A TYPE OF SILENT DISCHARGE INVOLVING CATALYSIS.

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The complications occurring at the solid surfaces in contact with electrical discharges are not generally appreciated. As a result of considerable study of chemical reactions in corona discharges the fact that the solid-gas interface introduces variable factors has become more and more evident. From a knowledge of the phenomena involved in contact catalysis it has become increasingly clear that these two apparently unrelated phenomena may be interdependent. The result of this dawning consciousness has led to a study of catalysis in chemical reactions in corona discharges, the first report of which is given here.

The theory of the action of a dielectric material in an electric field was first given by Faraday[1], who showed that the attraction between charged bodies is inversely proportional to the dielectric constant of the

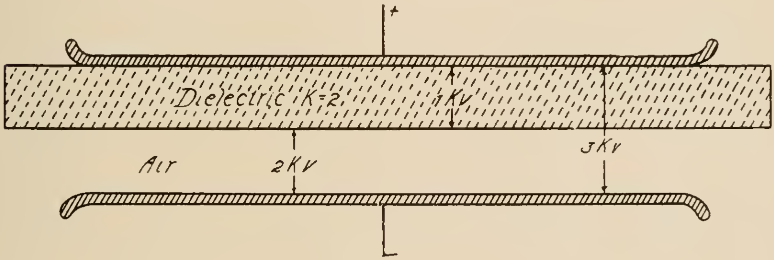

Fig. 1. The interposition of a dielectric material of constant 2 has increased the potential drop in the remaining air space from 1.5 to 2 Kv.

material separating them. Then, when equipotential lines are drawn (normal, of course, to the lines of force), they will be spaced in proportion to the dielectric constant of the material used. The term, specific inductive capacity, is more illustrative of the effect but its length militates against its use. If sheets of dielectric material, such as glass, are placed against one or both of parallel electrodes without filling the whole space between them, there will be a distribution of equipotential lines as given in figure 1. The equipotential lines are close together in the gas filled space so that there is a large potential gradient in the gas. It may be helpful to remember the analogy to contour lines on a map. If the potential is sufficient the gas "breaks down", that is, some of the molecules are ionized and a silent or corona discharge is set up. The presence of solid dielectric *tends* to prevent sparking or arcing over, so that with a suitably designed apparatus it is possible to fill the whole of the space with a corona of high density. If a rod of glass or other dielectric material is placed between parallel electrodes the effect of the lines of force is as given in figure 2[2]. On placing two

[1] Jeans. Electricity and Magnetism. 4th Ed. pp. 126-135 (1920).
[2] Jeans, loc. cit., p. 228.

"Proc. 38th Meeting, 1922 (1923)."

rods in contact it is seen (figure 3) that the space of closest contact is one of high potential gradient. This device of using glass rods in an electric field has been tried out at Purdue by K. B. McEachron[3], who has obtained some high yields of ozone.

Similar reasoning would show that a sheet of dielectric material between two parallel electrodes would produce no distortion of the field. This theory has been tested experimentally by C. W. Rice[4] using glass cylinders with experimental conditions such that there were no "end effects". It was found that the presence of the cylinder always lowered the arc-over voltage. The condition of the surface and especially the nature of the gas or vapor adsorbed on it were found to have important effects. Moisture is always very potent in aiding the arc-over[5]. These observations led to the idea that the mechanism of this promotion of arc-over was catalytic in nature. Just as solid surfaces promote chemical reactivity by adsorbing the reacting substances and activating them by loosening their bonds so here the adsorbed molecules

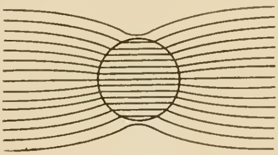

Fig. 2. The lines of force in an electric field are distorted by a rod or sphere of dielectric material.

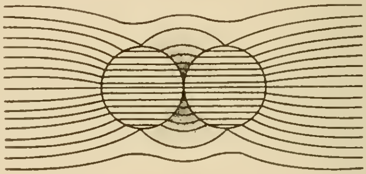

Fig. 3. Two such bodies in contact distort the lines of force as shown. The maximum discharge in the gas occurs in the shaded areas.

in an activated condition would be much more easily ionized and would aid materially in establishing a path of discharge[6].

