

ORGANIC REACTIONS IN GASEOUS ELECTRICAL DISCHARGE  
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(Received September 4, 1930)

## ABSTRACT

An apparatus is described for subjecting vapors to an electrical discharge. Vapor pressure and current are variable. Different fractions of the gaseous reaction products can be collected and their rates of accumulation measured. A study of n-decane vapor with this apparatus, with current values of from 0.5 to 2.5 m.a., voltage approximately 450 volts, and pressures from 0.2 to 4.5 mm of mercury, indicates that electric conduction in gases may follow an electrochemical equivalence law similar to Faraday's law of electrolytic conduction in liquids. Evidence has been obtained showing the amount of reaction to be proportional to the current, and independent of voltage and vapor pressure. Among the reaction products is a wax-like substance which deposits on the cathode only. The rate of production of gaseous reaction products has been measured for various values of discharge currents and vapor pressure. Curves and tables are given showing the relation between molecular size and rate of production of various fractions of the gaseous reaction products, for a series of seven normal paraffin hydrocarbons. A brief theoretical discussion is given.

## INTRODUCTION

OF THE many investigations of electrical discharges in gases the greater part has been carried out with stable gases, whereas gases which undergo chemical changes in the discharge have been comparatively neglected. The work described below is the first set of a series of measurements which may eventually include all available hydrocarbons, and possibly also some oxygen-containing compounds, such as alcohols, ethers, ketones and esters. The purpose of the investigation is to try to shed some light on chemical action in electrical discharge, and to contribute something to the knowledge of the relation between molecular structure and chemical reactions, especially in regard to hydrocarbon chain structure.

## APPARATUS AND PROCEDURE

The apparatus (Fig. 1) consists of a bulb *E* for containing the liquid hydrocarbon, the discharge chamber *D*, the trap *T*, the mercury vapor pump *P*, and the storage chamber *S*, from which tubes *G* and *F* lead to a McLeod gauge and oil pump respectively. The bulb *E* can be immersed in a constant-temperature bath and runs made at constant vapor pressure. The discharge chamber *D* consists of a two-liter Pyrex bulb; the purpose of the large volume being to minimize any possible influence of the walls on the chemical

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action. The two aluminum disk electrodes are about 2.5 cm in diameter and about 8.5 cm apart. They are mounted on heavy, glass-covered tungsten wires which in turn are sealed through ground glass stoppers, so that the electrodes may be removed from the bulb for cleaning. The trap *T* is of the ordinary type except that there is a ground joint near the top to facilitate cleaning, and the inside tube is cut shorter than usual and is flared at the end to prevent clogging by frozen hydrocarbons. The storage chamber *S* has a capacity of about 13 liters. The electrical energy for the discharge is supplied by a transformer in series with a single kenotron.

When the apparatus is in operation a continuous current of vapor flows from *E* to *T* where it condenses. The chamber *D* is therefore filled with hydrocarbon vapor whose pressure is determined by the temperature of *E*. In the few cases where runs were made at temperatures higher than that of

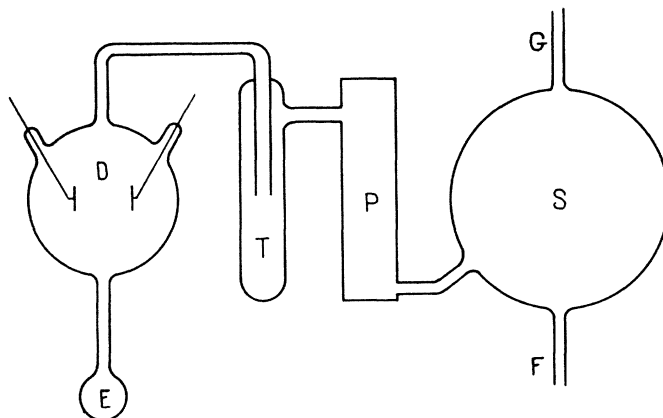


Fig. 1. Diagram of apparatus.

the room, *E* was removed, the hydrocarbon was placed in *D* itself, and *D* was entirely immersed in a constant-temperature bath. The runs were all made with such a high rate of vapor flow from *E* to *T* that all gaseous reaction products were swept out of *D* before there was any appreciable reverse reaction. This was shown by the fact that the results were independent of the vapor pressure, and consequently of the rate of flow. The discharge may therefore be considered as taking place through essentially pure hydrocarbon vapor.

