

## Conduction of Electricity in Highly Insulating Liquids\*

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Investigations have been made on the natural conductivity, and on the conductivity induced by gamma-rays in isooctane and liquid oxygen. The characteristics of the two types of conductivity are so very different that it may be concluded that the natural conductivity is not due to stray radiation or to cosmic rays. The curves for the natural conductivity are such that the current increases much faster than the field. Evidence is presented supporting Plumley's theory that the observed conductivity is due to

dissociation of the liquids by the field, and against the view that it has a thermionic origin at the cathode, or the view that it is due to radiation. The prediction that the logarithm of the current should be a linear function of the square root of the field is verified. The much larger currents induced by gamma-rays rise at first rapidly and then more slowly in a manner indicating a slow approach toward saturation. The results fit Jaffé's formula satisfactorily.

### INTRODUCTION

RELATIVELY few investigations on the electrical conductivity of highly insulating liquids have been made. In comparison with the immense amount of work which has been done on the electrical conductivity occurring in, and imparted to, gases, it is evident that much remains to be done in accumulating information about the corresponding phenomena in highly insulating liquids. The first publication in this field was that of P. Curie,<sup>1</sup> who found that the electrical conductivity of petroleum ether, carbon tetrachloride, carbon disulphide, and benzene was increased by exposure to gamma- or x-rays, an investigation suggested, of course, by the effect of these rays on air. Later, other investigators studied the current-voltage characteristics of hexane and similar liquids when exposed to gamma-rays,<sup>2</sup> the mobilities,<sup>3</sup> the coefficient of recombination,<sup>4</sup> and the coefficient of diffusion of the ions. Jaffé<sup>2</sup> made an important contribution to the understanding of the current-voltage characteristics of hexane when irradiated by gamma-rays. In his 1908 paper he considered the

current to be accounted for as the sum of two separate currents; one of these rising to a saturation value like the current in a gas, while the second is an ohmic current. In 1913 he discarded this view in favor of a theory according to which the ions are produced in very densely packed columns isolated from each other. These columns are the tracks of the photoelectrons ejected by the gamma-rays. An important feature of this theory was that it gave a quantitative relationship between the current and the field, a relationship which expressed the great difficulty of securing saturation, as a result of the ease with which recombination occurs in the tightly packed columns of ions. This theory has been extended successfully to cases of ionization in compressed gases.<sup>5</sup> The most recent application of Jaffé's theory is that of Mohler and Taylor,<sup>6</sup> and later Taylor<sup>7</sup> alone, who used it successfully in their work on ionization in carbon disulphide by x-rays. While there is no reason to suppose that Jaffé's theory is inadequate, it is certainly desirable to extend the scope of investigations on the conductivity imparted to liquids by ionizing radiations.

When all ionizing agents such as x-rays and radium are removed, it is found that there still exists a residual or natural conductivity in these liquids. However, there is no general agreement as to its characteristics. In the first place, the

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<sup>1</sup> P. Curie, *Comptes rendus* **134**, 420 (1902).

<sup>2</sup> G. Jaffé, *J. de Phys.* **5**, 263 (1906); *Ann. d. Physik* **25**, 257 (1908); *Le Radium* **10**, 126 (1913); *Ann. d. Physik* **42**, 303 (1913).

<sup>3</sup> I. Adamczewski, *Acad. Polonaise Sci. et Lettres, Bull.* **5-7A**, 217 (1934); *Acta Phys. Polonica* **3**, 235 (1934); *Ann. de physique* **8**, 309 (1937).

<sup>4</sup> H. J. Van der Bijl, *Ann. d. Physik* **39**, 1, 170 (1912); C. Bialobrzewski, *J. de phys. et rad.* **7**, 329 (1936).

<sup>5</sup> J. W. Broxon and G. T. Meredith, *Phys. Rev.* **54**, 9 (1938); J. Clay, *Rev. Mod. Phys.* **11**, 123 (1939).

<sup>6</sup> F. L. Mohler and L. S. Taylor, *J. Research Nat. Bur. Stand.* **13**, 659 (1934).

<sup>7</sup> L. S. Taylor, *J. Research Nat. Bur. Stand.* **17**, 557 (1936).

residual conductivity of a supposedly pure insulating liquid can be reduced by a factor of a thousand or more by treating it in such a way as to remove traces of water. Such treatment may be prolonged refluxing with an agent like sodium or phosphorus pentoxide, or exposure to a high electric field. When a reasonably low limiting value of the conductivity has been reached, the next question is to find how it originates. Some authors<sup>8</sup> believe that the residual conductivity should be attributed to cosmic and similar radiations. Other physicists<sup>9</sup> interpret their investigations to mean that the conductivity is due to a thermionic emission from the cathode combined with a Schottky effect. This has been criticized by LePage and DuBridge.<sup>10</sup> The most recent work is that of Plumley<sup>11</sup> who interprets his experiments to support the potential dissociation theory, which was originally proposed by Onsager<sup>12</sup> for very weak electrolytes. According to Plumley's view there are even in the purest hydrocarbons such as hexane a very small number of ions resulting from the spontaneous dissociation of molecules. A favorable orientation of the molecules with respect to the field increases the number of dissociations, the number increasing rapidly with the strength of the field. The investigations, while often supporting the point of view of the various authors, are seldom complete enough to decide definitely against alternative theories. For example, in the experiments for which the thermionic point of view was suggested, there was no systematic investigation of how the current depended on the volume of the liquid between the electrodes. For a given field, the thermionic theory would imply no dependence on the volume of the liquid, whereas all other theories would require for a given field a larger current, the greater the amount of liquid involved. However, it must be recorded that all who have worked on the residual conductivity of highly insulating liquids have found great

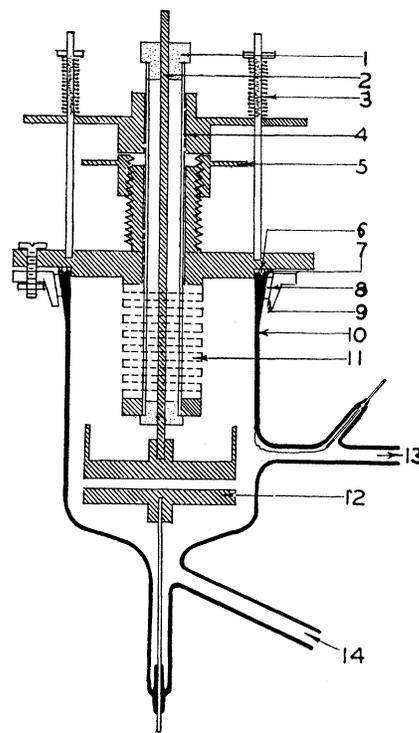


FIG. 1. Experimental cell I: (1) amber plug, (2) brass rod, (3) spring, (4) brass tube, (5) graduated brass disk, (6) 20-ampere Buss fuse wire, (7) mixture of paraffin and stopcock greases, (8) packing, (9) metal flange, (10) silvered glass jar, (11) sylvphon, (12) brass electrode, (13) outlet for the liquid, (14) inlet for the liquid.

difficulty in securing reproducible results. Frequently, for no apparent reason at all, the value of the observed current will change by a factor of two or so. Getting the liquid into a state where it will retain reasonably constant characteristics is often a tedious trial and error process.

This investigation was undertaken to study both the natural and induced conductivities under as varied conditions as possible in the hope that some of the ambiguities now existing as to interpretation could be removed. The liquids chosen for investigation were isooctane and liquid oxygen. The reason for choosing isooctane was that we were fortunate to secure a supply of very pure liquid through the courtesy of Dr. G. W. Waters of the Shell Oil Company at Wood River, Illinois. The conductivity was investigated not only as a function of the field but also as a function of the spacing between the electrodes, or what amounts to much the same

<sup>8</sup> G. Jaffé, *Ann. d. Physik* **28**, 326 (1909); M. C. Bialobrzewski, *J. de phys. et rad.* **7**, 329 (1936); A. Rogozinski, *Ibid.* **8**, 128S (1937); A. Rogozinski, *Phys. Rev.* **60**, 148 (1941).

