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# CONDUCTION AND BREAKDOWN IN LIQUID DIELECTRICS*

by

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# CONDUCTION AND BREAKDOWN IN LIQUID DIELECTRICS

## 1. INTRODUCTION

In Volume 1 of this series, Lewis[1] wrote a comprehensive review of conduction and breakdown in liquid dielectrics under the title 'The Electric Strength and High-field Conductivity of Dielectric Liquids'. Since then, a number of important papers in this field have appeared and it is therefore timely to review the current ideas of the subject. Thanks to Lewis's thorough treatment, we have been able to confine our attention mostly to papers which have appeared since 1957.

Many of the papers which are of direct interest to us were presented at an international symposium on the subject of liquid dielectrics which was sponsored by the Electrochemical Society, and held in May, 1959.[2] Some twenty-eight papers were presented on the subjects of conduction and breakdown in liquids, and allied phenomena, by investigators from England, France, Germany, Italy, and the United States. Many other papers have appeared in the literature, and it is impossible to deal adequately with all of them; consequently, the authors have had to establish some sort of criterion for selection. In so doing, we have chosen to consider mainly those papers specifically concerned with the mechanism of conduction and breakdown in highly purified organic liquids, and so, reluctantly, have had to omit a number of very interesting papers.

## 2. LOW FIELD CONDUCTION

The problem of making a satisfactory measurement of the d.c. conductivity of an insulating liquid has long been recognized. The troublesome dependence upon the magnitude and time of application of the test voltage makes it necessary to specify these variables for a quoted value of conductivity. Even so, values cited by different investigators, for the same liquid under apparently comparable conditions of purity, often differ by several decades. Indeed, the reproducibility by a single investigator using the same sample and equipment leaves much to be desired. In spite of these troubles, a d.c. measurement is convenient to make and will no doubt continue to be used, since it provides useful information about the purity of the liquid.

A thorough and systematic study of several of the phenomena associated with d.c. measurements at very low fields ($< 1\,\mathrm{kV\,cm^{-1}}$) has been made by Hart and Mungall.[3] Although this study was confined to chloroform and chlorobenzene, whose resistivities lie in the intermediate range ($10^{11}\,\Omega\,\mathrm{cm}$), the conductance phenomena associated with these liquids exhibit many features in common with insulating liquids having higher resistivities in the range $10^{15}$–$10^{20}\,\Omega\,\mathrm{cm}$.

These workers used an evacuated circulating still with five conductance cells, identical except for the composition of the electrodes which were made of tantalum, monel, nickel, platinum, and platinum–(20 per cent) rhodium, respectively. Each cell was fed continuously with liquid from a common distillation flask. The

measured value of liquid conductance was found to be dependent upon the impurities present, including dissolved air, and also upon the material of the cell electrodes (see Figure 1(a)). Only after a month of continuous distillation did the

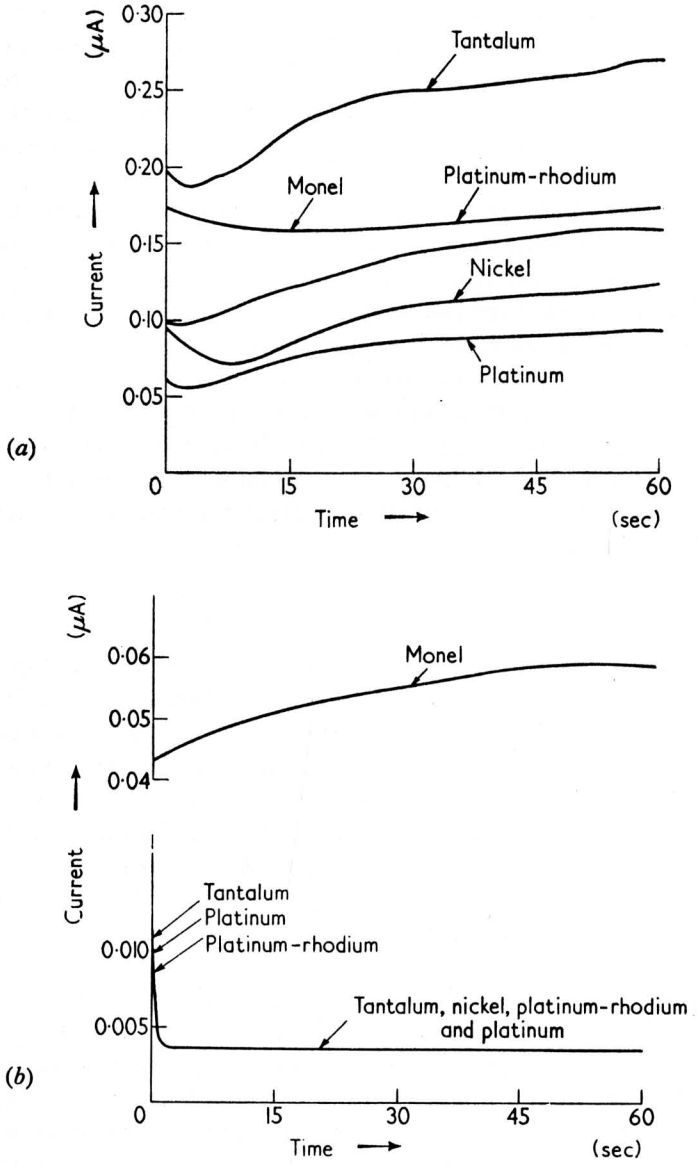



Figure 1. *The charging characteristics of chlorobenzene with electrodes of various compositions.* (*a*) *At beginning of experiment;* (*b*) *After 1 month continuous distillation. After Hart and Mungall*[3]

charging characteristics (current/time) and steady state conductances of all five cells become approximately the same (see Figure 1(b)). Furthermore, after a five month period of continuous circulation, the conductivity was still slowly, but definitely, decreasing with time.

Whenever a conductance cell is polarized by a d.c. voltage, an e.m.f. of opposite polarity to the charging voltage is developed across the electrodes. This causes a reverse current to flow in an external circuit after removal of the charging voltage. This current may flow for hours and is not to be confused with the very short time capacitive discharge current. A study of this phenomenon is often overlooked by investigators and thereby much valuable information is lost.

Hart and Mungall made detailed observations of the time decay of the counter e.m.f., as well as the charging current, and found both to be linear with a log time plot up to four decades in time. Such an observation, while interesting, is not definitive in elucidating the mechanism, since a wide variety of relaxation phenomena under the influence of a steady force depend upon time in this manner. A study of the temperature dependence of the relaxation process would have added to the usefulness of this work.

These investigators also made a direct measurement of the potential variation in a separate cell which had parallel-plate electrodes and was provided with probes. They found that the field was sharply enhanced near the cathode, slowly decaying as the anode was approached. As judged from the published curves, the field enhancement was of the order of threefold at the cathode, extending over about 5 per cent of the gap. The percentage enhancement remained roughly constant as the applied field was increased, indicating an 'ohmic' polarization.

At low field strengths (less than 10 $kV\,cm^{-1}$, for example) it is generally agreed that the residual conduction current in a highly purified insulating liquid, such as hexane, is due to trace amounts of impurity ions, and that the lower limit of current is ultimately determined by ionization of the liquid molecules themselves by external cosmic radiation.

To study prebreakdown conduction in these weakly conducting liquids, various kinds of experiments have been devised by workers in the field. Their efforts, in the main, have been directed toward increasing the conductivity to more readily measurable values by increasing the applied field strength or by ultra-violet irradiation of the cell. The latter has not been very successful, probably because it requires a quartz cell (or window) and the use of degassed liquid,[4] and early workers may not have recognized the importance of these requirements. Furthermore, the use of radiation including wavelengths of less than 2,000 Å produces charge carriers in the body of a hydrocarbon liquid as well as photoemitted electrons from the electrodes. This greatly complicates the analysis of the results. By the use of optical filters one may restrict the radiation to somewhat longer wavelengths ($>$ 3,000 Å) and thereby inject electrons from the cathode without the complication of charge generation in the body of the liquid itself. LeBlanc[5] and Morant[4] have exploited this technique in recent years, although some years ago Dornte[6] had observed enhancement of current in pure hydrocarbon liquids by irradiation with an unfiltered source. Recently, Sletten[7] has called attention to the stabilization of currents in hexane by dissolved oxygen.

After an electron is injected into the liquid by some process, such as photoinjection, it is of interest to know whether it (1) acts as a free particle, (2) is attached to a neutral hydrocarbon molecule to become a negative ion, or (3) exists in an intermediate, partly trapped, partly free state, as suggested by Crowe.[8] A free electron would be expected to have a much larger mobility than a trapped electron so that a measurement of the mobility should enable one to identify the charge

carrier. A knowledge of the mobility is of importance, not only in the theory of conduction *per se*, but also in making space charge calculations and in the interpretation of time lag phenomena in liquid breakdown.

Toward this end, LeBlanc[5] has reported upon a new experimental technique whereby he made a direct measurement of the drift mobility of electrons in *n*-hexane. The time for a bundle of electrons to drift between plane parallel electrodes immersed in the liquid was measured. The applied field strength was always kept below 2 kV cm$^{-1}$ so that there was no possibility of collision ionization. Electrons were injected from the cathode (aluminium) by illumination with a high intensity pulse of ultra-violet light, the duration being short compared to the

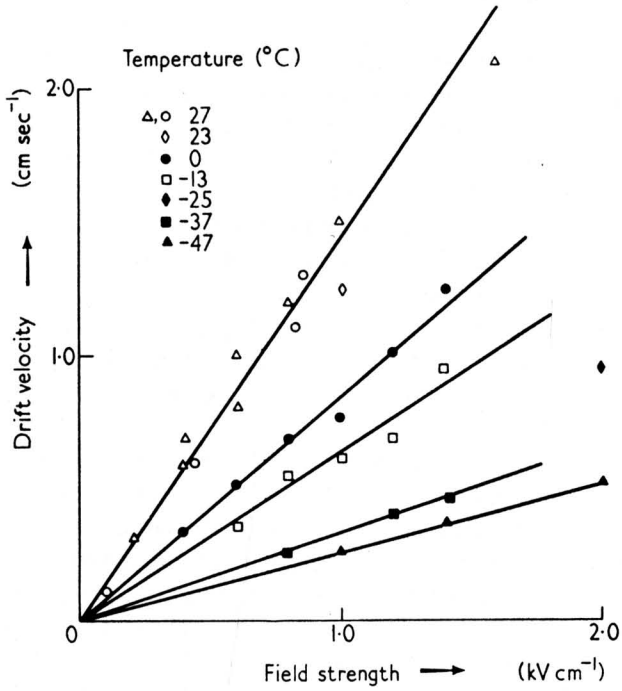



Figure 2. *The dependence of electron drift velocity upon field strength at various temperatures. Liquid n-hexane. After LeBlanc*[5]

transit time of the electrons. The transient current produced in the external circuit followed closely the expected behaviour; some departure from the ideal pulse shape was found and was ascribed to emission of electrons from the edge of the cathode and lateral diffusion. These effects caused the appearance of a tail at the end of the induced current pulse. The measurements were made with two different electrode separations as a function of applied field and some observations were made at different temperatures in the range 27 to −47°C. The results are shown in Figure 2.

From the slopes of these lines, LeBlanc calculated the electron drift mobility as a function of temperature, the value in liquid hexane at 27°C being $1{\cdot}4 \pm 0{\cdot}1 \times 10^{-3}$ cm$^2$V$^{-1}$sec$^{-1}$. The value in liquid heptane was the same within experimental error. This value of mobility is small ($10^5$ times smaller than the value for a free electron in liquid argon) but a little larger than ionic mobilities

in aqueous solution ($10^{-3}$ to $10^{-4}$ $cm^2V^{-1}sec^{-1}$). As shown in Figure 3, the drift mobility was found to change with the absolute temperature $T$ according to the relation

$$\mu = \mu_0 \exp(-\Delta u/\mathbf{k}T) \qquad \ldots(1)$$

Here $\mu_0 = 0{\cdot}3 \pm 0{\cdot}2$ $cm^2V^{-1}sec^{-1}$ and $\Delta u = 0{\cdot}14 \pm 0{\cdot}02$ eV.

The product of mobility and liquid viscosity changed with temperature, indicating a violation of Walden's rule (see Figure 3). LeBlanc points out that the small value of mobility and anomalous behaviour with respect to Walden's rule

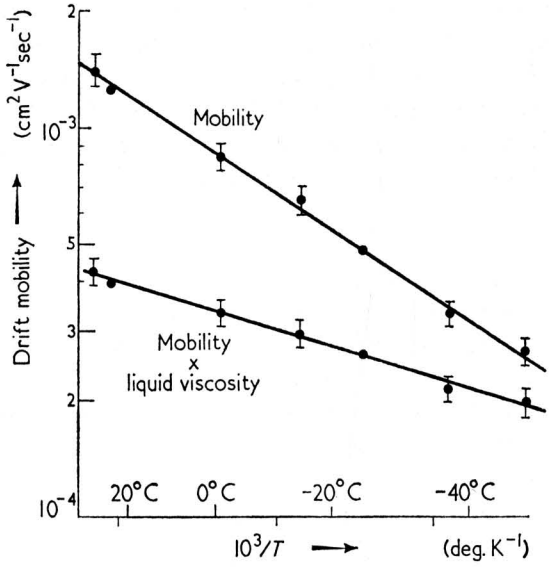



Figure 3. *The dependence of the drift mobility of electrons in n-hexane upon temperature (upper curve). The dependence of mobility times liquid viscosity upon temperature (lower curve). After LeBlanc*[5]

are two important pieces of evidence for the fact that one is measuring the mobility of neither a free electron nor a negative molecular ion. Additional evidence against the latter is provided by a comparison of the carrier mobilities in hexane and heptane. Considering both the size of the molecule as well as the increased viscosity, one would expect the mobility in heptane to be about 1·5 times that in hexane, if the charge carriers were negative molecular ions. This is well beyond the limits of the experimentally observed ratio of $1{\cdot}1 \pm 0{\cdot}2$.

Since his measurements indicate an intermediate value of mobility, LeBlanc has proposed mechanism (3) mentioned above. According to this model, an injected electron travels some distance $\lambda$ before being trapped. After a time $\tau$ the electron escapes from the trap and travels another free path before being trapped again. Since $\lambda$ is much smaller than the total interelectrode distance, then the electron drift mobility will be given by

$$\mu = \frac{\mu_e \lambda}{c(\tau + \lambda/c)} \qquad \ldots(2)$$

Here $\mu_e$ is the mobility an electron would have in the absence of traps and $c$ is the average thermal speed of the electron ($\sim 10^7$ cm sec$^{-1}$ at room temperature). Neglecting $\lambda/c$ in comparison to $\tau$, and assuming that $\tau$ will decrease exponentially with increasing temperature, then equation (2) may be written in the form of equation (1). In this manner, the observed value of $\Delta u$ is interpreted as being the average trapping energy, and the small value (0·14 eV) is an indication of relatively shallow traps.

The mobility of the electron would be expected to be dependent on electric field, and LeBlanc discusses this to some extent. He reasons that at fields of the order of 1 MV cm$^{-1}$ the energy gained by an electron in travelling across a trap of molecular dimensions will be comparable to the observed small values for the trapping energy. This would lead to an increase in the rate of escape from traps and hence an increase in the drift mobility. Quantum mechanical tunnelling would further enhance this mobility. Assuming classical processes only, and square-well traps of radius $a$, LeBlanc gives the expression for the field dependence of mobility

$$\mu = \mu_0 \exp[-(\Delta u - Ea)/\mathbf{k}T] \qquad \ldots(3)$$

The experimental technique of LeBlanc has been extended to high fields by Chong and Inuishi[39] and will be discussed in Section 3.

