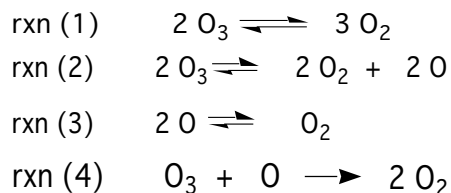# THE HISTORY OF OZONE. V. FORMATION OF OZONE FROM OXYGEN AT HIGH TEMPERATURES (1)

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Introduction

In his 1884 book on the principles of mobile equilibria, van't Hoff (2) presented the generalization that, in an equilibrium system, an elevation of temperature would favor the endothermic reaction. Twenty years later, Nernst, as part of his efforts in developing the third law of thermodynamics (3), derived an expression for calculating the equilibrium constant for a reaction at any temperature. These ideas were expressed specifically in relation to ozone in a 1903 lecture by Nernst at the University of Göttingen as reported by Kremann (4). In agreement with van't Hoff, the formation of ozone was favored by increasing temperature. Nernst considered the equilibrium between two molecules of ozone and three of oxygen (rxn 1) to be composed of equilibria between ozone and oxygen plus atomic oxygen (rxn 2) and between oxygen and 2 atoms of oxygen (rxn 3); rxn 4 was not considered:

$$\text{rxn (1)} \quad 2\,O_3 \rightleftharpoons 3\,O_2$$

$$\text{rxn (2)} \quad 2\,O_3 \rightleftharpoons 2\,O_2 + 2\,O$$

$$\text{rxn (3)} \quad 2\,O \rightleftharpoons O_2$$

$$\text{rxn (4)} \quad O_3 + O \longrightarrow 2\,O_2$$

This report describes the proof that such an equilibrium exists at high temperature and the 35-year struggle to establish the chemistry and the quantitative relationships involved.

Early Studies

Although Andrews and Tait (5) had reported in 1856 that ozone decomposed "instantaneously" at temperatures above 230° C, the formation of ozone from air or oxygen at higher temperatures was recorded nearly 50 years before Nernst's lecture. In fact, in the same year as Andrews and Tait's publication, Van der Willigen reported (6) that the gas above a platinum wire heated to redness by an electric current possessed a strong odor of ozone. Four years later Le Roux (7) confirmed this result by examining the gases exiting from a chimney containing an electrically heated platinum wire and added the observation that a positive starch-iodide test was obtained. Additional reports which appeared before Nernst's ideas include work by Saint-Edme (8), Böttger (9), Troost and Hautefuille (10), Helmholtz (11), Dewar (12), Elster and Geitel (13), and Brunck (14). Böttger was the first (see below) to employ an explosion for the high temperature conditions required to form ozone. Explosion of an oxygen-hydrogen mixture afforded a gas mixture which gave a positive starch-iodide (perhaps due to the presence of hydrogen peroxide, see below). Bichat and Guntz (15) were sufficiently enthusiastic about thermal formation of ozone to suggest that its formation in the silent discharge was not an electrical phenomenon at all; the function of electricity was simply to heat the apparatus. Ewell

reviewed the subject in 1909 and wrote (16):

> The methods so far used are relatively inefficient but great improvements are expected in the near future.

We are still waiting.

While almost all of these experiments provided ambiguous identification of ozone (odor and starch-iodide paper, which could indicate nitric oxide or hydrogen peroxide as well as ozone), the work of Troost and Hautefeuille (10) is worthy of note. They seem to have been the first workers to realize the generality of the apparent paradox of formation of substances at temperatures much above their normal decomposition points. The distinction between thermodynamic and kinetic control of reactions had not arrived in chemistry at that time. Such thermal phenomena were observed in a number of inorganic systems. For example (rxn 5), silicon sesquichloride decomposed to silicon dichloride and elemental silicon on heating at temperatures well below 1000° C but regenerated the sesquichloride upon heating to about 1200° C and rapid cooling of the melt.

$$\text{rxn (5)} \qquad 2\ Si_2Cl_3 \ \rightleftharpoons \ 3\ SiCl_2 \ + \ Si$$

Troost and Hautefeuille also studied thermal formation of ozone from oxygen using the so-called hot-cold principle of Deville (17). The apparatus consisted of a ceramic outer tube which could be heated to high temperature by a flame and a water-cooled inner tube. Passage of oxygen through the annular space of a silver inner tube resulted in the formation of silver peroxide when the outer tube was heated to approximately 1200° C. When the silver tube was replaced by tubes of unreactive material in other experiments, examination of the apparatus after the heating was interrupted showed a strong odor of ozone, a positive starch-iodide test, and decolorization of indigo by the condensate on the outer wall of the inner tube. When water-cooling of the inner tube was omitted, no ozone was evident.

