support to Wurtz’s effort in the late 1860s in asking for more government support for research facilities.

To someone unfamiliar with the history of 19<sup>th</sup>-century chemistry, I would advise the reader to begin with the “Introduction” and especially the last chapter: “A Summing Up.” This will give one a sense of the flow of the chapters in the book and provide some of the historiographical considerations for the structure of the book. Rocke’s Dexter award address, “Celebrity Culture in Parisian Chemistry,” in the *Bull. Hist. Chem.*, **2001**, 26, 81-91, would also be beneficial to read.

In Rocke’s hands Wurtz’s life serves as the focal point for a much larger narrative: the development of French chemistry and its comparative (dis)advantage over German chemistry. Is it possible to tell a grand story, a macro-history that accurately reflects the critical intellectual, social, institutional, and material factors and themes, which are inevitably interwoven and interrelated without succumbing to a hagiographic one-dimensional story about an individual? Rocke invites us to evaluate his attempt.

The book’s introduction details the difficulties and challenges faced by someone examining 19<sup>th</sup>-century French science. Take, for example, the supposed simple fact of determining a person’s date of appointment. The details are frequently clouded by the institutional structure of *cumul* in which an individual could hold multiple appointments at different research institutions simultaneously. In the Parisian network there were indeed many such instances. At one point in 1845 Wurtz held positions in the Faculté de Médecine, the ?cole Centrale, and Dumas’s private laboratory.

In rapid review, Chapters 1 and 2 present two of the leading lights of the chemical realm: Liebig and Dumas, both of whom played an important role in the career of Wurtz. The book's next four chapters focus on Wurtz. In Chapter 3 Rocke recounts Wurtz's education, his participation in Liebig's laboratory in Giessen, and his research on hypophosphorous acid. Chapter 4 locates Wurtz in Paris, finding his way through the politics of academic appointments as evidenced in the careers of Gerhardt and Laurent. The next two chapters, 5 and 6, describe Wurtz's research: cyanic esters, amides, primary amines, and his acceptance of the theory of types as well as his use of structural theory. Chapter 7, "The Campaign," recounts Wurtz's involvement with the *Bulletin* of the Société chimique, his research on glycol, lactic acid, oxalic acid, and the events surrounding the famous Karlsruhe Conference of 1860. In Chapter 8 Rocke presents further details of Wurtz's struggles with his principal Parisian rival, Marcellin Berthelot. The next chapter, 9, describes efforts to renovate laboratory science in France. "The Atomic War," namely, the struggle between using atoms or equivalents in chemistry and its aftermath, are described in great detail in Chapter 10.

The penultimate chapter gives us a glimpse of Wurtz in his "later years." Details are provided on Wurtz's efforts to convince his French colleagues to adopt the 'modern' atomic-structural point of view, by arguing that the flowering of contemporary German chemistry was a consequence of French seeds falling on fertile ground ("chemistry is a French science"); his mature research school; his political involvement; his role as dean of the Faculty of Medicine; and some of his family life.

Why did Wurtz not receive more acceptance (or win victory) for his arguments in favor of atomic weights, atomic theory, and structural theory by his contemporaries? And why have modern historians of science paid him so little attention? This is the subject of the concluding chapter, in which Rocke describes some of the broad cultural aspects of the French chemical community: its celebrity cult, its pedagogy, institutional structure, laboratory facilities, and the causes for the general decline of French chemistry.

This is an outstanding book. It places Wurtz, his scientific ideas, and his strategies for advancing those ideas in its appropriate cultural context. Ideas do indeed become embodied or incarnate in the ebb and flow of historical events. *Dr. Arie Leegwater, Calvin College, Grand Rapids, MI 49456-4301.*

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*Robert Boyle (1627-1691): Scrupulosity and Science.* Michael Hunter, Boydell & Brewer, Inc., Rochester, NY; Woodbridge, UK, 2000, \$90.

The famous chemist Robert Boyle has received enormous attention from historians of late. His complete works (in 14 volumes) were republished during 1999-2000 in a critical edition enriched with the first publication of much material left in manuscript form by the great man. Last year, Boyle's surviving correspondence was published for the first time in its entirety, filling another six substantial volumes. When we consider the dozen or more scholarly monographs on Boyle that have appeared since about 1990, it is no exaggeration to say that the Boyle we now know seems a wholly different (and certainly a more interesting) man than the iconic "Father of Chemistry" we thought we knew previously and whom most scientists associated primarily with a simple law describing the pressure and volume of gases.