In many theories of conduction in liquids, it is commonly assumed that electron emission into a liquid occurs in a manner similar to emission into a vacuum. The effect of the liquid is neglected, apart from the fact that the vacuum work function of the cathode is lowered by the factor $1/\epsilon$ where $\epsilon$ is the dielectric constant,[9] and Poisson's equation is written as

$$\frac{\partial^2 V}{\partial x^2} = \frac{-4\pi\rho}{\epsilon} \qquad \ldots(4)$$

This approach has not been very successful in correlating the magnitude of the observed currents with the work function of the cathode corrected in this manner.[10] Furthermore, the current emitted into a pure insulating liquid is usually two or three orders of magnitude smaller than the current emitted into a vacuum by the same electrodes.[4] This is the reverse of what would be expected on the basis of the simple concept presented above.

In an effort to clarify this situation, Morant[11] has reasoned that, in addition to the work function potential barrier, there is an additional barrier due to a space charge layer formed by electrons injected into the liquid by the metallic electrode. Such a potential arises in a manner similar to the formation of the junction potential between two dissimilar metals—the so-called contact e.m.f. Morant has applied the theory of the metal–semiconductor contact to the case of the metal–insulating liquid interface and has calculated a total barrier height, consisting of both the work function and space charge barrier. He computes the latter to be about 1·0 eV in a typical well purified hydrocarbon liquid and shows that the presence of such a space charge tends to make the conduction current much less sensitive to the cathode work function. Although the estimated magnitude of this barrier may be open to some question, the general concept seems to be sound.

Morant[11] has demonstrated the existence of the space charge potential by an ingenious experiment. As shown in Figure 4, a movable cone is immersed by varying amounts into a metal cup filled with pure hexane, while the potential across

the system is measured on a sensitive electrometer. When the metal cone is gradually immersed into the liquid, this potential steadily rises. As might be anticipated, there are some difficulties with spurious charging of the electrometer by metal-to-metal contact e.m.f., and a troublesome change in capacitance of the circuit due

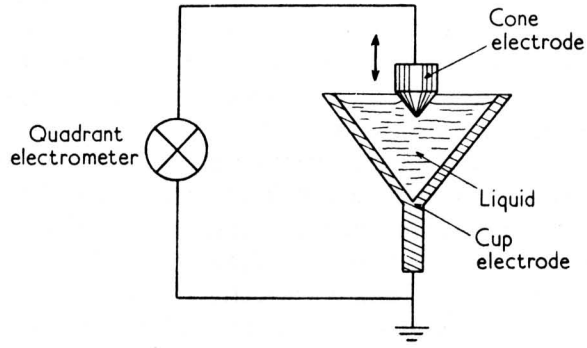



Figure 4. *Experimental arrangement for detecting space-charge potential at metal–hexane interface. After Morant*[11]

to geometry changes (see Figure 5). However, these effects may be taken into account, and there is little doubt as to the existence of the space charge potential barrier.

Additional experimental evidence of the space charge layer at the electrode has been published by Morant in a later note.[4] In this experiment degassed hexane was sealed into a conductance cell at a pressure of $10^{-6}$ mm Hg; the cell was

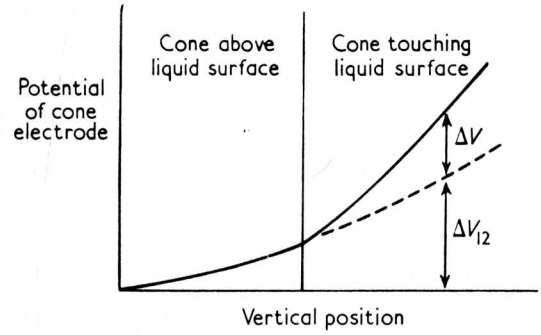



Figure 5. *The potential of the cone electrode in Figure 4 as a function of its vertical position. After Morant*[11]

equipped with a side arm bulb into which all the hexane could be frozen out with liquid nitrogen. Such an arrangement permits the photoemission into a vacuum to be compared directly with the emission from the same electrodes into hexane. Morant noted a two to three decade decrease in emission current when the electrodes were immersed in liquid, but a more important observation was the radical change in the character of the voltage–current dependence. The current emitted into the vacuum reached a saturation level in the expected manner, but the current emitted into hexane showed a distinct lack of saturation.

In addition, Morant measured the spectral response of the aluminium cathode, with and without hexane. He found that the photoelectric threshold was about the same in the two cases, viz., 4·1 eV (corresponding to a wavelength of 3,000 Å), and that the threshold wavelength increased slightly as the applied voltage was increased. This increase in threshold wavelength, as well as the lack of saturation, tends to support the existence of the space charge layer at the cathode which causes a diminution of the importance of the vacuum work function barrier. On the other hand it is rather surprising to find the photoelectric threshold to be about the same for emission into a vacuum and into a liquid.

Swan[12] has re-examined the experimental data of Williams[13] and Stacey[14] on ion mobilities in liquid argon and liquid helium. Previous analysis of these results appeared to indicate that ionic mobilities in these liquids could not be interpreted in terms of gas kinetic theory. Swan's analysis shows that for positive ions in liquid argon the results had been incorrectly calculated, and that Hassé's[15] modified form of Langevin's equation for ion mobility gives good agreement with the experimental results. This equation for mobility (equation (5)) takes into account elastic collision scattering, and also polarization scattering in the medium

$$\mu = \frac{A}{[\delta(\epsilon-1)]^{1/2}}\left(\frac{M+m}{m}\right)^{1/2} \qquad \ldots(5)$$

In this equation, $\mu$ is the ion mobility, $\delta$ is the gas density, $\epsilon$ is the dielectric constant, and $m$ and $M$ are the masses of the atom and ion, respectively. $A$ is a function of a parameter $Z$ where

$$Z^2 = \frac{8\pi S^4 \delta \mathbf{k} T}{(\epsilon-1)\mathbf{q}^2 M}$$

Here $S$ is the sum of the atomic and ionic radii, and $\mathbf{q}$ the electronic charge.

Using this equation, Swan[12] has calculated the mobilities of positive ions in liquid argon at 90°K and helium at 4·2°K: these are, respectively, $3{\cdot}24\times10^{-3}$ $cm^2V^{-1}sec^{-1}$ and $3{\cdot}4\times10^{-2}cm^2V^{-1}sec^{-1}$. These values compare very favourably with the corresponding experimental results of 2·8 to $3{\cdot}2\times10^{-3}$ $cm^2V^{-1}sec^{-1}$ (Williams[13]) and $3{\cdot}6\times10^{-2}$ $cm^2V^{-1}sec^{-1}$ (Meyer and Reif[16]).

Equations of this type are inapplicable when the energy gain per mean free path becomes comparable with the thermal energy. The negative carrier in liquid argon is known to be a free electron, but the application of Wannier's high-field equation[17] to the measured values of mobility leads to a value for cross-section, which is about 100 times smaller than the gas cross-section. Swan[12] attributes this discrepancy to the presence of small quantities of impurities. This is corroborated by the observation by Bortner, Hurst, and Stone[18] that very small concentrations of oxygen and nitrogen can appreciably increase the drift velocity of electrons in gaseous argon.

On the basis of their analysis, Williams and Stacey[14] had concluded that some electron multiplication was probably taking place at the highest fields in their experiments on liquid argon. However, Swan's subsequent analysis indicates that the probability of ionization is much less than had previously been thought.

Measurements of the mobilities of ions in liquid helium[13] indicate that usually the negative carrier is not a free electron, and the evidence suggests that impurities (particularly dissolved oxygen) are acting as trapping agents for the electrons.

## 3. HIGH FIELD CONDUCTION

The most widely accepted theories of liquid conduction at high fields are covered in detail in Lewis's review;[1] therefore, it is only necessary to recapitulate them and list their mathematical expressions for convenient reference. While conduction at high fields is still not completely understood, important papers bearing on each of the processes discussed below have appeared in the literature during the past few years.

### 3.1. Theories of Conduction

At high field strengths (say, greater than $0\cdot1$ MV cm$^{-1}$) the conduction process is known to involve emission of electrons from the cathode by either (1) cold emission, sometimes called field emission, in which electrons tunnel through the surface potential barrier, or (2) field enhanced thermionic emission, usually referred to as Schottky emission. The latter process is a consequence of the lowering of the work function barrier by the applied field so that appreciable thermionic currents are emitted even at room temperature.

Cold emission is described by the Fowler–Nordheim equation[19]

$$I = 6\cdot2\times10^{-6}\frac{F^{1/2}S}{\phi^{1/2}(F+\phi)}E^2\exp(-6\cdot8\times10^7\phi^{3/2}/E)\text{ amperes} \qquad \ldots(6)$$

$F$ is the Fermi level of electrons in the metal and is usually taken to be 5 eV, $\phi$ is the work function, $S$ is the emitting area in square centimetres, and $I$ is the current in amperes. As predicted by this equation, conduction data may often be expressed in linear form by a plot of $\ln I/E^2$ versus $1/E$ but the values for $\phi$ and $S$ calculated from the slope and intercept of this line are frequently of unreasonable magnitude. These difficulties can be resolved to some extent by invoking the presence of an oxide layer on the cathode and by taking account of the field enhancement at the tips of emitting asperities on the cathode surface.

The emission of electrons through a surface barrier layer has been analysed by Stern, Gossling, and Fowler.[20] They derive the expression

$$I = 6\cdot2\times10^{-6}\frac{F^{1/2}S}{(F+\phi_1)\phi_1^{1/2}}E^2B\exp(-6\cdot8\times10^7\phi_2^{3/2}/E)\frac{\phi_1}{\phi_2}\text{ amperes} \qquad \ldots(7)$$

where $\phi_1$ is the work function of the metal, $\phi_2$ is the work function of the oxide layer, and $B$ is the barrier term given by the expression

$$B = \exp\left[-6\cdot8\times10^7\frac{\phi_1+\phi_2+(\phi_1\phi_2)^{1/2}}{\phi_1^{1/2}+\phi_2^{1/2}}a\right]$$

Here $a$ is the layer thickness in centimetres. This equation is seen to be of the same form as the Fowler–Nordheim equation with the addition of the factor $B$ which takes into account the presence of the barrier layer.

Schottky, or field enhanced thermionic emission,[21] is described by the equation

$$J = J_t\exp\frac{4\cdot4}{T}\cdot\sqrt{(E/\epsilon)}\text{ A cm}^{-2} \qquad \ldots(8)$$

Here $J_t$ is the thermionic current density and is given by the Richardson–Dushman equation

$$J_t = AT^2 \exp(-b_0/T) \qquad \ldots(9)$$

$A$ and $b_0$ are emission constants of the cathode material, the latter being proportional to the thermionic work function.

The effect of field enhancement due to microscopic surface roughness is taken into account in the above equations by making the substitution

$$E = ME_a$$

in which $M$ is a multiplication factor and $E_a$ is the applied field. Calculated values for $M$, even for highly polished surfaces, may be as large as ten.[22]

Attention is called to the extreme sensitivity of the current in the above equations to the assumed values for the work functions and barrier thickness. For example, from equation (9) at a temperature of 450° K the thermionic current will increase by a factor of $10^5$ when $b_0$ is reduced from 25,000 to 20,000° K.

It may be remarked that the weight of experimental evidence seems to indicate that Schottky-type emission, rather than cold emission, is the more plausible mechanism in liquid conduction at fields near breakdown. In principle, one may distinguish between these two important types of field emission by making conduction measurements as a function of temperature, but, as yet, the evidence is inconclusive.

In addition to electrode processes for increasing the conduction at elevated fields, charge carriers may be generated in the liquid itself by field dissociation of either impurities or the liquid molecules themselves.[10, 23] This effect arises because the equilibrium constant for an undissociated molecule and its ions will increase with increasing field. The Onsager equation[24] for the dissociation of a weak electrolyte adequately describes this phenomenon, and the limiting form of the equation at high fields is

$$K(E) = K(0)\sqrt{\left(\frac{2}{\pi}\right)}\cdot(8b)^{-3/4}\exp\sqrt{(8b)} \qquad \ldots(10)$$

$K(E)$ is the equilibrium constant at field $E$ and

$$8b = 77\cdot 2E/\epsilon T^2$$

Assuming that the positive and negative ions of the dissociated molecule contribute equally to the current, and that the mobility is independent of field in the range of interest, then the current should be proportional to $E\sqrt{[K(E)]}$. The linear test plot for this kind of conduction consists of a graph of $\ln IE^{-5/8}$ vs $\sqrt{E}$. Since the corresponding plot for Schottky emission is $\ln I$ vs $\sqrt{E}$, it is difficult to distinguish between these two mechanisms of charge production when measurements are made with the usual range in field strengths.

We must also consider the possibility that charge carriers may be generated by collision ionization of liquid molecules or of easily ionized impurities in a manner analogous to the Townsend model[25] of conduction in gases. With this kind of charge production

$$J = J_c \exp(\alpha d) \qquad \ldots(11)$$

where $J_c$ is the current density emitted at the cathode via either Schottky or cold emission. The ionization coefficient $\alpha$, as well as $J_c$, will be strongly field dependent and so the only satisfactory method for detecting and measuring a multiplication process involves the determination of the gap width dependence of conduction currents at constant field strength. According to equation (11), a plot of $\ln I$ versus the gap width $d$ at constant $E$ would yield a straight line of slope $\alpha$. Since the production of charge carriers by this process would be expected to be favoured at high fields, it is important to make measurements at fields up to, and including, breakdown. Consequently, the experimental conditions (pure liquid, suitable electrode configuration, etc.) must be such that breakdown will occur at the highest possible value.

All the above processes for charge generation are strongly field dependent; hence it is very difficult to separate them simply on the basis of test plots. Furthermore, test plots often yield absurd values for the emission parameters, and, in such cases, a predicted straight line alone constitutes weak evidence for the applicability of a theory. The fact that different mechanisms may be operative in different ranges of field strength and under different degrees of sample purity, coupled with the fact that the processes may be interdependent, can result in very complicated behaviour.

The importance of flat electrode systems whose separation may be varied over wide limits cannot be overemphasized. This demands rather exacting mechanical arrangements for achieving and checking the planarity of the surfaces as well as for the measurement of small gap widths. Spherical surfaces under high stress have an emitting area which increases with increasing stress even when held at constant separation. In addition, the area under high stress is a function of electrode separation. Therefore, the use of a spherical electrode introduces additional complications into an already difficult problem, making the analysis of the results almost impossible.

### 3.2. D.C. Conduction Studies

A survey of the papers dealing with d.c. measurements at high fields shows that most of the early studies were made at field strengths less than about 25 per cent of the breakdown value. It is suspected that one of the principal reasons for this restriction is the appearance of widely fluctuating currents at higher fields, making the measurements of a current quite difficult. Green,[26] House,[27] and Sletten[7] succeeded in extending their d.c. current measurements above 1 $MV\,cm^{-1}$.