<sup>9</sup> E. B. Baker and H. A. Boltz, *Phys. Rev.* **51**, 275 (1937).

<sup>10</sup> W. R. LePage and L. A. DuBridge, *Phys. Rev.* **58**, 61 (1940).

<sup>11</sup> H. J. Plumley, *Phys. Rev.* **59**, 200 (1941).

<sup>12</sup> L. J. Onsager, *J. Chem. Phys.* **2**, 509 (1934).

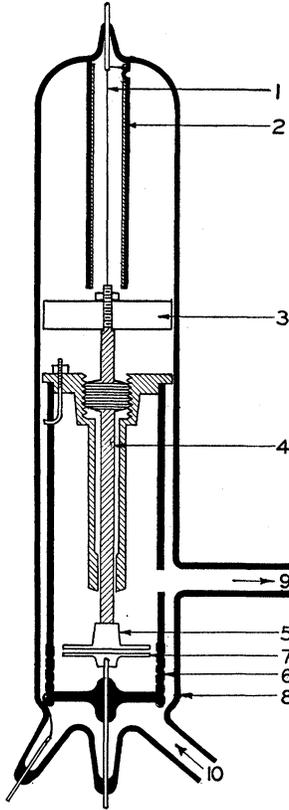


FIG. 2. Experimental cell II: (1) fine nickel wire, (2) brass cylinder, (3) soft ion bar, (4) brass rod, (5) brass electrode, (6) fine nickel screen, (7) copper electrode, (8) guard ring, (9) outlet for the liquid, (10) inlet for the liquid.

thing, the volume of the liquid. Measurements were also carried out at different temperatures.

#### APPARATUS

The apparatus and methods employed may be conveniently discussed under several headings.

##### 1. The Conductivity Cells

In all, four cells were used in this investigation. Two of them had parallel plate electrodes, the spacing between which could be adjusted so that the effect of distance between the electrodes on the observed current could be investigated. Two others had concentric cylindrical electrodes. One of these cells was easy to shield with lead for investigating a possible cosmic-ray origin, and the other was specially designed for investigating the effect of temperature.

Cell I: A diagram of this cell is shown in Fig. 1; the dimensions of interest are the radius of the electrodes, 2.4 cm, the pitch of the screw,  $1/24$ th of an inch. By means of the sylvon it is possible to vary the distances between the electrodes from zero to 6 mm. The insulation of the upper electrode, which is the one connected to the electrometer, consists of two pieces of amber. The upper piece is made vacuum tight by Sealstix. The glass part of the apparatus is made from standard Pyrex glass pipe. The junction between its flange and the brass disk is made vacuum tight by a gasket of fuse wire fitted into the groove in the flange in place of the more usual rubber gasket. Care was taken to ensure that the faces of the two electrodes were accurately parallel. The inside of the glass was coated with evaporated silver, which was electrically grounded to act as a shield for the upper electrode. The liquid did not rise above the level of the side tube (13).

Cell II: This all glass cell is shown in Fig. 2. The upper electrode, in this cell connected to the

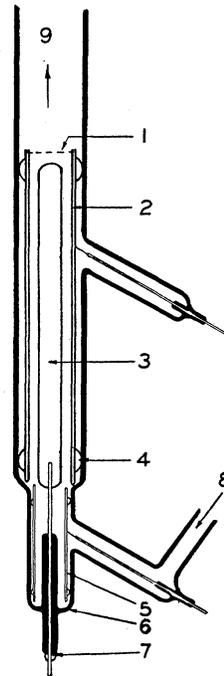


FIG. 3. Experimental cell III: (1) nickel screen, (2) monel cylinder, (3) dural rod, (4) blobs of solder, (5) brass cylinder, (6) guard ring, (7) Dennison's "number 4 express" sealing wax, (8) inlet for the liquid, (9) outlet for the liquid.

high voltage, is a brass disk 2.88 cm in diameter which can be moved up or down by manipulating a magnet in the vicinity of the soft iron bar (3). The lower electrode (connected to the electrometer) is a copper disk supported by a strong tungsten wire which is sealed into a glass spider at the end of the inner glass tube (6); on the surface of the glass tube (6) is a grounded nickel screen. The metal cylinder (2) prevents a corona discharge from the fine wire (1) from giving trouble. Great care was taken to ensure parallelism between the electrodes.

Cell III: This cell, designed to study the effect of external radiation, is shown in Fig. 3. It has two concentric cylindrical electrodes, the outer one of monel 9.6 cm long, 1.11-cm internal diameter, and the inner one of dural 9.2 cm long and 0.635-cm outside diameter. Blobs of solder serve to center the monel tube. Care was taken to secure exact centering. Cylinder (5) serves as a guard ring. The end (7) is covered with a good grade of sealing wax to ensure high insulation. The outside of the tube, above the sealing wax, is painted with Aquadag which is grounded. When the liquid is circulating in the system, it flows in through the tube (8) and leaves the tube through (9).

Cell IV: The cell (Fig. 4) is designed to be inserted in a thermos jar to allow investigations to be made at different temperatures. The dural rod (6) is 8.62 cm long and 1.68 cm in diameter. The monel cylinder (7) has an inside diameter of 2.42 cm. There are guard rings both inside and outside the cylinder (4) which is evacuated. At (1) there is amber insulation. Continuous circulation of the liquid is not possible with this cell. The liquid is distilled into the cell through (8); it can be tipped back into the distilling flask and the process repeated.

## 2. Treatment of the Isooctane

In order to secure low and reasonably steady residual currents, it is necessary to remove the constituents (whatever they may be) which are associated with a high conductivity (say  $10^{-16}$  mho/cm) which is to be found even in the purest liquid obtainable commercially. The method finally adopted was to reflux the liquid over metallic sodium for a long time in a closed system including the conductivity cell. A simple design

of the distilling and refluxing system is shown in Fig. 5. By increasing the heat input to the distilling flask, it was possible to arrange for the newly distilled liquid to pass through the conductivity cell back into the flask in a continuous cycle. In this way any suspended matter that might have been present in the cell initially was eventually removed. The conductivity sometimes obtained in this work is the lowest on record,  $3 \times 10^{-20}$  mho/cm. (Since the relationship be-

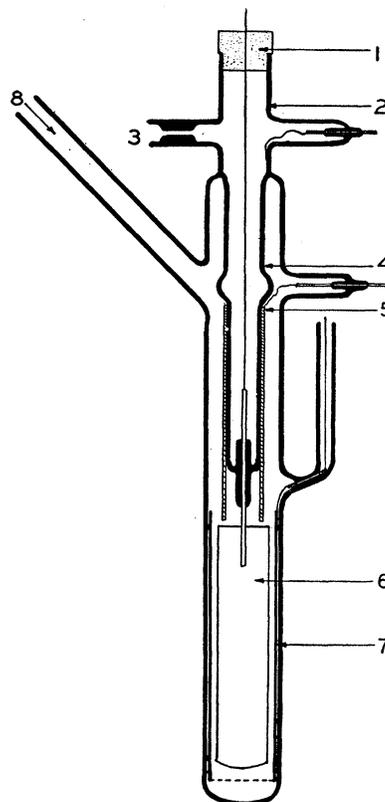


FIG. 4. Experimental cell IV: (1) amber plug, (2) Aquadag film, (3) to diffusion pump, (4) Hanovia "Liquid Bright Platinum" paint serving as a guard ring, (5) brass cylinder, (6) dural rod, (7) monel cylinder, (8) glass tube connected to a two-way stopcock.

tween current and voltage is not linear, no precise meaning can be attributed to this unit; it is, however, a short and convenient unit for comparing results.)

