A Chemical Study of the High Frequency Corona Discharge.

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All commercial methods of making ozone take advantage of the chemical properties of a corona or silent discharge. In order to prevent the undesirable spark discharge from forming it is necessary to use some device such as a dielectric. Glass, micanite or similar insulating material interposed between two electrodes is a great aid in the formation of a discharge suitable for ozone production. Dielectrics have several disadvantages; they cannot be used at high temperatures; they are apt to be easily broken mechanically and finally they are subject to annoyingly frequent punctures. Moreover, a dielectric undergoes progressive changes which are apt to have considerable effect on the yield of ozone.

The high frequency discharge has certain advantages which have made desirable some investigations of its availability for ozone production. Because of the time necessary to build up a spark discharge from small electrodes it is possible in a suitably designed tube to have brilliant corona discharges without the use of dielectrics.

In 1896 Nikola Tesla,[1] observing the production of ozone in air subjected to the discharge from certain forms of his high-tension high-frequency coils, applied for a patent. The electrodes were parallel plates; these do not produce a form of discharge very suitable for ozone production, so that this apparatus has not achieved any commercial success. The use of a high-frequency corona discharge in reducing the molecular weight of hydrocarbons so as to render them suitable for use as gasolene has been described by Cherry.[2] By this means, he has eliminated the dielectric, which, at the temperatures used (up to 480°), would give considerable trouble. Other investigators[3] working with frequencies as high as 1,200 cycles apparently have found optimum frequencies for certain conditions.

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[1] N. Tesla. U. S. Patent 568, 177 Sept. 22, 1896.

[2] L. B. Cherry *Trans. Am. Electrochem. Soc.* 32. 345 (1917). U. S. Patent 1229, 886 July 12, 1917. Doubtless a certain amount of cracking occurs under the given conditions. Indeed the use of a corona discharge primarily for cracking has been more recently patented. Schmidt and Wolcott. U. S. Patent. 1307, 931, June 21, 1919. The use of high frequency for polymerization of acetylene has been described by Kaufman, *Ann.* 417, 34 (1918).

[3] Shenstone and Priest, *J. Chem. Soc.* 63, 938 (1898) concluded that the maximum efficiency is to be obtained with a 16 cycle discharge. Further discussion of the effect of frequency has been given by Rideal, Ozone, Van Nostrand, 1920, pp. 105-107, but it must be remembered that uncertainties as to meter readings and as to the effect of other uncontrolled variables render the conclusions drawn there of doubtful value. A comparison of a number of ammeters placed in the primary circuit of an induction coil operated on direct current showed that none of them registered the same value or even the true value as obtained from oscillographs. The maximum deviation was about 25 per cent. However, the tendency to use 500 cycles whenever available for commercial production of ozone must have some significance.

Experimental: Preliminary experiments were made with a small Tesla coil. One side of both the secondary and primary was grounded, the other end of the terminal ending in a platinum wire supported on the inside of a bell, similar to the method proposed by H. Guilleminot,[4] so that the corona discharge, which is produced under suitable electrical conditions, may ozonize the air. The Tesla coil was supplied with energy from a small induction coil. The concentrations of ozone were very small and the power yield was only 2-5 g. per killowatt hour on a basis of gross input into the induction coil. A more suitable arrangement for securing a corona discharge is a wire passing through the axis of a tube,[5] as previously used for the study of the direct current corona. At first a No. 29 platinum wire was placed in a five-inch aluminum tube. The results obtained were quite variable and it was thought that the variability of the direct current which excited the induction coil was responsible; but on applying storage battery current, the improvement was not great. An oscillographic study of the secondary current and of the voltage from a tertiary coil wound on the induction coil showed a very inconsistent wave form. Various make-and-breaks were tried without success. A 5,000 v. Thordarson type H-1 transformer was substituted and with a fairly constant source of alternating current gave results which were very much more consistent.