House[27] was able to cope with the erratic currents in hexane encountered near breakdown ($1{\cdot}4\ MV\,cm^{-1}$) through the use of a high speed electronic diverter circuit to reduce sample decomposition and electrode damage by the prebreakdown current bursts. Only after a tedious 'conditioning process' could stable and reproducible currents be observed at high fields. The same effect was reported by Tropper in his study of prebreakdown currents in transformer oil.[28] These current bursts have been ascribed to a variety of causes including (1) gas removal from surface layers in the form of bubbles, (2) sporadic removal of oxygen to expose sites of low work function, (3) impurities moving into the high field region of the test gap, (4) and particles coming to rest upon the cathode. It has also been suggested[1] that the conditioning process in hydrocarbon liquids is associated

with the formation of polymer layers on the electrodes to produce more stable surface conditions.

A recent discovery by Sletten[7] is concerned with the elimination of the conditioning process. He observed the usual violent current fluctuations with well degassed hexane, and a prolonged conditioning period, but, with dissolved air in the sample, no conditioning was necessary. In Figure 6 the dashed line shows the conduction current of degassed hexane measured by House[27] with careful conditioning. Sletten's measurements with dissolved air (oxygen) and no conditioning are shown as solid lines. It is clear that the presence of dissolved oxygen permits measurement without conditioning at fields near breakdown, but the mechanism is not at all clear.

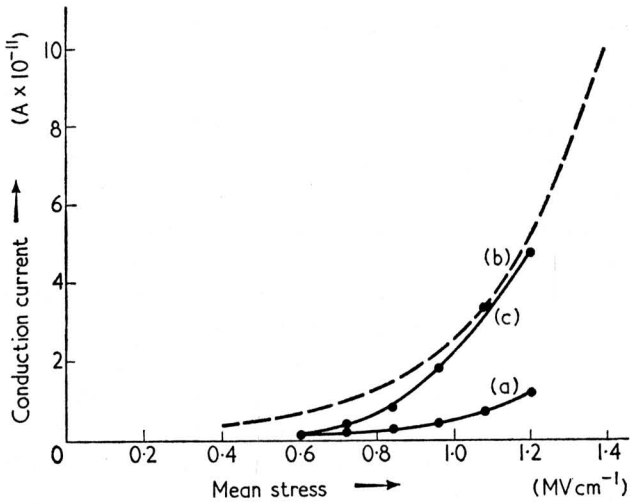



Figure 6. *The conduction current of liquid hexane as a function of the mean stress. (a) Purified hexane saturated with air; (b) Purified and degassed hexane; (c) Commercial hexane saturated with air. After Sletten*[7]

Additional experimental evidence bearing on the effect of dissolved oxygen on conduction in hexane, has been presented by LeBlanc,[29] using the photo-injection technique described earlier.[5] He found that the photo-injected current pulses disappeared when degassed liquid samples were equilibrated with a 100 mm Hg partial pressure of oxygen. It required about ten minutes for the complete disappearance of the pulse after admitting oxygen to the system. Partial pressures of oxygen less than 100 mm Hg did not produce any observable effect. The effect was reversible, i.e. removal of the dissolved gas restored the sample to its original behaviour. This reversibility would indicate that the oxygen does not undergo chemical combination. However, it is not entirely clear whether this is a volume effect in the liquid or an electrode surface effect. The oxygen would provide deeper electron traps (approximately 0·5 eV) than the shallow ones suggested by LeBlanc's experiments,[5] and thereby reduce the probability of thermal untrapping at room temperature. Perhaps the use of flat electrodes of different areas and spacing would help to separate the surface and volume effects.

Coelho and Bono[23] have reported upon some interesting measurements of d.c.

conduction in hexane and heptane under very inhomogeneous field conditions. The electrode geometry consisted of a 1 mil wire surrounded concentrically by a 1 cm diameter cylinder. In the absence of space charge, the field arising from this configuration is calculable and the use of such a geometry is helpful in separating cathodic and anodic effects. Coelho and Bono noted the usual conditioning process, the currents measured after conditioning being some decades lower than the starting values. The effect was more pronounced with the wire negative, supporting the idea that conditioning involves the elimination of regions of high emissivity on the cathode.

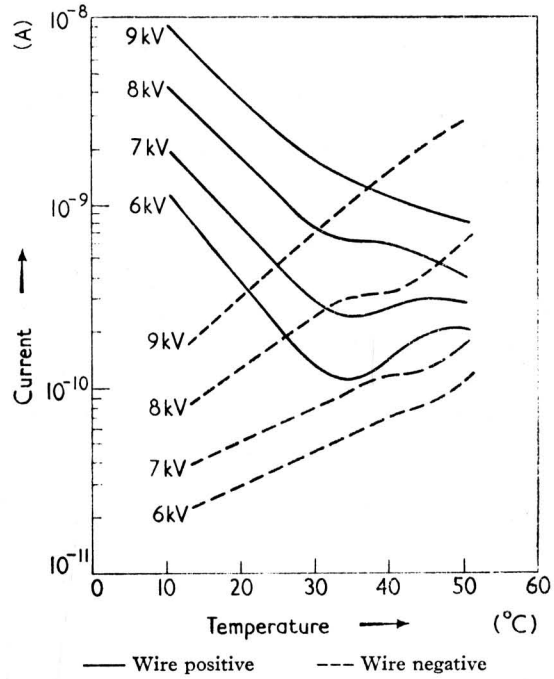



Figure 7. *The dependence of d.c. conduction current of n-hexane upon temperature for wire-cylinder geometry. The potentials of the wire are given beside the appropriate curve. After Coelho and Bono*[23]

Their results are shown in Figure 7 where the current after conditioning is plotted against the temperature for several different applied voltages. They made the unexpected observation that, at room temperature, the currents with a positive wire were about ten times higher than those measured with the wire negative. One might have expected the current to be higher with the wire as cathode if field emission were important. Furthermore, as the temperature was increased to 50° C, the currents measured with the wire positive and negative approached the same values. To test for field dissociation, a plot of $\ln(IE^{-5/8})$ versus $\sqrt{E}$ for the positive wire currents was made as discussed in sub-section 3.1. An excellent straight line was found whose slope is within 15 per cent of the theoretical value. This has been taken to show the importance of field induced dissociation of impurities near the wire.

This mechanism, however, fails to account for the observed temperature dependence and polarity effect. This is explained by Coelho and Bono as follows. For the particular geometry of the cell, the field (in MV $cm^{-1}$) at the wire surface is about 100 times the applied voltage and decreases rapidly with the reciprocal of the distance from the wire. The authors reason that when the wire is positive, negative ion space charge enhances the applied field at the wire. On the other hand, when the wire is negative, the electron space charge arising from field emission decreases the field at the wire below the geometric value. (Apparently, the presence of positive ion space charge is ignored.) An increase of temperature causes diffusion of both space charges, decreasing their effect and tending to make the field at the wire approach the geometric value. In Figure 7 the currents with both positive and negative wire are increasing with about the sixth power in field. It might have been expected that the two characteristics would differ somewhat if only one were space charge limited. Furthermore, $I$ is proportional to $E^{3/2}$ or $E^2$ for space charge limited currents in gases and solids, and it is surprising to note such a strong dependence on $E$ for space charge limited emission from a wire, unless the space charge is very localized.

### 3.3. **Pulse Conduction Studies**

The authors recognized some years ago that the use of short pulses of voltage to measure conduction currents had several important advantages over prevailing d.c. methods. Among these advantages are that (1) pulse breakdown fields are higher than with d.c.; (2) troublesome polarization effects may be minimized; and (3) undesirable chemical effects, such as wax formation on the electrodes, may be avoided.

Although considerable progress has been made in recent years in the measurement of electric strengths of liquids through the use of pulse techniques, conduction current measurements have continued to rely on d.c. Presumably, this is due to the experimental difficulties inherent in making reliable measurements of currents under short pulse conditions. With the advances that have taken place in electrometer design and in pulse techniques during the past few years, it has become possible to surmount these difficulties and Watson and Sharbaugh[30] have described a method for making pulse conduction measurements in insulating liquids.

The method is based on the fact that a voltage pulse $V_a$ applied to a series circuit consisting of resistance $R$ and capacitance $C$, leaves behind on the capacitor a charge proportional to $(V_a/R)\tau$. Here $\tau$ is the pulse duration, which must be short compared to the time constant $RC$. This charge is conveniently measured after the termination of the pulse, and from a knowledge of its magnitude and the pulse duration the average conduction current is readily calculated.

Watson and Sharbaugh made a comparison of the results obtained with d.c. and their pulse method using identical electrodes and liquid samples. As shown in Figure 8, the results obtained with the two techniques were quite different. Firstly, the absolute magnitudes of the pulse currents were orders of magnitude greater than for d.c.; and secondly, in the time range $10^{-2}$–$10^{-6}$ sec the magnitude of the pulse currents were approximately independent of the applied voltage duration, whereas in the d.c. case the currents decreased markedly with time. On the basis of this and other results, there is good evidence for suspecting that d.c. conduction

current measurements in liquids are more complex than pulse measurements, and that the latter may be more reliable as a guide to prebreakdown phenomena.

Macfadyen and Helliwell[31] have described a second method for the measurement of conduction currents under pulse conditions through the use of a Schering bridge circuit. The successful operation of a bridge circuit with microsecond pulse voltages is a formidable task, involving, among other things, a carefully balanced pulse transformer to couple the oscilloscope detector to the bridge circuit. These authors successfully overcame the circuit problems and their paper is mainly concerned with the experimental aspects of the method. The use of an oscilloscope to

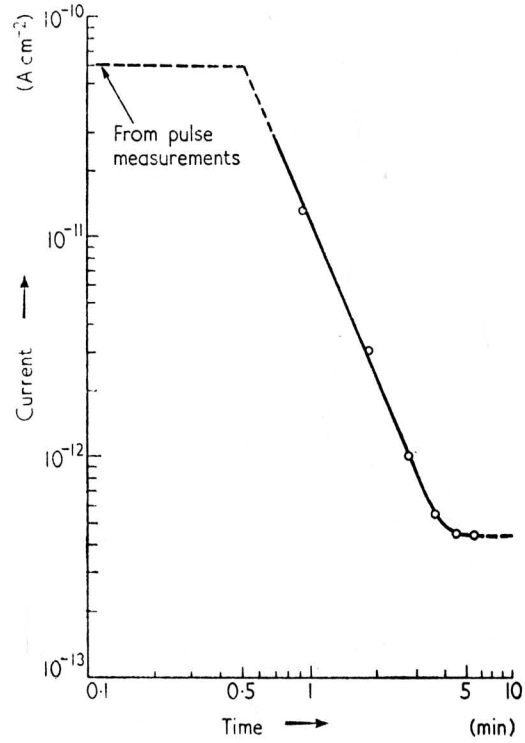



Figure 8. *A comparison of the magnitudes of conduction currents in n-hexane measured under d.c. and pulse conditions (1,500 V; 10 mil gap; stainless steel electrodes). Solid line shows time dependence with d.c.; dashed line extrapolated from pulse measurements. After Watson and Sharbaugh*[30]

detect bridge unbalance permits the observation of the current as a function of time, although this feature was not particularly exploited by Macfadyen and Helliwell. Unfortunately, their measurements were made at a single gap and over a limited range of field strengths. Their observations at high fields were limited by breakdown in the liquid which occurred at about 0·5 MV cm$^{-1}$. In order to reach higher fields with this electrode geometry it may be necessary to condition the electrodes. The experimental results of Macfadyen and Helliwell are shown in Figure 9 where the observed current is plotted on a linear scale against field strength. They suggest that at these large current densities space charge limited

emission probably occurs; however, with flat electrodes the local emission in the vicinity of cathode asperities could be space charge limited even though the total current varies with the fifth power of voltage as shown in Figure 9.

One of the most controversial points in the interpretation of conduction in liquids concerns the presence (or absence) of an electron multiplication in the liquid. Those who interpret behaviour at high fields by means of a Townsend model are prone to favour the existence of a multiplication, or '$\alpha$-process', and some have published d.c. conduction data which are consistent with this model.[27, 33–35]

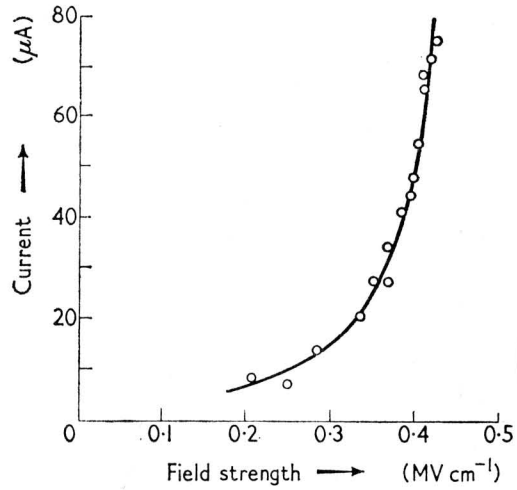



Figure 9. *The dependence of conduction current upon field strength for n-hexane under pulse conditions. After Macfadyen and Helliwell*[31]

On the other hand, there are others who doubt the existence of an $\alpha$-process in liquids and have measurements to support their point of view.[26, 36] As indicated earlier, most of these studies have been confined to fields less than about 25 per cent of breakdown. House[27] and Green[26] were the first workers to succeed in making conduction measurements up to field strengths in the vicinity of breakdown.

These two investigators found the usual contradictory evidence concerning the existence of collisional ionization. Green[26] observed no catastrophic current increase up to a field of $1 \cdot 06$ MV cm$^{-1}$, and set an upper limit of $\alpha$ equal to 2 at fields above $0 \cdot 8$ MV cm$^{-1}$, if it existed at all. House[27] thought he had positive evidence at fields of $1 \cdot 5$ MV cm$^{-1}$. However, both of these investigations suffered from the use of spherical electrode geometry which, as discussed above, makes the analysis of results very difficult.

Watson and Sharbaugh[37, 38] overcame these difficulties by using flat electrodes with their pulse technique to investigate conduction in hexane up to the highest fields reported for the breakdown of hexane between conditioned flat electrodes. As shown in Figure 10, currents were measured over a wide range of fields ($0 \cdot 04$ to $1 \cdot 4$ MV cm$^{-1}$) and at several gap widths in order to determine whether or not an $\alpha$-process exists in the liquid. These authors concluded there was no evidence for multiplication at fields up to $1 \cdot 2$ MV cm$^{-1}$, but observed

marginal indication of the beginning of the process at $1 \cdot 3$ MV cm$^{-1}$. Further evidence would be required to establish the existence of the process with certainty, the lower limit of detection in this experiment corresponding to a value of $\alpha d$ equal to about $0 \cdot 1$.

Having concluded that electron multiplication in the gap is relatively unimportant, Watson and Sharbaugh assume that the observed dependence of bulk current on the applied field (approximately ninth power) is explicable in terms of electron emission from the cathode and examined the various possible emission mechanisms.