Michael Hunter has been in the vanguard of Boyle studies, as an editor of both Boyle's *Works* and *Corre-*

*spondence* and as a prolific author of scholarly papers on Boyle and his Restoration milieu. The present volume is a collection of ten papers on Boyle (eight of them previously published in journals or collections) plus an introduction. The topics range widely across various aspects of Boyle's career and persona. The first paper is an important contribution (published first in 1995) on "How Boyle Became a Scientist," which examines how and why Boyle first turned to the study of natural science during his early twenties, and away from his original activities in writing devotional and moralizing tracts. Three subsequent papers deal with how Boyle's moral concerns, particularly his examination of his conscience, affected his work. We read here about his casuistical interviews with his confessor, the potential moral roadblocks to Boyle's otherwise avid pursuit of alchemy, and the seeming "dysfunctionality" which plagued Boyle and which resulted from his over-anxious, even obsessive, concerns about taking right actions. This last paper is of special interest on a wider scale, since it serves to

remind historians that our objects of study do often fail to act “rationally” (at least by our definition), and so the task of judging causes for their actions requires a great deal of finesse and understanding.

Glimpses of Boyle’s curious (in both senses of the word) mind are provided by two further papers. One examines how the surviving Boyle Papers (housed in over 40 volumes at the Royal Society in London) tell us something about the English philosopher’s mental landscape and method of work. The other, one of the papers published here for the first time, examines the rather obsessive “apologies” that Boyle regularly prefixed to his publications. These prefaces gave excuses for what Boyle perceived (often correctly) as the imperfect or seemingly disorganized state of his text, or fended off potential charges of plagiarism, or apologized that the book was being published at all or at the present time (being either late or premature). Readers accustomed to the modern state of scholarly publication will find this study both enlightening and amusing.

Boyle was interested in medical practices and their reforms, and accordingly he published several books on the subject. But two papers here indicate how there would have been several more if Boyle had not held his thunder. In one case, Boyle suppressed a critique of the contemporary medical establishment partly on the grounds that he was an outsider to it. In the other paper, Hunter shows how Boyle’s hot, youthful enthusiasm for

reforming medicine and the free communication of medical knowledge cooled significantly over time as a more mature Boyle came to understand the real social, political, and economic complexities of medical practice. The penultimate paper examines Boyle’s interest in magic and how his concern over his reputation made him wary of revealing the depth of these interests. The volume is rounded out by a paper on the “Dilemma of Biography:” namely, the difficulty subsequent scholars have had in constructing a biography of Boyle. Boyle’s interests and activities were wide-ranging. This situation complicated matters first by making a comprehensive biography all but impossible (even to his near contemporaries), and second by ensuring that there were always topics of interest to Boyle which, to quote one eighteenth-century student of Boyle, were “not suited to the genius of the present age,” and thus had to be downplayed or dismissed.

This dilemma of biography continues in modified form to the present day. How does one fit the “new Boyle” into the narrative of the “Scientific Revolution”? Most of the papers in this book, and indeed the whole brunt of recent Boyle studies, show how quite a few facile categorizations or dichotomies, such as ancient/modern, scientific/nonscientific, science/magic, rational/irrational, need to be rethought and amended if we are to do justice to our historical characters by understanding them aright. *Lawrence M. Principe, Johns Hopkins University, Baltimore, MD 21218.*

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*Histories of the Electron: the Birth of Microphysics.* Jed Z. Buchwald and Andrew Warwick, Ed., MIT Press, Cambridge and London, 2001. xi + 514 pp, Cloth, ISBN 0-262-02494-2. \$55.

The discovery of the electron or, more correctly, the discovery of the suite of properties that have been attributed to the electron, initiated the electronic age of science in the early years of the 20<sup>th</sup> century. Although subdivision of the atom had been hypothesized by energeticists and spectroscopists during the 19<sup>th</sup> century, no one could have foreseen that the electron would emerge from its origins as the unit carrier of electrical charge to become the focus of early 20<sup>th</sup> century physics and workhorse of chemistry. Physicists were the first to discover, explore, and explain the remarkable properties of the

first subatomic particle and needed to confront the complexities of a massy particle bearing wave/particle duality. But some chemists began to suspect that the electron held the key to atomic valence, molecular bonding, structure, and even reaction tendencies. Modern chemists now move effortlessly (maybe superficially on occasion) from discussions of electrons as negatively charged particles to others in which electron density is spatially distributed in atomic and molecular orbitals. The electron has become fundamental to chemical explanation; and consequently a book such as this, which presents the context of its discovery and theoretical interpretation, has potential interest to chemists.