Acting on a suggestion by Warburg, Wartenberg (18) in 1910 reported the results of a study of the absorption spectrum of ozone in the region around 2537 Å at various temperatures up to 2000 K. He argued that ozone at high temperature was too unstable to survive cooling and that only by examining the hot gas directly would it be possible to obtain information on the presence of ozone. This in spite of the fact that, in 1906, Fischer and Marx (19) had measured ozone partial pressures greater than 1×10^{-4} atm in cooled samples of oxygen after passage over a Nernst glower at 2000 K. Such a concentration would most probably have been detected

in Wartenberg's experiments. These were performed using an oxygen-filled cell with a 10-cm light path in a heated oven; the spectrometer included a mercury vapor lamp as light source and a photocell to detect radiation between 2200 and 2500 Å. He obtained no evidence for the presence of ozone. The implications of this work were completely ignored by other workers, possibly because spectroscopy was not sufficiently established in the minds of most chemists at that time. Wartenberg himself drew no conclusions. The result lay dormant in the literature until 1932 when Harteck (see below) went back to such experiments using equipment of greater sensitivity than Wartenberg.

Formation of Ozone in Flames

Another source of ozone at high temperature was the flame; this might well involve both temperature and participation of reactive intermediates present in flames. The first report was published in 1867 by Pincus in an obscure source (20) and then reported briefly in *Annalen der Physik* in 1871 (21). He found that a flame of purified hydrogen and oxygen gave a condensate with a very strong smell of ozone. Neither Loew (22) nor Than (23) was aware of this work when both published their reports of ozone in flames in 1870. Loew's experiment was very simple; he blew a strong stream of air over a Bunsen flame into a beaker. Examination of its contents revealed the characteristic ozone odor, and the product liberated iodine from potassium iodide and gave a positive test for ozone with guaiacum paper. Than, using a similar procedure, reported that only flames of hydrogen-containing substances produced ozone while burning carbon did not. His intriguing explanation was that an oxygen atom was required for reaction with an oxygen molecule to give ozone; such atoms were not formed with carbon since its reaction with oxygen consumed an entire oxygen molecule. Than's procedure was adopted by Hofmann and Kronenberg (24) for a lecture demonstration.

Other reports during the 19th century of ozone in flames were due to Blochmann (25), Radulocoitsch (26), Cundall (27), Manchot (28), Loew (29), and Bose (30). Hofmann (24) described a lecture demonstration using the Than conditions.

The formation of ozone in flames seemed to some workers to offer a practical procedure for its preparation. What could be simpler than to blow air over a flame for instantaneous production of ozonized air? Patents were awarded in the 1870s to Loew (31), Rumine (32), Turner and Vanderpool (33), and Swan (34), among

others. Loew's patent described an apparatus in which a number of air inlets blew streams of air over a bank of Bunsen burners. In fact, the substances prepared in most, if not all, of these procedures were undoubtedly oxides of nitrogen and hydrogen peroxide.

C. F. Schönbein had a highly developed sense of smell which played a key role in his discovery of ozone (35). However, the literature provides many examples of erroneous identification of ozone based on odor by others who lacked Schönbein's olfactory talent. Furthermore, the starch-iodide test is not specific for ozone; it will give positive results with oxides of nitrogen and with hydrogen peroxide. Since odor and the starch-iodide test were often the only means for identifying the ozone produced in most of the work described above, it is not surprising that considerable criticism was directed toward the identification of ozone in thermal and flame reactions. Critics included Leeds (36), Ilosvay (37), and St Edme (8). In fact, Clement (38) claimed in 1904 that all of the early reports of ozone formation were due to the formation of low concentrations of nitric oxide. Engler (39), in his 1879-80 series of review articles on ozone chemistry, commented that it was unfortunate that the evidence for ozone formation was ambiguous but that the considerable number of reports lent some weight to the claims made. He also commented prophetically that there was a real possibility that oxygen atoms could be formed at high temperature and could then combine with O_2 molecules to form ozone which, of course, would be very short-lived under the conditions of reaction. Short-lived is the key word here.

By the beginning of the 20th century improvements in techniques and the possibility for testing Nernst's theoretical contribution led to intensive investigations of thermal equilibria of gases (oxygen, hydrogen and oxygen, nitrogen and oxygen, etc.). Nernst (with Jellinek) (40) succeeded in achieving good correspondence between experiment and theory in a study of the temperature dependence of the equilibrium constant in the system N_2, O_2, 2 NO. This reaction was of considerable interest from the practical point of view as an approach to fixation of atmospheric nitrogen and was also investigated by Haber (41) and others.