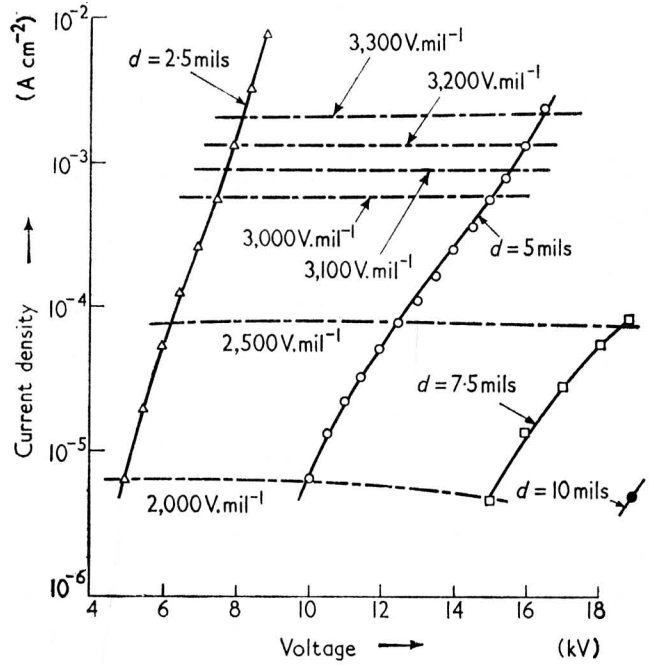



Figure 10. *The dependence of conduction current density upon voltage at different electrode separations (in n-hexane). Lines of constant field strength are shown as dashed lines. After Sharbaugh and Watson*[37]

On the basis of test plots and the assumption of realistic emission parameters, the authors conclude that the currents originate either by Schottky emission or by field emission from asperities on the cathode. It is possible that these currents are space charge limited at the tips of the emitting points. In the case of field emission, the current magnitude would be strongly influenced by an oxide layer on the cathode as discussed in sub-section 3.1. Using equation (7) the authors calculate the active emitting area $S$, composed of the sum of all the areas of the cathode asperities, to be of the order $10^{-3}$ of the total cathode area. At $1 \cdot 3$ MV cm$^{-1}$ the measured current density was $10^{-3}$ to $10^{-2}$ A cm$^{-2}$; hence the local current density at the emitting points is computed to be about 1 A cm$^{-2}$. Such a calculation assumes that the sum of all the local currents is linearly related to the local emission and this would only be true for the hypothetical case of identical emitting points.

Chong and Inuishi[39] have reported upon the measurement of the mobility of electrons in hexane and benzene at field strengths up to the region of breakdown. The experimental technique of LeBlanc[5] was used, i.e. a pulse of electrons was injected with a light pulse whose duration was short compared to the transit time of the electrons. However, instead of observing the time variation of the current in the external circuit, the current was integrated with respect to time and the build-up of charge was observed directly on an oscilloscope. The transit time of the charges is then simply the time elapsed during the linearly rising portion of the charging curve. Chong and Inuishi generated photo-currents whose magnitude was about $10^{-9}$ A cm$^{-2}$ (about $10^3$ larger than those used by LeBlanc). Apparently, this higher current was achieved by the use of high intensity light pulses and a magnesium cathode.

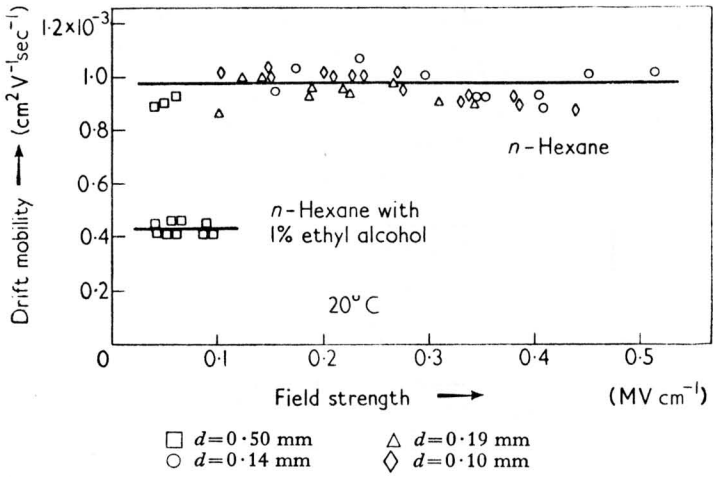



Figure 11. *The dependence of drift mobility upon field strength. After Chong and Inuishi*[39]

The results of Chong and Inuishi for the drift mobility of electrons in hexane are shown in Figure 11, as a function of field strength. It will be noted that their value of $1{\cdot}0 \times 10^{-3}$ cm$^2$ V$^{-1}$sec$^{-1}$ at 20° C is independent of field strength up to 0·5 MV cm$^{-1}$, and agrees well with the value of $1{\cdot}4 \times 10^{-3}$ cm$^2$V$^{-1}$sec$^{-1}$ measured by LeBlanc at 27° C and 2 kV cm$^{-1}$. By measuring the temperature dependence of mobility and using equation (1), Chong and Inuishi derived a value of $\Delta u = 0{\cdot}16$ eV. Furthermore, the product of mobility and liquid viscosity was not independent of temperature, indicating a violation of Walden's rule. These workers conclude from the low value of mobility, the lack of field dependence, and lack of fulfilment of Walden's rule that either (1) the electron attaches to neutral hydrocarbon molecules or (2) the electron induces a local region of polarization in a manner analogous to the 'polarons' in solids suggested by von Hippel.[40]

A value of $0{\cdot}45 \times 10^{-3}$ cm$^2$V$^{-1}$sec$^{-1}$ was measured for the mobility of electrons in benzene at 20° C. In this case the temperature dependence followed more closely that required by Walden's rule, indicating a charged entity of molecular dimensions. This observation and the fact that the value of mobility lies in the range of ionic mobilities, together with the increased difficulty in the purification

of benzene, suggests that in this case the mobility of an electron attached to an impurity ion is being measured.

A few measurements were made on hexane and benzene doped with 1 per cent ethyl alcohol at a single temperature and gap spacing. In both cases, the measured mobility was decreased by about one-half. Unfortunately, the lack of data on the temperature dependence precludes the possibility of testing for negative ion conduction, which might be expected in the case of the doped liquids.

In these experiments the existence of electron multiplication at high fields might have been inferred in either of two ways: (1) from an exponential growth of the induced charge as a function of time at a given field and constant injected charge, or (2) from the growth of the maximum induced charge for increasing field strength when a constant number of electrons were photo-injected. The linear growth of charge versus time and the absence of phenomenon (2) provide negative evidence for electron multiplication in the volume of the liquid, although a spurious multiplication was noted with unconditioned electrodes. Since this effect disappeared after conditioning, Chong and Inuishi attributed this to adsorbed gases on the cathode.

## 4. ELECTRICAL BREAKDOWN MEASUREMENTS

The search for reproducible values to assign to the breakdown strengths of liquids has been a long one, but with the widespread use of microsecond pulse techniques the values obtained by various workers are now in fair agreement. Even so, few people are bold enough to speak of an *intrinsic* breakdown strength of a liquid, as it has become increasingly evident that imperfections (such as asperities on the electrodes, suspended particles, etc.) play an important role in determining the onset of breakdown.

### 4.1. Pure Organic Liquids

Kao and Higham[41] have investigated the effects of hydrostatic pressure, temperature, and voltage duration on the electric strengths of various organic liquids, under well controlled conditions. The liquids under examination included hexane, heptane, decane, benzene, toluene, chlorobenzene, methyl and ethyl alcohols, and carbon tetrachloride. Most of the measurements were made using stainless steel electrodes and the majority of the results reported were for a single breakdown with each liquid sample and pair of electrodes, so that the usual conditioning process was avoided; the reason for adopting this technique was to ensure that the by-products of one breakdown could not affect subsequent results. The range of pressures studied ran from 0 to 350 lb in$^{-2}$ (gauge) though some sub-atmospheric results were also included. A range of pulse widths from 0·5 $\mu$sec to 1 msec was used.

The liquids tested included several polar and non-polar materials, and all exhibited a marked increase in breakdown strength with increasing applied hydrostatic pressure. Some of these results are shown in Figure 12. The results given were obtained on degassed liquids in a 200 micron gap between $\frac{1}{4}$ in. diameter electrodes of stainless steel, using a pulse width of 4·5 $\mu$sec.

The initial slopes of the curves, near atmospheric pressure, vary somewhat but are of the order of 5 per cent increase in strength per atmosphere; this is almost

one-third of the effect reported by Edwards[44] for benzene at sub-atmospheric pressures.

Some measurements were made on *n*-hexane at pressures below atmospheric, using 5 $\mu$sec pulses, and a distinct minimum in the breakdown strength was found at an absolute pressure of 45 mm Hg; the presence of this type of minimum had previously been reported for transformer oil, stressed with alternating voltages,[42, 43] but its appearance under microsecond pulse conditions had not been observed before.

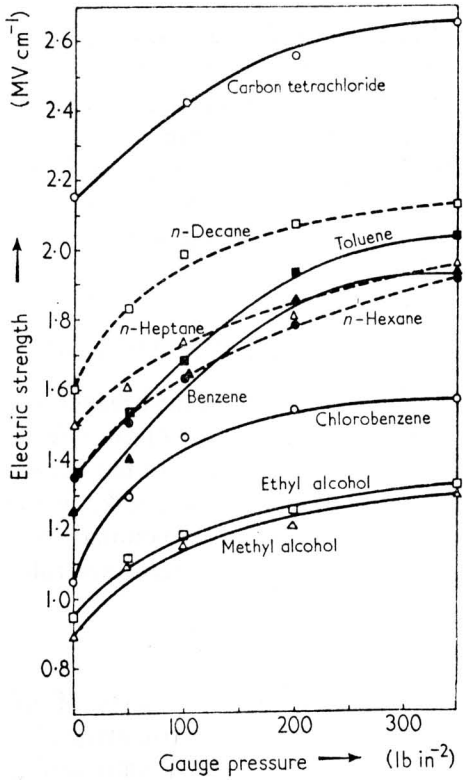



Figure 12. *The dependence of the electric strength of some organic liquids upon applied pressure (Degassed liquids; electrodes, $\frac{1}{4}$ in. diameter, stainless steel; gap length, 200 microns; pulse length, 4·5 $\mu$sec). After Kao and Higham*[41]

Kao and Higham also reported on their measurements of the temperature dependence of breakdown strength. The compounds tested include *n*-hexane, *n*-heptane, and *n*-decane among the non-polar liquids, and methyl alcohol, ethyl alcohol, and chlorobenzene among the polar liquids. There is a general fall in breakdown strength with increasing temperature, with a sharp fall towards the boiling point, and a marked rise near freezing point.

As is well known, when breakdown strength is measured as a function of pulse width, for pulses longer than a certain time (called the critical time, or critical pulse width $\tau_c$), the strength is independent of pulse width, and breakdown occurs at or after $\tau_c$. For pulse widths less than the critical pulse width, the strength of

the liquid depends strongly upon time and increases rapidly as shorter pulses are used. It is already known from the work of Edwards,[44] Goodwin and Macfadyen,[33] Crowe,[8] and others that $\tau_c$ increases with gap width. Kao and Higham report $\tau_c$ for two gap widths, giving 1 $\mu$sec for a 33 micron gap, and 3·5 $\mu$sec for a 200 micron gap.

Kao and Higham[41] have measured the breakdown time lags for *n*-hexane at several temperatures and pressures, as shown in Figure 13. They find that the critical time lag is virtually independent of applied hydrostatic pressure, but there appears to be some increase in time lag at the lowest temperature. This is believed

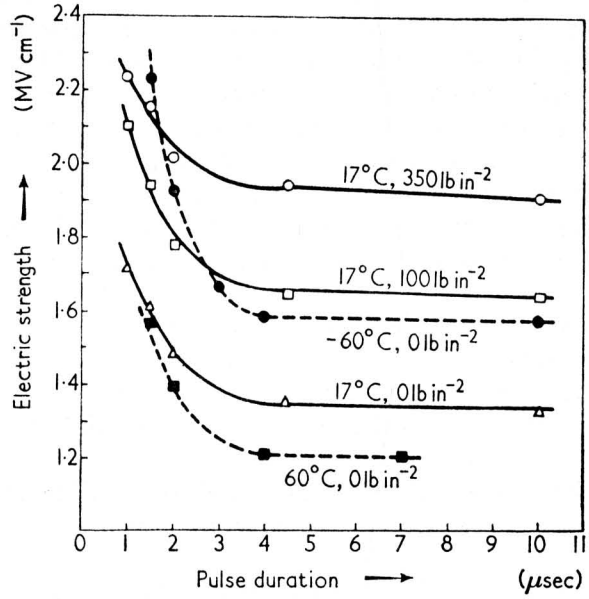



Figure 13. *The dependence of the electric strength of liquid n-hexane upon applied pulse width as a function of temperature and pressure (electrodes, ¼ in. diameter, stainless steel; gap, 200 microns). After Kao and Higham*[41]

to be the first time that this important parameter has been measured as a function of either pressure or temperature. They have also measured the time lag as a function of chain length in the paraffin series, and find that $\tau_c$ is independent of chain length—this is in agreement with the findings of Crowe, Sharbaugh, and Bragg,[45] but contrary to the results of Goodwin and Macfadyen.[33]

Some time lag measurements were made by applying single long duration pulses, the time lag to breakdown being recorded oscillographically. It was found that this technique gave results appreciably different from those of the multiple pulse method, viz., shorter time lags and lower breakdown strengths. The effect is difficult to explain, but suggests that with the multiple pulse technique one is conditioning the gap in some way.

Ward and Lewis[46] have described an experimental and theoretical investigation of statistical time lags in liquid hydrocarbons, in which they cast some doubt upon the usual interpretation of breakdown time lags. Using *n*-hexane and stainless steel electrodes with a gap width of 50 microns, time lags were measured using a step-function of voltage lasting for about 0·1 msec. The time lags were

recorded by means of the technique of Saxe and Lewis.[47] From these measurements it was found that the time lags were random, but decreased as the stress increased. Moreover, at each stress there was a substantial number of long time lags. Thus, at a stress of 1·8 MV cm$^{-1}$, time lags greater than 1·5 $\mu$sec were not infrequent, whereas at this stress one would not normally expect to find time lags much longer than 0·25 $\mu$sec.

Ward and Lewis also measured the breakdown strength of *n*-hexane using a conventional multiple pulse technique. According to their statistical model (see Section 6) the probability of breakdown at a given stress should increase with the number of trials at each stress level. Experimentally it was found that the level of breakdown strength, for a given length of pulse, did in fact depend upon the number of pulses which one chose to apply to each stress.

We note, however, that the results of Ward and Lewis using step-function voltages are contrary to the findings of Kao and Higham,[41] who found that their single pulse measurements consistently gave shorter time lags than their multiple pulse technique.

Some results on the effect of dissolved gases on the breakdown strength of *n*-hexane have been reported in two papers by Sletten.[7,48] The measurements were made using 1 cm diameter spherical electrodes of chromium and of stainless steel. Some of the measurements were made with d.c. voltage, and others with rectangular voltage pulses of 1·5 $\mu$sec duration.