Although this book’s title offers little enticement to curious chemists (or to tentative reviewers), it does

contain a rewarding collection of articles that have a great deal of chemical interest and offers great value for the price. The book is one of a series entitled the Dibner Institute Studies in the History of Science and Technology and is, like others in the series, a collection of edited articles drawn from workshops focussed on selected themes. The essays in *Histories of the Electron* were first presented at two meetings held in 1997 to commemorate the centenary of the electron's purported discovery by J. J. Thomson at the Cavendish Laboratory in 1897. The subtitle reflects the electron's distinction as the first microphysical particle to be discovered, with the understanding that the "microworld" is comprised of objects smaller than the wavelength of visible light. All articles but two were written by historians and philosophers of science, but historians and philosophers who know their science very well. Their studies on various aspects of the electron are grouped around four themes: the experimental discovery of the electron and its major properties; questions of priority and the nature of discovery; accommodation of the electron in nuclear physics, chemistry and electrical science; and the electron as a real entity.

The first section, entitled "Corpuscles and Electrons," contains four chapters that explore the experimental and conceptual environment in which the electron appeared. George Smith discusses Thomson's three classic papers of 1897, 1898, and 1899, which presented the results of experimental work on cathode rays and led Thomson to conclude that the rays consisted of negatively charged "corpuscles" with a very high charge to mass ratio. (Thomson avoided use of the word "electron" coined in 1891 by George Stoney for the basic unit of electrical charge). Further, the negative rays differed in fundamental ways from positive rays and were composed, he concluded, of subatomic particles. For these contributions, Thomson is properly judged to be the seminal figure in electron history; but depending on how one defines discovery, he may not be the electron's unique discoverer. Isobel Falconer demonstrates how local context affects historical analysis by comparing early British and German accounts, the former emphasizing Thomson's work and the latter that of Lorentz and Zeeman. Graeme Gooday adds that the impact of Thomson's results was unclear for several years, during which time the electro-technology of the period bounded along. After about 1910, as the particulate properties of the electron became more widely accepted, Thomson's students worked diligently to place their mentor at the center of the discovery process. Benoit Lelong writes that it was even possible to explain many of the cathode

ray results by a theoretically more conservative hypothesis involving ionized hydrogen atoms, as the Frenchman Paul Villard did before converting to Thomson's interpretation. In sum, these opening chapters confirm that the discovery of the electron is not the rational, individualistic process succinctly presented in modern science texts; only the logical reconstruction of historical events makes it seem so.

The second section of the book, entitled "What was the Newborn Electron Good For?," is loosely organized around the theoretical status of the new particle and its incorporation into experimental physics. Theodore Arabatzis circumvents the claim of antirealist philosophers that it is impossible to specify compelling criteria for the discovery of an unobservable entity such as the electron by redefining discovery as the formation of consensus within the scientific community. On this view Zeeman, who obtained good values for the charge to mass ratio of the atomic component responsible for the electromagnetic splitting of the sodium D line in 1896, Lorentz and Larmor all have significant roles. Helge Kragh investigates the electron's brief life as the potential "protyle," the ultimate particle of all matter, a hypothesis that was dashed by the discovery of other subatomic particles later in the 20<sup>th</sup> century. Such particulate views of the electron were, however, intimately interconnected with explanations of phenomena in electrochemical, electro-dynamical, and magneto-optical researches. The electron seemed to be as ubiquitous as the ether, but just as elusive. Ole Knudsen describes the work of one of Thomson's most successful students, O. W. Richardson, who initiated the study of thermal electron emission and extended the range of phenomena explicable by electron theory. Walter Kaiser gives another example of the theory elaboration in his report of work beginning in 1900 on electrical conduction in metals, work that began by transferring concepts from the kinetic theory of gases to an "electron gas" of charged electrons of fixed mass moving freely within a metal.