For this catalytic action of promoting creepage along the surface the name, "creepage corona" is proposed. In any discharge involving dielectrics there will be two effects, that of the specific inductive capacity in increasing the discharge density and the creepage action in increasing the discharge current. In addition, the purely catalytic effect on any chemical reactions of the solid-gas interfaces will produce effects which

[3] McEachron and George. Purdue Univ. Eng. Exp. Sta. Bul. No. 9. pp. 58-108 (1922).

[4] C. W. Rice. Trans. Am. Inst. Elec. Eng. 36, 1947 (1917).

[5] This action of moisture is due to the polarity of the water molecule. Replacing the polar water with nonpolar oil lowers the creepage effect and raises the arc-over potential.

[6] G. V. Hevesy. Z. Physik. *10*, 80-3 (1922), who found that small crystalline conglamerates had fifty times the conductivity of large crystals, explains the results as due to "loosened spots" in the crystal lattice which would result in an irregularity in the order of the ions especially at the surfaces. H. S. Taylor. Chem. Age. *30*, 309; J. Franklin Inst. *194*, 1 (1922), explains the catalytic action of reduced copper on the reduction of copper oxide at the point of contact of the two phases, as due to a distortion of the adsorbed reducing gas when in contact with the different electronic configurations in the two phases.

superimposed on the other, are apt to be rather too complicated for theoretical treatment. The conclusion that the effects are in large part catalytic, is seen to be justified from the following experiments.

EXPERIMENTAL. A Liebig condenser forms a convenient laboratory apparatus for testing the effects of different dielectric materials upon various combinations of gases. The outer jacket with its cooling water running through serves as one electrode and it is convenient to use an aluminum wire at the axis of the tube for the other electrode. Aluminum is covered with a very coherent coating of oxide which decreases its catalytic activity, apparently as far as the corona discharge is concerned. A small experimental transformer with the ratio of 120:1 was used and the connections are given in figure 4. The power actually supplied to the tube has not been determined in these first experiments. The secondary voltage was simply obtained from the transformer ratio

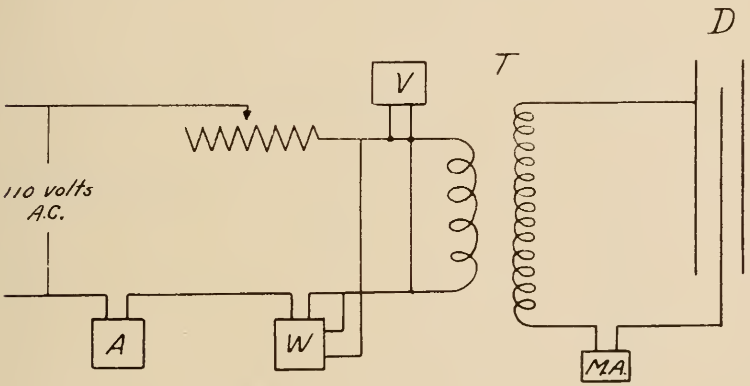

Fig. 1. Diagram of connections.

and the reading of the voltmeter. Air, carbon monoxide and mixtures thereof freed from carbon dioxide and moisture have been studied. The arrangement of the apparatus is indicated in figure 5.

The dielectric materials experimented with have included fragments of ordinary glass rods, of quartz glass, of earthenware (clay marbles) with and without impregnation with beeswax. Crystalline hematite, as well as white and blue flint were also used in addition to glass wool. Some experiments were made with no fragments of dielectric material around the inner wire electrode. The actual density of the space when packed with glass fragments was twice that when packed with glass wool. The surface of the glass wool, was however immensely the greater, resulting in enhanced chemical effects.

Some of the curves obtained for ozone formation[7] in air are given in figure 6 while figure 7 gives similar results for nitric acid yields. Figure 8 gives typical curves for the simultaneous production of both ozone and nitric acid in contact with white flint. With the increase in

[7] Proc. Ind. Acad. Sci. 1921, p. 159, for details of analysis.