## 3. Use of Liquid Oxygen

Investigations of liquid oxygen were carried out only with cell IV. The apparatus was very carefully washed and then dried thoroughly.

The tube (8) was connected through a suitable two-way stopcock which allowed one first to produce a vacuum in the apparatus and then to admit oxygen through a filter from a tank at a pressure of about 12 lb./in.<sup>2</sup> above atmospheric pressure. On immersing cell IV in a thermos bottle of liquid air it was possible to fill it with liquid oxygen. It is believed that, though traces of water may be responsible for the conductivity in isooctane above the limiting value finally reached, they cannot be a cause of trouble in liquid oxygen for traces of water would be frozen to the walls and unavailable to form ions.

#### 4. Measurement of Current

The currents measured ranged all the way from  $10^{-11}$  down to  $10^{-16}$  ampere. They were measured by means of the Western Electric D-96475 electrometer tube mounted in a vacuum. The grid of the tube was grounded through one of a set of S. S. White resistors whose values ranged from  $4.06 \times 10^{11}$  to  $2.4 \times 10^9$  ohms. The tube was used in the well-known balanced circuit set-up described by Penick.<sup>13</sup> A sensitivity of 200,000-mm divisions per volt was obtained, so that with a resistor of  $4.06 \times 10^{11}$  ohms, a deflection of 1 mm indicated a current of  $1.2 \times 10^{-17}$  amp. This sensitivity was seldom used except when the current to be measured was extremely low. For high currents care was taken to use a resistor

between the grid and the cathode which limited the voltage change on the grid to less than 0.05 volt. This was necessary to secure linearity in the system.

#### 5. High Voltage Supply

The investigation included measurements on the current through the liquids with voltages as high as 6000 volts. Slight fluctuations in the voltage applied to the cells can produce effects which will completely mask a small current. Constant voltage can be secured by means of a sufficient number of B batteries. In this investigation voltages as high as 1485 volts were provided by means of B batteries. It was impracticable to use B batteries for higher voltages. An electronic high voltage supply was designed and constructed which had the following characteristics: (1) Constant voltages up to 5500 volts could be produced at will. The constancy was comparable to that of a bank of B batteries. Tests showed that the output voltage changed by less than 0.1 volt in a time interval of ten minutes. The fluctuations were often considerably less than this. (2) The device gave high voltages of either sign with no difference in the constancy of the output. (3) No detectable ripple could be observed. An account of the high voltage supply will be published elsewhere.

### EXPERIMENTAL RESULTS

#### Induced Conductivity (Isooctane)

##### 1. Dependence on Field and Volume

The conductivity induced by gamma-rays in highly purified isooctane was investigated in all the cells. Only with cells I and II was it possible to study the way in which the current depends on the spacing for any given electric field. (It was possible of course to investigate the dependence on field with all four cells.) Typical results for the current obtained with isooctane in cell II irradiated by gamma-rays are shown in Fig. 6. It is clear that the current is almost, but not quite, independent of the direction of the electric field. This asymmetry is a spurious effect and is to be attributed to the small contribution to the observed current from the "dead" region around the back of the electrode which is connected to the electrometer. The direction of the current in

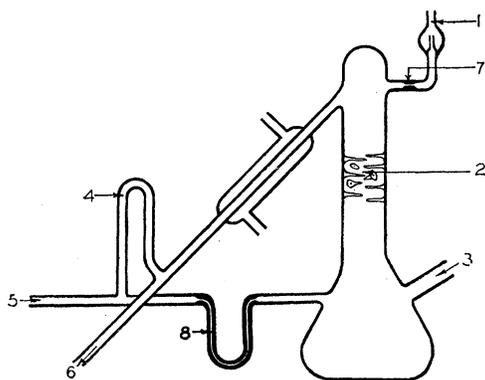


FIG. 5. Distilling system: (1) to Wood's metal seal off device, (2) indentations, (3) entrance for the liquid and sodium, (4) glass tube for equalizing the pressures between the cell and the reservoir, (5) inlet for the liquid from the cell, (6) outlet for the liquid to the cell, (7) constriction, (8) capillary.

<sup>13</sup> D. B. Penick, *Rev. Sci. Inst.* **6**, 115 (1935).

this region is not affected by the sign of the voltage on the other electrode; hence, the small asymmetry. This interpretation was verified by using one cell with a lead shield so arranged that the direct ionization of the "dead" region by the radium is greatly reduced; it was found that this shielding reduced the small asymmetry very greatly. The current increases noticeably with the field showing that saturation calls for much higher fields. Results of this kind were obtained by Jaffé<sup>2</sup> with hexane many years ago.

He proposed an interpretation according to which the ionization due to the photoelectrons ejected here and there in the liquid by gamma-rays takes place in very short columns densely packed with ions. The difficulty of obtaining saturation is due to the strong initial recombination within the columns. Jaffé developed a formula expressing the value of the current at any field in terms of the mobility, diffusion, and recombination coefficients of the ions. The formula is

$$\frac{1}{I_A} = \frac{1}{I_\infty} \left[ 1 + \frac{\alpha N}{7.85bw} \frac{1}{X} F\left(\frac{b^2 w^2 X^2}{2D^2}\right) \right], \quad (1)$$

where  $I_A$  is the current per unit area at a field  $X$ ,  $I_\infty$  the saturation current at infinite field,  $N$  the number of ion pairs produced per cm length of a column,  $b$  the initial diameter of the column within which the ions are found, and  $\alpha$ ,  $w$ , and  $D$  are the recombination, mobility, and diffusion coefficients, respectively, of the ions.  $F(b^2 w^2 X^2 / 2D^2)$  is a complicated function of the argument which approaches unity when the argument is sufficiently large. In practice this is secured by using a high enough field so that Eq. (1) becomes

$$\frac{1}{I_A} = \frac{1}{I_\infty} \left( 1 + S \frac{1}{X} \right). \quad (2)$$

Here  $S$  is  $\alpha N / 7.85bw$ . The validity of this theory may be tested by plotting  $1/I_A$  against  $1/X$ . If the plot results in a curve which is practically straight for all values of  $X$  above a certain value then one can infer that the theory applies. Moreover, the intercept of this line (when extrapolated) on the ordinate through the origin gives the value of  $1/I_\infty$ . It is thus possible,

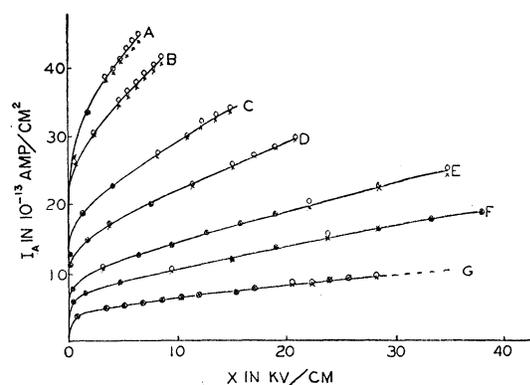


FIG. 6. Variation of induced current with field strength in isoctane irradiated by constant radiation from 2000  $\mu$ g radium. Curves A, B, C, D, E, F, and G represent results when  $d=0.848, 0.636, 0.371, 0.265, 0.159, 0.106,$  and  $0.053$  cm. Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode of cell II.

assuming the validity of Jaffé's theory, to calculate the value of the saturation current. The slope of the line in such a graph has the value  $S/I_\infty$ .

