be in error by more than one-third of an entropy unit, one unit, or two units, respectively.

We shall not discuss the table further at this time, except to point out that the atomic entropies show with respect to atomic weight, or atomic number, the same sort of periodicity that occurs in other important atomic properties. In certain rough calculations this fact may be utilized in the estimation of the entropies of elements for which experimental data are not yet available.

Table VIII. Atomic Entropies.

Hydrogen (*g*)	15.9 *b*
Helium (*g*)	29.2 *b*
Lithium	7.6
Beryllium	7.3
Diamond	0.6 *a*
Graphite	1.3 *a*
Nitrogen (*g*)	22.8 *b*
Oxygen (*g*)	24.1 *b*
Sodium	12.2 *a*
Magnesium	8.3 *a*
Aluminum	6.9 *a*
Silicon (met.)	4.7 *a*
Sulfur (rhomb.)	7.6 *b*
Sulfur (monocl.)	7.8 *b*
Chlorine (*g*)	25.7 *c*
Argon (*g*)	36.4 *b*
Potassium	19.7 *c*
Calcium	11.0 *a*
Titanium	6.6
Chromium	5.8
Manganese	7.3
Iron	6.6
Nickel	7.2
Cobalt	7.2
Copper	8.0 *a*
Zinc	9.8 *a*
Bromine (*l*)	18.5 *c*
Zirconium	9.5
Molybdenum	7.5
Ruthenium	6.9
Rhodium	7.6
Palladium	8.9
Silver	10.2 *a*
Cadmium	11.6
Tin	11.5
Iodine	15.7 *b*
Lanthanum	13.7
Cerium	13.8
Tungsten	8.4
Osmium	7.8
Iridium	8.7
Platinum	10.0
Gold	11.0
Mercury (*l*)	17.8 *b*
Thallium	14.6 *a*
Lead	15.4 *a*
Thorium	13.6
Uranium	11.1

Berkeley, Cal.

[Contribution from the Chemical Laboratory of the University of Illinois.]

CHEMICAL REACTIONS IN THE CORONA. I. OZONE FORMATION.

By F. O. Anderegg.

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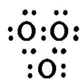
Introduction.

Among the problems which are attracting attention at the present time the question of the nature of the forces which hold the atoms together in the molecule is of great importance. The most probable suggestion is that these forces are due to the electrons and positive nuclei of the different atoms acting on each other according to laws still obscure. Most of the articles which have been published on this problem are of a speculative nature. If the forces are electrical it seems obvious that some electrical method might be used advantageously in their study. Ionization, often followed by chemical reaction, is found to occur in solutions of electrolytes and sometimes in gases. A tremendous amount of work has been done with electrolytes in solutions of various solvents. These studies have led to the development of many interesting relationships, but there are so many complications in any study of liquid solutions that it is difficult to get much conception of the fundamental intramolecular forces. In spite of the fact that a much greater amount of work has been done on ions in solutions than on gaseous ions, more is known about the latter. In gases the ions have far greater freedom of movement than in liquids. The structure is simpler and it is much easier to control and alter conditions. Ionized gases with charged atoms and molecules are often capable of causing chemical action and so may well lend themselves to the study of those forces which bind the atoms together. For instance, to cause a reversible reaction like $N_2 + O_2 \rightleftarrows 2NO$, to shift toward the right by purely thermal means would require a very high temperature for appreciable yields, but with the ionization of gases resulting from various forms of electrical discharge similar yields can be secured at far lower temperatures. It seems probable, then, that the presence of ions in gases is the cause of new combinations of the atoms. It is very desirable when studying fundamental relationships to work with conditions as little complicated as possible. For this purpose there is available one reaction which involves the presence of only one element, oxygen, which is changed into ozone under suitable conditions. The following is a discussion of a *theory of ozone formation* which is applied to the various known types of ozone formation:

The oxygen atom is supposed to possess six electrons in the outer shell. According to G. N. Lewis[1] the two atoms in the molecule may be held together in two different ways, between which there may be several gradations. The oxygen molecule may be represented by either of the Formulas A $:\ddot{O}::\ddot{O}:$, or B, $:\underset{\cdot}{\ddot{O}}:\underset{\cdot}{\ddot{O}}:$. In the first form the atoms are held together by two valence bonds while in the second there is only the one bond holding them together, each atom possessing an extra, unsatisfied valence. It is supposed that a valence bond is due to the coupling together of two electrons which tend to make a fairly stable union. In form B each atom has an extra unbalanced electron and we have an arrangement similar to the usual conception of the ethylene molecule. In its second form the oxygen molecule would be highly reactive as, indeed, oxygen is well known to be.

[1] THIS JOURNAL, 38, 778 (1916).