Using the same procedures which were successful in the nitrogen-oxygen system, Clement (38), a doctoral student in Nernst's laboratory, made a valiant effort to study the oxygen-ozone equilibrium by blowing a very rapid (flow rates up to 1 m/s) stream of air over a Nernst glower (2200 K), an arc lamp (3000 K), or an electri-

cally heated platinum wire but obtained no evidence for ozone formation. As noted above, he concluded that all of the earlier experiments claiming ozone formation were incorrect. He abandoned thermal formation of ozone and went on to study its thermal decomposition for his doctoral thesis. His results indicated "that, at 1000 K, the concentration of ozone would be reduced by a factor of 1000 in 0.7 milliseconds," and the conclusion was that the decomposition of ozone at elevated temperature was too rapid to allow for its detection.

Proof of Ozone Formation at High Temperature

A concerted attack on the problem came from the laboratory of F. Fischer, with five publications on the subject appearing in 1906-7. A particular advantage was the emergence in 1902 of a simple analytical method for distinguishing qualitatively between ozone, nitric oxide, and hydrogen peroxide. This employed the "tetrabase paper" developed by Arnold and Mentzel and by Chlopin (42), which is prepared by absorbing an alcohol solution of p,p'-bis-dimethylaminodiphenylmethane on filter paper and drying. Exposed to gas vapors, this reagent gives a blue-violet coloration with ozone, a yellow color with nitric oxide, and remains colorless with hydrogen peroxide. While not as sensitive as starch-iodide paper, it provides a distinctive identification of gases present. Another, less sensitive procedure for identifying ozone in the presence of nitrogen oxides and hydrogen peroxide was reported by Manchot (28). Ozone vapors impinging on a silver surface maintained at 250° C led to formation of a black deposit of silver peroxide, whereas no effect was observed with nitric oxide or hydrogen peroxide at this temperature. Wartenberg (43) pointed out that the rapid decomposition of ozone molecules to molecular oxygen and oxygen atoms at this temperature meant that the active reagent was probably atomic oxygen.

In the first paper, by Fischer and Braehmer (44), the authors addressed the question of whether or not ozone is actually formed from oxygen in thermal reactions and in flames. They found (to this author's surprise), that devices such as an electrically heated platinum wire (protected from oxygen by a coating of zirconium and yttrium oxides) or a Nernst glower or various flames and arc lamps (possible photochemical as well as thermal reaction), if ignited and allowed to stabilize under ambient conditions, could then be immersed in liquid air or liquid oxygen without extinguishing their operation. One imagines that the procedure would be an exciting

one. Thus both extremely high and low temperatures could exist in very close proximity. Ozone (and oxides of nitrogen), if formed, would be cooled to very low temperature extremely rapidly. After most of the liquid had evaporated, any nitric oxide formed was filtered, the blue filtrate examined with tetrabase paper, and analyzed iodimetrically. Flames investigated included hydrogen, carbon monoxide, acetylene, hydrogen sulfide, sulfur, charcoal, and wood. In all cases, ozone was formed as well as traces of nitric oxide when liquid air was used; hydrogen peroxide was not observed unless the atmosphere was enriched in water vapor. Definite evidence for the presence of ozone was obtained with a Nernst glower operating at about 2000 K. A maximum ozone concentration of about 1 wt.% was obtained in the first work. One year later, Fischer and Marx (45) reported an improved version of the apparatus with which they obtained blue drops of ozone and a final concentration as high as 4%, much greater than predicted by theory. They suggested that a fractionation process was operative, perhaps due to the 71° difference in boiling point between ozone (bp -112° C) and oxygen (bp -183° C). Thus the formation of ozone at high temperature was definitely established.

Equilibration Studies

After the demonstration that ozone was indeed formed from oxygen at high temperatures, further work—until the subject became dormant with the outbreak of World War II—was concentrated on efforts to establish equilibrium conditions and show that the Nernst relationship applied. Both Riesenfeld and Wartenberg (46) used the following expression (eqn 1) derived from Nernst's general treatment where 68,000 is twice the heat of dissociation of ozone (cf rxn 1) to calculate the equilibrium concentration of ozone, usually expressed as partial pressure of ozone (pO_3) at one atmosphere total pressure.

$$K_p = 3logpO_2 - 2logpO_3 = 68,000/4.57 \cdot T + 1.75 \cdot logT$$
$$+ 8 \times 10^{-5} \cdot T + 2.6 \qquad \text{eqn 1}$$