The third section, entitled "Electrons Applied and Appropriated," contains papers of greater relevance to chemists. Laurie Brown investigates the various suggestions for the location of electrons in the atom, either within or outside of the nucleus, with special emphasis on Heisenberg's theories on nuclear electrons. Lillian Hoddeson and Michael Riordan advocate that the electron's reality was reinforced for scientists and engineers when it was put to work in devices such as the vacuum tube amplifier. Mary Jo Nye suggests the electron entered chemistry in three stages— as a material particle in the valence bond, as a participant in reaction

mechanisms and then in resonance theory, with the key participants being Robert Robinson, Keith Ingold, and Linus Pauling. The electronic aspects of chemical explanation are presented as an evolutionary advance because nothing important in the chemical corpus had to be discarded to make room for it. Kostas Gavroglu focuses on the developments which enabled physicists and, later, chemists to bring the quantized electron into comprehensive theories of bonding and valence. After Heitler and London's successful use of electron spin in 1927 to explain the 2-electron bond in molecular hydrogen, others such as Mulliken and Pauling extended the "quantum mechanical" methods of electronic bonding to larger molecules, thus giving the methods greater chemical utility. The chapters in this section bring the electron into its modern chemical environment where it manifests itself as a particle or wave, as need requires. But the story does not end here.

The concluding section, simply entitled "Philosophical Electrons," does what philosophy does best—render asunder the reconstructed logic of favored explanations. Peter Achinstein dismisses the sociological interpretation of discovery as consensus in place of a person-oriented, conscious, and even wilful path to discovery. By his criteria, Thomson fulfilled enough of the requirements to merit recognition as a discoverer, maybe. How surprising it is to have a philosopher leave an argument as an open question. Margaret Morrison uses the concept of electron spin to explore the problems inherent in affirming the reality of an entity independently of the ways in which it is investigated. Electron spin, so crucial to the electron's behaviour, still lacks consensus as to its physical nature. Jonathan Bain and John Norton use electron theories to dispute the philo-

sophical tenet that, since all theories in the history of science have been false (in the sense that none has been complete), the methods of science do not generate true theories—dubbed, obviously enough, the "pessimistic induction." They argue, contrarily, for an "optimistic induction" in which science advances through a series of theories that correct the errors of predecessors while providing ever improved representations of phenomena. Such a progressionist view is likely in harmony with the history of science most of us chemists are comfortable with. The book concludes with a chapter by Nicholas Rasmussen and Alan Chalmers, in which they investigate early uses of the electron microscope in biology and physics to conclude that instruments often interact synergistically with theory. The interaction of theory and practice is normally quite complex and event-specific, so much so that "science might be much more heterogeneous and complex than philosophers have long been imagining." No chemist will dispute this claim.

This book is packed with scientific, historical, philosophical, and sociological information in each of the four sections. It helps us view, from the perspective of the 21<sup>st</sup> century, the enormous renovation of chemical thought in the previous century made possible by the discovery of the electron. In addition it provides, for those wishing it, an accessible account of various issues current in the history, sociology, and philosophy of science illustrated by a scientific example of great interest and subtlety. If you do not wish to have it for yourself, make sure your library orders it. It is quite likely that, after reading the book, you will present electron theory to your colleagues or students in a very different way. *M. C. Usselman, Department of Chemistry, University of Western Ontario, London ON N6A 5B7, Canada.*

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*Liebigs Lehrer. Karl W. G. Kastner (1783-1857): Eine Professorenkarriere in Zeiten naturwissenschaftlichen Umbruchs.* Martin Kirschke, GNT Verlag (Verlag für Geschichte der Naturwissenschaften und Technik), Berlin, Diepholz, 2001, 450 pp, 38.50 Euro.

When Richard Wagner felt the need to create room for his music, he decided to destroy not only the reputation of Felix Mendelssohn, whose music was considered the pinnacle of musical achievement, but also all music created by Jews which he described as derivative and unoriginal. Something similar must have occurred

to Justus Liebig. After having worked closely with his teacher Karl Kastner and greatly helped by him over a long period, Liebig in 1840, at age 37, let loose a diatribe against chemistry in Prussia, making fun of *Naturphilosophie*, the reigning romantic perspective on natural phenomena. Not only by implication, but by name, he singled out Kastner as a leading exponent. Ever since, Kastner has tended to be derided or ignored. Yet in his time he was considered one of the greatest German chemists, equally versed also in physics, botany, and pharmacy. Liebig chose to be his student in Bonn because of his eminence; and when Kastner moved to

Erlangen, Liebig went with him. Kastner helped him when he wanted to study in France, obtaining a stipend for him from the Grand Duke; and even after the verbal blast, Kastner continued in various ways to be of assistance.