If a neutral oxygen atom came in contact with form B there would be a strong tendency to form the neutral molecule of ozone,  $\begin{array}{c} :\overset{..}{\underset{..}{O}}:\overset{..}{\underset{..}{O}}: \\ :\ddot{O}: \end{array}$. The electrons not being symmetrically placed about the nuclei a strain results so that ozone is in an unstable condition and readily tends to decompose. The heat of decomposition of ozone by direct measurement is about +34,000 calories.[1] This value is the resultant of the force required to split two extra atoms out of two ozone molecules and of the force with which these two atoms unite to form a molecule, regardless of the order in which these steps may occur. It seems likely that an atom would have to come in contact with the unsaturated form of molecule B at just the right angle and with a suitable velocity in order to produce ozone. Collision between two atoms would result in the formation of a molecule with consequent degradation of energy as heat.

Apparently the formation of ozone requires oxygen atoms which may be derived from molecular oxygen or from some compound of oxygen with other elements. On this basis, in accordance with the mass-action principle, any factor which increases the atomic oxygen concentration ought to raise the yield of ozone. Let us examine those reactions by which ozone is formed either directly or as a by-product and it will be seen that this proposed viewpoint is not incompatible with the facts.

Methods of Ozone Formation.

I. Oxygen in a Nascent or Atomic Condition Often Contains Ozone.

Oxygen containing some ozone may be set free from some of its compounds by electrolysis, by the action of elemental fluorine on water and by the action of sulfuric acid on certain peroxides, peracids and persalts. In the electrolysis of dilute sulfuric acid the yield of ozone depends on the anode current density. By using an extremely small anode it is possible to secure as high as 23.4% of the gas in the triatomic combination.[2] That means that nearly one-third of all the oxygen atoms set free have joined together in triplets. Some ozone would be formed by the direct simultaneous collision of three atoms but according to the theory of probability only an infinitesimal quantity. The greater part of the formation of ozone is probably due to the impact of an atom with the more reactive oxygen molecule B.

II. Oxygen Atoms from Oxygen Molecules.

Oxygen molecules may be broken up into atoms in a variety of ways. Ionization of a gas usually brings about some dissociation into atoms which are usually charged but which sometimes lose their charge and become neutral. There are several ways in which a gas is ionized and in most,

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[1] Stephan Jahn, *Z. anorg. allgem. Chem.*, 60, 357 (1908).

[2] Fischer and Braehmer, *Ber.*, 38, 2623, 2630 (1905).

although not all, of the types of ozone formation to be described there is an accompanying ionization: 1. Many different kinds of *electrical discharges* are accompanied by ionization of the gases and usually by some ozone formation. However, if the temperature rises above 100°, the velocity of the decomposition is too great to allow appreciable yields of ozone. The spark, corona and especially the silent discharge among others cause ozone formation. Whenever ozone is formed by means of an electrical discharge light is produced.[1] Warburg[2] believes that only so long as the ions have a velocity sufficient to produce light will they cause ozonization.

2. The particles shot off in *radioactive disintegrations* ionize gases and are capable of bringing about the production of some ozone.[3]

3. Light of a sufficiently short wave length, known as *Schumann light*, can also ionize gases. The energy, measured as potential fall, required to ionize oxygen is 9 volts per unit charge[4] which corresponds to the extremely short wave length of $\lambda = 133.3\mu\mu$, calculated with the aid of the quantum theory. Such light is absorbed before it penetrates more than 1 or 2 cm. at atmospheric pressure so that little work has been done by it. Between $\lambda = 200\mu\mu$ and visible light lies the region of ordinary *ultraviolet light* to which most photochemical reactions are due. With the exception of mercury and anthracene vapors ultraviolet light does not cause ionization of any substances although it does produce ozone. Goldstein,[5] working with a vacuum discharge in a quartz tube, observed that ozone was formed in the air outside of the tube and that the yield was greater the brighter the light. Warburg,[6] working on the relation between the amount of energy absorbed and ozone formation to test out Einstein's law, has observed both an ozonizing and deozonizing effect according as the concentration of the ozone is above or below the equilibrium produced by any particular wave length. Of the two steps in the reaction by which ozone is formed the first, according to which the oxygen molecule is split into atoms, is the important one. Here we have an instance of the dissociation of a molecule uncomplicated by the presence of ions. Ultraviolet light is apparently capable of separating some of the oxygen molecules. The Lewis molecule B would be in an especially favorable condition to be split up. To set oxygen free from water requires energy

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[1] J. J. Thomson and Threlfall, *Proc. Roy. Soc. London*, **40**, 340 (1886).

[2] *Ann. Phys.*, [4] **17**, 1 (1905).

[3] P. and M. Curie, *Compt. rend.*, **129**, 823 (1899).

[4] *Engineering*, 99, 277 (1915); Frank and Hertz, *Verh. deut. physik. Ges.*, **15**, 929 (1914); **16**, 12, 457 (1914).