Description of Electrical Set-up. A very steady source of alternating current at 110 v. was applied through variable resistance to a Thordarson transformer of type H-1 whose ratio was 1:50. A condenser made of three concentric aluminum tubes, having a capacity of 0.0007 microfared, was placed in parallel with the high voltage terminals. A zinc spark gap with variable adjustment was used in an atmosphere of ether vapor. The Tesla coil was composed of four turns of wire in the primary and 200 in the secondary with an air core. The frequency was measured with a Kolster decremeter calibrated by the Bureau of Standards. The wave length varied according to the size of the wire in the tube and according to whether the measuring apparatus was connected to the tube or to the wire. With No. 29 wire, the wave length was 185 m. for the tube and 2000 m. for the wire, while with No. 16 wire, these values had increased to 260 and 300 m. respectively. The frequency, then, was in the range between 1 and 1.6 million cycles per second. Variations in the width of the spark gap and in the power-input had no effect on the wave length. Attempts to change the frequency by changing the capacity of the primary or secondary circuit of the Tesla coil or by changing the inductance of the secondary had no effect on the frequency but resulted in reducing seriously the secondary current as well as the corona discharge. Evidently an optimum set of dimensions of the circuit can be obtained for each tube according to its capacity. No attempt was made to work out the relationships involved. The electrical circuits used in this work were such as to give optimum discharge in the tube used. In other

[4] H. Guilleminot, *Compt. rend.* 136, 1653 (1903) describes an apparatus but gives no data as to its chemical possibilities.

[5] F. O. Anderegg, *J. Am. Chem. Soc.* 39, 2581 (1917).

words, the circuit must be "tuned" according to the dimensions of each discharge tube used.

Air dried by passing through sulphuric acid wash bottles and over freshly cracked potassium hydroxide was passed into one end of the corona tube at constant pressure. The flow rate was measured with the usual type of flowmeter. The corona tube was 193 cm. long and had an internal diameter of 4.65 cm. The volume with side arms was 3,402 cc. The wire was passed through small holes in glass plates which were cemented to the aluminum tube by a special wax[7] which has shown itself to be very resistant to the action of ozone. Inlet and outlet tubes were made by screwing short lengths of aluminum tubing into holes in the side of the tube near the end, and inside of these, glass tubes were sealed tight with the special wax. The first part of the absorption apparatus was made entirely of glass and the absorbing liquid was standard alkali by means of which nitrogen pentoxide, formed in the discharge, could be absorbed. The amount of ozone absorbed by the small volume of solution used was found to be well within the experimental error. To absorb the ozone two Erlenmeyer flasks were used. The rubber stopper in the first Erlenmeyer flask was protected by a very thin coating of beeswax, which was unaffected by the ozone during experiments lasting more than a year.

The procedure was to pass a corona discharge through still air enclosed within the tube or through air which was flowing through the tube at a definite rate. The pressure in the tube was maintained constant at 750 mm. The temperature was that of the room, 22-30°. Changes in temperature of 10° were shown to produce only very slight variations in yields. Results are given for different wires under various conditions of flow rate of air and under varying electrical conditions. The amperes, volts and watts of the primary circuit of the Thorardson transformer were recorded as well as the voltage across the spark gap. The current in the secondary of the Tesla coil was measured with a hot wire ammeter and reached values as high as half an ampere at 6,000-8,000 v. when the gross input into the system was less than 150 watts. A very poor power factor in this part of the circuit is thus indicated. The power factor of the circuit which excites the transformer ranged from a very low value for the feeblest coronas to 50-70% for the most intense discharges.

The material as well as the size of the wire produced changes in the discharge with corresponding changes in the chemical reactions. A platinum wire was at first used because of its supposed chemical inertness, but platinum is a material which has been found to be one of the most active catalytic substances known. Its catalytic properties seem to depend upon surface absorption and it has been noted that with continued use, as in the oxidation of ammonia, it becomes, apparently, badly corroded. This is, of course, not a true corrosion but a very large

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[7] A wax that will withstand the action of ozone and oxides of nitrogen and yet possesses desirable mechanical properties, is made by melting 5 parts of rosin, adding 3 parts of red sealing wax and then stirring in 2 parts of beeswax. Harding and McEachron, J. Am. Inst. Elec. Eng., April, 1920.

increase in the surface.[6] A platinum wire that had been used as an electrode for corona work was found to have suffered similarly. And with the increase in the surface there was a notable increase in a "lag

