6. Summary

The equation of state proposed by Beattie and Bridgeman has been applied to mixtures of methane and nitrogen by use of a simple method for calculating the values of the constants of the mixture from those for the pure gases. The constants R, a, B_0, b and c which contain the dimension of density to the first power are combined linearly, thus $B_{0x} = B_{01}(1 - x) + B_{02}x$; the A_0 constant contains the dimension of density to the second power and hence the square root of A_0 is combined linearly, $A_{0x} = [\sqrt{A_{01}}(1 - x) + \sqrt{A_{02}}x]^2$.

It is concluded that it is possible to write a single equation by means of which pressures for the entire series of mixtures of methane and nitrogen, including the pure gases, can be calculated from the temperature, density and composition.

The satisfactory nature of the agreement between observed and calculated pressures for the mixtures of methane and nitrogen leads to the expectation that this method of combining the constants will prove applicable to mixtures of other gases. The general equation of state for mixtures is presented in Equation 3 and the virial form in Equation 4. This equation of state is completely algebraic and can be used for the integration in terms of elementary functions of many thermodynamic relations.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE FORMATION OF OZONE IN THE ELECTRICAL DISCHARGE AT PRESSURES BELOW THREE MILLIMETERS[1]

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RECEIVED MAY 17, 1928 PUBLISHED JANUARY 8, 1929

Ozone formation in the electrical discharge has been studied chiefly at atmospheric pressures under conditions which give a non-uniform distribution of ionization. The purpose of this investigation was the study of the factors involved in the formation of ozone in an electrical discharge at low pressures, under conditions of somewhat greater uniformity. Pressures below three millimeters of mercury were employed and a high precision in the chemical analysis was demanded for these minute quantities of ozone.

In a previous communication from this Laboratory[2] the influence of the electrodes was studied down to 14 mm. and the ratio of electrode area to

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[1] This communication is based on a thesis submitted for the degree of Doctor of Philosophy at the University of Wisconsin in 1926, under the direction of Farrington Daniels.

[2] Newsome, THIS JOURNAL, 48, 2035 (1926).

the volume of the discharge was made large. In the present research this ratio was made as small as possible in order to minimize the influence of the electrodes.

In one other research using a Siemens ozonizer and alternating current,[3] the pressure range has been carried down to 27 mm.

Apparatus and Procedure

The apparatus is shown in Fig. 1. The electrodes E, E′ of the discharge tube T were connected to a source of high potential, S. An adjustable alcohol-xylene rheostat, R, of high resistance, was used for stabilizing and regulating the current. The induction coil, C, served to initiate the discharge, and the air gaps B, B′ in the circuit prevented the short circuiting of the battery through the secondary of the coil. The potential drop across the tube was indicated by a Braun electrostatic voltmeter, V.

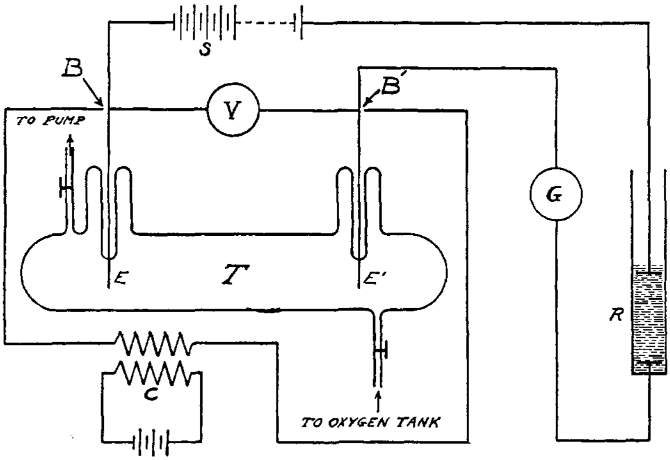

Fig. 1.—Discharge chamber and electrical connections.

The discharge tube was of soft glass about 60 cm. long and 7.2 cm. in diameter, with electrodes 45 cm. apart. These tubes had all-glass seals, but later another tube was used in which the electrode holders were sealed in with wax at a ground-glass joint to facilitate the interchange of different kinds of electrodes and to permit variation of the electrode distance.

Pressures within the discharge tube were read with a modified McLeod gage capable of measuring quickly and accurately from 3 mm. to 0.01 mm. of mercury. A Hyvac oil pump was used for evacuating the discharge tube down to 0.001 mm. The voltage for maintaining the discharge was obtained from 36 B batteries,[4] in series, giving a total potential of over 1600 volts. The current through the tube was measured with a shunted galvanometer which was calibrated to 0.05 milliampere. The electrodes of platinum, gold, aluminum and carbon were 0.4, 0.4, 1 and 2 mm. in diameter, respectively, and each was 3 cm. long. The electrodes of platinum foil were 1 cm. wide and 3.5 cm. long.