[5] *Ber.*, **36**, 3042 (1902).

[6] *Verh. deut. physik. Ges.*, **15**, 194 (1915); *Sitsb. kgl. preuss. Akad.*, **1914**, 872; **1915**, 42; cf. also Fischer and Braehmer, *Ber.*, **38**, 2623, 2630 (1905); Franz Fischer, *Physik. Z.*, **10**, 453 (1906).

represented by 1.25 volts. It would take much less energy to merely separate two oxygen atoms, accordingly, from quantum considerations; ordinary ultraviolet light possesses much more energy than is needed for this reaction. It would seem that the vibration of the ultraviolet light tends to cause the oxygen bonds to be loosened, producing more or less completely, a dissociation effect analogous to the *thermal action* at very *high temperatures*.

4. Since the formation of ozone is an endothermic reaction, the *higher* the *temperature* the greater the amount of ozone in equilibrium with the oxygen. From the heat of reaction determined by calorimetric methods and the free energy calculated from electromotive-force measurements, the equilibrium concentrations may be calculated for any temperature.[1] The experimental results are all lower than the values calculated because of the great difficulty in lowering the temperature quickly enough to prevent the decomposition of the ozone formed.[2] Another complication in the experimental work is the tendency of hot bodies to cause the ionization of any gases with which they come in contact. This criticism applies to the work of Fischer and his associates in which the hot pencil of the Nernst lamp was used as the source of heat. Such an incandescent body is a great ion breeder. This thermal equilibrium suggests that there is a certain amount of dissociation of the oxygen molecule at the higher temperatures although to a far less extent than with iodine. The concentration of oxygen atoms is very small for there are three possibilities: if the atom comes in contact with another atom a molecule results; if it comes against a molecule, ozone may be formed; and finally, if it should happen to collide with an ozone molecule two molecules of oxygen should result. Accordingly, ozone of a greater concentration than very slight traces would be unstable at ordinary temperatures. The only reason for its existence is that the velocity of the second step of the decomposition $O + O_3 \longrightarrow 2O$ is so small at ordinary temperatures.[3] Above 100° this velocity becomes very much larger so that an equilibrium is soon reached.

5. Ozone is formed incidentally in certain slow oxidations at low temperatures. When the elements phosphorus, sulfur or arsenic are placed in a tube and moist air is drawn over them they are oxidized with an accompanying luminescence. By increasing the velocity of the air current the cloud of luminescence may be drawn completely away from the element being oxidized. This light is supposed by Bloch[4] to be caused

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[1] Stephan Jahn, *Z. anorg. allgem. Chem.*, 60, 332 (1908).

[2] Fischer and Braemer, *Ber.*, **39**, 363, 940 (1906); Fischer and Marx, *Ibid.*, **40**, 443, 1111 (1907); Clement, *Ann. Phys.*, [4] **14**, 334 (1906); Pollitzer, "Ber. chem. Affin.," p. 101.

[3] Warburg, *Ann. Phys.*, [4] **9**, 781 (1902).

[4] *Compt. rend.*, **147**, 842; **148**, 775 (1910).

by the oxidation of a lower to a higher oxide. When phosphorus and sulfur are oxidized in this way considerable amounts of ozone are formed, but none has been detected during the oxidation of arsenic. The distinguishing feature between phosphorus and sulfur when acted upon by moist oxygen is, that the products from the former contain ions which will discharge an electroscope, while the sulfur gases seem to possess no such ions. Part of the ozone formed in the oxidation of phosphorus may be due to the presence of these ions but there are only enough ions to produce a very small part of all the ozone formed. An explanation is, that the oxygen molecule, coming in contact with the lower oxide, uses up one atom before the other atom has time to combine with the substance being oxidized. Another atom from a second molecule completes the oxidation of the phosphorus. To oxidize sulfur dioxide to the trioxide would require only one oxygen.

When the vapor from ether and similar organic substances comes in contact with oxygen at the hot surfaces of platinum it is oxidized with the formation of some ozone. This is a surface reaction and, as long as the stream of air and vapor come in contact, the heat of reaction causes the wire to glow. A body that sends off light in this manner causes some ionization in the gases which come in contact with it although probably but a small part of the ozone would be formed here by ionic processes. The fact that the yield of ozone depends on the velocity of the air tends to show that one atom of the oxygen molecule may become detached on coming in contact with a carbon atom while the other atom is carried away by its velocity before it has its chance to combine with carbon or hydrogen. According to this view ozone should be formed during most combustions and it doubtless would be but for the unfavorable condition of the high temperatures usually involved, which allows the ozone to reach an almost immediate equilibrium with oxygen. In the reactions just discussed, the current of air tends to carry away the free atoms before they have become warm enough to decompose very rapidly.