E. H. Riesenfeld and Beja (47, 48) realized that the dissociation of oxygen into atomic oxygen (rxn 2) would be significant at high temperatures. The bond dissociation energy of oxygen was not known at the time (1920-23); unfortunately Riesenfeld and Beja assumed a value of 80 kcal/mol, significantly lower than the correct value (117.3 kcal/mol), to derive the partial pressure of atomic oxygen in equilibrium with oxygen at various temperatures. They then calculated the partial pressures of the three component mixture of atomic oxygen, oxygen, and ozone. The results are shown in the figure, where it can be seen that pO_3 reaches a maximum value of about 1.3×10^{-7} atm. at 3500 K and that atomic oxygen becomes the major component of the mixture at temperatures above about 4000 K. Eight years later Briner and Susz (49) recalculated using a value of 130 kcal/mol for the bond
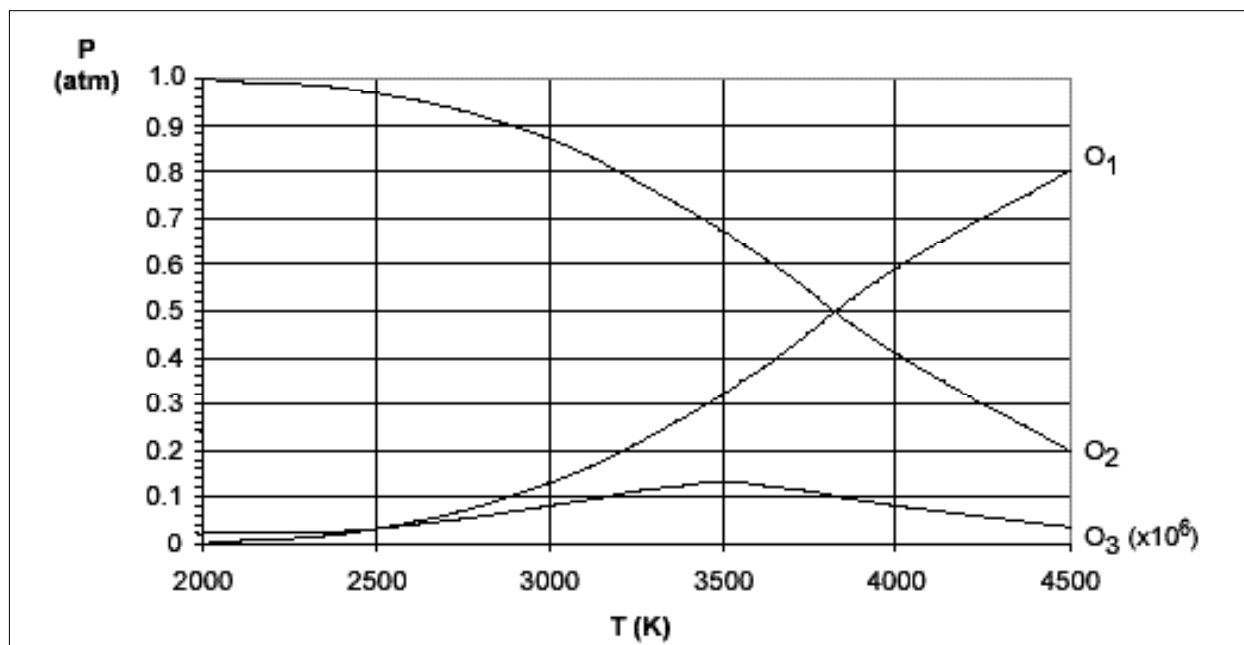

Figure. *Calculated equilibrium partial pressures (total one atm) of atomic oxygen (O_1), oxygen (O_2), and ozone (O_3, pO_3 shown is multiplied by 10^6) vs temperature (K) adapted from Riesenfeld and Beja (Ref. 47, 48).*

dissociation energy of oxygen, again incorrect but this time on the high side. Finally, in 1935 (50), they used the correct value of 117.3 kcal/mol, whereupon their results paralleled closely those of Riesenfeld and Beja. The maximum partial pressure of ozone was calculated to be 2.2×10^{-7} atm at 3500 K, while partial pressures of atomic oxygen and oxygen were 0.24 and 0.76 atm., respectively, at this temperature.