The samples of hexane were dried, filtered, and degassed, and could be maintained in the test cell in either the degassed state or saturated with dry gas, as

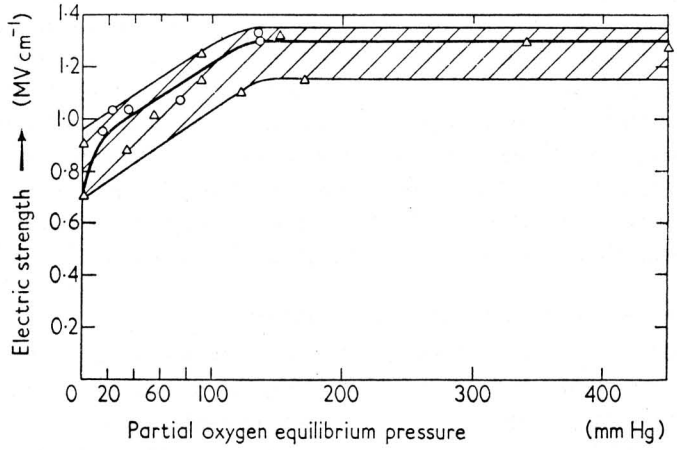
Table 1. The Influence of Gas Content on the Electric Strength of *n*-hexane

| Test voltage | Liquid | Electrodes | Mean Strength (MV cm$^{-1}$) | Coefficient of variation (per cent) |
|---|---|---|---|---|
| D.C. | Degassed | Chromium | 0·88 | 17·1 |
| D.C. | High air content | Chromium | 1·33 | 6·4 |
| D.C. | High oxygen content | Chromium | 1·33 | 6·2 |
| D.C. | High nitrogen content | Chromium | 0·89 | 10·7 |
| 1·5 $\mu$sec pulse | High air content | Stainless steel | 1·55 | 12·3 |
| 1·5 $\mu$sec pulse | Degassed | Stainless steel | 0·90 | 5·5 |

required. The results which are quoted in Table 1 show that when the air or oxygen content of the liquid is large, the strength is high and the coefficient of variation is small. With degassed and nitrogen-saturated liquid, the strength is lower and the spread increases. It is particularly surprising to find the marked effect of dissolved gas under microsecond pulse conditions, in contradiction to the findings of Edwards[44] on benzene, and of Sharbaugh[49] on the *n*-alkanes.

In the later communication,[48] Sletten reports some results which modify his previous findings; he states, as before, that oxygen content increases the electric

strength of hexane under d.c. conditions, but that no oxygen effect was found under microsecond pulse conditions. As before, no effect was observed under either d.c. or pulse conditions with dissolved nitrogen, hydrogen, or carbon dioxide. The effect of dissolved oxygen content on the d.c. strength of hexane is shown in Figure 14.




△ Values obtained with dissolved oxygen
○ Values obtained with dissolved air (oxygen content calculated)

Figure 14. *The dependence of the electric strength of n-hexane upon dissolved oxygen. After Sletten*[48]

Sletten[48] reported an interesting observation which had been made by Ward on air-saturated hexane; Ward found that prestressing the gap with a direct voltage prior to impulse testing increased the subsequently measured impulse breakdown voltage. The increase was largest when the direct voltage used for prestressing was opposite in polarity to the impulse voltage, and strengths as large as $2 \cdot 5$ MV cm$^{-1}$ were measured.

Table 2. Breakdown Strengths Measured with a 10 μsec Rectangular Pulse (Phosphor-bronze electrodes)

| Liquid | Edwards' maximum value (MV cm$^{-1}$) | Highest value previously reported in the literature (MV cm$^{-1}$) |
|---|---|---|
| Carbon tetrachloride | 4·79 | 2·48 |
| Chloroform | 2·53 | 2·07 |
| Methylene chloride | 2·36 | — |
| *n*-Hexane | 2·46 | 1·37 |
| Benzene | 1·83 | 1·45 |
| Ethyl alcohol | 1·63 | 1·27 |

Edwards[50] has called attention to the influence of small particles on the breakdown strength of liquids. Using an improved form of the apparatus described earlier by him,[44] Edwards measured individual values of electric strength which were 20–100 per cent higher than the highest average values reported previously in the literature; these are shown in Table 2. In addition to an increase in the

'mean' values of electric strengths, their 'spread' also increased considerably, being $\pm 50$ per cent in the case of methylene chloride. Presumably Edwards' values listed in the Table are the highest of a broad distribution of results.

Edwards attributes this rise in strength to the increased attention given to the elimination of minute particles from the breakdown gap. He suggests that if the method of electrode polishing is well controlled, particles as small as 1 micron may give rise to the lower but reproducible values of electric strength listed in the last column of Table 2. Some caution must be exercised in the selection of the highest values in a distribution of experimental results. Thus, the 20–100 per cent differences reported in Table 2 may be somewhat exaggerated. One clue as to the reason for these anomalously high results may lie in the statement by Edwards concerning the importance of electrode polishing. Phosphor-bronze surfaces are prone to high chemical reactivity and could form barrier films which would give rise to higher strengths. The matter needs further clarification.

### 4.2. Liquefied Gases and High Density Vapour

Because of the many complications which arise from the use of organic liquids in breakdown experiments, and the problem in interpretation of results when one has broken them down, it is naturally tempting to consider using simpler liquids. The simplest known liquids are the liquefied rare gases, and two groups of workers have recently followed the example of Kronig and van de Vooren[51] in making measurements on liquids of this type.

Blaisse, Boogart, and Erne[52] have measured the breakdown strengths of helium-I, helium-II, and liquid nitrogen. Swan and Lewis[53] have measured the strengths of liquid argon, oxygen, and nitrogen.

Many mechanical difficulties arise when working with an electrode system in a cryostat, and one cannot easily change or rotate the electrodes to obtain fresh surfaces. Blaisse, Boogart, and Erne, therefore, chose an electrode material with a high melting point (tungsten) and thus minimized electrode damage due to the breakdowns. They found that the surface damage to the tungsten was much less than with other electrode materials. The electrode configuration used was a sphere-to-plane, as this has the advantage that minor misalignment of the electrodes has only a second-order effect upon the gap spacing. Gap lengths from 50 to 300 microns were used. By moving the sphere and plane laterally with respect to each other, a fresh area on the plane electrode could be used. The plane was therefore used as the cathode.

The measurements, which were made with d.c., are summarized in Figure 15 in which the breakdown voltages of helium-I, helium-II, and nitrogen are given as a function of gap width. Each point is the average of at least five breakdowns, which were the highest of twenty to fifty discharges. In view of the difficulties attending these experiments, such as particles, bubbles, etc., all of which tend to give spuriously low breakdown voltages, this can be considered a legitimate statistical procedure, though it would have been useful to learn the standard deviation of all the results.

Within the limits of experimental accuracy, the breakdown strengths were independent of gap spacing. Moreover, the strengths of helium-I and helium-II were found to be virtually the same (viz., $0 \cdot 72$ MV cm$^{-1}$ for helium-I at $4 \cdot 2°$ K, and $0 \cdot 70$ MV cm$^{-1}$ for helium-II at $1 \cdot 3°$ K). The breakdown strength of liquefied

nitrogen at 65°K between tungsten electrodes was 1·6 MV cm$^{-1}$. This latter value is appreciably greater than that reported by Kronig and van de Vooren,[51] but this may have been partly due to the different electrode material used.

Swan and Lewis[53] have reported on the influence of electrode surface conditions on the breakdown strength of liquid argon, oxygen, and nitrogen, under d.c. stresses. They used gas of the highest commercially available purity, and before entering the test cell, it was passed through a phosphorus pentoxide drying tube, and a sintered glass filter of 1 micron pore size.

The temperature and pressure in the test cell were measured throughout the tests, but it was found that the small pressure changes experienced did not affect the breakdown voltage of the samples. A 25 kV stabilized d.c. supply was used,

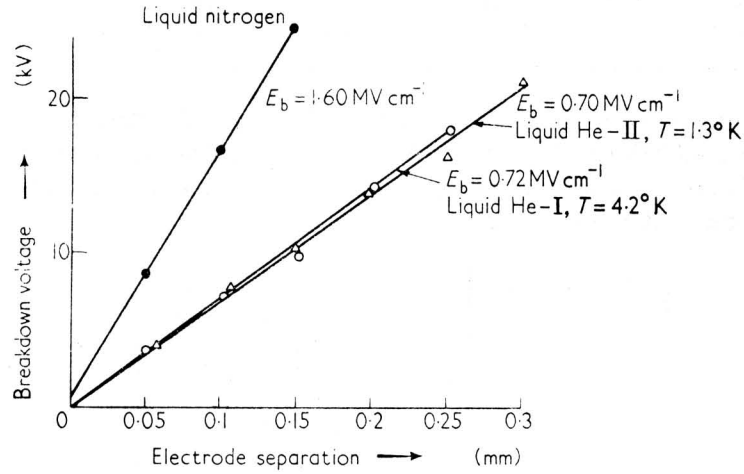



Figure 15. *The dependence of the d.c. breakdown voltage of liquefied gases upon electrode spacing. After Blaisse, van den Boogart, and Erne*[52]

with an electronic trip circuit to remove voltage from the electrodes within 1 $\mu$sec after breakdown. By this means, repeated breakdowns could be made on the same electrode surfaces without noticeable deterioration.

Several electrode materials were used, including platinum, gold, copper, brass, and stainless steel. The electrodes were spherical and highly polished.

With some electrode materials, an oxidizing technique was used to study the effect of thickness of surface oxide on breakdown strength. After cleaning, the metals were exposed to air for various times which were taken as a measure of the oxide thickness. Gap widths from 20 to 100 microns, and the separation of the electrodes could be controlled to an accuracy of 1 micron.

Some of the results obtained by Swan and Lewis are shown in Figure 16. The measurements were obtained with platinum electrodes. The measurements made with other electrode materials are shown in Table 3. The coefficients of variation of the measurements were less than 10 per cent. Swan and Lewis ascribe this to the efficacy of their current diverter circuit.

The breakdown measurements show that argon has the lowest strength of the three liquids, but the relative strengths of nitrogen and oxygen seem to depend entirely upon the electrodes used, nitrogen being the stronger between platinum

electrodes but weaker between stainless steel, etc. As shown in Table 3, no correlation of breakdown strength with work function has been found.

Measurements were made on argon, with the addition of small percentages of oxygen, and a marked effect was observed. For example, the addition of 20 per cent

Table 3. Breakdown Strength ($MV\,cm^{-1}$) as a Function of Electrode Material

| Electrodes | Work function | Argon | Oxygen | Nitrogen |
|---|---|---|---|---|
| Stainless steel | — | 1·40 | 2·38 | 1·88 |
| Brass | — | 1·01 | 1·44 | 1·62 |
| Copper | 4·47 | 1·40 | 1·81 | — |
| Gold | 4·58 | 1·16 | 1·24 | 1·50 |
| Platinum | 5·29 | 1·10 | 2·00 | 2·24 |

oxygen to argon between stainless steel electrodes raised the strength from 1·66 $MV\,cm^{-1}$ to 2·42 $MV\,cm^{-1}$. Swan and Lewis suggest that the major part of this increase is due to electrode oxidation, and the remainder to electron attachment processes in the bulk of the liquid.

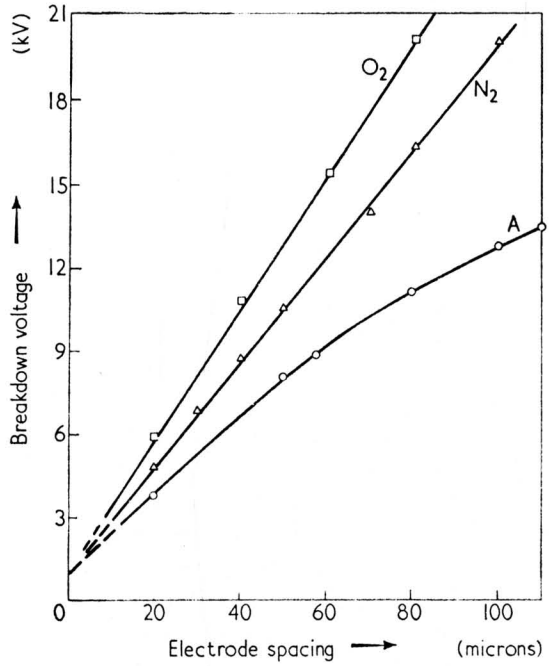



Figure 16. *The dependence of the d.c. breakdown voltage of some liquefied gases upon electrode spacing. Stainless steel electrodes. After Swan and Lewis*[53]

Measurements on argon between electrodes having various degrees of electrode oxidation show very interesting trends, as shown in Figure 17. The results for brass and stainless steel (both of which oxidize readily) change considerably with

oxidation time, whereas gold and platinum show no change, as one would expect. The interpretation of these results is difficult, but one possibility is that the emission from the cathode goes through a minimum as the oxide layer increases. However, it is difficult to reconcile this with the rather surprising result which has come from this study on the importance of the anode material in determining the breakdown strength of liquid argon. For example, with a stainless steel anode and an aluminium cathode, the strength was almost the same as for two stainless steel electrodes, but reversal of electrode polarity gave a strength equal to that for a pair of aluminium electrodes.

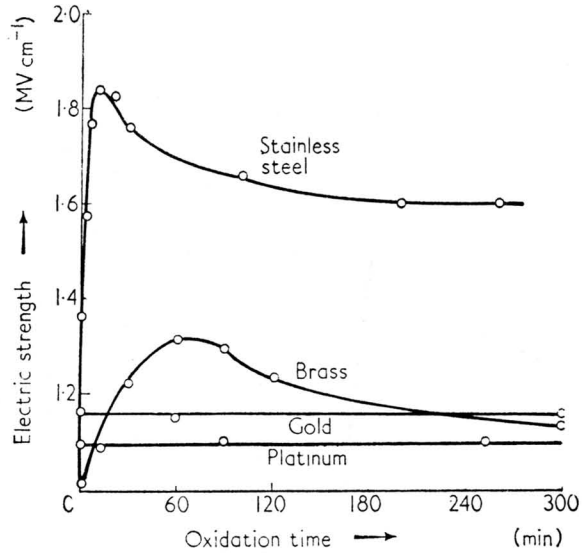



Figure 17. *The dependence of the electric strength upon the electrode oxidation time. After Swan and Lewis*[53]

Some years ago Young[35] studied the breakdown strength of carbon dioxide in the critical region, and concluded that there was no discontinuity in strength in going from the vapour to the liquid phase. Sharbaugh and Watson[54] have reported on the electric strength of hexane vapour at temperatures above critical, under uniform field d.c. conditions. The density of the vapour was computed from the observed temperature and pressure. Departures from ideal gas behaviour were taken into account by using compressibility data computed according to the method of Pitzer[55] et al.

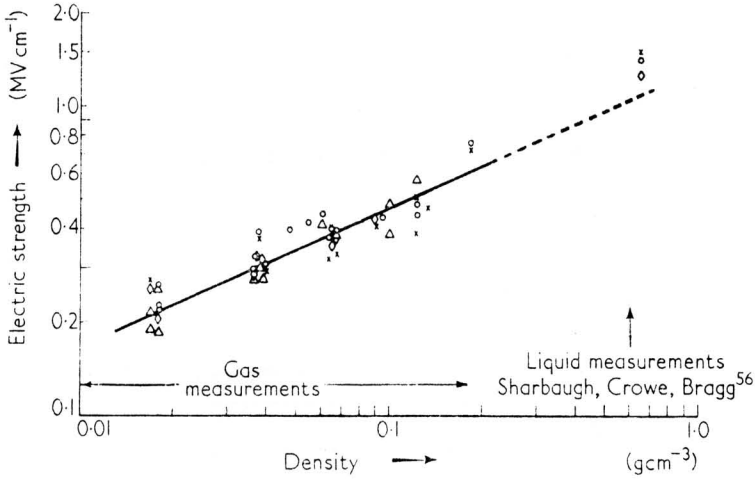
For breakdown fields below $0{\cdot}15$ MV cm$^{-1}$, the breakdown process could be completely described by means of the Townsend mechanism. At higher pressures, the strengths fell below those computed from Paschen's similarity law, indicating that at high fields other processes such as field emission, or field assisted thermionic emission come into play.