The whole tube was filled with a uniform blue glow during the discharge but the

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[3] Warburg and Rump, *Z. Physik*, **32,** 245 (1925).

[4] These batteries were kindly donated by the French Battery Co., Madison, Wis.

light was much more intense and somewhat lavender in shade around the electrodes, particularly around the negative electrode. The region of intense glow appeared to extend out about a millimeter from the electrodes under most of the conditions.

Carefully purified oxygen was used in the earlier experiments but subsequent experiments showed that the traces of hydrogen present in the electrolytic oxygen from a tank had no appreciable effect on the yield of ozone under the conditions of these experiments.

Preparatory to making a determination the tube was alternately exhausted and filled with oxygen several times to remove the nitrogen remaining in the tube. At a pressure of oxygen of about 2 mm. a current of 4 milliamperes was passed through the tube for five minutes to "age" the electrodes.

"Aging" was necessary since preliminary experiments had shown that with fresh electrodes the results were discordant and somewhat lower. This aging phenomenon was also observed by Anderegg[5] and Newsome.[2] After the preliminary discharge, the tube was twice evacuated and filled with oxygen to remove the ozone produced in the aging process. No ozone remained absorbed on the walls or electrodes after this treatment, as shown by the potassium iodide test.

After filling again with oxygen and evacuating to the desired pressure, the discharge was passed through the tube for a definite period of time while the current was carefully controlled and the voltage recorded. The tube was then disconnected and into it was carefully admitted about 80 cc. of 2% potassium iodide solution. After shaking intermittently for half an hour the solution was run out, acidified with dilute sulfuric acid and titrated with *M*/1000 sodium thiosulfate solution, 1 cc. of which is equivalent to 0.000024 g., or 3.03×10^{17} molecules of ozone. Freshly prepared starch was used as an indicator and the titrations were carried out in 100-cc. Nessler tubes. The end-point was accurate to about 0.1 cc. of thiosulfate solution.

Experimental Results

The variables of time, pressure, current, electrode area, electrode distance and electrode material were studied and the results are summarized[6] in Figs. 2, 3 and 4 and in Tables I, II and III.

The points in Figs. 2, 3 and 4 indicate the agreement to be expected. In general the yields of ozone increase slightly with successive check experiments.

TABLE I

VARIATION IN YIELD OF OZONE WITH DISTANCE BETWEEN ELECTRODES

Pressure, 1.9 mm.; current, 2 milliamperes; time, 30 seconds; platinum wire electrodes.

Dist. bet. elect., cm.	Potential drop, volts	Molecules of ozone $\times 10^{-16}$	G. of ozone per k. w. hour	Dist. bet., elect., cm.	Potential drop, volts	Molecules of ozone, $\times 10^{-16}$	G. of ozone per k. w. hour
6.5	560	18.5	1.6	37.5	875	29.8	1.6
6.5	560	19.7	1.7	37.5	875	31.9	1.7
6.5	560	22.8	1.9	45.0	1035	26.4	1.2
6.5	560	21.6	1.8	45.0	1035	36.4	1.7
24.0	760	23.7	1.5	45.0	1035	31.3	1.4
24.0	760	22.2	1.4				

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[5] Anderegg, THIS JOURNAL, 39, 2581 (1917).

[6] Complete details are recorded in the thesis filed in the Library of the University of Wisconsin.

TABLE II

VARIATION IN YIELD OF OZONE WITH ELECTRODE AREA

Pressure, 1.9 mm.; platinum electrodes; current, 2 milliamperes; average results.

Cathode	Anode	Dist. bet. elect., cm.	Potential drop, volts	G. of ozone × 10^6
Smooth wire	Smooth wire	24	760	18.1
Etched wire	Etched wire	24	700	17.8
Foil	Foil	24	600	23.6
Smooth wire	Smooth wire	37.5	875	24.3
Smooth wire	Foil	37.5	825	26.9
Foil	Smooth wire	37.5	750	46.2
Smooth wire	Point (wire broken off)	45	1250	28.8

TABLE III

VARIATION IN YIELD OF OZONE WITH ELECTRODE MATERIAL

Pressure, 1.9 mm.; time, 30 seconds; current, 2 milliamperes; distance between electrodes, 24 cm.