A number of serious experimental difficulties were involved in the attempts to study such equilibria. These included: a) analysis for the low concentrations of ozone formed, which were sometimes at the limits of quantitative methods available at the time (cf for example 47, 48); b) the need for very pure, dry gases in order to ensure that hydrogen peroxide or oxides of nitrogen were not formed; c) technical problems involved in design and construction of suitable apparatus for an extremely short transition time between a very hot region and ambient or cooler temperature; and d) maintaining constant temperature and measuring temperature in the reactive region of the apparatus. The following methods used in these studies are discussed briefly and the results presented in Table 1; the last column, calculated partial pressure of atomic oxygen (pO), will be discussed later:

1. Blowing a very rapid stream of oxygen or air over a Nernst glower.

a. Analysis of ozone concentration as a function of time (19) *(entry 1a). b. Analysis of ozone concentration as a function of temperature* (51) *(entry 1b).* As noted earlier, this procedure had been used successfully by Nernst (with Jellinek) (40) to study the thermal equilibrium between nitrogen, oxygen, and nitric oxide. Calculated values for the yield of nitric oxide correlated well with experimental results over the temperature range 1800-3200 K. As noted earlier, Clement (38) concluded that the decomposition of ozone was too rapid for it to survive. Fischer and Marx (19) increased the gas flow rate to as high as 90 m/s and detected ozone in the product gas. The products of thermal reaction of air depend on the interplay of reaction rate constants. Ozone is formed and decomposed rapidly at high temperature, while nitric oxide is formed slowly and decomposes at a rate many orders lower in magnitude than ozone. Thus high flow rates favor ozone formation and survival, while slow flow rates favor formation of nitric oxide and destruction of ozone. This could be demonstrated nicely by varying the flow rate of air over a Nernst glower with tetrabase paper as an indicator, the color of tetrabase paper changing from yellow to blue as the flow rate was increased.

Entry 1a shows that varying flow rates did not significantly affect ozone formation. This was inferred as evidence that complete survival of ozone was occurring; otherwise the higher flow rates would have given significantly higher amounts of ozone. Note that pO_3 is approximately four orders of magnitude greater than the value calculated from theory. Entry 1b (51) demonstrates that pO_3 increases with increasing temperature as expected. When moist gas was used in these experiments, hydrogen peroxide could be detected; its reaction with ozone made quantitative studies unattractive. Temperature of the glower was determined optically.

2. Immersion of an operating Nernst glower into liquid oxygen (44) *(entry 2).*

This procedure has been discussed earlier. As can be seen from the table, pO_3 increased steadily with reaction time, giving values much larger than predicted by theory. Presumably the limitation on conversion is evaporation of the liquid oxygen; otherwise the method might even have practical value.

3. Exploding ozone or ozone-oxygen mixtures (47, 48, cf ref. 9) *(entry 3).*

Having developed techniques for safely isolating pure ozone (1) in the early 1920s, Riesenfeld and Beja were in the desirable position of being able to approach the ozone-oxygen equilibrium from the ozone side. Ozone itself and mixtures with oxygen can be exploded by a spark. The explosion temperatures were calculated from thermochemical data for ozone and for a series of mixtures with highly purified oxygen at 10% composition intervals; these ranged from 2880 K for pure ozone to 2397 K for a 1:1 mixture. The explosions were performed in a 127-cc heavy-walled flask with sealed platinum electrodes, providing the spark to initiate the explosion. A series of ozone-oxygen mixtures were prepared, exploded, and analyzed for ozone concentration by the iodimetric technique; this was shown to be just sufficiently sensitive for the very low ozone concentrations obtained. The results reported from mixtures ranging in explosion temperature from 2459-2880 K were scattered within the range $2\text{-}4 \times 10^{-8}$ atm.

4. Rapid flow of oxygen through a heated capillary (entries 4a,b).

Riesenfeld's last essay into thermal formation of ozone appeared in 1939 (52) and corrected earlier 1925 work (53). It involved directing a stream of oxygen at a rate of 1 m/s through 0.9-1.3 mm i.d. heated capillary

Table 1. Experimental and Calculated Results of Equilibrations of Oxygen, Ozone, and Oxyhydrogen Mixtures.