A plot of the electric strength data, taken in the range 100 to 400 lb in$^{-2}$ at gap widths of $2{\cdot}5$ to 25 mils is shown in Figure 18, in which strength is plotted as a function of vapour density. For comparison, values for liquid hexane (density $0{\cdot}65$ g cm$^{-3}$) measured by Sharbaugh, Bragg, and Crowe[56] are included. The difference in the liquid strengths for gap widths of $2{\cdot}5$, 5, and 25 mils is due to the

area effect observed when liquid measurements are made with hemispherical electrodes (see Section 6).

From the Figure it can be seen that although the measurements in the vapour phase extend to the critical density there is still a considerable gap between measurements in the vapour phase, and those in the liquid. In spite of this, the vapour phase results appear to extrapolate to the liquid results, suggesting continuity throughout the entire region.

More recently Sharbaugh and Watson[57] have extended their high temperature experiments to higher pressures and have included the liquid as well as the vapour phase in their measurements. The results are more complex than appeared at




Gap length: × 2·5 mils; ○ 5 mils; ◇ 10 mils; △ 25 mils

Figure 18. *The dependence of the electric strength of hexane vapour at high density. After Sharbaugh and Watson*[54]

first;[54] using microsecond pulse techniques it has been found that the strength of hexane vapour rises considerably in the range 600 to 1,600 lb in$^{-2}$. Furthermore, the measurements in the liquid phase at temperatures just below critical and densities above critical have indicated strengths which are lower than in the vapour of the same density. However, the strengths of liquid and vapour converge as one approaches the critical point.

### 4.3. Commercial Liquids

An investigation of the influence of gas pressure on the electrical breakdown strength of cable oil has been made by Priaroggia and Palandri.[58] The tests were made at room temperature with 50 c/s a.c., using an oil with a viscosity of 25 cS at 20° C. The measurements were made as a function of gas pressure, from $6 \times 10^{-6}$ mm Hg up to atmospheric pressure.

It was found that the spread of results was considerable unless the gas dissolved in the oil was in complete equilibrium with the gas above the oil surface. In order to minimize this problem, the oil was allowed to equilibrate for 24 hr before each measurement, and only one breakdown was made on each sample.

From these measurements has come the surprising conclusion that the strength of the oil is absolutely independent of the gas pressure over the range tested. The strength of the oil was 400 kV(r.m.s.)$cm^{-1}$ (560 kV(peak)$cm^{-1}$) which, although low in comparison with values measured on pure liquids, is high in comparison with industrial tests.

Tropper[28, 59] has given a resumé of the studies of his group on the mechanisms of breakdown and conduction in transformer oil. Throughout these studies, careful control of the gas content and amount of suspended material has been maintained through the use of a closed system. Special attention was given to the electrode conditioning process which resulted in either an 'upward' or 'downward' progression in breakdown strengths, depending on the gas content of the oil. Normally, the electrodes were conditioned in oil saturated with air at atmospheric pressure and Tropper concluded that the conditioning process is one of establishing equilibrium conditions of adsorbed air on the electrode surfaces.

Breakdown was always preceded by a pronounced conduction current (10 to 20 $\mu$A between $\frac{1}{2}$ in. diameter spheres) which depended only upon the applied field. The onset of appreciable conduction current occurred at about 0·6 MV $cm^{-1}$ and there was no connection between the magnitude of this current and the observed breakdown strength. Samples which were passed through a 15-micron pore filter showed larger conduction currents than those filtered through a 1 micron filter.

Samples with different amounts of dissolved air were prepared by allowing degassed oil to equilibrate in a closed system with different partial pressures of air. Tropper's results for low and high gas contents are shown in Figures 19 and 20, respectively. An initial rise in breakdown strength and a decrease in prebreakdown conduction current were observed with the addition of very small amounts of dissolved air. These effects are similar to those reported for hexane[7] and have been attributed to the presence of dissolved oxygen. On the addition of still more air, there is a sharp decrease in strength to about 50 per cent of the maximum as shown in Figure 19. This minimum is followed by a slower increase to the general level of strengths observed at saturation. A minimum of this type has previously been reported by Clark.[60]

The effect of sub-atmospheric pressures on the breakdown strength of both degassed and air-saturated oil was also studied. As expected, a marked pressure dependence of the saturated oil samples was observed, but practically none was found for the degassed oil.

According to Tropper, two important processes are involved in the mechanism of breakdown in oil: (1) field emission of initiatory electrons at the cathode due to high applied fields, and (2) multiplication of these by collisional ionization until a critical electron yield is reached and breakdown ensues. The attainment of this critical electron yield will depend on the gap width as well as the initiatory current. At small gaps (approximately 10 microns) process (1) must be enhanced to make up for the deficiency of process (2). This introduces marked conditioning, electrode area effects, and a dependence of strength upon cathode material; all of these are observed experimentally. On the other hand at large gaps ($>$ 1,000 microns) the importance of process (1) is minimized and these electrode effects tend to disappear.

An observed fluorescence of the oil provides evidence that electrons having an

energy of several electron-volts are present prior to breakdown. Tropper reasons that electrons of this energy can lead to chemical degradation of the oil into gaseous products. When the concentration of gas exceeds its solubility in the oil, bubbles will form which will lead to breakdown. The observed dependence of strength upon air content and applied pressure strongly reinforces the argument concerning the importance of the gaseous phase in the breakdown process. The maximum in

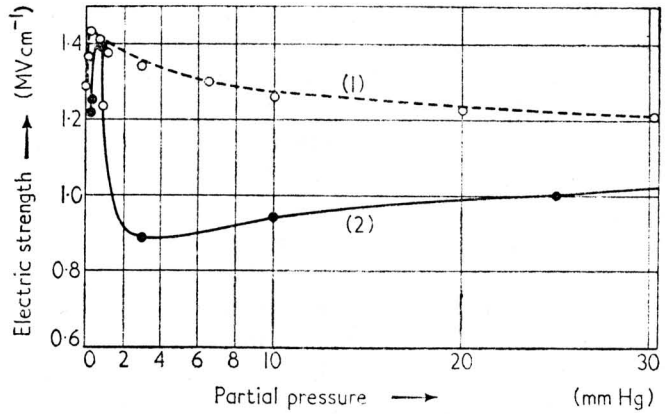



Figure 19. *The variation of the electric strength of transformer oil with small amounts of dissolved air. After Tropper*[28]

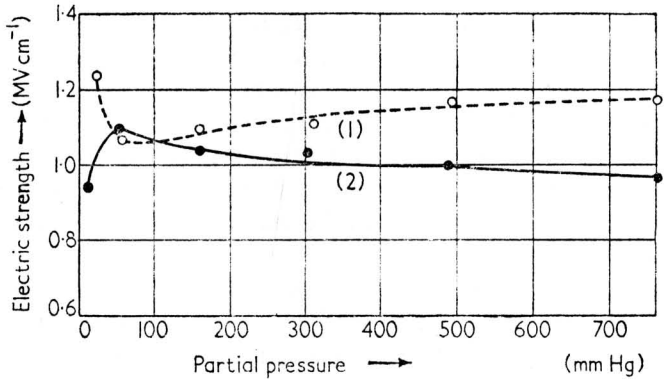



Figure 20. *The variation of the electric strength of transformer oil with large amounts of dissolved air. After Tropper*[28]

strength shown in Figure 19 at low air content is attributed to electron trapping. The subsequent decrease is ascribed to the greater ease of microbubble formation, suspended dust serving as nucleation sites. The final rise in strength is attributed to a field distortion effect of the positive ion space charge.

Sharbaugh, Cox, and Ast[61] have reported on the effect of electrode shape and spacing, electrode composition, filtration, and wave shape upon the pulse breakdown of transformer oil. They showed that suspended dust of the order of 2–5 microns diameter became increasingly important as the gap spacing was decreased: at 1·5 mil spacing, filtered oil had a breakdown strength about 20 per

cent higher than unfiltered oil, as shown in Figure 21. In contrast to the findings of Tropper,[59] they observed a twofold decrease of the strength when the separation of 1 in. diameter hemispheres was increased from 1·5 to 50 mils. Using flat electrodes with a Rogowsky profile, the strength dropped considerably with increasing area, in agreement with the findings of Weber and Endicott.[62] Most of the decrease in strength could be ascribed to the increase in electrode area; a small dependence upon volume of oil under stress was observed but could not be established as being statistically significant.

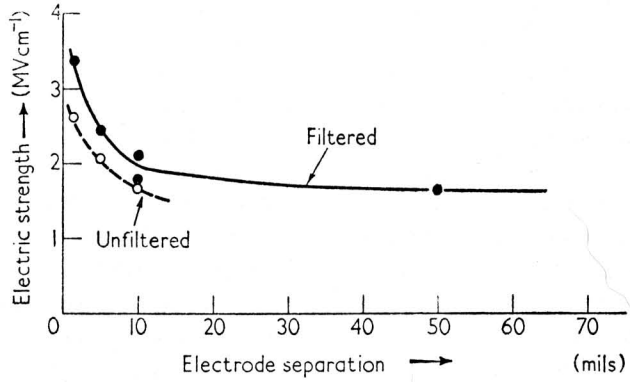



Figure 21. *The dependence of the electric strength of transformer oil upon electrode separation (1 in. diameter spherical electrodes, stainless steel). After Sharbaugh, Cox, and Ast*[61]

## 5. MISCELLANEOUS HIGH FIELD PHENOMENA

### 5.1. Light Emission and Gas Evolution from Liquids under Electric Stress

Some years ago Race[63] observed that visible light was emitted from an insulating liquid when under high electrical stress. This work went unnoticed and the effect was recently rediscovered in transformer oil.[64–66] It has also been found that a trace of anthracene causes electroluminescence in hexane at high fields.[65] These observations constitute evidence for the presence of free electrons with an energy of at least 2·5 eV in these liquids at high stress.

It has been suggested that the well known evolution of gas from highly stressed oils is associated with these relatively high energy electrons, causing chemical dissociation of the liquid molecules. However, the other observations seem to indicate that the majority of gas is generated by electrons which have been accelerated inside microbubbles in the liquid.[67]

Race[63] was the first to report on light emission from an insulating liquid under electrical stress. Using 60 c/s a.c. fields, his observations of this phenomenon were made on 'Dowtherm', which is a mixture of about 75 per cent diphenylether and 25 per cent diphenyl. Uniform field electrodes of 1 in. diameter were used, and a diffuse blue glow became visible at fields of about one-quarter of the breakdown stress. The glow continued with increasing brilliance up to breakdown (0·75 $MV cm^{-1}$), and photographs of the luminescence were published. Attempts

were made to obtain electroluminescence in mineral oil but with no success. In Dowtherm, it was found that a few centimetres partial pressure of air or Freon-12 would completely quench the glow.

Dakin and Berg[64] have reported upon their observation of light emission from transformer oil under high stress. The light emission was detected by a photographic plate, which was immersed in the oil, between the electrodes. The luminous spots occurred at random on the surface of the plane electrode, with a concentration of spots at the sharp edges of the electrodes.

While investigating prebreakdown currents in transformer oil, Darveniza[65] found that visible light was emitted from the high stress region at d.c. fields in excess of 600 kV cm$^{-1}$. Tests were carried out in uniform fields between 1 cm diameter nickel and stainless steel electrodes, with a gap spacing of 89 microns. The colour and frequency of the emitted light were similar to the blue fluorescence observed when the oil was excited with an ultra-violet source.

No chemical analysis was available on the composition of the oil, but it was known that traces of unsaturated polycyclic aromatic compounds were present (in fact, these give rise to the optical fluorescence of the oil). From this it was inferred that the light emission under electric stress was due to excitation of molecules of this type. To test this hypothesis, observations were made using spectroscopic grade hexane, and hexane samples doped with scintillation grade anthracene and *p*-terphenyl. No visible light was observed with pure hexane up to fields of 1·1 MV cm$^{-1}$, but light emission characteristic of the dissolved impurity was observed in the doped hexane samples.

Darveniza[65] reported that in the range from 600 to 950 kV cm$^{-1}$ filamentary luminous streamers completely bridged the oil gap from cathode to anode, and there was no apparent change in intensity along their length. At higher stresses, the glow appeared to become diffuse over the high field region. The light intensity increased exponentially with increasing field, but no noticeable change occurred in the spectrum of the emitted light. The experiments were repeated as a function of applied pressure; no variation in the light intensity was observed.

Dakin and Berg[66] have refined their earlier experimental observations on light emission from oils under electrical stress. A metal electrode was observed face-on through a glass window coated with a transparent semiconducting tin oxide, which was used as the second electrode; photographic observations through the window indicated that the luminous spots were always associated with the negative electrode. The light was attributed to fluorescence of the oil molecules, excited by field emitted electrons from asperities on the cathode. The threshold field appeared to be in the range 50–250 kV cm$^{-1}$, depending upon the degree of polish on the electrodes, so that the local stress might well have been an order of magnitude greater than the applied stress in the regions where luminosity was observed.

The light emission was not affected by applied hydrostatic pressure over the range 10 mm Hg to 2 atm.; this experiment eliminates the possibility that the light was being emitted from discharges in microbubbles. Dakin and Berg suggest that this observation helps to explain the origin of gas evolution from highly stressed oils, since the electrons exciting the fluorescence require very little more energy to decompose hydrocarbon oil molecules.