Recent writers have begun to revise the general viewpoint and have stated their shock at Liebig's ingratitude. Thus the Liebig biographer William H. Brock in his *Norton History of Chemistry* (p 200): "In later life Liebig was rude about Kastner's chemical competence and decidedly ungracious towards him; but without Kastner's support and patronage Liebig might well have remained a small-town hardware salesman."

In his book *Karl Kastner* Martin Kirschke explores the Liebig episode in detail; but the book covers far, far, more. It reminds me of Alan Rocke's biography of Hermann Kolbe, where Rocke deliberately chose a lesser yet very able man to illuminate a period. Rocke actually begins his book with a reference to Liebig's unfair criticism of German chemistry. Kirschke makes clear that he is certainly not writing a hagiography. Instead his book lifts a forgotten man out of obscurity and uses him as a vehicle to illuminate an early chemical transformation.

The book is a doctoral dissertation submitted to the University of Regensburg, where the presence on the history-of-science faculty of Christoph Meinel and Carsten Renhardt alone suffices to indicate the blisteringly high standards expected of a doctoral candidate. The book does not disappoint. It places Kastner in his social, religious, academic, and political milieu. In the process we learn of the development of chemistry, and often of other sciences, at the universities of Jena, Heidelberg, Halle, Bonn, and Erlangen. Kastner's many books and the journals he edited are described in detail, and the reader is surprised at the emphasis Kastner placed on empirical evidence, on experimental confirmation. He was interested in commercial applications of chemistry and was the author of books on experimental chemistry and experimental physics that were widely used. And he was up to date. He discussed galvanic electricity as well as some of Humphry Davy's researches, including Davy's invention of the miner's safety lamp.

There are some fascinating aspects to Kastner's very appealing life. He experienced the French occupation and participated in the wars of liberation against Napoleon, being in charge at one point of four field hospitals. When it was all over, he was in Britain for four months

raising relief funds for German widows and orphans and came home with a sizeable sum voted by the British parliament. When the Erlangen town-gown tensions had reached the point that the students, Liebig of course among them, left the university *en masse*, Kastner served as the go-between, trusted by both students and administration, to bring the students back to Erlangen. He was a very popular lecturer; and Liebig was not the only student of Kastner of interest to later historians. Another future scientist of renown was Pierre Louis Dulong of the Dulong and Petit Rule. Kastner also taught August Goethe, the son of the poet. Kastner was married and had several children but only one reached the age of 45. All his life he sought adequate laboratory space and equipment for his students and for his own research, but the authorities were slow to recognize the significance and importance of practical instruction and independent research. Only with Liebig's instructional laboratory in Giessen do we see this essential training component for all chemists adequately recognized by the authorities. Nevertheless, even during the many years Kastner had to work in his own home, he was known for his analyses of the waters of mineral springs and was sought for advice regarding their safety.

Kastner is variously labeled as representing the romantic and *Naturphilosophie* traditions and as being a Kantian. The latter designation helps explain Kastner's insistence that all theorizing should be based on observable evidence. In the absence of laboratories he used lecture demonstrations extensively. *Naturphilosophie* sought for a vision of unity, linking phenomena in the heavens, for instance, to living systems and chemical processes observable in the laboratory. It was opposed to mechanistic and reductionist views and was suspicious of mathematical formulations, looking for qualitative rather than quantitative laws.

In defense of Liebig it should be said that Wöhler and Berzelius also made fun of *Naturphilosophie*. And although in 1840 Liebig ridiculed the concept of a vital force in chemistry, he felt the need for it in order to explain various physiological processes, as Kenneth Caneva points out in his *Robert Mayer and the Conservation of Energy*.