No.	Lit.	Method	T (K)	Conditions	pO_3 (atm) Expt.	Calcd[a]	pO^b (atm)
1a	c	Oxygen blast over Nernst glower	2000	Flow rate 30 m/s 57 96	3.2×10^{-4} 6.1×10^{-4} 3.5×10^{-4}	1×10^{-8}	5×10^{-4}
1b	d	Oxygen blast over Nernst glower	2135 2310 2476	Flow rate 44 m/s	2.2×10^{-4} 3.9×10^{-4} 4.4×10^{-4}	1.4×10^{-8} 2.4×10^{-8} 2.8×10^{-8}	1×10^{-3} 3×10^{-3} 8×10^{-3}
2	e	Nernst glower in liquid oxygen	2000	25 min 50 125 360	7.8×10^{-4} 1.4×10^{-3} 3.1×10^{-3} 6.4×10^{-3}	1×10^{-8}	5×10^{-4}
3	f	Explode ozone, ozone-oxygen mixtures	2148 2459-2888	Varying ratios $O_3:O_2$	$<0.2 \times 10^{-8}$ $2\text{-}4 \times 10^{-8}$	$3.5\text{-}8.4 \times 10^{-8}$	
4a	g	Flow O_2 through heated capillary	900 1000 1100 1400	Flow rate 2 m/s	1×10^{-7} 1×10^{-6} 2×10^{-6} 6×10^{-6}	4×10^{-13} 3×10^{-12} 1×10^{-11} 4×10^{-10}	6×10^{-12} 2×10^{-10} 8×10^{-10} 4×10^{-7}
4b	h	Flow O_2 through heated capillary	<1273 1423	Flow rate 5-12 l/hr	5×10^{-7}	4×10^{-10}	5×10^{-7}
5	i	Flow $H_2 + O_2$ through heated capillary	873 1150-1273	Flow rate 660 cc/min	3×10^{-7} 2×10^{-6} 3×10^{-5}	5×10^{-13} 2×10^{-11} 9×10^{-11}	

a. Partial pressure of ozone calculated from equation 1. b. Partial pressure of oxygen atoms calculated from equation 2. c. Ref. 19. d. Ref. 51. e. Ref. 44. f. Ref. 47, 48. g. Ref. 52, 53. h. Ref. 54. i. Ref. 55.

tubes at temperatures ranging from 900 to 1400 K to a cooled region at the exit of the capillary and subsequent iodimetric analysis. Temperatures were measured optically. Once again, the experimental values were significantly higher than the calculated ones. This work was criticized by Wartenberg (54) (entry 4b), who claimed that the actual temperatures were as much as 400° higher than reported in the publication because of improper use of the optical pyrometer. In his brief 1940 paper Wartenberg reported, with minimal experimental detail, that he had repeated the Riesenfeld experiment with proper temperature measurement at flow rates of 5-12 l/hr. He was unable to detect ozone at temperatures below 1273 K but could measure the ozone concentration at 1423 K; $pO_3 = 5 \times 10^{-7}$ atm, three orders of magnitude greater than the calculated value.

5. Rapid flow of oxygen-hydrogen mixtures through a heated capillary (55) (entry 5).

The hydrogen-oxygen system ("oxyhydrogen") had been studied by numerous workers who had definitely established that hydrogen peroxide is formed in such flames or heated systems and found indications for ozone as well (56). The first detailed study of both products was reported in 1920 by Wartenberg and Sieg (55), who used a nonexplosive hydrogen-oxygen mixture (9 H_2:1 O_2 by volume), which flowed at rates between 600-1400 cc/min through a 1-mm i.d. quartz tube heated to temperatures between 600-1000° C. Rapid cooling afforded a condensate containing water and hydrogen peroxide that was weighed and analyzed for peroxide; the collected gases were shown to contain ozone by tetrabase paper and analyzed quantitatively by iodimetry. As can be seen in Table 1, the amounts of ozone formed were 5-6 orders of magnitude larger than the calculated values. It was concluded that ozone was formed by some additional mechanism, perhaps the thermal decomposition of hydrogen peroxide to give water and atomic oxygen (rxn 6), the

latter being the precursor of the ozone observed. rxn (6)

rxn (5) $2\ Si_2Cl_3 \rightleftharpoons 3\ SiCl_2 + Si$

The amounts of hydrogen peroxide formed were larger than those of ozone; the reaction between ozone and hydrogen peroxide yielding water and oxygen was not taken into account, nor was the fact that a thermal reaction occurs between ozone and hydrogen (57).

Riesenfeld (58) also investigated the hydrogen-oxygen system with a study of flames from very fine capillaries (0.2-0.4 mm i.d.) using varying ratios of hydrogen to oxygen. Water cooling of the gases formed resulted in condensation of water and hydrogen peroxide; the permanent gases were passed into KI solution for iodimetric analyses. With excess oxygen (molar ratio O_2: $H_2 = 3.3$:1) and a flow rate of 0.6 liter/hour, nearly equal partial pressures of ozone and hydrogen peroxide ($pO_3 = 18.8 \times 10^{-6}$ atm; $pH_2O_2 = 20.3 \times 10^{-6}$ atm) resulted, while under stoichiometric conditions (1 O_2:2 H_2 ratio, flow rate 5.85 liter/hr) there was a moderate increase in hydrogen peroxide ($pH_2O_2 = 38 \times 10^{-6}$ atm) and no detectable ozone formation. With excess hydrogen the partial pressure of hydrogen peroxide increased to 244×10^{-6} atm without any ozone formation. Riesenfeld argued that these results negated Wartenberg's proposal that hydrogen peroxide was the precursor of ozone. However, this argument ignores the fact that ozone formation would not be possible without sufficient oxygen available for reaction with atomic oxygen; Riesenfeld (59) later abandoned his objection.