The directly observed experimental results collected in Fig. 6 are replotted in Fig. 7. It is clear that these "Jaffé plots" have straight portions which can be extrapolated back to the ordinate at the origin which corresponds to an infinite field. The characteristics of this family of curves are presented in Table I. Here  $d$  is the spacing between the electrodes. The fourth column is quite significant for it shows that  $I_\infty$  is almost exactly proportional to  $d$ , as it should be if the total number of ion pairs is proportional to the available volume. On the other hand, the fifth column shows that the currents observed for an experimentally obtainable field  $X=20$  kv/cm are not quite proportional to the spacing between the electrode. It is to be expected that with the larger spacings, the currents would deviate further from the saturation value, as is found to be the case.

## 2. Dependence on the Intensity of Radiation

In order to determine the intensity variation of the current induced in the liquid at room temperature, current-intensity runs were taken for different fields in a cell of concentric cylinder type, whose construction is similar to that of cell III. The intensity of radiation was varied by

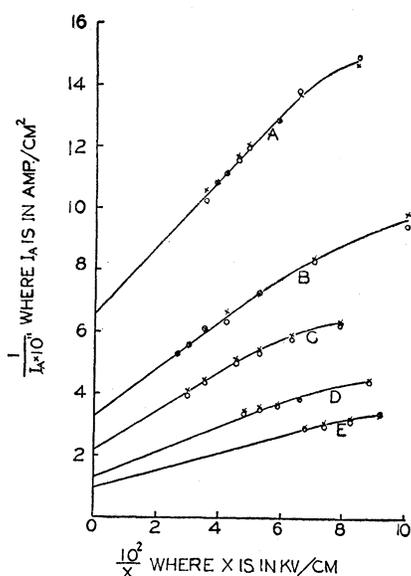


FIG. 7. Inverse current and inverse stress (field strength) relationship for isooctane irradiated by constant radiation of 2000  $\mu\text{g}$  radium. Curves *A*, *B*, *C*, *D*, and *E* represent the results when  $d=0.053, 0.106, 0.159, 0.265, 0.371$  cm, respectively. Open circle and cross represent the results when positive and negative voltages are applied to the high voltage electrode of cell II.

using different calibrated gamma-ray standards supplied by the Bureau of Standards. Figure 8 shows what one obtains when the intensity of radiation is selected and the current measured at various fields. It is clear that the present results agree with those obtained by Adamczewski,<sup>14</sup> who measured the ionization current through hexane with various intensities of x-rays.

With a fixed value of field strength the induced current was measured as a function of the intensity of radiation. A typical curve is shown in Fig. 9. It is a rather remarkable phenomenon that the relationship between the induced current and intensity of radiation is quite linear, a fact which, in principle, enables us to use the ionization in such a liquid to indicate the intensity of radiation. If the radiation is sufficiently strong and if the liquid inside the ionization chamber is fairly pure, so that the induced current is much greater than the residual current, the author believes that this kind of measurement may be developed into a dependable and accurate method of measuring radiations.

<sup>14</sup> I. Adamczewski, Acta Phys. Polonica 3, 246 (1934).

### 3. Dependence on Temperatures

The effect of temperature on the currents through isooctane as a function of the field was studied by means of cell IV. Figure 10 shows the results obtained when the field was set at some selected value and the temperature varied. Figure 11 shows what one obtains when the temperature is selected and the current measured at various fields. It is clear that for any given field the currents are larger the higher the temperatures. This can be explained qualitatively by the fact that viscosity decreases with increasing temperature and when viscosity decreases, the ions in the column are more readily separated from each other so that closer approach to the saturation current is obtained.

The results in Fig. 11, together with some others not shown, are replotted as Jaffé plots in Fig. 12. It is interesting to note that all the lines, when extrapolated, hit the ordinate at the origin at substantially the same place, indicating that for each curve we have the same  $I_\infty$ . This is as it should be, for with the radium placed in a fixed position with respect to the cell, one would expect the same total number of ion pairs to be produced whatever the temperature may be. (It is true that a change in density with temperature could affect the absorption of gamma-rays slightly and this would change the total number of ion pairs produced per unit volume. However, this is probably too small an effect to make a noticeable change in  $I_\infty$ .)

From Fig. 12 we find an empirical relation between the value of  $S$  and  $T$  to be  $S = \text{const.}/T^{1.28}$ . Since  $S = \alpha N/7.85bw$  it is likely that  $N$  and  $b$  are but little affected by the temperature so that the principal factors varying with the temperature are  $\alpha$  and  $w$ , the recombination and mobility coefficients, respectively. Thus measurements of the slopes of the straight lines in the Jaffé plots

TABLE I. Characteristics of curves of Fig. 7;  $d$  is the space between electrodes.

$d$	$\frac{10^{-11}}{I_\infty}$	$I_\infty \times 10^{-12}$	$\frac{I_\infty \times 10^{-12}}{d}$	$\frac{I_{20}}{I_\infty}$	$S \times 10^{12}$
0.053	6.6	1.51	2.85	0.550	10.9
0.106	3.3	3.02	2.845	0.465	7.3
0.159	2.2	4.53	2.845	0.412	6.2
0.265	1.33	7.51	2.83	0.397	4.03
0.371	0.96	10.04	2.81	0.405	2.83

can be used to indicate the way in which  $\alpha/w$  changes with the temperature.

In cells containing electrodes of different materials, the magnitude of the current was quite independent of which electrode was the cathode, a result entirely in accord with the view that the conductivity due to gamma-rays is a volume effect in the liquid and not a surface effect at the electrodes.

No time lag in the value of the observed current was noticed when the field was changed. This result is not in agreement with that found by Taylor<sup>7</sup> for ionization of carbon disulphide by x-rays. Our statement is subject to the proviso that conclusions cannot be drawn as to time intervals less than about three minutes as the resistance condenser factor of our set-up was of this order.

It may be concluded that the phenomena observed when isooctane is irradiated by gamma-rays may be attributed to the formation of ions in the liquid and that the results are described adequately by Jaffé's theory.

#### Induced Conductivity (Liquid Oxygen)

Because of the experimental restrictions imposed by the low temperature of liquid oxygen, it was impracticable to use either cell I or II to determine the effect of changing the spacing.

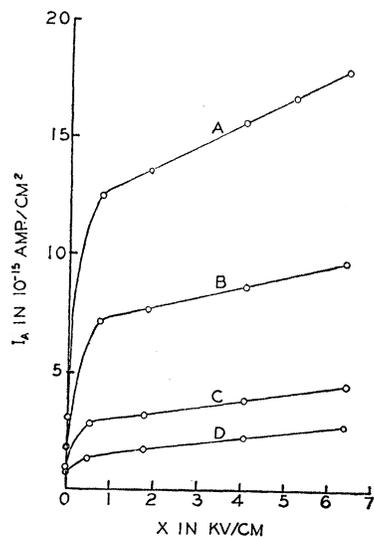


FIG. 8. Variation of induced current with field strength in isooctane at room temperature ( $T=297^{\circ}\text{K}$ ). Curves A, B, C, and D represent the respective results when the amounts of radium are 100, 50, 20, and 10  $\mu\text{g}$ .

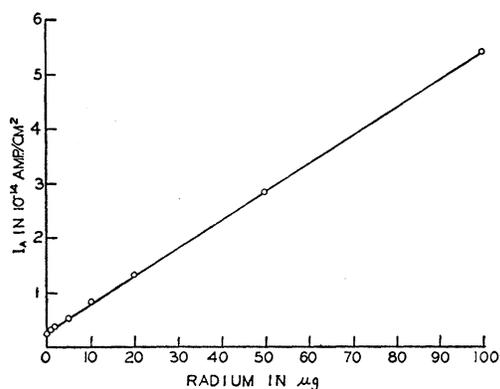


FIG. 9. Variation of induced current with intensity of radiation at  $X=5830$  v/cm.