We need to remember that Joseph Priestley clung to phlogiston ideas rather than espousing Lavoisier's system and yet found it possible to do perfectly sound chemistry using the older language. And we are finding that with the espousal of a new language certain insights of the older system are lost, only to be rediscovered many years later. Modern science has gone through a long

period of searching for local order irrespective of the larger picture, in the faith that in the end all the pieces will fit together. Yet the longing of Kastner and others for a unitary, holistic view of nature is never submerged

completely and is the motivation of many who make major contributions to our science. *Theodor Benfey*, 909 Woodbrook Drive, Greensboro NC 27410; and the Chemical Heritage Foundation [benfeyot@nr.infi.net](mailto:benfeyot@nr.infi.net).

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*Imaging a Career in Science: The Iconography of Antoine Laurent Lavoisier.* Marco Beretta, Science History Publications/USA, Nantucket, MA, 2001; xvii + 126 pp, clothbound and jacketed, ISBN 0-88135-2294-2, \$29.95.

According to the author in his introduction, the only other attempt at putting together a survey of images of Lavoisier—in the author's words "iconography"—was published by Pierre Lemay in the 1930s, a "superficial but useful survey." Beretta, inspired by newer findings of references to paintings and sculptures portraying Lavoisier, undertook the project he feels Lemay and some others never accomplished: a thorough survey of the iconography of Lavoisier and an interpretation of these images as insight into Lavoisier's intellectual background and professional career. To the present author this seems a gargantuan goal for someone who must be equally competent as an historian of chemistry and art. Roald Hoffmann, in his foreword, expresses the view that we the readers have a better understanding of Lavoisier through this critique of the many renditions of Lavoisier, some verifiable and many of questionable authenticity.

To be sure, readers are presented with a generous collection of images of Lavoisier in the form of a "Select Catalogue of Lavoisier's and Madame Lavoisier's Iconography" (pp 77 – 111), many of which are reproduced in the catalogue section or elsewhere in the text. The 1806 engraving by Brossard de Beaulieu appears twice (pp 13, 29). Unfortunately some images within the text are not given their corresponding catalogue designation. The pivotal image, around which all discussion rests, is the famous and familiar portrait of M. and Mme. Lavoisier painted by Jacques Louis David in 1788. In possession of family heirs until 1925, when it was purchased by John D. Rockefeller, the portrait passed to the Rockefeller Institute in 1927 and was acquired by the Metropolitan Museum of New York in 1977. It is the sole subject of Chapter 2; any images before David are treated in Chapter 1. The significant contributions of Mme. Lavoisier as illustrator form the basis for Chap-

ter 3, "The Chemical Revolution in Action." Not only did she provide artistic elaboration for her husband's writings, as is well known; she also created many illustrations to promote the 'new chemistry.' Beretta describes an allegorical performance, probably organized by Mme. Lavoisier, at the Arsenal in 1788 or 1789. In this staged inquisition on phlogiston, she played the role of a priestess, with Stahl as the victim. "The Iconographic Myth," the last chapter, is a description of the use of artistic renditions of Lavoisier as a means of glorifying his image in the decades after his death.

It is not surprising that Beretta, as a historian of chemistry, should defer to two recent publications by historians (M. Vidal, 1995; A. Donovan, 1996) on David's creative works, including the Lavoisier portrait. Vidal reads a wealth of information from Mme. Lavoisier's gaze directed, not at her husband, but at the artist; and Beretta seems to confirm this "evidence" that she is mediator between science and art—not merely her husband's muse. There are many examples of supposition in 'reading' meaning from the art. David might have drawn inspiration for the portrait from Tangena's 17<sup>th</sup>-century engraving of Descarte (p 40); it is "perhaps not unlikely" that *Hommage rendu à la mémoire de Lavoisier* (1807) was done by Mme. Lavoisier (p 47). Beretta acknowledges several colleagues by name and three anonymous referees for their suggestions and criticisms, but a few inconsistencies have slipped by. One is the contradictory information on Fontana's instrument, variously dated as 1777 (p 37) and 1780 (p 38). In fact, Partington gives the date as 1781. One hopes this error is the exception rather than the rule. No name is attached to the translation, for which the author acknowledges financial support; but some mistakes have been overlooked ("laying;" p 34; "loosing," p 44).

Whether the treatment by Beretta measures up as to scholarly treatment or not, the book is a handsome collection of black and white and colored reproductions of many fascinating likenesses of Lavoisier, but also of a variety of other forms: Mme. Lavoisier's painting of Benjamin Franklin and her self portrait, for example. *Paul R. Jones, University of Michigan.*

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