It is believed that, for the formation of ozone, oxygen in an atomic condition is required. The atoms may or may not be charged and this is a very important point. The ions tend to pull apart the molecule into the more reactive atomic condition. If the atoms that do react are not charged, then the action of ions is only an indirect cause of chemical reaction. Of course, there is chemical reaction between gaseous ions especially if oppositely charged. From the discussion just given it seems evident that while atomic oxygen is required for the production of ozone the presence of ions may or may not be incident to this reaction. The reactive modifications of two other gases are without charge although both are formed under the influence of ions. Strutt has concluded from his experiments[1] that the active modification of nitrogen produced by a condensed discharge was composed probably of uncharged atoms. Duane and Wendt[2] have shown that the reactive modification of hydrogen produced by α-radiation is composed of uncharged particles.

The Corona.

To test these views and to throw some light on the relationships between ionization and chemical reaction the study of certain of the chemical reactions in the corona has been begun. At first it is proposed to study the formation of ozone from oxygen in the corona discharge. This reaction is a comparatively simple one. There is present only the one element for oxygen is readily prepared and purified in reasonably large quantities. Although quite a large variety of ions in oxygen is possible (electrons, atoms charged with a single or double negative or positive charges, molecules of oxygen or ozone bearing charges), there would be fewer kinds of ions present where ozone is formed than in almost any other reaction in which gaseous ions take part. Another advantage of this reaction is that the analysis of ozone is a very convenient one and seems to be fairly accurate. The first phase of this reaction studied concerns the production of an equilibrium between ozone, oxygen molecules and oxygen atoms whether charged or uncharged. That oxygen does occur in the atomic condition seems probable from the increase in pressure which is observed as soon as the corona discharge is turned on and which seems to be caused by an increase in the number of particles in the gas as noted first by Farwell.[3] This has been doubted by Arnold[4] but has since been proved by Warner[5] along half a dozen different lines of evidence to be due to the ionization of the gas and not to the heat effect which does develop with time. There are, therefore, present oxygen atoms to form ozone according to the viewpoint developed above. It is hoped that evidence as to whether these atoms are charged or not will be brought forward in investigations now under way.

The corona is an electrical discharge accompanied by various light phenomena from which it gets its name. By impressing sufficiently high potentials on a wire the air is broken down and some leakage occurs from the wire. Such a loss is of considerable importance in long distance transmission of high voltage alternating or direct currents. The alternating corona has been studied by a number of electrical engineers who have obtained many empirical results. The direct current corona has, of course,

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[1] *Proc. Roy. Soc. London,* **85**, 219, 377 (1911); **86**, 56, 105, 262 (1912); **87**, 179, 302 (1913); **88**, 539 (1914); **89**, 187 (1914); **91**, 303 (1915).

[2] *Phys. Rev.,* [2] 10, 116 (1917).

[3] *Proc. Am. Inst. Elec. Eng.,* **33**, 1693 (1914); cf. also Kunz, *Phys. Rev.,* [2] **8**, 28 (1916); and Warner, *Ibid.,* [2] **8**, 285 (1916).

[4] *Phys. Rev.,* [2] **9**, 93 (1917).

[5] *Ibid.,* [2] **10**, 483 (1917).

received less attention, although in the Physical Laboratory of this University considerable work has been done in studying some of the relationships between the different variables which may affect the discharge.[1] Recently, W. W. Strong[2] has proposed to get at the theory of fume precipitation by studies involving the direct current corona.

The corona probably offers the most favorable conditions for the study of gaseous ionization at atmospheric pressure. There are other forms of discharge at atmospheric pressure, such as the arc and spark discharges, which are extremely complex. The silent discharge used for the commercial production of ozone is made less simple by the glass-covered electrodes which act like condensers. The work that has been done in this University on the purely physical relationships is of great assistance in any work of a chemical nature and coöperation from some of these investigators may be expected. Moreover the form of apparatus, which will be described later, is a convenient one for experimentation. In spite of the number of variables, such as dimensions of tube, pressure and temperature of the gas, it is not difficult to keep practically all constant. Finally, the constancy and ease of control of the potential available are of great help in making a success of the proposed studies.

Experimental.

Oxygen was prepared by the electrolysis of 15% sodium hydroxide solution with nickel electrodes. Hydrogen was removed by hot copper oxide. A 20% solution of sodium hydroxide absorbed any carbon dioxide. Moisture was removed by passing the gas through a bead tower containing concentrated sulfuric acid, through a 20 cm. tube containing fused potassium hydroxide and, finally, through a similar tube containing phosphorus pentoxide.