Either liquid air, or a slush of carbon dioxide snow and ether was used as a refrigerant for the trap *T*, depending upon what fraction of the gaseous products it was desired to collect. With carbon dioxide cooling, n-hexane vapor was found to pass easily through the trap, while n-heptane was stopped. Since the vapor pressures of these two substances at  $-77^{\circ}\text{C}$  are about 0.1 and 0.02 mm of mercury respectively, it can be concluded that substances of vapor pressures below 0.02 mm at the temperature of the trap will not pass, whereas those of vapor pressures above 0.10 mm will pass. This means, for example, that in the normal paraffin series, with liquid air cooling, only

H<sub>2</sub>, CH<sub>4</sub> will pass, while with carbon dioxide cooling H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, . . . , C<sub>6</sub>H<sub>14</sub> will pass, and higher members of the series will be stopped.

Runs were made on seven normal paraffin hydrocarbons, n-pentane, n-hexane, n-heptane, n-octane, n-decane, dodecane, and n-tetradecane. All were obtained from the Eastman Kodak Company, and were of the highest degree of purity provided by them, except n-pentane which was the "practical grade." However it is believed that small amounts of impurities have no appreciable effect on the phenomena reported here, since in a series of about fifty runs, made on the same sample of n-decane, the results toward the end of the series were the same as at the beginning. A similar observation was made also with some of the other hydrocarbons, but the number of runs was not so great.

### RESULTS

The discharge was run with currents from 0.5 to 2.5 m.a. for the n-decane measurements, and 1.0 m.a. for the other substances. The voltage could not be varied independently; it made wide fluctuations (sometimes as large as 25 percent) about 500 volts for all compounds. In appearance the discharge was essentially the same for all hydrocarbons investigated. There was only a very slight visible glow around the cathode, and frequently none at all. The glow was most apparent at the lower pressures, and hardly perceptible at all at pressures as great as 1.0 mm. The most conspicuous feature was the large number of sparks scintillating on the surface of the cathode. The sparks were small and bluish, and appeared in about equal numbers on the back and front of the disk. At the beginning of a run, when only a thin layer of wax had formed, they appeared evenly distributed, but later on, became more or less concentrated in small regions or spots. These spots finally became black as if the wax had been carbonized. Sparks also appeared on the surface of the anode, but they were much fewer in number and did not shift about, remaining fixed and glowing for minutes at a time. They were yellow or white rather than blue in color.

Previous work has shown that in general the effect of an electrical discharge in a hydrocarbon gas is to cause an apparently complicated chemical reaction resulting in solid, liquid and gaseous products. With the writer's apparatus the solid products were deposited mostly upon the cathode with slight traces of deposits on the glass walls, the gaseous products were pumped over into the storage chamber *S*, while the liquid products (if any) condensed in the trap. However, no evidence of liquid products was found, the same sample of n-decane having been run through the apparatus about fifty times without showing evidence of contamination or change of any sort.

The wax which formed on the cathode has not been analyzed by the writer, but analyses of similar, if not identical compounds by others<sup>1</sup> indicate

<sup>1</sup> S. C. Lind, *The Chemical Effects of Alpha Particles and Electrons*, The Chemical Catalog Co., 1928, Amer. Chem. Soc. Monograph No. 2, page 158. C. F. Hirshfeld, A. A. Meyer, L. H. Connell, *Study of the Mechanism of Cable Deterioration*, Detroit Edison Co., printed but not published by the Association of Edison Illuminating Companies, 1928, page 111.

that it is a complex hydrocarbon of high molecular weight. It is insoluble in all common organic solvents.

The gases produced by the discharge were pumped into the chamber *S*. Typical curves showing the pressure increase are given in Fig. 2, in which

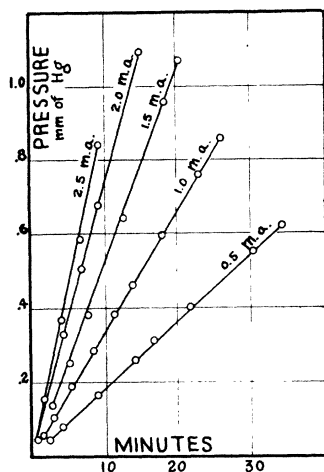


Fig. 2. Pressure-time curves for n-decane for various values of discharge current.