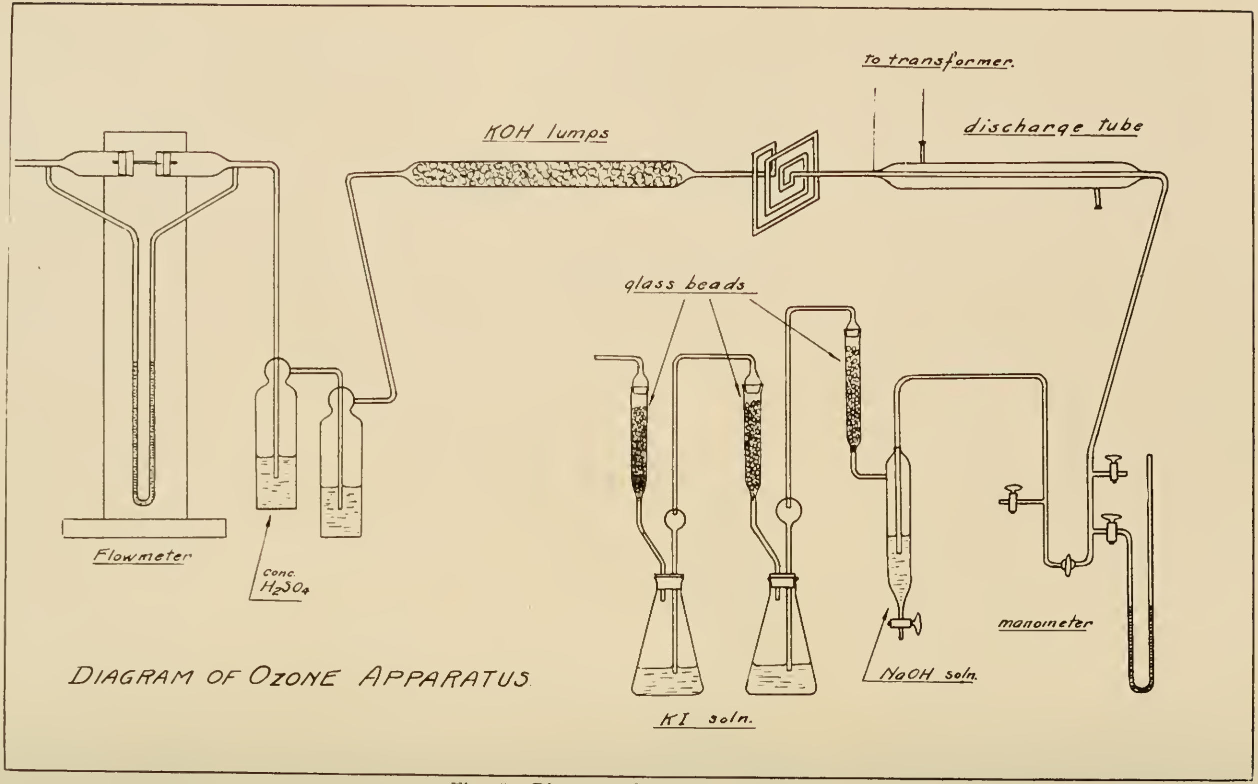

Fig. 5. Diagram of ozone apparatus.

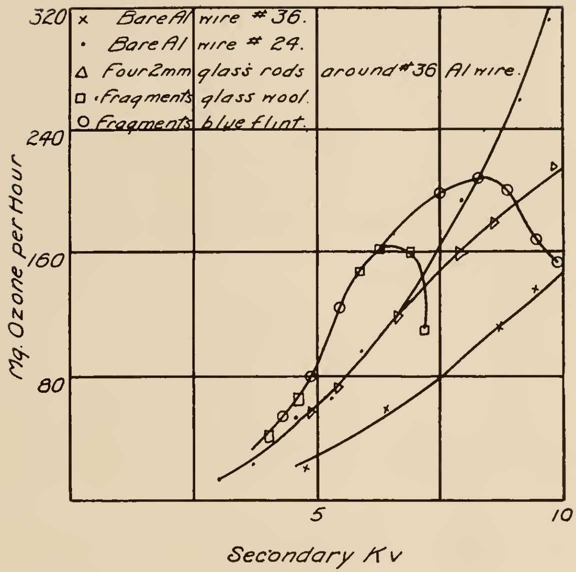

Fig. 6. Ozone formation with and without fragments of dielectric material in contact with the discharge.