In their work on the evolution of gas from liquid dielectrics under electric stress, Basseches and Barnes[67] observed a faint blue discharge between their electrodes

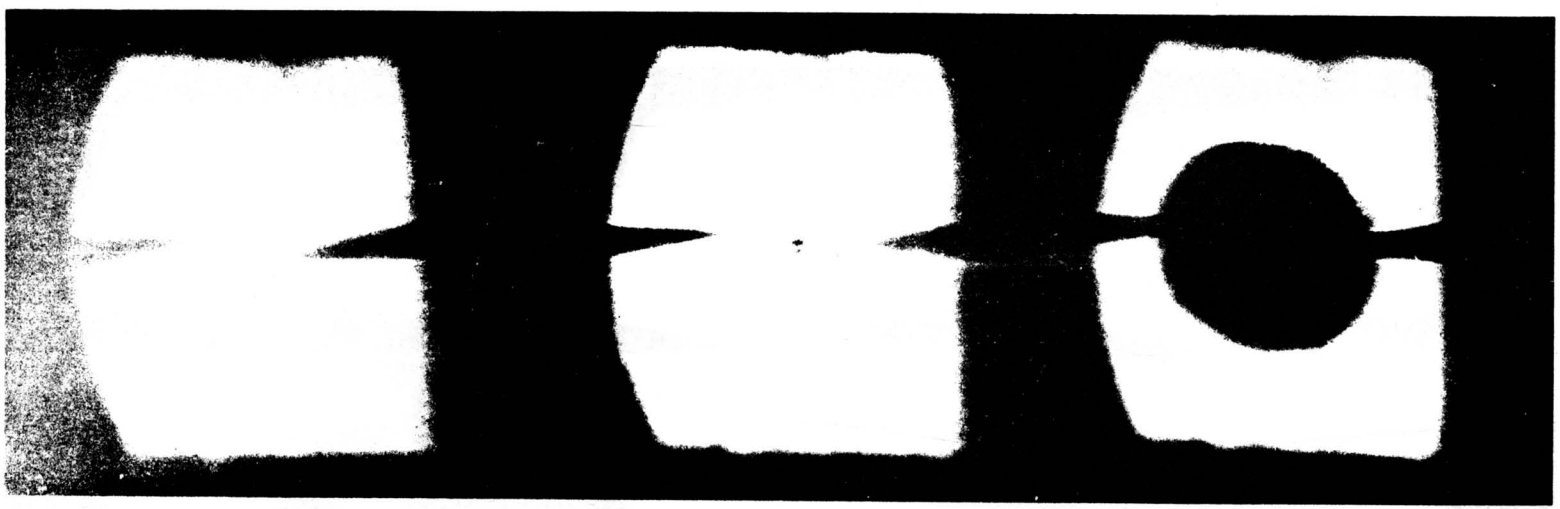


Plate I. *High speed Schlieren photographs of pre- and post-breakdown phenomena in n-hexane (After Hakim and Higham[68])*

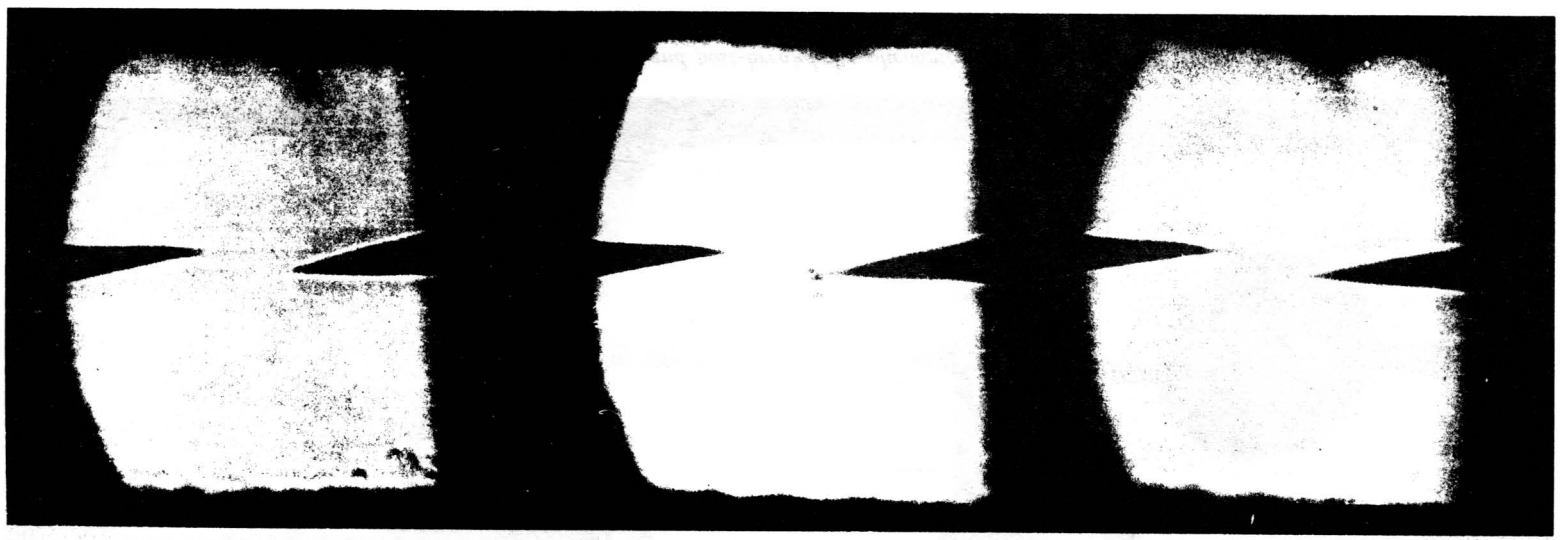


Plate II. *High speed Schlieren photographs of pre-breakdown phenomenon in n-hexane (After Hakim and Higham[68])*

when gassing was taking place. However, unlike the previous workers, these authors conclude that the gas evolution is probably associated with the presence of microbubbles in the liquid. They found that the rate of gas evolution from a mineral oil was dependent upon the applied hydrostatic pressure, which suggests that a discrete gas phase is essential to the gassing process. Basseches and Barnes assume that there are bubble nuclei which are stabilized at the electrode surfaces and that some electrons, which are emitted from the electrodes, enter the gas phase and are accelerated in the field until they come into collision with the hydrocarbon molecules at the margin of the bubble; under suitable circumstances this results in the breaking of a carbon–hydrogen bond, and ultimately leads to the evolution of hydrogen.

Here we see the usual complement of conflicting evidence, so characteristic of the field of liquid dielectrics; on the one hand there is this strong evidence for an electronic process in the liquid (the key experiment here seems to be that of Darveniza on the pure and doped hexane samples): on the other hand, we see very good evidence for the bubble hypothesis. However, there is no reason why both theories should not hold in their own particular circumstances—the former, in a clean, gas free system; the latter in a gassy liquid.

### 5.2. Optical Studies of High Field Phenomena in Liquids

With the development of high speed photographic and other techniques, new methods of study of prebreakdown and breakdown processes in liquids have become possible. In this section, we consider some recent studies which yield valuable information about high field phenomena in liquids.

Hakim and Higham[68] have used a rotating mirror camera, in conjunction with a Schlieren optical path, to photograph density changes occurring in hexane prior to breakdown. In order to obtain separate frame exposures from the 'streak' camera, they used a multiple flash light source, which was synchronized with the camera, and the high voltage impulse generator.

At fields in the breakdown region, they found that after voltage was applied to the gap, a region of different refractive index formed near the cathode. In the case of point–point and point–plane gaps, this region assumed an irregular shape. Plate I shows a photograph of the sequence of events leading to breakdown in a point–point gap in hexane. The individual frames correspond to the firing of successive light sources and the events are separated in time by the rotating mirror. The region of different (and presumably, lower) refractive index appears a few microseconds after the voltage pulse is applied, and breakdown follows shortly afterwards. The spark is a self-luminous event and therefore appears to overlap the second frame on the film; the third frame shows a large vapour bubble caused by the postbreakdown arc. The results are somewhat difficult to interpret and Hakim and Higham have refrained from elaborating on this point. However, the photograph suggests either a region of low density, or a large number of small vapour bubbles, which are ejected from the high field region near the cathode. One other interesting observation made by Hakim and Higham is that it is possible for these regions to form, and subsequently to die away without a breakdown of the gap. A sequence of this type is shown in Plate II. The results of this work may provide evidence in favour of the thermal mechanism of breakdown in the microsecond region.

A short paper by Nagao[69] describes the use of a bubble chamber to study pre-breakdown phenomena in liquids. This work does not seem to have been pursued beyond the preliminary stage, and only a few results have been published. In some respects the technique is similar to that used by Koppelmann[70] in his study of the behaviour of dissolved air during the breakdown of liquid dielectrics. The major difference is that Nagao used pulse techniques, whereas Koppelmann was restricted to d.c.

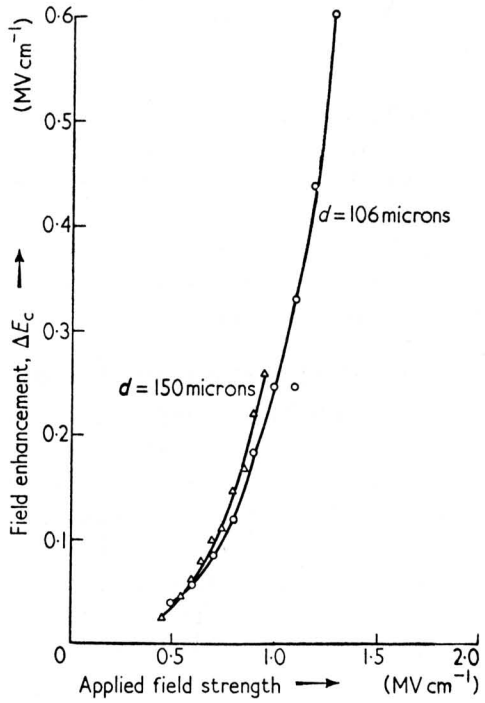



Figure 22. *Enhancement of cathode field in chlorobenzene. After Goodwin*[71]

The liquid used in the experiments was diethyl ether; the liquid was not degassed and no purification was specified. The electrodes used were a point and a sphere, so that a highly divergent field was produced. It was found that if the chamber was expanded without the application of voltage, or, conversely, a sub-breakdown voltage was applied without expansion of the chamber, then no bubbles were observed in the gap. With both expansion and a sufficiently high voltage, however, bubbles were photographed in the gap. Irrespective of polarity, the most copious bubbles were observed on the surface of the sphere; the photographs also show an intense filamentary region of bubbles extending from the vicinity of the point electrode and bridging most of the gap.

Many theories of electrical breakdown in liquids invoke the presence of positive ion space charges in the vicinity of the cathode at fields approaching breakdown. Goodwin[71] has used the electro-optical Kerr effect to measure the local fields in liquids, and has been able to demonstrate that, at fields in the range 0·5 to 1·3 MV cm$^{-1}$, considerable enhancement of the field at the cathode occurs in

monochlorobenzene, as shown in Figure 22. There was also evidence that the conduction process was occurring in filamentary channels.

Unfortunately, the sensitivity of the method was insufficient to show these effects in liquids with small Kerr coefficients, such as *n*-hexane or benzene. Moreover, the use of a highly polar material such as chlorobenzene leads to some difficulty in interpretation, since it is possible that the space charges observed were due to ionic charge carriers created by the high field dissociation of the liquid, and not by electron impact ionization, as assumed by Goodwin. The dissociation of chlorobenzene is described by the equation

$$C_6H_5Cl \rightarrow C_6H_5^+ + Cl^-$$

Onsager[24] has shown that at high fields, dissociation of the type described by the above equation is greatly enhanced. If, now, one assumes that the phenyl ion is much less mobile than the chloride ion, then the observed enhancement of the cathode field can be accounted for. On the other hand, even with a considerable difference in ionic mobilities, some enhancement of the anode field should occur, and Goodwin does not mention any such effect.

The observations of Hart and Mungall[3] indicate that even at low fields, appreciable enhancement of the cathode field occurs in liquids such as chlorobenzene; this is consistent with the hypothesis that the space charge observed by Goodwin was due to the ionic carriers from the dissociation of the liquid.

In the absence of further information regarding ionic mobilities in non-aqueous systems at high fields, one must conclude that this elegant experiment is rather inconclusive: that it demonstrates the presence of a positive ion space charge is beyond doubt, but the source of the ions is open to question.

## 6. MECHANISMS OF ELECTRICAL BREAKDOWN

In the search for an adequate theory to explain the electrical breakdown of liquid dielectrics, two distinct schools of thought have existed for many years. On the one hand, there are those who explain the breakdown of liquids in terms of a model which is essentially an extension of the gaseous breakdown mechanism. They assume that at high fields, conduction electrons are free to be accelerated in the field and undergo ionizing collisions with the liquid molecules; a mean free path for the electrons in the liquid is defined, and this mean free path is related to the scattering cross-section of the liquid molecules. In this way, a relationship is deduced between the electric strength and the molecular structure of the liquid.

On the other hand, it has long been thought that bubble formation may play an important role in the breakdown of liquids. These bubbles may be formed in the test gap by one of a number of possible mechanisms; they may be created either from gas dissolved in the liquid, coming out of solution in regions of high stress, or they may be due to vaporization of the liquid itself.

Many secondary effects may also promote breakdown. For example, suspended particles may enter the gap, and give rise to high local fields; bubble formation may take place, either by the electrolysis of impurities, or the dissociation of the liquid by electron bombardment. These processes are commonly operative in the breakdown of commercial liquids, though suspended particles frequently cause low breakdowns in otherwise highly purified liquids.

## 6.1. The Electronic Theory of Breakdown in Liquids

Several early workers[25] put forward theories in which the electrical breakdown of liquids is determined by a runaway collision ionization process. More recent investigators have elaborated upon the model and have assumed that the current is initiated by field emission from the cathode, and grows by electron multiplication. The associated positive ion space charge enhances the cathode field and can result in a catastrophic increase in current.

Young[35] proposed this mechanism for the breakdown of carbon dioxide at high pressures, and Goodwin and Macfadyen[33] applied the concept to liquids. Since then, Lewis[72] and others[45] have modified and extended the model.

We consider first the mechanism of emission from an electrode into a liquid. As indicated in Section 3, the Schottky equation fits most conduction data fairly well, and consequently, many people have thought in terms of field assisted thermionic emission from the cathode into the liquid. However, it is difficult to see how such an emission process can be reconciled with the breakdown results obtained at very low and very high temperatures. For example, the measurements of Blaisse, Boogaart, and Erne[52] and Swan and Lewis[53] on liquid nitrogen at a temperature of 65° K give breakdown strengths of the order of 1·6 to 2·0 MV cm$^{-1}$. These are virtually the same as the values measured by Sharbaugh and Watson[73] on high pressure nitrogen gas at room temperature. Also, when the breakdown strength of hexane vapour above the critical temperature (approximately 500° K) is extrapolated to a density equal to the liquid phase at room temperature, one obtains a value which is of the order of, or greater than, the liquid breakdown strength.

Thus, breakdown measurements which have been made over a wide range of temperatures show strengths which vary remarkably little—yet if one assumes a reasonable value for the work function, the thermionic emission term should change by an enormous amount (see Section 3). This suggests that the cathode process postulated in the breakdown mechanism is true field emission, or 'cold emission', which is independent of temperature. This is in contrast to the conclusion from the conduction studies; it remains for this discrepancy to be resolved.

Once the electron has been injected into the liquid, it gains energy from the applied field. In the electronic theory of breakdown in liquids, it is assumed that at sufficiently high fields some of the electrons will gain more energy from the field than they lose to the molecules in non-ionizing collisions. These electrons are accelerated until they gain sufficient energy to ionize the liquid molecules, and thus build up an electron avalanche. The observation of light emission from liquids under high stress[63–66] (see Section 4) is direct evidence that electrons having an energy of at least 2·5 eV can exist in liquids. It is, therefore, quite plausible to argue that further acceleration up to ionization energy is possible.

The condition for the onset of an avalanche in the liquid can be expressed in the form of an energy balance equation

$$\mathbf{q}E.\lambda = c\mathbf{h}\nu \qquad \ldots(12)$$

where $E$ is the applied field, $\lambda$ is the electron mean free path, $\mathbf{h}\nu$ is the quantum of energy lost by the electron in exciting the molecules, and $c$ is an arbitrary constant.

This equation was proposed by von Hippel[74] for ionic crystals; it has been applied to liquids by a number of authors,[45, 56, 75-77] and Lewis has recently re-examined the hypothesis in detail.[72] In liquids there are a large number of collision processes by which electrons can lose energy; these are of varying degrees of importance and include elastic, vibrational, and excitational processes, but their complexity is such that it is difficult to include more than one energy loss mechanism in a calculation.

Lewis has concluded that the vibrational collisions account for the major energy loss in the hydrocarbon liquids, and that the carbon–hydrogen bond vibrations act as the principal energy sink. This has been used to set up a breakdown criterion similar to that expressed in equation (12), and so it has been possible to relate breakdown strength to molecular structure.