Theory vs Experiment

From the results presented in Table 1 it is immediately obvious that entry 3, the explosion of ozone and of ozone-oxygen mixtures, is the only procedure that gave experimental results in approximate agreement with those calculated for pO_3 from eqn 1. We note that this is the only procedure that does not involve the initial presence of a large excess of oxygen. Unfortunately, the measured ozone partial pressures were at the limit of sensitivity of the iodimetric procedure used and were scattered over the range $2-4 \times 10^{-8}$ atm without any observable trend. Riesenfeld and Beja expressed themselves as satisfied that they had achieved agreement between theory and experiment. The desirable addition of confirming experiments was never reported. It might, for example, have been possible to modify the procedure to provide larger amounts of ozone and thereby increase the precision of measurement.

The outstanding feature of all the other experiments, where equilibrium was approached from the oxygen side, is the absence of any correlation between eqn 1 and experimental values for pO_3. The latter are orders of magnitude larger than the calculated values in every case. The failure of a theory to give results that agree with experiment is often taken as a strong indication that something is wrong with the theory. In these cases, however, the opposite was true, perhaps because of the enormous influence Nernst had in his time. In all cases the authors concluded that the processes involved were not purely thermal ones or that the experimental procedures were faulty. The final conclusion (see below) is that the interpretation was faulty; experimenters were measuring a quantity different from what they thought.

Among the rationalizations presented to account for the observed results were the following. Riesenfeld proposed that, in the experiments involving gas flowing rapidly through a heated capillary (entry 4), there was a wall effect which distorted the results. Both he and Wartenberg also suggested that the combination of translational and thermal energy involved in experiments with very high flow rates through capillary tubes could lead to ionization ("Ionenstoss"). Ionization was also proposed to occur with electrical devices such as Nernst glowers. In such cases, the ozone-forming process was suggested to be similar to that occurring in the silent discharge.

The breakthrough in understanding came with a 1932 paper by Harteck (60) following the 1910 paper by Wartenberg (18) on his failure to detect ozone absorption in heated oxygen samples by examination of UV absorption, as cited earlier. Harteck used a 100-cm cell at 2023 K with a slow flow of oxygen at one atm pressure. Using mercury lines at 2804, 2655, 2537, and 2482 Å and photometric analysis, he could detect no ozone absorption and set an *upper limit* of 4×10^{-6} atm for pO_3 at 2000 K contrasting with experimental values (see Table 1) greater than 1×10^{-4} atm. The conclusion was inescapable. The ozone measured, except in entry 3, was not formed in the hot section of the apparatus and, therefore, was not related to the thermal equilibrium between oxygen and ozone. Earlier workers had been barking up the wrong tree. Harteck derived an equation for calculation pO at various temperatures, but the values he obtained for pO were higher than the values observed experimentally for pO_3.

The results clearly implied that the ozone found experimentally is formed as the hot gas cools to its final temperature in the cooling section of the apparatus. This

gas contains a very small pO_3, given by eqn 1, a very small pO given by eqn 2, and oxygen itself at 1 atm. The reactions possible as the gas cools are those of atomic oxygen in the presence of O_2 and O_3, namely dimerization (rxn 2), reaction with ozone (rxn 4), and addition to oxygen (rxn 1) to form ozone. Six years later Wartenberg (61), who earlier had dismissed the thermal cleavage of oxygen to atoms as unimportant, took the interpretation a step further by arguing that the reaction $O + O_2 \rightarrow O_3$ was diffusion controlled in the rapidly cooling gas. The relative rates of formation of the products would be determined by the relative amounts of each present. The enormous excess of oxygen at the temperatures employed meant that the almost exclusive reaction of O atoms would be the formation of ozone. If this were correct, ozone could be used as a label for oxygen atoms; pO_3 measured *experimentally* would be equal to pO at the exit of the oven plus the negligible partial pressure of any ozone present. The situation would be more complicated at higher temperatures where pO would be significantly larger. Interestingly, Riesenfeld, who was the first to suggest the importance of the dissociation of oxygen into atoms as a factor in the reactions at elevated temperatures, did not arrive at this interpretation of the results.