Cell IV was used for studies on liquid oxygen. The direct experimental measurements are plotted in Fig. 13. (To facilitate comparison, the light dotted line shows the curve for isooctane at  $273^{\circ}\text{K}$  in the same cell. The curves are adjusted arbitrarily to coincide at 10 kv/cm.) The curve for liquid oxygen indicates that saturation is much harder to attain in it than in isooctane. The corresponding Jaffé plot is shown in Fig. 14. The intercept on the ordinate at the origin is so small that it would be almost useless to use the curve to determine the value of  $I_{\infty}$ . However, the value of  $I_{\infty}$  is of the order 30 times more than  $I_A$  at 10 kv/cm, whereas, in the case of isooctane, the value of  $I_{\infty}$  is only of the order 2 times more than  $I_A$  at 10 kv/cm (for  $T=273^{\circ}\text{K}$ ). If the  $273^{\circ}\text{K}$  curve for isooctane is transferred to Fig. 14 and adjusted so that  $I_{\infty}$  is the same for both, we find that the Jaffé plot for isooctane is the lower curve. The  $S$  for liquid oxygen is thus much larger than the  $S$  for isooctane.

The high value of  $S$  can be attributed principally to the factors  $\alpha N/w$ .  $N$  may well be considerably larger for liquid oxygen than for isooctane because the oxygen molecules offer a larger cross section to the gamma-ray photoelectrons than do the isooctane molecules. Little can be said as to the quotient  $\alpha/w$  since no measurements have been made to determine these constants in liquid oxygen.

#### Natural Conductivity (Isooctane)

##### 1. Dependence on Field and Volume

The investigation of the natural conductivity in isooctane and similar liquids, that is, the

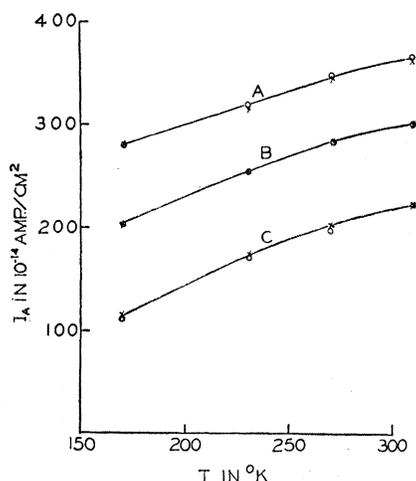


FIG. 10. Variation of induced current with absolute temperature in isooctane irradiated by constant radiation from 4000  $\mu\text{g}$  radium. Curves *A*, *B*, and *C* represent the results when  $X=14,850$ , 8088, and 1348 v/cm, respectively. Open circle represents the results when positive voltages are applied to the high voltage electrode of cell IV, and cross represents the results when negative voltages are applied to the high voltage electrode.

residual conductivity' to be found in the absence of ionizing agents such as radium, is full of experimental difficulties. The currents to be measured are so small that it is difficult to secure reproducible results. This is also accentuated by the need for measurements at high voltages as well as at low voltages. Slight variations in the absolute value of the high voltage, which may be quite insignificant in a relative sense, often produce electrostatic induction effects of a magnitude comparable with the current being measured. There is no agreement among previous investigators as to the nature and origin of the natural conductivity. It has been attributed to (1) radiation, probably cosmic rays, (2) thermionic emission from the cathode, (3) cold emission from the cathode,<sup>15</sup> and (4) dissociation induced by the field. In order to effect a discrimination between these views it is desirable to study the conductivity as a function of several variables in one and the same investigation. Thus for a given field, the current should be independent of the spacing between the electrodes, if the explanation be either (2) or (3). The supporters of these theories have not made this particular test.

The dependence of the current through iso-

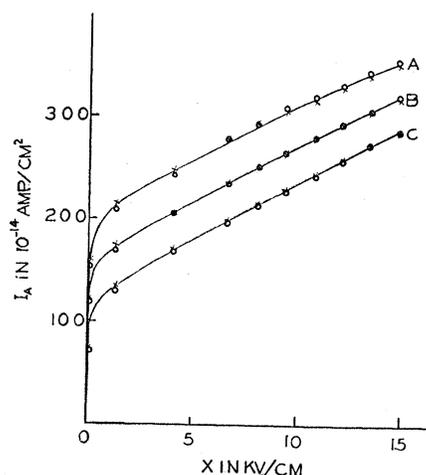


FIG. 11. Variation of induced current with field strength in isooctane irradiated by constant radiation from 4000  $\mu\text{g}$  radium. Curves *A*, *B*, and *C* represent the results when  $T=315.3$ , 260.6, and 210°K, respectively. Open circle represents results when positive voltages are applied to the high voltage electrode of cell IV, and cross represents results when negative voltages are applied to the high voltage electrode.

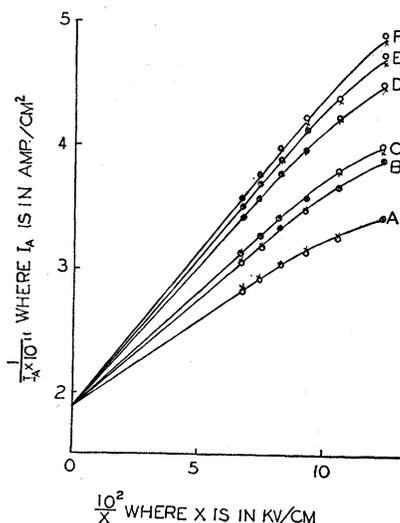


FIG. 12. Variation of inverse current and inverse stress (field strength) curves with the absolute temperature in isooctane irradiated by constant radiation from 4000  $\mu\text{g}$  radium. Curves *A*, *B*, *C*, *D*, *E*, and *F* represent the results when  $T=313.3$ , 273, 260.6, 230, 210, and 191°K, respectively. Open circle and cross represent the results when positive and negative voltages are applied to the high voltage electrode of cell IV.

octane on spacing was investigated in cells I and II. Although the same amount of effort was spent on the experiments involving these two cells, the ultimate conductivity (at the same field) ob-

<sup>15</sup> R. W. Dornte, *Ind. Eng. Chem.* **32**, 1529 (1940).

tained after prolonged refluxing and circulation was about 20 times less in II than in I. This is typical of much of the work in the field. Many cells with refluxing and circulating systems have been tried out. Often two systems, substantially identical, yield widely different ultimate conductivities. Figures 15 and 16 give directly the values of the currents per unit area as a function of both the spacing and the field. It is to be noted that the current is independent of the sign of the potential applied to the high voltage electrode. This was also found later with cells III and IV where the electrodes are made of different metals. Had the current been due to a thermionic emission at the cathode, it would have depended very greatly on the nature of the cathode. We may conclude, therefore, that these experiments give no support to explanations (2) nor indeed to (3). Another characteristic to be noted is that the curves for the natural conductivity are entirely different in shape from the curves for the conductivity induced by gamma-rays. This result makes it extremely unlikely that one can attribute the residual conductivity to feeble radiations of the gamma-ray type. Figure 17 shows that the currents observed in cell I are strictly proportional to the spacing between the electrodes, or what amounts to the same thing, to the volume of the liquid between the electrodes. Figure 18 shows how the currents in cell II depend on the spacing. While it is clear that these currents also definitely increase with the spacing,

they are not strictly proportional to the spacing. It may be that this is to be attributed to the great difficulty in making measurements in this region. (Over one-half of points in Fig. 18 correspond to  $I_A$  less than  $10^{-15}$  amp./cm<sup>2</sup>.) On the other hand, since the currents in Fig. 18 are so much smaller than those in Fig. 17 it may well be that the way in which the lines pass above the

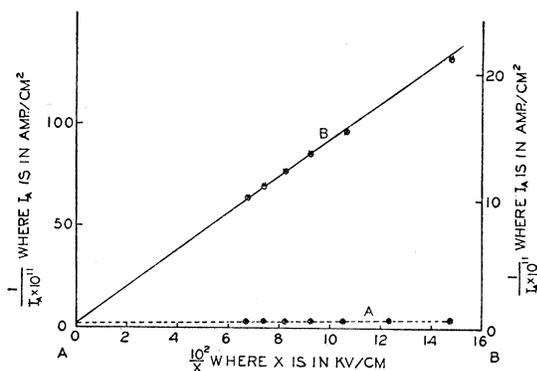


FIG. 14. Inverse current and inverse stress (field strength) curves. Curve A (dotted curve) represents the results when isooctane was irradiated by 4000  $\mu\text{g}$  radium at  $T=273^\circ\text{K}$ . Curve B (solid curve) represents the results when liquid oxygen was irradiated by 4500  $\mu\text{g}$  radium at  $T=90^\circ\text{K}$ . Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode of cell IV.