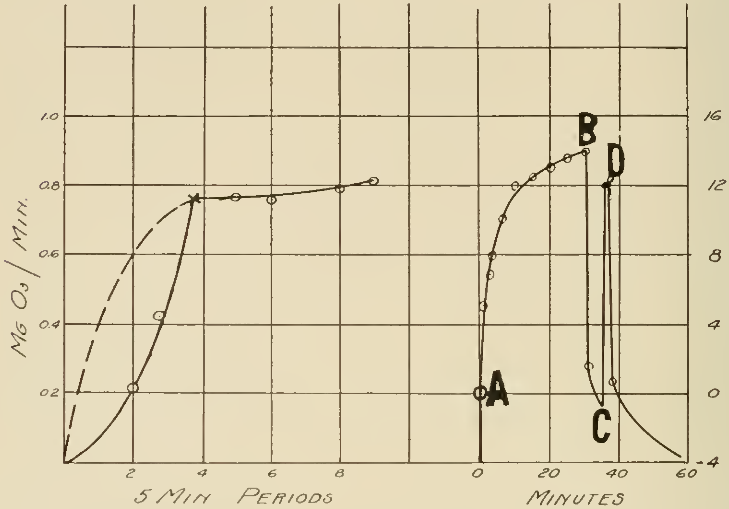

FIG. I. FIG. II.

Fig. I. The "lag effect" due to a platinum wire. A continuous discharge was passed through air flowing at the rate of 190 cc. per min. so that the air in the tube would be renewed in 18 min. The continuous line indicates the actual results for successive five min. periods. The break in this curve occurs with the elimination of the lag effect. The dotted curve shows the normal course of ozone production without any complicating lag effect.

Fig. II. Evidence of an "ionization pressure". The discharge was passed through enclosed air and the pressure was followed by a manometer containing a pure paraffin oil. At A and C the current was turned on and at B and D it was turned off. The jumps are too great to be caused by the rise in temperature.

effect". In Fig. 1 the continuous line follows the actual results obtained in a typical run. Air was passed through the apparatus continuously at a rate of 190 cc. per minute, so that the air in the tube was replaced every 18 minutes. After five minutes of discharge the outcoming air was analyzed for ozone during the second five-minute period in one analysis apparatus and during the third five-minute period in another apparatus. Average yields of ozone per minute during each five-minute period are given. The air that comes out of the tube at first contains less ozone than after it has had a chance to come in contact with the discharge during its whole passage through the tube. Because of the very marked electric wind the effect of any slower rate of flow along the walls than in the middle was largely eliminated.

[6] *Ibil*, p. 2593. A considerable amount of material is accumulating in this laboratory as to the properties and nature of this lag. It will be assembled in a separate publication. For the illustration of the charge on the surface of platinum see Rideal and Taylor, Catalysis in Theory and Practice, Longmans Green & Co., 1919.

The longer the time spent in the discharge the greater the concentration of the ozone, but, owing to the reverse decomposition of the ozone, which occurs simultaneously, the increase in ozone concentration with time should be logarithmic as indicated by the dotted curve. The lag effect has operated against ozone production at first.

An iron wire was also found to be unsuitable because of the large magnetic losses with high-frequency currents. A copper wire was found to be much more suitable, although it became gradually oxidized and covered with more or less nitrate with some "lag effect", although much less than with platinum wires. Aluminum was found to be the best material for ozone production.

An interesting "ionization pressure" has been noted at the University of Illinois by Kunz and his students.[7a] The same effect was observed with the high-frequency corona. In Fig II are plotted some results. The discharge was passed through enclosed air and the pressure changes were followed by means of a manometer filled with the purified paraffin oil called "stanolax". At A the discharge was started and stopped at B; after three minutes it was started again at C and at the end of one more minute of discharge was again discontinued. The sharp breaks are mostly due to the ionization pressure. They are much too sharp and extended to be caused simply by the heating of the gas. At the end the pressure drops below that of the atmosphere, indicating some kind of condensation reaction such as ozone formation.