the time of duration of the discharge is plotted horizontally, and the pressure in *S*, vertically. Curves are given for five different values of discharge current from 0.5 to 2.5 ma., as indicated. The graphs are straight lines

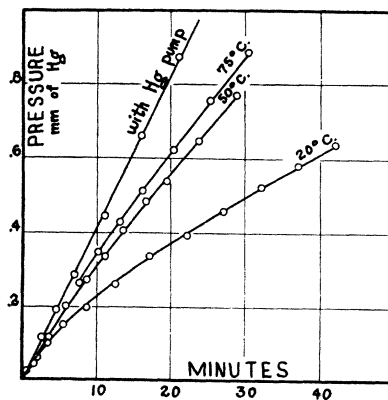


Fig. 3. Pressure-time curves showing effect of accumulation of reaction products on rate of reaction in n-tetradecane.

through the origin. Runs of a duration of 80 minutes showed no departure from this linear relationship. This is true in spite of the fact that at the beginning of the run the electrodes were clean whereas at the end the cathode

was coated with a heavy layer of wax. It seems that the wax deposit on the cathode has no effect on the production of gas.<sup>2</sup>

A linear relation between pressure and time is not found unless the gaseous products are removed from the reaction chamber sufficiently fast. If the mercury pump *P* is not in operation the products will be removed from *D* only by the pumping action of the vapor stream flowing from *E* to *T*. In most cases this will not effect a complete removal. Fig. 3 shows graphs for n-tetradecane. The three curved lines were obtained with the liquid hydrocarbon held at 20°, 50°, and 70°C, as shown. The straight line was obtained with the pump *P* in operation. It can be seen that the curved lines have at the origin the same slope as the straight line, but their slope decreases as the

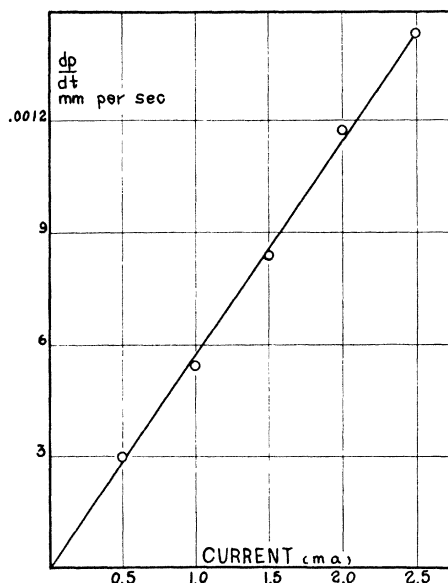


Fig. 4. Proportionality between discharge current and rate of reaction in n-decane.

discharge continues. This is probably due to the accumulation of reaction products in *D*, and consequent reverse reactions, or conduction of current by non-reacting ions. These hypotheses are supported by the fact that as the temperature of the liquid hydrocarbon is raised, and the rate of flow of vapor from *E* to *T* thereby increased, the pumping action of the vapor stream increases, the reaction products are more efficiently swept from *D*, and the curves approach closer to the straight line. A similar result was obtained with n-decane.

Plotting the slopes of the lines of Fig. 2 against discharge current, a straight line passing through the origin is obtained, as shown in Fig. 4.

<sup>2</sup> J. C. McLennan, M. W. Perrin, H. J. C. Ireton, Proc. Roy. Soc. **125**, 246 (1929), bombarded with cathode-rays a similar wax formed from acetylene and found no evidence of gas evolution.

The numerical data are given in Table I. This indicates that under the conditions of this experiment, the relation between current and rate of reaction is of the type,

$$dp/dt = ki \quad (1)$$

where  $k$  is a constant depending only on the kind of hydrocarbon, and  $i$  is the current. In other words it seems that conduction in gases may follow an electro-chemical equivalence law similar to Faraday's law of electrolytic conduction in liquids. It appears quite certain however, that the mechanism in the case of gases must be very different from that of electrolysis.

TABLE I. Rate of production of gas in *n*-decane vapor for various values of discharge current.

Current (m.a.)	$dp/dt$ ( $-77^{\circ}\text{C}$ )
0.5	0.000300
1.0	.000546
1.5	.000842
2.0	.001180
2.5	.001441

The rate of reaction has been found to be independent of pressure and the voltage between the electrodes. There is some evidence that it is independent also of the distance between the electrodes. These points are discussed somewhat more in detail below.