Ernst Hermann Riesenfeld, 1877-1957. Photograph courtesy of Mrs. Harald Riesenfeld.

By 1938 spectroscopic measurements had established the value of 117.3 kcal/mol for the bond dissociation energy of oxygen. The partial pressure of atomic oxygen had been determined over a wide range of temperature and could be closely approximated between 1000 and 3000° C by the empirical equation 2.

$$log(pO) = - 60,350/4.57 \cdot T + 3.466 \qquad \text{eqn 2}$$

Wartenberg's 1938 experiment used highly purified oxygen flowing through a tube (22 cm long, 8 mm i.d.) in a heated oven which abutted directly on a water-jacketed metal capillary (0.5 mm i.d.) leading to a KI-starch solution for analysis. Reproducible values for pO_3, shown in Table 2, were obtained at flow rates of 6 l/hr. The agreement between experiment and calculation is remarkably good.

Comparison with the results in Table 1 shows that there is also a reasonably good fit between calculated pO and measured pO_3 except for entry 1b, where temperatures in the range 2100-2500 K were used. Here pO_3 values are an order of magnitude lower than pO, possibly because some ozone was destroyed at the higher temperatures. The temperatures given in entry 4a were reportedly incorrect, as noted earlier.

To the best of our knowledge, there has been no further work on thermal formation of ozone since Wartenberg's 1940 paper (54). It would appear that the only type of procedure which could give information on the ozone-oxygen equilibrium is one in which the analysis is made on the heated sample of oxygen using an analytical method of sufficient sensitivity to measure the ozone concentration directly, as Wartenberg had suggested in 1910. This is what Harteck attempted by UV measurement with a one-meter path length; unfortunately, in that case the ultraviolet measurement was not sufficiently sensitive for the predicted pO_3 of about 1×10^{-8} atm. Apparently, the problem has been either too difficult or not of sufficient interest to tempt any investigators since

Table 2. Comparison of Experimental and Theoretical Results from Heating Oxygen Gas Followed by Rapid Cooling[a].

No.	T (K)	Exptl. pO_3[b] (atm)	Calc. pO[c] (atm)
1	1283	0.1 x 10-6	0.14 x 10-6
2	1423	1.51 x 10-6	1.53 x 10-6

a. Flow rate 6 l oxygen per hour.
b. Measured values of partial pressure of ozone.
c. Calculated values for partial pressure of oxygen atoms at the given temperature, from eqn 2.

1940 although modern analytical methods could probably provide answers.

The only remotely related work we have found is that of Romanov et al. (and references therein (62)), who obtained ozone by passing air over heated crystals of magnesium and bismuth oxides. The result was explained on the basis of release of oxygen atoms from the crystals.

It is tempting to take a very critical attitude towards the progress of work described in this paper. If, for example, Wartenberg or other workers in the field had considered the implications of his 1910 failure to detect ozone in samples of oxygen heated to about 2000 K, the solution to the problem might not have had to wait over 20 years for correct interpretation. However, one should realize that these were formative years in physical chemistry and that the necessary information, in this case the quantitative dependence of oxygen dissociation upon temperature, was not available. A similar situation in pre-Schönbein ozone chemistry was the failure of van Marum (35) to decide that arcing air or oxygen produced a new compound. The tools to treat such a situation were not available in the 1780s.

Summary

A considerable number of early reports of formation of ozone by heating air and from a variety of flames were largely due to erroneous identification of nitric oxide as ozone by smell and starch-iodide test. However, despite the well known thermal instability of ozone, it was clearly established that it is formed from oxygen under these conditions. Detailed studies followed Nernst's work on the third law of thermodynamics, and a number of attempts were made to establish the equilibrium composition of the ozone-oxygen mixture as a function of temperature despite the considerable experimental difficulty involved. The only experiments which gave values compatible with theory were those in which the equilibrium was approached from the ozone side by use of explosions of ozone and oxygen-ozone mixtures; these were at the limit of sensitivity of the analytical methods available at the time. In all other experiments, amounts of ozone formed were far in excess of theoretical prediction. In fact, it was finally established that the quantity being measured when thermal reactions of oxygen were investigated was the concentration of oxygen atoms formed by thermal dissociation of oxygen molecules.

The presence of water vapor or its formation by combustion of hydrogen leads to formation of hydrogen peroxide in flames or upon heating moist oxygen. The oxyhydrogen flame produces hydrogen peroxide and also, if sufficient oxygen is present, ozone. The formation of ozone was suggested to proceed via the intermediacy of oxygen atoms formed by thermal decomposition of hydrogen peroxide.

ACKNOWLEDGMENTS

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