The corona tube was 28 cm. long and its diameter was 4 cm. The outer cylindrical electrode was of gold foil 0.1 mm. thick with a diameter of 3.6 cm. Connection to it was made by a long platinum wire which made a complete circle outside the foil. The foil was supported by three rings of thin glass rodding. A slit 1.5 cm. wide allowed the discharge to be observed. The appearance of the discharge is interesting. If the connections are continuous so that there is no arc in series the whole length of the wire is surrounded by a uniform glow when positively charged. If the wire is charged in the opposite manner there are a few brushes or beads scattered more or less regularly along its length. If an arc is intro-

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[1] Earlier work was done by Watson, *Electrician*, **63**, 828 (1909); **64**, 707, 777 (1909–10), and by Schaffers, *Compt. rend.*, **157**, 203 (1913). Contributions from the Physical Laboratory of the University of Illinois are by Farwell, *Proc. Am. Inst. Elec. Eng.*, **35**, 1693 (1914); Davis and Breese, *Ibid.*, **36**, 143 (1917); Kunz, *Phys. Rev.*, [2] **8**, 28 (1916); Booth, *Ibid.*, [2] **10**, 266 (1917); Warner, *Ibid.*, [2] **8**, 285 (1916); [2] **10**, 483 (1917); Crooker, *Ibid.* (forthcoming publication).

[2] *Met. Chem. Eng.*, **16**, 748 (1917).

duced in series there develop some brushes on the positive wire while on the negative wire the brushes are more or less extinguished by a glow running all along the wire. The effect of the arc is simply one of interruptions. There is no reversal of the current.[1]

The source of power was forty direct current dynamos each rated at 500 volts and 0.5 ampere. These were run by three motors, current for which came from a motor generator which was controlled by a constant potential device so that the fluctuations of the potential were less than 1%. This device is necessary to eliminate variations in the power house circuit. The voltage from these machines could be regulated by means of field switches and by means of a rheostat in series with the motors. The dangerously large current was cut down by a water resistance. The negative terminal of the dynamos was grounded to decrease the risk. All connections were either soldered or made through mercury cups. The potential difference was given by a Kelvin electrostatic voltmeter. The strength of the current was measured by a sensitive d'Arsonval galvanometer on a shunt between the corona tube and the ground.

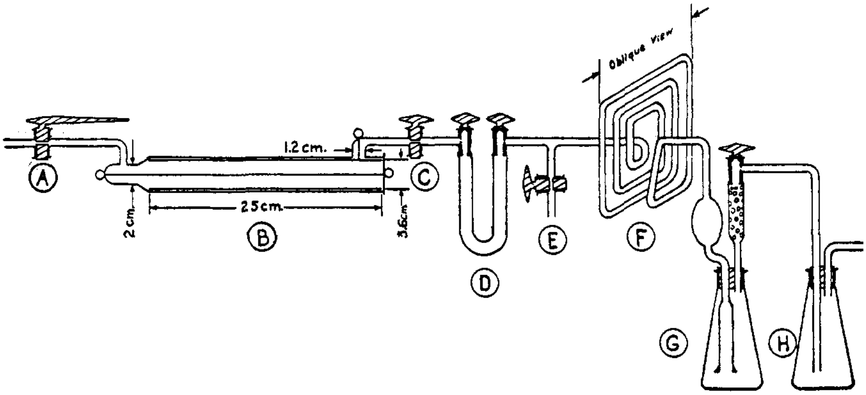

Fig. 1.

After the discharge the apparatus was connected to a vacuum pump so that the oxygen and ozone mixture could be slowly drawn through tube D containing phosphorus pentoxide which had been completely oxidized by resubliming in a current of oxygen. Then the gas passed through a stout Erlenmeyer flask containing 30 cc. of 2 *N* potassium iodide. The salt from which this solution was prepared has been recrystallized till neutral to phenolphthalein. This solution was poured into the flask through the bead tower so that the gas would be further scrubbed. The gas then passed through a similar flask containing more potassium iodide solution and finally through a calcium chloride tube. By pumping out the gas from the discharge tube down to about 3 cm. pressure and then

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[1] Crooker, *Phys. Rev.* (forthcoming publication).

washing with three or four portions of oxygen to a pressure of 7–10 cm. of mercury, of the original gas in the tube there would remain less than one part in 2000. When the ozone had been practically all removed from the tube stopcock C was closed and oxygen was allowed to enter the corona tube at a reasonable rate while air was admitted to the adsorption flasks through E. The solution on the beads was washed down into the flask and after barely acidifying with dilute sulfuric acid the iodine liberated was titrated with freshly standardized 0.0025 *N* sodium thiosulfate solution. By using very well-diffused light the end point could be obtained within a drop or two. The thiosulfate solutions were standardized against arsenious oxide after standing at least one week after they were made up.[1] Pure oxygen was passed through these absorption flasks for six hours without any trace of iodine being liberated. Evidently the ionization of a gas produced by bubbling is too slight to have any effect here. The second flask was used as a check to see if all the oxygen was absorbed in the first flask. Usually after working all day there was no trace of iodine to be observed in it. Once after using the same solution in the second flask for four days a slight trace of color accumulated which was discharged by a single drop of the thiosulfate solution, as compared with over 600 cc. required for the first flask during this period.