Electrode material	Potential drop, volts	G. of ozone × 10^6	Electrode material	Potential drop, volts	G. of ozone × 10^6
Platinum	760	18.7	Carbon	725	16.6
Platinum	760	17.5	Aluminum	600	24.2
Gold	760	19.2	Aluminum	600	69.2
Gold	760	18.5	Aluminum	600	84.5
Carbon	725	18.0	Aluminum	600	91.2

Interpretation of Experimental Results

Time.—In a closed tube the yield of ozone does not increase directly with the duration of the discharge, since an equilibrium is soon reached

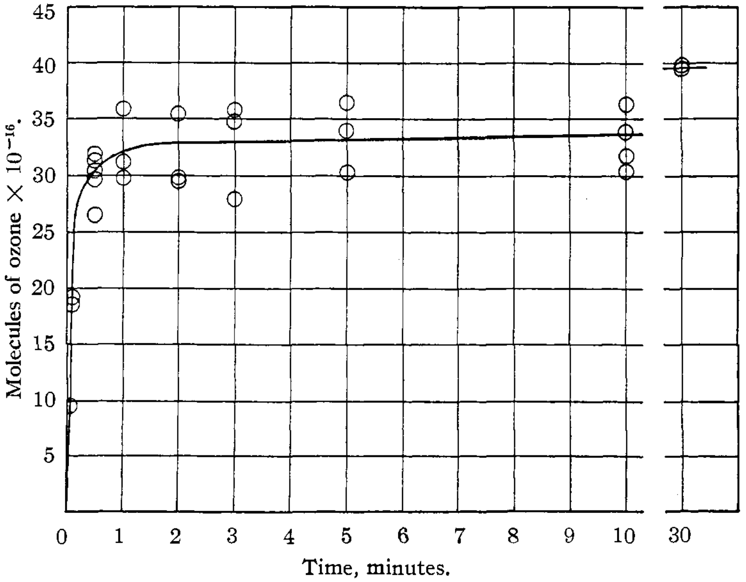

Fig. 2.—Variation in ozone yield with time. Pressure, 1.9 mm.; current, 2 milliamperes; potential drop, 850 volts; electrodes of platinum wire.

and the ozone is decomposed as fast as it is formed. The yields approach a limiting value, as shown in Fig. 2, and the yields per faraday and per kilowatt hour decrease with longer periods of time. During the first thirty seconds, however, the quantity of ozone is approximately proportional to the input of electricity, that is to the time, because the equilibrium mixture has not been reached and the concentration of ozone is so low that its decomposition is less important.

Pressure.—In Fig. 3 it is seen that the yield of ozone is greater at the higher pressures, perhaps on account of the greater number of collisions. Since the yield is limited by equilibrium conditions, it is not to be expected that the yield of ozone will vary directly with the pressure.

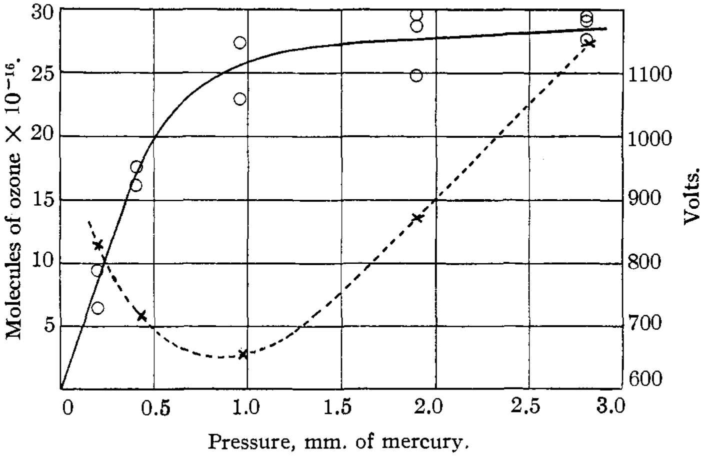

Fig. 3.—Full line: variation in ozone yield with pressure; broken line: variation in voltage with pressure at constant current; time, 30 seconds; current, 1 milliampere; electrodes of platinum wire.

Current.—Since the formation of ozone depends on the formation of ions, the yield must depend on the electrical energy input rather than on the current, for the current and the time constitute only the capacity factor of the electrical energy. Fig. 4 shows that as much ozone is formed with 1 milliampere as with 6 milliamperes. These facts indicate that the energy of which 1 milliampere is the capacity factor is sufficient to bring about in thirty seconds a state of approximate equilibrium and therefore it is not to be expected that more current (or energy) will result in a greater ozone yield.