(1) *Effect of pressure.* Table II gives  $dp/dt$  for different pressures, with carbon dioxide cooling on the trap. It will be seen that  $dp/dt$  is constant,

TABLE II. Rate of gas production and vapor pressure.

Hydrocarbon	$t^{\circ}\text{C}$	V.P. (mm Hg)	$dp/dt$ ( $-77^{\circ}\text{C}$ )
dodecane	0		0.000645
	22		640
n-decane	0	0.20	547
	22	1.25	555
	24	1.50	539
	40	4.50	533
n-octane	-15	.90	523
	0	2.95	511
n-heptane	-20	.63	800
	-17	.80	867
	0	11.45	816

within the experimental error, over a wide range of pressures, for a given compound. In the case of n-heptane the pressure change is over 1700 percent, whereas the corresponding change in  $dp/dt$  is only 2 percent. The vapor pressure data for dodecane were not available, but are probably similar to those of n-decane.

(2) *Effect of voltage.* Although it was not possible to determine the effect of different voltages by independently varying the potential difference between the electrodes, the automatic fluctuations in this quantity during the course of the runs served the purpose. These voltage changes were commonly as large as 25 percent yet no effect due to them was noticeable. The pressure-time curves were always straight lines as shown in Fig. 2. Hence it appears that if the current is held constant, the rate of reaction is unaffected by changes of potential difference between the electrodes.

(3) *Effect of electrode spacing and shape.* For the n-decane runs, two discharge bulbs were used, which were similar except that the distance between the electrodes was 5.5 cm in one and 8.5 cm in the other. The first gave as an average  $dp/dt = 0.000546$ , while the single run made with the latter gave  $dp/dt = 0.000521$ . Since the positive column was longer in the second case than in the first it can be concluded that in the case of n-decane any action which may occur in the positive column must be negligible in comparison with that occurring near the cathode.

As a further test of the locus of the reaction a point electrode about 1.0 mm in diameter and 1.0 cm long was substituted for the disk-shaped cathode. The electrode spacing was 8.5 cm. This gave  $dp/dt = 0.000660$ , an increase of about 27 percent over the rate obtained with the disk electrode. This indicates that the reaction goes to completion in the gas phase rather than on the electrode surface, but the difference is not sufficient to make the result conclusive.

Results similar to these have been obtained by a few other workers for other substances. Kirkby<sup>3</sup> studied the synthesis of water in the glow discharge and obtained a linear relation between current and amount of water formed. He also observed that most of the action occurred in the neighborhood of the cathode and that this was independent of pressure. Günther-Schulze<sup>4</sup> found the rate of reaction to be proportional to the current for the synthesis of water in the glow discharge for currents from 20 to 120 ma. The rate was independent of pressure. He found similar results for the synthesis of ammonia. A. Keith Brewer and J. W. Westhaver<sup>5</sup> have made an extensive study of the synthesis of ammonia, and also nitrogen dioxide. They also find proportionality between current and rate, and independence of pressure. They show that most of the reaction occurs in the neighborhood of the cathode and that it apparently goes to completion in the gas phase rather than on the surfaces of the walls or cathode.

The rates of gas production for each of the seven normal paraffin hydrocarbons are given in table III, and shown graphically in Fig. 5. These rates are for a current of 1.0 m.a. The subscripts -77 and -182 indicate the use of carbon dioxide and liquid air, respectively, as the refrigerant on the trap.

<sup>3</sup> P. J. Kirkby, *Phil. Mag.*, [6] **7**, 223 (1904); **9**, 175 (1905); **13**, 289 (1907); *Proc. Roy. Soc. A***85**, 151 (1911).

<sup>4</sup> A. Günther-Schulze, *Zeits. f. Physik* **21**, 50 (1924).

<sup>5</sup> A. Keith Brewer and J. W. Westhaver, *J. Phys. Chem.* **33**, 883 (1929); **34**, 159 (1930); **34**, 554 (1930).

TABLE III. Rate of gas production for normal paraffins (discharge current = 1.0 m.a.)