Typical results are given in Figs. III, IV and V. In Fig. III a No. 33 copper wire was used and the data for one spark gap width

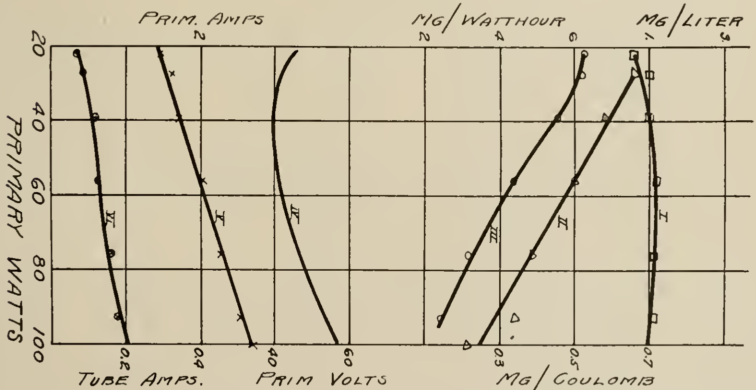

Fig. III. A No. 33 copper wire was placed co-axially in an aluminum tube. The air flow rate was 280 cc. per min. The spark gap-width was 1.2 mm. Six variables are plotted against the gross primary watts as abscissa. I. gives the concentration curve in mg. per liter (g. per cu. M.). II. expresses the yield of ozone in mg. per coulomb of current flowing into the discharge tube. The efficiency of ozone production is plotted in curve III. in terms of mg. per watt hour (g. per kilowatt hour). The other three curves give the electrical readings; IV. for the primary volts; V., the primary amperes and finally VI. gives the amperes of the discharge current as measured by a hot-wire ammeter.

[7a] *Phys. Rev.* 8, 285 (1916) ; 10, 483 (1917).

are given. Results with other spacing of the spark gap with this wire and with other sizes of copper wire are essentially similar. With a No. 18 wire of copper or, better, aluminum, the efficiencies are increased two or three times, while the concentrations are often doubled. In this figure the points of interest are the similarity of the curves for primary amperes and for tube amperes, a direct proportionality usually existing. The voltage, on the other hand, as a rule requires a high value in order to start the spark gap and then falls to a minimum. In most cases, the efficiency of the process as expressed in g. per kilowatt-hour (mg. per watt-hour) runs closely parallel to the curve for the yield of ozone per coulomb as calculated from the hot-wire milliammeter in the tube circuit. Usually, also, the concentration is increased at the expense of efficiency, although there are certain conditions where this generalization does not hold. In Fig. III the efficiency is constantly decreasing because in the short distance of the spark gap the tendency of the spark is to change over in characteristics toward a power arc,

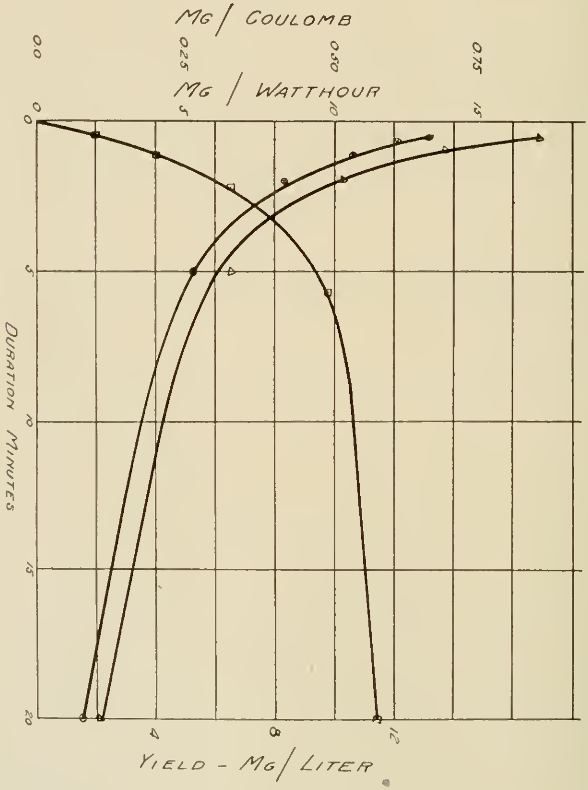

Fig. IV. Enclosed air was subjected to discharge in the same tube provided with a No. 12 wire. The gross power input into the tube was 65 ± 2 watts. The spark-gap was set at 2.0 mm. Note the reciprocal relation of the concentration and efficiency curves, characteristic of *nearly* all chemical reactions in corona discharges.