Electrode Distance.—The full effect of increasing the distance between the electrodes is quite complicated but the chief factor is probably the greater energy input caused by the greater potential drop across the tube required to maintain a constant current. In Table I it is interesting to note that as the electrode distance increases the ozone yield increases, but the yield per kilowatt hour remains practically constant.

Electrode Area.—Table II shows that in most cases the yield of ozone is independent of anode area but somewhat dependent on cathode area. It is known that the potential drop is greatest at the cathode and that the ionization in the region around the cathode is much more intense than the ionization at the anode. Rideal and Kunz[7] found more ozone around the cathode than around the anode. An increase in the area of the cathode gives an increase in the volume of the cathode glow and increases the yield of ozone. The two experiments in which foil was used as the cathode are similar to those of Newsome[2] and suggest that in these two cases ozone may be decomposed at the anode.

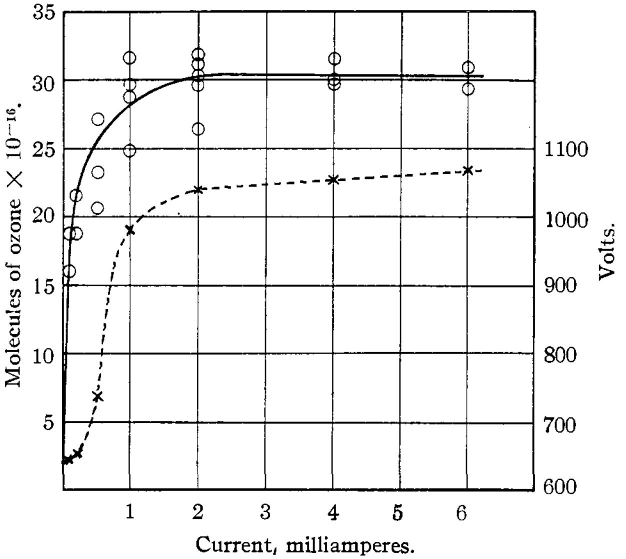

Fig. 4.—Full line: variation in ozone yield with current; broken line: variation in voltage with current at constant pressure; pressure, 1.9 mm.; time, 30 seconds; electrodes of platinum wire.

In the case of the etched electrodes, the volume of the cathode glow was the same as with the smooth electrodes and the yield of ozone was the same. The surface of the etched electrodes must have been greater than the surface of the smooth electrodes, but since the yield of ozone was no greater it may be concluded that the formation of ozone in these experiments was not strictly a surface phenomenon.

Electrode Material.—The data of Table III indicate that, with the exception of aluminum, the yield of ozone is independent of the electrode

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[7] Rideal and Kunz, *J. Phys. Chem.*, **24**, 379 (1920).

material. This fact supports the view that under the conditions of the experiment, with small electrodes and low pressures, the formation of ozone occurs chiefly through the formation of gaseous ions in the discharge, probably in the vicinity of the cathode. In the work of Newsome[2] the conditions were different and the large electrodes led to the decomposition of the ozone at the surface after its formation.

An examination of the experimental data suggests that the influence of the electrodes was not completely eliminated in the present investigation, for a preliminary aging was found necessary, and even after the aging process there was an unmistakable tendency for each successive experiment of a series to give a slightly greater yield. The effect was so small, however, as to be nearly negligible in all cases except in that of the aluminum electrodes.

The results with aluminum electrodes are interesting. In the present investigation with small aluminum electrodes the ozone yield was high, while in the work of Newsome[2] with large aluminum electrodes and small current density the yields were very low. These two researches taken together appear to furnish a good example of the catalytic behavior of an electrode, giving an abnormally high yield when the ionization around the electrode is great and abnormally low yield when the ionization is small.

Theoretical Discussion

Before consideration of a possible mechanism of ozone formation it is necessary to make a calculation concerning the number of ions which is theoretically possible.

Taking the maximum potential necessary for the complete dissociation and ionization of oxygen as 23 volts,[8] it is easily calculated that 3.7×10^{-11} erg is required to form a pair of atomic ions in oxygen. The largest yield of ozone obtained in this investigation is the one corresponding to a current of 0.1 milliampere in Fig. 4, in which the time was thirty seconds, the potential drop 640 volts and the number of molecules of ozone produced 16.1 and 18.8×10^{16}. The energy input was 1.9 joules, giving an average yield of 26 g. of ozone per kilowatt hour. If all the energy of the discharge was used in making monatomic oxygen ions, it would be possible to produce during this thirty-second period 5.2×10^{17} pairs of ions ($1.9 \times 10^{7} \div 3.7 \times 10^{-11} = 5.2 \times 10^{17}$). Since 1.8×10^{17} molecules of ozone was obtained, the ratio of molecules of ozone to calculated ion pairs is 1/2.8.