Hydrocarbon	Formula	$\frac{dp}{dt}$ ( $-77^{\circ}\text{C}$ )	$\frac{dp}{dt}$ ( $-182^{\circ}\text{C}$ )
n-pentane	$\text{C}_5\text{H}_{12}$	—	0.000208
n-hexane	$\text{C}_6\text{H}_{14}$	0.000757	.000173
n-heptane	$\text{C}_7\text{H}_{16}$	.000828	.000167
n-octane	$\text{C}_8\text{H}_{18}$	.000510	.000163
n-decane	$\text{C}_{10}\text{H}_{22}$	.000546	.000174
dodecane	$\text{C}_{12}\text{H}_{26}$	.000642	.000291
n-tetradecane	$\text{C}_{14}\text{H}_{30}$	.000702	.000346

The rates are expressed in mm of mercury per second increase in pressure in the storage chamber S.

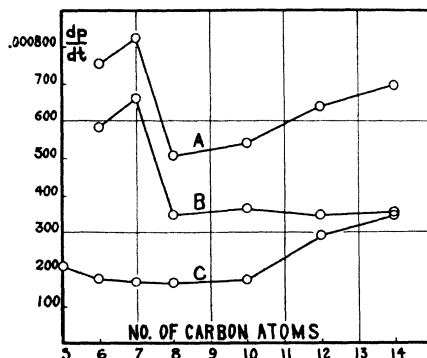


Fig. 5. Relation between molecular size and rate of reaction. Curves A and C represent data taken with carbon dioxide and liquid air respectively as refrigerants. Curve B was obtained by subtracting C from A.

In Fig. 5, curve A represents the rates of gas production with carbon dioxide cooling, curve C with liquid air cooling, while curve B was obtained by subtracting C from A. Although the writer has made no analyses of the gases collected, some idea of their composition may be obtained from these curves. Obviously they must be hydrocarbons or hydrogen. As was stated above, those having a vapor pressure greater than 0.1 mm at the temperature of the trap will pass through it, whereas those whose vapor pressure is less than 0.02 will be stopped. Hence the gases represented by curve C likely include hydrogen and methane, their vapor pressures being well above the limit. Ethylene, propylene and acetylene may also be present, for their vapor pressures, although not available for this temperature, may also be above the limit. Hirshfeld, Meyer, and Connell<sup>6</sup> have analysed the gases given off when liquid normal paraffins are rayed with cathode-rays from a Coolidge cathode-ray tube and found them to be made up of from 72 to 91 percent of hydrogen, 1.8 to 3.0 percent of methane, and 6.3 to 26.4 percent of undetermined light hydrocarbons. Reference to Fig. 5 will show that in a

<sup>6</sup> C. F. Hirshfeld, A. A. Meyer, L. H. Connell, *Study of the Mechanism of Cable Deterioration*, 1929. (See reference 1.)



gaseous electrical discharge a considerably smaller percent of hydrogen is obtained, curve *C* representing the maximum possible amount. On the other hand, the light hydrocarbons are present in larger amounts as shown by curve *B*. This may be due to the lower energy of the impacting electrons in the gaseous discharge. Or, it may be due to the longer period of bombardment in the cathode-ray experiments, in which the liquid hydrocarbons were exposed to the rays for periods of a few hours length. Polymerization and condensation may therefore have progressed further.

Heptane and hexane show a much greater production of light hydrocarbon gases than the others, as is shown by the hump in curve *B*. For these two substances the pressure-time curves (with carbon-dioxide as refrigerant) were not straight lines, as shown in Fig. 2, but broken lines each made up of two straight sections; the second section in each case was less steep than the first. This was due to the presence of hydrocarbon gases which condensed in the McLeod gauge, as soon as the difference in the mercury levels became equal to their vapor pressure at room temperature. The break for n-heptane occurred at a difference in mercury levels of about 120 mm, while that for n-hexane occurred at about 140 mm. No breaks in the pressure-time curves were found for any other substances.

#### DISCUSSION

Previous work<sup>1,5,7</sup> indicates that chemical action in electrical discharge is initiated by positive ions. Once positive ions are formed the reaction appears to take place in one of two ways, (1) by a *chain mechanism* such as postulated by Bodenstein,<sup>8</sup> in which "there is formed an unstable intermediate product, rich in energy, which on further reaction gives rise not only to the final product, but also to another intermediate product which regenerates the same process again and again," or (2) by a *clustering process*, such as has been assumed by Lind in connection with his work on  $\alpha$ -ray bombardment, and according to which positive ions attract surrounding neutral molecules forming an ion cluster which reacts chemically upon neutralization.