The experiments were made at room temperature (24 ± 3°); the gas was always at atmospheric pressure (740 ± 5 mm.) at the start of each discharge. In a closed tube the density of the gas would remain constant. Coincident with the increase in temperature there is an increase in resistance. When the potential was maintained at a constant value the current strength fell off with the time, dropping sharply at first and then more slowly so

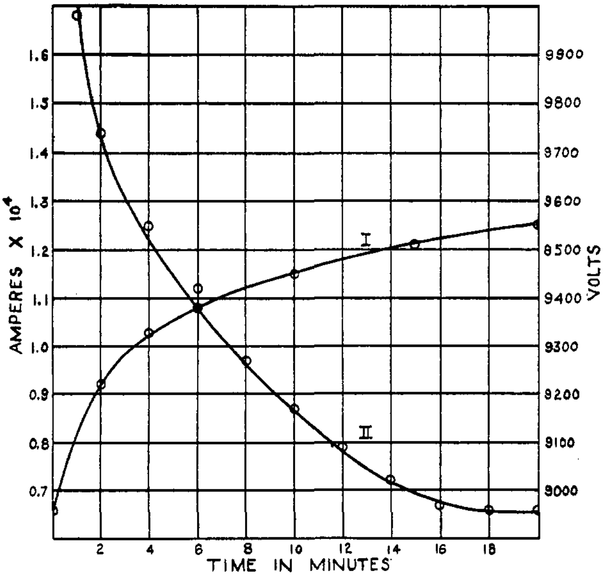

Fig. 2.

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[1] Treadwell and Hall, "Analytical Chemistry," 2, 676 (1915); Bates and Vinal, This Journal, 36, 916 (1914); Riesenfeldt and Bencker, *Z. anorg. allgem. Chem.*, 9 , 167 (1916).

that the curve (Fig. 2, Curve I) approaches a line parallel to the time axis asymptotically. Curve II shows the relationship between the time and voltage at a constant current strength of 1.25×10^{-4} ampere.

CURRENT-VOLTAGE RELATIONSHIP.

Wire positive.		Wire negative.	
Amperes $\times 10^4$.	Volts.	Amperes $\times 10^4$.	Volts.
2.00	7910– 8300	1.25	8960– 9550[1]
2.77	8960– 9260	2.50	9880–10280
3.75	9370– 9650	3.75	10400–10600
6.25	9680–10440	5.00	10800–11240
		7.50	11600–12480

These data are the extreme values observed during a 20-minute run. The results plotted in Figs. 3 and 4 represent all that were secured when the current was constant and there was no arc in series. The following results were obtained, partly during one day and partly the next day,

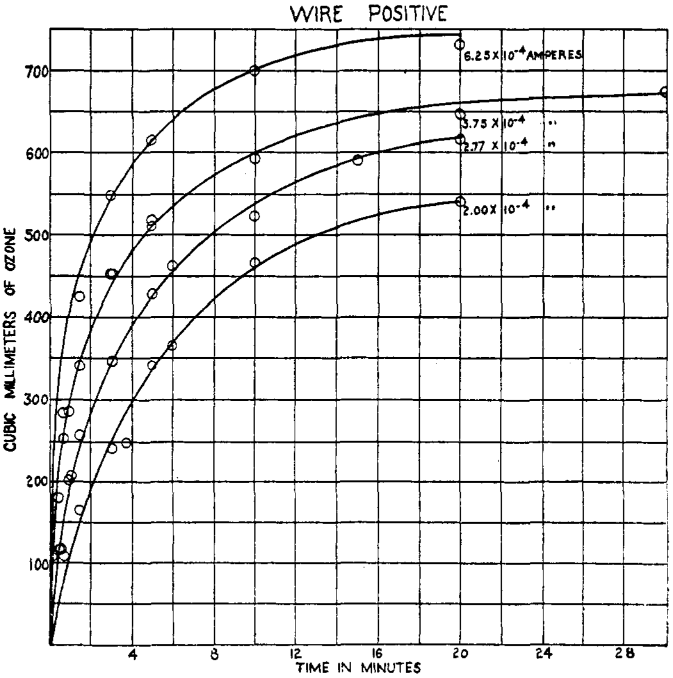

Fig. 3.

with a positive wire and a current strength of 2.77×10^{-4} ampere for the 3-minute interval: 345, 340, 350, 335 and 360 cu. mm. of ozone. To change this value, the one used in the curves, to percentage divide by 3000.[2] From the slopes of the curves near the origin it seems likely that

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[1] Cf. Fig. 2, Curve I.