so that the energy expended in the tube is not proportional to the primary energy. In Fig. IV, where air enclosed within the tube is subjected to discharge for different periods of time, the concentrations are increased with time but at a loss of efficiency owing to the simultaneous decompositions of ozone, such as occurs also with very low frequencies or direct current.[8] In this way, concentrations up to 15 g.

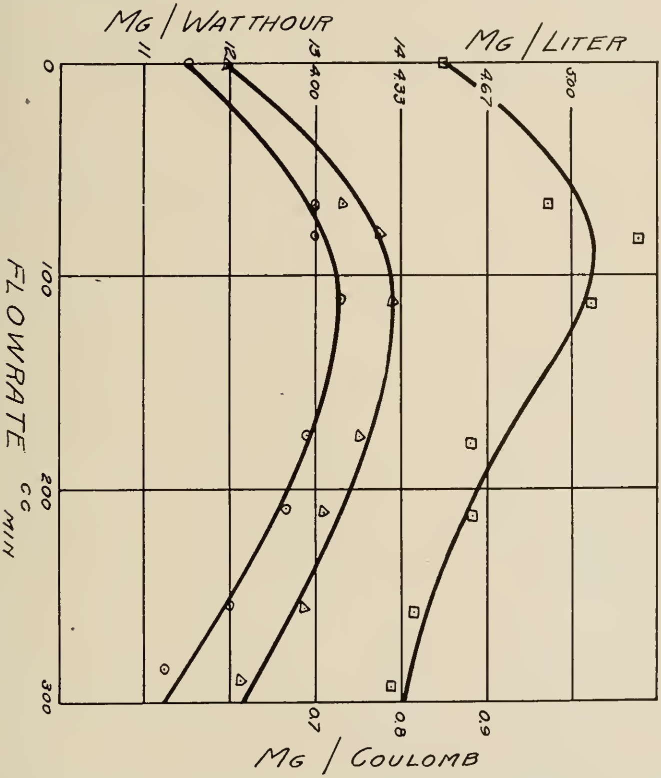

Fig. V. The rate of flow of air through the tube was varied. The length of discharge was 1 min., after which the tube was swept out completely. A No. 18 wire was used and the primary power was 75 2 watts. The spark-gap was set at 2.00 mm.

per cubic meter (mg. per liter) were obtained. In Fig. V an optimum flow rate is indicated for the given conditions. Similar optima have been previously obtained with different types of 60-cycle ozonizers.[9]

The size of wire has a marked effect on the optical and chemical properties of the discharge. Around a fine (No. 33) wire there is a

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[8] Chassy, *Compt. rend.* **133**, 789 (1901) with a Berthelot ozonizer and 60 cycle current. Anderegg, *loc. cit.*, gives curves for a direct current discharge in oxygen. The shapes of these curves have been checked by A. C. Grubb and J. K. Stewart working independently in this laboratory with current rectified by a kenotron.

[9] Ray and Anderegg, *J. Am. Chem. Soc.* **43**, 967-78 (1921), observed an optimum flow rate with the 60 cycle discharge in apparatus A. It was also noted with the very large apparatus E for both ozone and nitric acid production.

weak, nearly uniform glow extending only 4 or 5 mm. from the wire before it tends to break into a spark. With No. 24 wire, fine streamers or brushes are noticeable which become the chief characteristic of the discharge around a No. 18 wire. A No. 12 wire was tried, but the effect was to reduce the radius of curvature so much that sparks were the only form of discharge which could be produced.[10] A No. 16 wire gave the same effect, but, remembering Vosmaer's experiments on space distribution,[11] a number of small points were filed on this wire from which magnificent brushes would be thrown out sometimes to distances estimated as half of the radius. The resonance range under these conditions is narrow and easily overstepped, so that while the discharges most brilliant optically and most effective chemically occurred around a No. 16 wire with points, yet very small surges of power tended to throw them over into sparks with greatly diminished yields. Better total yields are obtained with smaller wires, thus sacrificing erratic for more reliable, although less intense, effects.