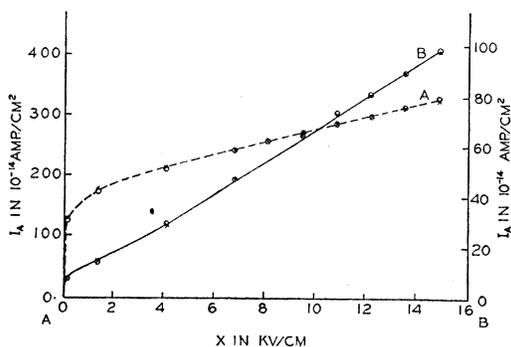


FIG. 13. Variation of induced current with field strength. Curve A (dotted curve) represents the results when isooctane was irradiated by 4000  $\mu\text{g}$  radium at  $T=273^\circ\text{K}$ . Curve B (solid curve) represents the results when liquid oxygen was irradiated by 4500  $\mu\text{g}$  radium at  $T=90^\circ\text{K}$ . Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode of cell IV.

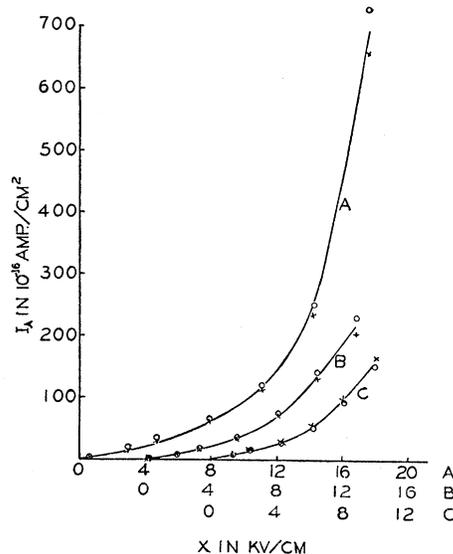


FIG. 15. Variations of residual current and field strength curves for isooctane. Curves A, B, and C represent the results when  $d=0.318, 0.424,$  and  $0.530$  cm. Open circle and cross represent the results when positive and negative voltages are applied to the high voltage electrode of cell I.

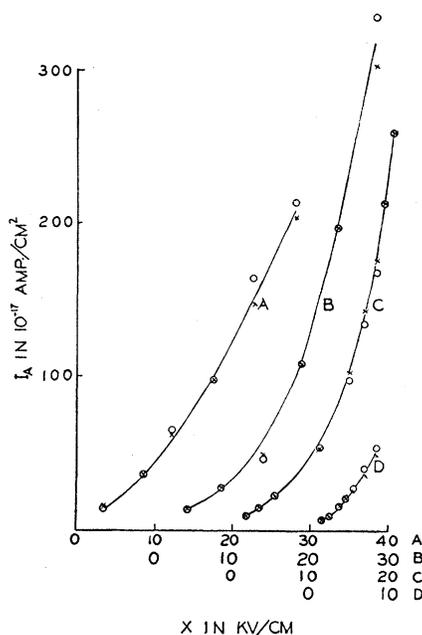


FIG. 16. Variation of residual current and field strength curves for isooctane. Curves A, B, C, and D represent the results when  $d=0.053$ ,  $0.106$ ,  $0.265$ , and  $0.636$  cm, respectively. Open circle and cross represent the results when positive and negative voltages are applied to the high voltage electrode of cell II.

origin indicates the superposition of two effects, a small one (possibly due to radiation) whose characteristic curve cuts the zero ordinates above the origin and a larger one which is proportional to the spacing. In Fig. 17 the larger effect is possibly so enhanced that the small effect is swamped. It is perhaps unprofitable to speculate further on the point. Clearly more experimental work should be done.

Plumley<sup>11</sup> has applied the potential dissociation theory to explain residual conductivity. According to this view a very small number of the molecules even in the purest hydrocarbons are dissociated into ions. Other molecules on the verge of dissociation will be dissociated by a field if their orientation be favorable. Plumley gave a formula for the number of dissociated molecules, which, therefore, also leads to an expression for the current in terms of the temperature  $T$  and the field  $X$ . The formula is

$$I_A = C \exp \left[ \frac{2e}{kT} (eX/300D)^{\frac{1}{2}} \right]. \quad (3)$$

Here  $C$  is proportional to the number of dissociated molecules at zero field. The exponential

term describes the way in which a field  $X$  increases the degree of dissociation;  $k$  is Boltzmann's constant,  $e$  the unit charge, and  $D$  the dielectric constant. This theory can be tested by plotting  $\log_{10} I_A$  against  $X^{\frac{1}{2}}$ . If it is correct, a straight line should be obtained and its slope should be  $2e^{\frac{1}{2}}/2.3kT300^{\frac{1}{2}}D^{\frac{1}{2}}$ . The "2" enters the equation through a particular assumption as to the nature of the force between the ions. If a straight line with a slope differing from the calculated value be obtained from the experimental results, it may be inferred that while the theory, in the main, is satisfactory, the correct form of the force between the ions has yet to be found.

In Figs. 19 and 20 we have re-plotted the results given in Figs. 15 and 16 for cells I and II, respectively. Insofar as the plots are straight lines one may infer that the potential dissociation theory is satisfactory. The slopes of the lines in Fig. 19 are substantially the same, a result which we should expect for there is nothing in the theoretical expression for slope which depends on the spacing between the electrodes. In these observations, however, the variation in spacing is not very great. When this variation is made large, the curves of Fig. 20 are obtained; here the slopes are very different for the different spacings. This cannot be accounted for by Plumley's

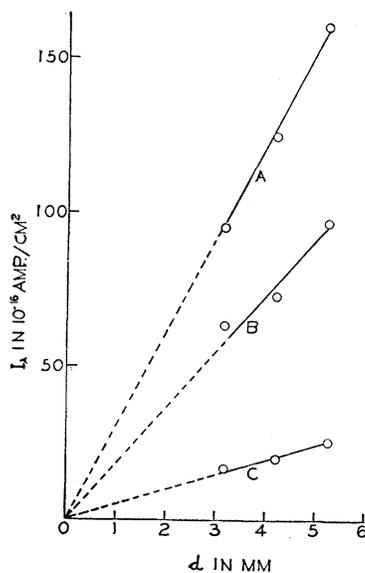


FIG. 17. Variation of residual current with electrode spacing at constant field strength. Curves A, B, and C represent the results when  $X=10$ ,  $8$ , and  $4$  kv/cm, respectively.

theory. The theoretical value of the slope  $2e^3/2.3kT300^3D^3$  is 0.0092 at 297°K. For cell I (Fig. 19) the experimental value is 0.0215, while for cell II (Fig. 20) it ranges from 0.0105 to 0.0183.

2. Dependence on Treatment of the Isooctane

Observations were made on the residual current through cell II during a period of six weeks. This cell together with its distilling flask forms a closed system. The first observations were made after circulation for about twenty-four hours. Results about three times larger in magnitude than those represented in Figs. 16 and 18 were obtained. During the course of repeated distillation and circulation the current values slowly diminished to the limiting values shown in Figs. 16 and 18. The slope of the  $\log I_A$  against  $X^3$  lines also diminished by roughly 20 percent.