It seems that a satisfactory theory of chemical action in electrical discharge should be in harmony with the above hypotheses, and in addition should explain the following experimental facts: (1) proportionality between current and rate of reaction; (2) independence of rate of reaction on pressure; (3) occurrence of the greater part of the reaction in the neighborhood of the cathode. (These facts are supported not only by the work reported in this article but also by that of Kirkby, Günther-Schulze, and Brewer and Westhaver, mentioned above.)

A simple mechanism which meets these requirements is the following: Consider the electrons leaving the cathode. These traverse the cathode potential drop and thereby acquire energy which is expended in collisions in

<sup>7</sup> S. C. Lind, *Science* **67**, 565 (1928).

<sup>8</sup> Max Bodenstein, *Chem. Reviews* **7**, 2, 215 (1930).

the dark space and negative glow. We assume that the positive ions formed by these collisions serve as the initiators of the chemical action, giving rise to either chain or cluster processes.

Proportionality between current and rate of reaction will follow from this hypothesis if there is a constant ratio between the current and the number of positive ions formed in the dark space and negative glow. The existence of such a ratio seems quite likely for the ranges of pressure and current under consideration. Such a constant ratio would exist (1) if there were a constant ratio between the current and the number of electrons leaving the cathode, or in other words, between the number of electrons leaving and the number of positive ions arriving; and (2) if there were a constant ratio between the number of electrons leaving the cathode and the number of positive ions formed in the dark space and negative glow. Both of these assumptions are in good agreement with the generally accepted ideas of the glow discharge, and it seems likely that they are valid.

Independence of the rate of reaction of pressure can be explained by the relation  $pd = \text{const.}$ <sup>9</sup>, where  $p$  is the pressure and  $d$  is the width of the dark space. From this it is clear that any change in pressure is compensated for by such a change in  $d$  that the amount of gas subjected to bombardment by electrons from the cathode remains constant. In other words, as the pressure changes the mean free path of the electrons changes so that the same number of collisions is made as before. Changes in pressure may be regarded as only magnifying or reducing the dimensions of the active region surrounding the cathode, but not affecting the total number of positive ions formed therein.

This picture disregards the action in the positive column. Any reaction which may occur there is probably due to the formation and recombination of ions which never reach the electrodes and hence have no relation to the current. In the experiments discussed here this action has apparently been small in amount, and could probably be made as small as desired by making the positive column sufficiently short.

The occurrence of the greater part of the reaction in the neighborhood of the cathode is obviously accounted for by this mechanism. It would be expected that the negative glow would be the seat of most of the reaction because of the high energy of the electrons and the high density of positive ions in that region.

Among the experimental results, which are not yet well-established, are: First, the apparent independence of reaction rate on electrode spacing, found in the case of *n*-decane. On the basis of the suggested mechanism this means only that in this case the amount of reaction in the positive column is negligible. Second, the independence of the reaction rate on voltage. It seems likely that the voltage fluctuations were caused by inconstant conditions on the wax-covered cathode surface. The cathode potential drop depends only on the nature of the gas, hence it must have remained constant, and thereby yielded a constant reaction rate regardless of the voltage across the electrodes.

<sup>9</sup> L. H. Dawson, *Phys. Rev.* **30**, 119 (1927).

The results presented in this article are not such as to distinguish between a chain and cluster mechanism. However, a cluster mechanism is indicated by the formation of the wax, which is apparently a hydrocarbon of high molecular weight such as would be formed by polymerization or condensation. It seems likely that these heavy molecules form on the surface of the cathode rather than in the gas phase, since such large clusters would probably be unstable in the gaseous state,<sup>10</sup> even though chemical forces were added to the ordinary forces of electrostatic induction between an ion and surrounding neutral molecules.

In conclusion the writer wishes to express his appreciation to those of the Departments of Physics and Chemistry of Cornell University who were helpful in this work, to Dr. H. A. Trebler for his interest in the problem and his valuable suggestions, and to Prof. Vladimir Karapetoff, who is in general charge of the above mentioned research program on insulation at Cornell University. He wishes especially to thank Mr. C. F. Hirshfeld, chief of research, and Mr. Alex Dow, president, both of the Detroit Edison Company, for the financial support which made the above described work possible, and for permission to publish the results.

<sup>10</sup> J. J. Thomson, *Conduction of Electricity Through Gases*, 3rd Ed., p. 66.