[2] The capacity of the tube is 300 cc. so to change from cu. mm. to percentage multiply by $100/(300 \times 1000)$ or divide by 3000.

the production of ozone might be proportional to the current strength if the gas were drawn through the apparatus fast enough to eliminate the decomposition effect of the discharge. It is expected to work out this point experimentally as well as the connection between the amount of ozone formed and the current and power consumption in the corona.

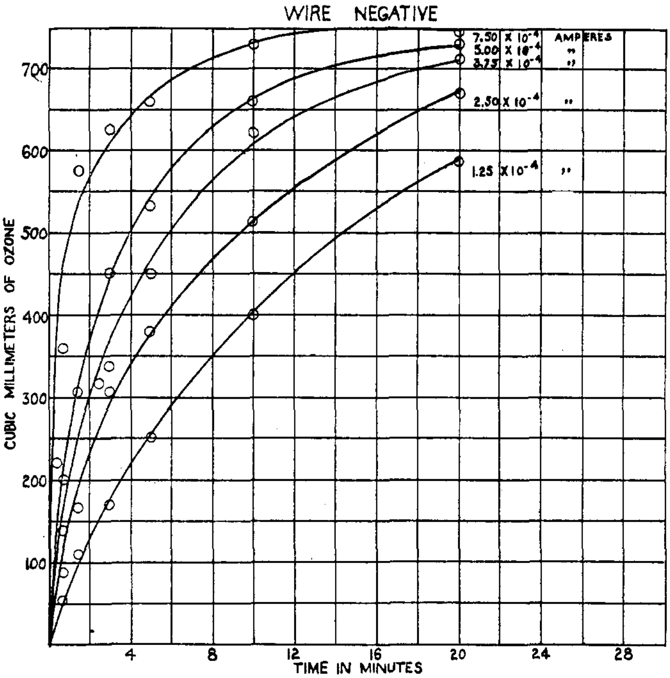

Fig. 4.

With the wire charged positively there is nearly as much ozone formed as when it is negative. These curves belong to a family of curves which have their origin in the same place and which tend to approach a common point as a limit. The greater initial slope of the larger current curves indicates that there is a greater ozonizing effect, but the smaller slope of these curves after about five minutes shows a greater deozonizing effect also. The resultant is probably the same in all cases with a final equilibrium which is independent of the magnitude of the current. The similarity in the two sets of curves is interesting as one would expect to find that the negative discharge with its numerous electrons is a better ozonizer. In this connection it would be of great interest to know in what part of the discharge the ozone is formed and that point is now being investigated.

With an arc 0.1 mm. long in series the galvonometer did not vibrate very much but when the gap was increased to 0.25 mm. there was considerable vibration. The spark gap had but little effect on the yields with the higher current strengths, but it did increase the initial amounts of ozone formed when smaller currents were used so that their curves would lie close to those for the larger currents.

A peculiar phenomenon has been observed. At the start of the work each day the yield of ozone was very much less for a given time and current than after the discharge had been passing for some time. Thus, if the current was maintained constant and the discharge was allowed to proceed for successive one-minute intervals, the yield per minute increased very fast at first, reaching constancy only after the sixth or seventh minute period. Usually this initial lag was eliminated by running the discharge for twenty minutes. An explanation for this phenomenon is being sought.

That ozone formation is a fairly suitable reaction for the study of some of these fundamental relationships has been appreciated by Warburg[1] who, especially assisted by Leithäuser, has devoted several years to the connection between the different variables which may affect the formation of ozone. They have worked under a variety of conditions and with several forms of apparatus. That part of their work which concerns the present article will be discussed here. Other points, including the theory of the commercial production of ozone, will be considered in future articles when similar experiments with the corona are described. Warburg[2] studied the ozone-oxygen equilibrium produced by an electrical discharge at various temperatures and found that the concentration of the ozone decreased with an increase in temperature caused by a greater deozonizing effect. The rate for the formation of ozone was found to be nearly constant at various temperatures. His apparatus consisted of two small bulbs of about the same volume connected by a sulfuric acid manometer. Oxygen containing a small amount of nitrogen was used since he had been able to detect no oxides of nitrogen when the nitrogen concentration was below 7%, provided there was no sparking. When a discharge was passed from a negatively charged point to a grounded wire there was no sparking at first, but if the point was charged positively the discharge was a spark discharge. By using a charged wire and a half cylinder of platinum he secured an arrangement like the corona tube. The current was supplied from an influence machine which produces great fluctuations of potential. Both bulbs were placed in a constant temperature bath and after turning off the discharge the apparatus was allowed to stand a few minutes so that the heat developed by the discharge might be removed and a correct reading of the manometer could be obtained. The amount of ozone formed was calculated for the volume decrease in the discharge bulb. When equilibrium was reached at any temperature the concen-

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[1] A series of articles from 1900–1915, *Sitzb. Akad. Wiss. Math. nat. Klasse;* and *Ann. Phys.,* [4].