When the liquid had been "purified" by prolonged distillation over sodium, exposure to a high electrostatic field for an hour did not produce any further reduction.

3. Time Lag

Some investigators report hysteresis effects in the current when the field is charged. No time lags of this sort were found in this investigation

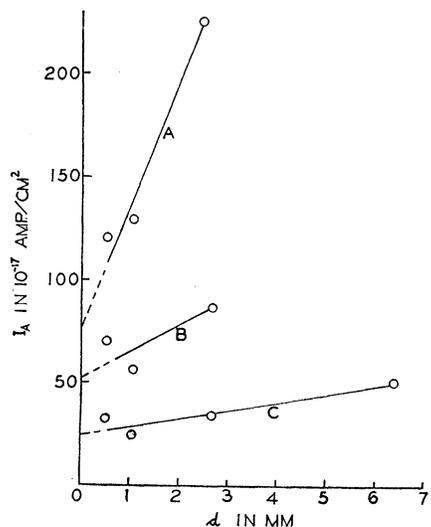


FIG. 18. Variation of residual current with electrode spacing at constant field strength. Curves A, B, and C represent the results when  $X=20, 14,$  and  $8$  kv/cm, respectively.

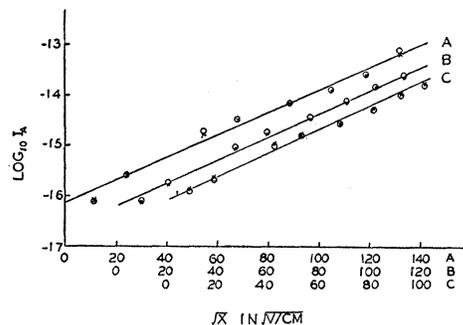


FIG. 19. Relation between  $\log_{10} I_A$  and  $X^3$  for isooctane. Curves A, B, and C represent the results when  $d=0.318, 0.424,$  and  $0.530$  cm. Open circle and cross represent the results when positive and negative voltages are applied to the high voltage electrode of cell I.

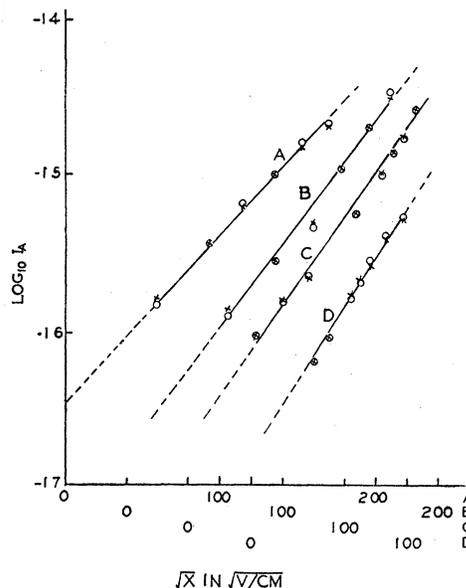


FIG. 20. Relation between  $\log_{10} I_A$  and  $X^3$  for isooctane. Curves A, B, C, and D represent the results when  $d=0.053, 0.106, 0.265,$  and  $0.636$  cm, respectively. Open circle and cross represent the results for positive and negative voltages applied to the high voltage electrode of cell II.

larger than the purely instrumental ones associated with the resistance capacitance characteristics of the circuit.

4. Effect of External Radiation

It was possible to surround cell III with 3 inches of lead and an extra inch on the top. No measurable change in the current at any field could be detected. On replacing cell III by a Geiger-Müller tube it was found that its response was cut down by 22 percent by the presence of

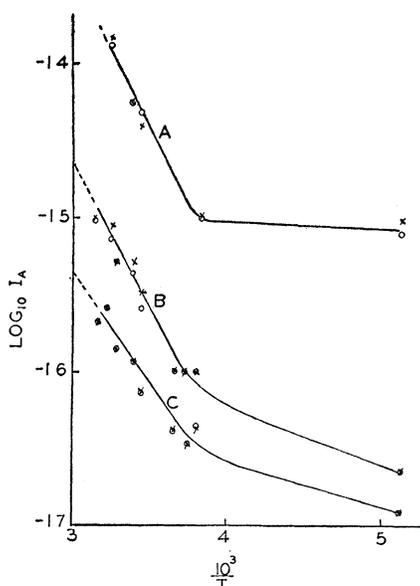


FIG. 21.  $\log_{10} I_A$  against  $1/T$  curves for isooctane. Curves A, B, and C represent the results when  $X = 14,850$ , 4010, and 1215 v/cm. Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode of cell IV.

the lead. It may, therefore, be inferred that little or none of the current through the isooctane in cell III could be attributed to cosmic radiations. Other investigators<sup>8</sup> have published results in support of the view that the residual conductivity in their experiments is due to radiation which can be reduced by shielding. The data are summarized in Table II.

It is difficult to understand why no evidence of an effect due to stray radiations was found in this investigation. The "conductivity" of the liquid was as low as that used by the other investigators. There is a difference which may perhaps be important. The volume of the cell used in this work was far smaller than in the cells used by the other investigators, while the field was larger. It is conceivable that had the current at fields below 1 kv/cm been large enough to measure accurately, a dependence on shielding would have been found.

Assuming that the residual conductivity of air is due to the formation of 3 ion pairs per cc per sec., and making reasonable assumption as to the method of predicting the ionization in isooctane, as suggested by Mohler and Taylor's work,<sup>6</sup> it may be concluded that the current to be expected

in isooctane is  $6 \times 10^{-16}$  amp./cm<sup>3</sup>. This is of the order of magnitude of the observed current below about 1 kv/cm, but unfortunately it is not easy to make decisive measurements on the effect of shielding when the current is so small. To secure further evidence in this direction it would be helpful to use a cell containing a much larger volume of liquid.

### 5. Effect of Temperature

Equation (3) indicates theoretically how  $I_A$  should depend on the temperature. According to this equation the relation between  $\log I_A$  and  $1/T$  should be linear. The experimental results are shown in Fig. 21. The most noticeable thing about these curves is the change in slope for the lower part of the temperature range. This has the effect that the current at low temperatures is larger than theory predicts.

It should be pointed out here that in the temperature range from 318°K to 263°K the slopes of  $\log_{10} I_A$  against  $1/T$  are of the same order of magnitude as those for toluene measured by LePage and DuBridge.<sup>10</sup> The only difference is that the present slopes of these plots decrease with a decrease of field, while those obtained by LePage and DuBridge increase with decreasing fields, as actually required by the potential dissociation theory. Again this difference can be reconciled by assuming that the observed current is composed of two effects, one due to cosmic radiation and the other due to the potential dissociation. The current measured by LePage and DuBridge is about 50,000 times larger than the current measured in the present investigation (at the same  $X$  and the same  $T$ ); thus, one would

TABLE II. Evidence for ionization of liquids by natural radiation.

	Jaffé	Bialobrzieski	Rogozinski	Pao
$v$	200	800	—	5.98
$X$	1500	900	—	19000
$r_1$	0.15	2	—	0.317
$r_2$	2.00	4	—	0.555
$I_v$	216	600	135	190000
$t$	3	5	7	8
$R$	0.66	0.61	0.28	0.00

In this table the following symbols are used:  $v$  = the effect volume of the liquid in cubic centimeters;  $X$  = the maximum field strength in volt/cm used in the investigation;  $r_1$  = radius of the inner electrode in cm;  $r_2$  = radius of the outer electrode in cm;  $I_v$  = the current density in number of ions/cc·sec. at  $X$ ;  $t$  = thickness of the lead used in cm;  $R$  = effect of the external radiation.

expect that, in their measurements, the potential dissociation effect overrides the other to show a result in accordance with the theory, while in our measurement the two effects may be of the same order of magnitude. By calculating the number of ions per cubic centimeter per second at  $T = 273^\circ\text{K}$  from Fig. 21, we found these values to be of the same order of magnitude as the value calculated for the cosmic ray alone, which is about 4240 ions/cc·sec. This tends to support the argument given above.