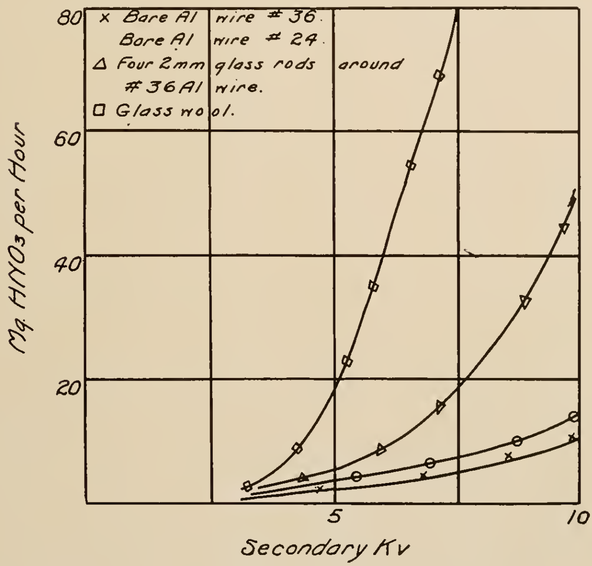

Fig. 7. Nitric acid formation with and without fragments of dielectric material in contact with the discharge.

the intensity of the discharge the amount of nitrogen activated increases. The ozone or ozone forming activated oxygen is used up to combine with this nitrogen and then to further oxidize to nitrogen pentoxide. Incidentally, with the increase in the intensity there is more local heating and catalytic decomposition of ozone. These sometimes have, with rising voltage, a periodic increasing and decreasing in which the opposite slopes of the ozone and nitric acid curves are the noteworthy feature. Blue flint has been found to be the best material for the production of ozone except at very high voltages when no dielectric material is desirable. Glass wool is much more effective than glass rods for the oxidation of nitrogen.

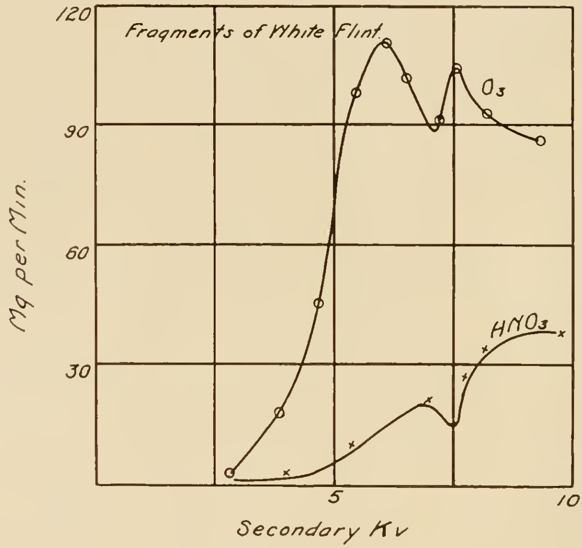

Fig. 8. Ozone and nitric acid formation in contact with fragments of white flint. Note the depressing action of the higher yields of nitric acid on ozone formation.

The curves for the decomposition of carbon monoxide are remarkably similar in shape to the curves for nitric acid production and so have not been given. The color of the discharge in carbon monoxide is worthy of remark. It is a pale light green, sometimes with a bluish tinge. With increase in air content it shifts over into the characteristic purple of resonant nitrogen. A tube which had been subject to discharge for some time was suspected to have carbon deposited on the fibers of the dielectric, glass wool. On letting in air and continuing the discharge some beautiful scintillations were observed. Little threads of fire would creep along the fibers and branch out to connecting fibers in a spectacular fashion. The notable differences in the results with different dielectric materials are due to catalytic action at the surfaces.