It must be emphasized that this ratio gives only the order of magnitude, for it is assumed that all the ions require the maximum energy of 23 volts for their formation and that there is no decomposition of ozone. These

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[8] (a) Smyth, *Proc. Roy. Soc.*, **105**, 116 (1924); (b) Franck and Jordan in "Anregung von Quantensprüngen durch Stösse," J. Springer, Berlin, **1926**, p. 275, give 20 ± 1 volt.

assumptions are valid only as first approximations. The ionization potential for *molecular* oxygen is 15 volts instead of 23 volts, and the resonance potential is about 8 volts. As a matter of fact oxygen can be converted into ozone by ultra-violet light, which corresponds to this resonance potential (158 $m\mu$) but other evidence indicates that the ionic reactions are more important in the electrical discharge. If 8 volts is taken as the energy necessary for ozone formation instead of 23 volts, the number of ozone molecules formed for a given energy input is three times as great and if 15 volts is taken, the ratio of molecules of ozone to calculated number of ion pairs becomes 1/3.6 instead of 1/2.8.

There is considerable decomposition of ozone even at the low concentrations, and a rough extrapolation of the yield per kilowatt hour to zero current indicates a yield about three times as large as the largest yield obtained in these experiments, namely, 3 × 26 g. per kilowatt hour. This extrapolation suggests an M/N ratio of approximately 1, if an ionization potential is used for the calculation, but the extrapolation is too inaccurate and the uncertainties of analysis for the short experiments are too great to draw any conclusions.

The discharge tube contained 2.3 liters of oxygen at 1.9 millimeters' pressure, or about 1.5×10^{20} molecules of oxygen. The number of pairs of ions produced in thirty seconds was about 5.2×10^{17}, or a ratio of about 150 molecules to 1 ion if the ions retained their charges as long as 30 seconds. Actually the ratio of the concentration of molecules to the concentration of ions was *much* greater than this, because the ions were discharged very rapidly.

The large excess of molecules over ions demands a predominating mechanism which involves reactions between ions and molecules, rather than between ions and ions. It must be borne in mind, however, that although the collisions between ions and molecules predominate greatly the collisions between positive and negative ions are not entirely fortuitous, since a force of attraction tends to draw them together.

The following reactions are offered as giving a possible mechanism for ozone formation in the electrical discharge. Several other intermediate steps also may be involved.

$$O_2 = O^+ + O^-$$

$$O^+ + O_2 = O_3^+ \text{ and } O^- + O_2 = O_3^-$$

$$O_3^+ + O_3^- = 2O_3 \text{ or } O_3^+ + O^- = 2O_2 \text{ and } O_3^- + O^+ = 2O_2$$

According to these reactions, one molecule of ozone should be produced by each pair of ions and this M/N ratio of 1 is not incompatible with the experimental results of this investigation.

Other mechanisms are possible such, for example, as the formation of an ion cluster surrounding an ionized molecule (instead of an ionized atom), but at least three oxygen molecules are required for each cluster in order that it may break up into O_3 molecules, and the mass spectrograph data so far available show a high concentration of charged atoms of oxygen and very low concentration of O_6 ions.

The author desires to express his appreciation to Professor Farrington Daniels for his guidance throughout this investigation and to E. I. du Pont de Nemours and Company for the fellowship held during a portion of the time this work was in progress.

Summary

1. The formation of ozone in the glow discharge has been investigated in a closed tube at pressures from 0.2 to 2.8 mm. The ozone was determined by chemical analysis.
2. The electrodes were small, minimizing any catalytic effect.
3. The effect of the following variables on the ozone yield has been studied: (*a*) duration of discharge, (*b*) pressure, (*c*) current, (*d*) distance between electrodes, (*e*) area of electrodes, (*f*) material of electrodes.
4. An equilibrium concentration of ozone was reached in less than a minute.
5. The yield of ozone increased with increasing pressure, but at a decreasing rate.
6. The yield of ozone increased with increasing cathode area.
7. The yield of ozone was independent of electrode material, except that aluminum gave abnormally high results.
8. The highest yield obtained was 26 g. per kilowatt hour, but all yields were low on account of the decomposition of ozone.
9. A calculation on the basis of ionization potentials indicates that the number of pairs of ions and the number of molecules of ozone produced are both of the same order of magnitude.
10. The predominating mechanism of ozone formation is possibly one involving collision between monatomic oxygen ions and neutral molecules.

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