The relationship between  $I_A$  and  $X$  at different temperatures is shown in Figs. 22 and 23. As  $T$  decreases from  $309^\circ\text{K}$  to  $195^\circ\text{K}$ , the slope decreases almost 13 percent. Theoretically, if Eq. (3) applies, the slope should increase about 38 percent.

The assumption made in this method of testing Eq. (3) is that every ion pair produced finds its way to the electrodes, which is the same thing as saying that we have a saturation current. Plumley<sup>11</sup> has established a criterion for testing whether or not saturation conditions prevail. On applying this test it would appear that we actually do have saturation. However, as the temperature is lowered the mobility of the ions decreases while the coefficient of recombination increases. Both factors act so as to diminish the degree of saturation as the temperature is lowered. This explanation is still to be confirmed.

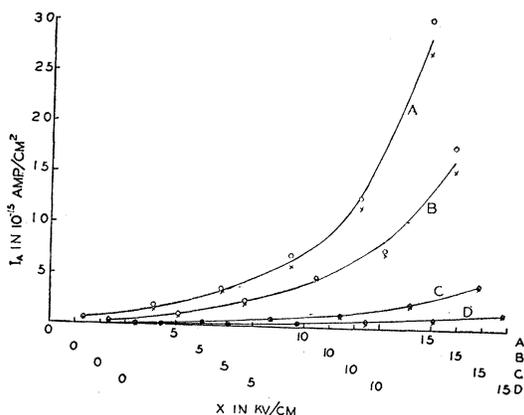


FIG. 22. Variation of residual current with field strength at constant temperature. Curves A, B, C, and D represent the results when  $T = 309.5, 296.7, 273,$  and  $195^\circ\text{K}$ , respectively. Open circle and cross represent the results for positive and negative voltages applied to the high voltage electrode of cell IV.

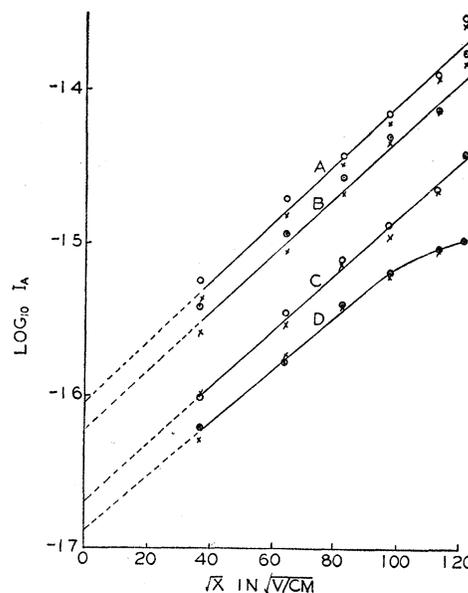


FIG. 23.  $\log_{10} I_A$  against  $X^{1/2}$  curves for isooctane. Curves A, B, C, and D represent the results when  $T = 309.5, 296.7, 273,$  and  $195^\circ\text{K}$ , respectively. Open circle and cross represent the results when positive and negative voltages are applied to the high voltage electrode of cell IV.

**Natural Conductivity (Liquid Oxygen)**

The current passing through liquid oxygen as a function of the field in the absence of radium is shown in Fig. 24. Cell IV was used so that these results are directly comparable with those for isooctane in Fig. 22. The outstanding results here are that, when the same cell is used, the current in liquid oxygen is much less than that in isooctane for fields below about 5 kv/cm; for higher fields, say 15 kv/cm, the currents are of the same order of magnitude. As a matter of interest, we tabulate the conductivity of isooctane obtained from curve C, Fig. 22, and that of liquid oxygen in Table III.

TABLE III. Comparison of natural conductivities of isooctane and liquid oxygen.

Isooctane ( $T = 273^\circ\text{K}$ )		Liquid oxygen ( $T = 90^\circ\text{K}$ )	
$X$	$\sigma_a$	$X$	$\sigma_a$
1348	7.3	1214	0.252
4050	7.9	4010	0.307
6760	11.0	6760	2.495
9460	12.5	9460	4.52
12140	17.9	12140	7.61
14860	26.1	13520	9.84
		14860	14.70

$X$  is the field strength in volt/cm;  $\sigma_a$  is the average of positive and negative conductivities in  $10^{-20}$  mho/cm.

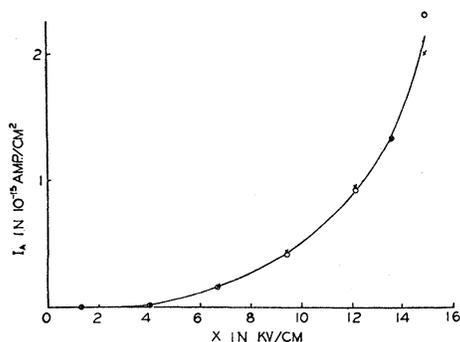


FIG. 24. Variation of the residual current with field strength in liquid oxygen. Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode of cell IV.

In order to compare the slopes of the straight lines representing  $\log I_A$  against  $X^{\frac{1}{2}}$  for liquid oxygen and isooctane the results shown in Fig. 24 are replotted. In Fig. 25 curve *A* represents the results for isooctane at  $T=273^\circ\text{K}$ , curve *B* for liquid oxygen at  $T=90^\circ\text{K}$ . It is noted that the liquid oxygen has a greater slope as predicted by the potential dissociation theory because of its lower temperature. The experimental slope for curve *B* is  $3.56 \times 10^{-2}$ , while the theoretical value is  $3.03 \times 10^{-2}$ .

In working with isooctane at ordinary temperatures there is always the slight possibility that the conductivity is due to the ions into which the last irremovable traces of water dissociate and not to charged molecules or fragments of molecules of isooctane. Such an explanation for the behavior of liquid oxygen cannot be sustained for it seems certain that any water that might

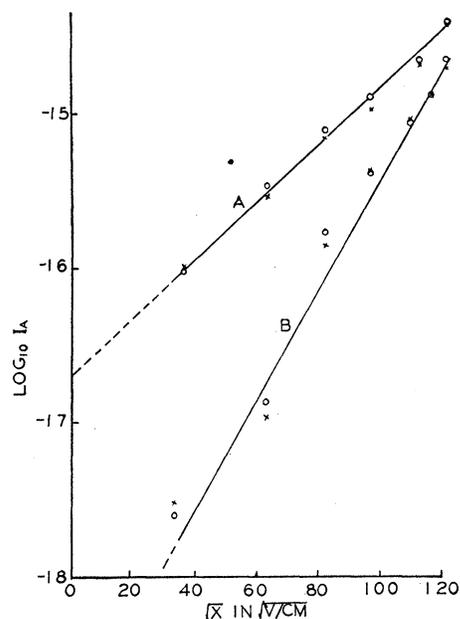


FIG. 25. Relation between  $\log_{10} I_A$  and  $X^{\frac{1}{2}}$ . Curve *A* represents the results for isooctane at  $T=273^\circ\text{K}$  and curve *B* represents the results for liquid oxygen at  $T=90^\circ\text{K}$ . Open circle and cross represent the respective results for positive and negative voltages applied to the high voltage electrode of cell IV.

happen to get into the apparatus would be firmly frozen to the solid surfaces.

#### ACKNOWLEDGMENT

The writer wishes to thank Professor A. L. Hughes for suggesting this investigation and for his continued interest and help while the experimental work was in progress.