[2] *Ann. Phys.,* [4] 9, 781 (1902).

tration of the ozone with the wire negative was about three times as great as with the wire positively charged. This was probably due to the greater velocity of the negative ions. In the corona apparatus used in the present investigation with the current constant no such difference in ozone formation was observed. The deozonizing effect was about the same for both positive and negative discharge. The results obtained by Warburg have been confirmed by Cermak[1] who worked with the point discharge.

The results obtained with other forms of discharge are, doubtless, often similar to those which can be obtained with the corona, but the greater number of uncontrollable variables have made it seem desirable to study some of the primary relationships where conditions could be under better control. It is also highly desirable to get definite data regarding the ionization and chemical reaction relationship and it is hoped that these studies will lead to securing of sufficient facts to clear up some of the vagueness now existing. J. J. Thomson concluded in his lectures before the Royal Institute in 1915[2] that there is very little evidence of ionization by chemical reaction. This would be expected since the energy produced by any chemical reaction is not great enough to cause the ionization of any of the elements except possibly the alkali metals. On the other hand, that chemical reaction often follows ionization is hardly to be doubted.

In the first part of the study of ozone it has seemed desirable to determine if an equilibrium is reached between the two forces in the electrical discharge which tend to cause the formation of ozone and then its decomposition. Warburg has studied this question with the apparatus described above. His work and that of Cermak have shown that there is a tendency to reach an equilibrium. In the corona the time required to reach an equilibrium would be dependent on the rate of diffusion. The question of whether ozone is formed at the central wire, as seems likely, or elsewhere and the calculations of diffusion will be taken up in the next article of this series.

The writer desires to express his sincere thanks to Jakob Kunz for several valuable suggestions and to A. P. Carman, head of the department of Physics in this University, for kind permission to use the corona apparatus.

Summary.

The great desirability of securing more knowledge as to the relationship between ionization and chemical action has been pointed out.

For the formation of ozone atomic oxygen is probably required. The various known types of reactions by which ozone is formed have been discussed and it has been shown that there is a strong probability of the

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[1] *Ber. deut. physik. Ges.*, 4, 268 (1906).

[2] *Engineering*, **99**, 251, 277, 303, 329, 356, 413 (1915).

presence of atomic oxygen in each case. Ozone may or may not be formed by means of gaseous ions. Because of the few species of ions present in oxygen its transformation into ozone is a suitable reaction for the study of the connection between ionization and chemical reaction. The corona apparatus gives a very favorable form of discharge for this purpose.

An equilibrium results between the oxygen and ozone caused by the presence of two opposing effects, ozonizing and deozonizing. At equilibrium in the corona it is probable that gases have the same concentration regardless of whether the wire is charged positively or negatively. Coincident with the increase in temperature in the discharge tube, caused by the degradation of energy, there is an increase in resistance.

The study of ozone formation is being continued.

URBANA, ILL.

[CONTRIBUTION FROM THE H. LOUGININE THERMAL LABORATORY OF THE PHYSICAL INSTITUTE OF MOSCOW UNIVERSITY.]

ON THE STANDARD UNIT IN THE THERMOCHEMISTRY OF ORGANIC COMPOUNDS.

BY W. SWIENTOSLAWSKI.

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In 1908, Em. Fischer and Wrede[1] published a paper about the heat of combustion of benzoic acid and cane sugar. As the measurement of heat capacity of calorimeteric systems, carried out in the Reichsanstalt by Jaeger and Steinwehr, has been expressed in kilo-joules, therefore, these quantities also were expressed in kilo-joules.

1 g. benzoic acid weight in air................	26,497 kilo-joules.
1 g. cane sugar weight in air..................	16,555 kilo-joules.

The authors proposed that the cited quantities might be used as standard units for the measurements of the heat capacity of all the calorimetric bombs. Verifying the constants of calorimetric bombs, used in W. Louginine's Thermal Laboratory of Moscow University, I noticed that the real heat capacity of the bombs was smaller than the one determined from the combustion of benzoic acid or cane sugar. These constants were computed with the aid of the Reichsanstalt data using 4.189 as the equivalent of the joule instead of a more probable value between 4.179 and 4.182.

This induced Popov and myself to determine the heat capacity of the Peters bomb of the Thermal Laboratory by two methods, which were described in our preceding papers,[2] and to measure again the heat of combustion of benzoic acid.

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[1] *Sitzb. k. akad. Wiss. Math. Nat. Klasse*, 1908, 129.

[2] *J. Russ. Phys. Chem. Soc.*, 46, 935, 1284, 1293, 1302 (1914).