Under the best conditions ozone was produced at an efficiency of from 15 to 17 g. per kilowatt hour calculated on a basis of gross power input. No attempt was made to determine the efficiency of the process on a basis of the power delivered from the secondary of the transformer because of the uncertainty in obtaining the tare of the transformer. However, certain considerations indicate that it had a rather large tare, so that with a properly designed transformer the efficiency would have been doubled, or possibly trebled. The loss of energy in the spark gap varied, of course, with conditions. To determine the value the spark gap was enclosed within a water-tight container and immersed in a large calorimeter which had been calibrated with electrical energy. The results at 80 and 110 watts gross input indicated a loss of the total energy supplied to the transformer of 12 and 15%.

The concentration of oxides of nitrogen produced in the corona discharge was 0.005-7% by volume. For every molecule of nitric oxide formed there were produced from 70 to 90 molecules of ozone. When, however (as around a No. 16 wire), a spark played more or less intermittently, the concentration of oxides of nitrogen as well as their ratio to ozone was materially increased. Two runs were made with a discharge in which almost continuous sparking predominated, accompanied by some corona. With a gross input of 120 watts, 41 mg. of nitric acid was obtained in 20 minutes at a flow rate of 95 cc. per minute, so that the concentration was about 0.8% by volume (21 mg. per liter). A 40-minute run at a flow rate of 200 cc. per minute produced 90 mg., reducing the concentration nearly half. The efficiency in each case was a little more than 1 g. nitric acid per kilowatt hour. This method offers little promise as a means of nitrogen fixation under these conditions but might be effective at high temperatures.

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[10] The larger wire increases the capacity and tends to throw the circuit out of resonance. With the reduction in radius of curvature of the smaller electrode, the condition of parallel plates is approached.

[11] Vosmaer, Ozone, Van Nostrand, 1916, pp. 56-64. Incidentally, this question of space distribution has resulted in a very larger variety of possible modifications, many of which have been patented.

It has been thought[12] that one of the benefits of a high-frequency discharge might be in setting up so great a vibration with the molecules as to loosen the bonds so that new combinations might take place. A simple calculation would show that the intensity factor of this form of energy is much too small to have appreciable effect in any way except, possibly, upon the loosest of secondary valence combinations. This resonance result must not be confused with the results produced by ionic bombardment of molecules in the large voltage gradients of the corona discharge; nor should it be confused with the very real chemical action of the ultra-violet radiation accompanying any corona discharge.

Summary.

1. This study of the production of ozone in a high-frequency corona discharge indicates that it is governed by the same laws that control its production in either low-frequency or direct-current corona discharges.

2. With the use of high frequency, the discharge apparatus itself is simplified through elimination of any dielectric. This point is of especial value for high temperature work.

3. On the other hand, the apparatus for supplying the electrical energy is much more complicated than for low frequency. This results in greater first cost and in increased energy losses, with consequent decreased efficiency.

4. The conditions which give the most intense discharge with greatest ozone production narrow the resonance range so that small surges of power tend to shift the discharge from corona to spark.

5. The high-frequency discharge is unsuitable for the oxidation of nitrogen. Where ozone is desired, the rather low concentration of oxides of nitrogen is an advantage, but even in the spark discharge the amount of nitrogen oxidized indicates a very low efficiency.

6. In order to use additional discharge units, it would be necessary to "retune" the high-frequency circuits.

7. Even a frequency of a million and a half cycles per second would have little, if any, effect in loosening the chemical bonds.

8. Some evidence is given of a "lag effect" when platinum wires are used.

9. The existence of an "ionization pressure" is indicated in a high-frequency corona discharge.

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[12] L. B. Cherry, *loc. cit.*, offers this explanation. But consideration of the energy of the radiation needed to activate carbon compounds indicates that it requires a frequency of 10^{14}-10^{15}, an order of magnitude quite different from the value of 10^5-10^6 cycles per second of the wireless waves set up in his discharge apparatus.