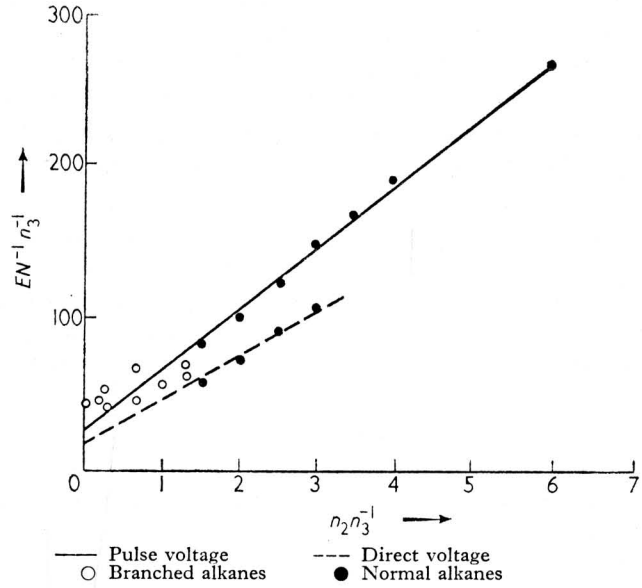



Figure 23. *Test plot of electric strength as a function of molecular structure for the liquid alkanes. After Lewis*[72]

The infra-red spectra of the hydrocarbon liquids suggest that the various groups CH, $CH_2$, and $CH_3$ behave independently, so that one may analyse a molecule in terms of its component groups, each acting as an independent collision centre. Thus, the mean free path of the electron $\lambda$ is given by

$$\lambda^{-1} = N \sum n_i Q_i \qquad \ldots (13)$$

where $N$ is the number of molecules per cubic centimetre, and $n_i$ is the number of groups having cross-section $Q_i$. Combining equations (12) and (13) and expanding the summation term for the $n$-alkanes, $C_nH_{2n+2}$,

$$EN^{-1} = k(n_2 Q_2 + 2Q_3) \qquad \ldots (14)$$

The suffixes refer to the $CH_2$ and $CH_3$ groups, respectively, and the constant $k$ includes $\mathbf{h}\nu$ and $c$. This equation suggests that a plot of $EN^{-1}$ versus $n_2$ should yield a straight line and, as shown in Figure 23, this is indeed the case. From the intercept of the line one can obtain $2kQ_3$, and the slope of the line gives $kQ_2$.

The measurements on the alkyl benzenes by Sharbaugh, Crowe, and Cox[78] can also be fitted by a model of this type,[72] although the resulting cross-sections $kQ_2$ and $kQ_3$ are considerably larger (about 100 per cent) than estimated from the alkanes. On the other hand, the estimate for $kQ_3$ obtained from measurements on a series of methyl silicones[79] is identical with that from the alkanes.

It might be expected that the cross-sections $Q_1$, $Q_2$, and $Q_3$ would increase progressively with increasing number of C—H bonds, but this in fact is not the case, and this casts some doubt on the validity of associating the electron energy loss with the C—H bond vibrations.

Adamczewski[80] has developed a theory which is similar to that of Lewis, with the difference that the major energy loss is ascribed to the C—C bond vibrations. An important difference is that an attempt is made to estimate the absolute values of the collision cross-section by assuming that it is equal to the longitudinal geometrical cross-section of the molecule. For example, in the normal alkanes the molecule is approximated by a cylinder of radius $r$ and length $l(n-1)$, where $2r$ is the mean distance between molecular axes, $l$ is the C—C bond length projected on to the axis of the molecule, and $n$ is the number of carbon atoms.

This gives a collision cross-section $Q = 2rl(n-1)$ and hence the mean free path $\lambda^{-1} = [2Nrl(n-1)]$. Using this approach Adamczewski has obtained good agreement with pulse measurements of breakdown strength.

From the work of Lewis and Adamczewski, it is apparent that a model of this type is consistent with the relative magnitudes of the breakdown strengths of liquids. However, the electronic theory of breakdown is less satisfactory when it is used to explain the breakdown time lag data. The formative time lags associated with electronic breakdown in gases, for example, are far too short to be comparable with time lags in liquids.

Goodwin and Macfadyen[33] associated the critical time lag $\tau_c$ (Section 4) with the movement of positive ions in the liquid. Crowe[8] was led to postulate a trapped electron model and identified $\tau_c$ with the transit time of the charge carrier. He inferred a carrier mobility which was fairly close to that measured later by LeBlanc[5] (Section 2). However, Crowe's conclusions were largely based upon a linear dependence of $\tau_c$ on gap width, and there is some evidence against this.[41]

It has been generally accepted that the statistical time lags in liquids are insignificant, even under microsecond pulse conditions, and breakdown theories have assigned the entire time lag to formative processes of one type or another. In contrast to this, Ward and Lewis,[46] following Saxe and Lewis,[47] have put forward the hypothesis that a significant statistical time lag does in fact exist and can be determined if the experimental results are correctly interpreted. Ward and Lewis suggest that the statistical time lag is the waiting time for electrons to appear from the cathode; they assume that the electrons are emitted at a rate $I$ per second, and that each electron has a probability $W$ of initiating a breakdown process whose formative time $t_f$ is small. $W$ will become zero at the breakdown threshold $E_0$, which is identified with the d.c. breakdown stress.

If a step-function of voltage is applied to a liquid, then the probability that breakdown will occur at that stress $E$ within the time interval $t$ to $t+\mathrm{d}t$ is

$$P(E)\,\mathrm{d}t = WI\exp[-WI(t-t_f)]\,\mathrm{d}t \qquad \ldots(15)$$

At the threshold stress $E_0$, $P = 0$. The probability of breakdown during a rectangular pulse of duration $\tau$ is

$$p(E) = 1 - \exp[-WI(\tau - t_f)] \qquad \ldots(16)$$

This will be zero for $E < E_0$ and $\tau < t_f$ and will tend to unity as $E$ increases.

The calculation for the multiple pulse experiment is best computed by using a continuous variable. The probability of a first breakdown occurring in the interval $E$ to $E + dE$ is

$$Q = \lambda p \exp\left(-\lambda \int_{E_0}^{E} p \, dE\right) \qquad \ldots(17)$$

where $\lambda$ is the number of pulses applied in a unit interval of stress. From this distribution function, Ward and Lewis have calculated the average breakdown

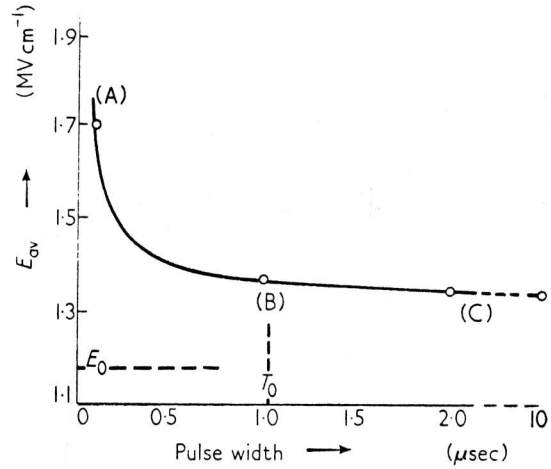



Figure 24. *Calculated breakdown stress as a function of pulse duration for a hypothetical liquid. After Ward and Lewis*[46]

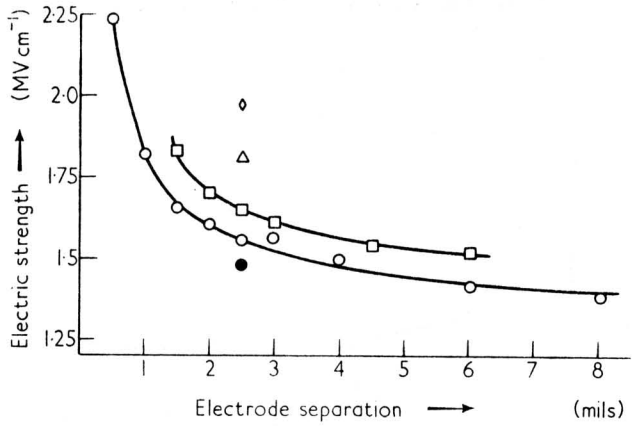
stress $E_{av}$, as a function of the pulse duration, for a hypothetical liquid. This is shown in Figure 24. The parts of the curve AB and BC depend mainly on $I$ and $W$, respectively. The curve was computed on the assumption that the formative time lag is zero. A more realistic value for $t_f$ would move the curve towards longer time lags. Even so, the agreement between the model and the practical case is fairly good. However, since all three of the variables, $I$, $W$, and $t_f$, are likely to be field dependent, it is difficult to put this model to a precise test.

Even so, there are a number of objections to associating the statistical lag with the emission of electrons from the cathode: LeBlanc[81] has pointed out that the increase in breakdown time lag with gap spacing is clear evidence that the time lag is formative and not statistical. One may still argue, of course, that this does not preclude the possibility of a small statistical lag, but it severely limits its magnitude.

Watson[82] has noted that the high field currents[37,38] which are observed in liquids under microsecond pulse conditions are 1 to 10 mA cm$^{-2}$ of cathode area,

and assuming a value for electron mobility of the order of $10^{-3}$ $cm^2V^{-1}sec^{-1}$, one obtains an electron emission rate of $10^{13}$ electrons $sec^{-1}$ $cm^{-2}$ from the cathode surface. It is so large that it is difficult to see how such copious emission can be consistent with an electronic statistical time lag of the order of a microsecond. Moreover, the current is strongly field dependent, so that one would expect a marked reduction in time lag if he were able to increase the field needed to cause breakdown. This can be done by increasing the hydrostatic pressure applied to the liquid, and Kao and Higham find virtually no change in critical time lag in going from atmospheric pressure to 25 atm, despite the very marked increase in breakdown strength.

In reply to these criticisms, Lewis[83] has pointed out that the experimental results on the direct measurement of time lags[46] show definite random fluctuations,




Electrodes: ◇ $\frac{3}{32}$ in. radius; △ $\frac{1}{8}$ in.; □ $\frac{1}{4}$ in.; ○ $\frac{1}{2}$ in.; ● $1\frac{1}{2}$ in.

Figure 25. *Electric strength of n-hexane as a function of electrode separation. After Sharbaugh, Bragg, and Crowe*[56]

indicating that there is a statistical process involved in the breakdown mechanism: the actual nature of the random event may or may not be associated with the cathode emission process, but this in no way invalidates the mathematical treatment of the time lags in terms of a statistical process.

One of the major pieces of evidence used in favour of the electronic theory of breakdown of liquids is the gap dependence of breakdown strength, shown in Figure 25 from the data of Sharbaugh, Crowe, and Bragg.[56] A plausible explanation of the phenomenon was that for an electron avalanche mechanism of breakdown, the multiplication factor $\alpha d$ must reach a certain critical size, as in certain types of gas breakdown.[84] By assuming a reasonable exponential dependence of the multiplication coefficient $\alpha$ upon field, a logarithmic dependence of breakdown strength upon gap was obtained, which was in fair agreement with the experimental observations.

However, the effect of electrode radius (Figure 25) does not fit into this picture, and later work suggests an entirely different interpretation of these observations. The measurements of Sharbaugh et al.[32] on the effect of electrode area on breakdown strength show clearly that for highly purified *n*-hexane measured between

uniform field electrodes having a Rogowski profile, the strength is strongly dependent upon electrode area; moreover, the strength under conditions of constant electrode area is independent of electrode separation. Following the implications of this, it was shown that the discrepancies between previous results for spherical electrodes of varying radii and spacing could be resolved on the basis of electrode area under stress. For spherical electrodes, the area under high stress increases with the product $ad$, where $a$ is the electrode radius and $d$ is the electrode separation. This should lead to a decrease in breakdown strength on the basis of the area effect, and suggests that the data of Figure 25 would lie on a common curve when strength is plotted against the product $ad$, as shown in Figure 26. The most

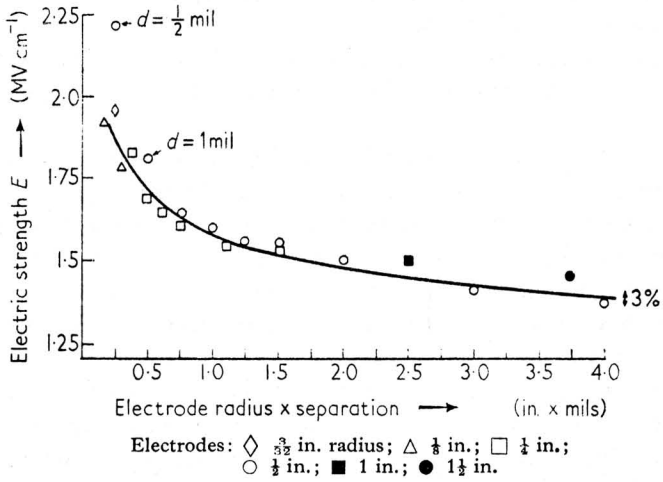



Figure 26. *Electric strength of n-hexane as a function of electrode radius times separation. After Sharbaugh, Cox, Crowe, and Auer*[32]

probable reason for this correlation between breakdown strength and electrode area is the presence of asperities on the electrode surface which contribute to the initiation of breakdown. The evidence for the importance of asperities, or active sites, on the electrodes has been summarized by Lewis.[1]

The electronic theory of breakdown, as generally understood, predicts the presence of an electron multiplication process or $\alpha$-process in the liquid. Indeed, some estimates, such as those of Goodwin and Macfadyen give values of $\alpha d$, as high as 10 at breakdown, but recent pulse measurements[38] (Section 3) have not been able to detect an $\alpha$-process in $n$-hexane, even at fields as high as $1 \cdot 2\,\mathrm{MV\,cm^{-1}}$. However, the observation of light emission from liquids (Section 5) at high fields shows that there are electrons of at least 2·5 eV in the liquid, so that collision ionization cannot be ruled out. One can only say that there are marginal indications of an $\alpha$-process at the highest fields studied and this sets an upper limit on $\alpha d$ of about $0 \cdot 1$ at $1 \cdot 3\,\mathrm{MV\,cm^{-1}}$.

At this stage the evidence both for and against the electronic theory of breakdown may seem to the reader to be inconclusive; there is, however, one point upon which the predictions of the electronic theory appear to be completely incorrect. There seems to be no good reason why the strength of a relatively imcompressible

insulating liquid should increase with pressure[41] if the breakdown mechanism is predominantly an electronic process. On the other hand, a breakdown mechanism involving a change of phase, would naturally lead one to expect a marked pressure dependence.

### 6.2. Cavitation Theories of Breakdown

The work of Kao and Higham[41] shows that there is a strong dependence of liquid breakdown strength upon applied hydrostatic pressure, even in the microsecond pulse range. These results clearly indicate, under their test conditions at least, that a change of phase is involved at a critical stage in the breakdown process.

Kao[85] has recently put forward a mathematical model for a bubble mechanism of breakdown, based upon these experimental findings.[41] He considers that a bubble is formed in the liquid by one of several processes, and that once formed, the bubble tends to elongate in the direction of the field under the influence of electrostatic forces. Breakdown in the bubble is thought to occur when it reaches a critical length.

Kao summarizes the possible causes for the formation of bubbles as: (1) gas pockets, which may exist at pits or cracks on the electrodes; (2) electrostatic repulsion in space charges, which may be sufficient to overcome surface tension; (3) dissociation of liquid molecules by energetic electrons giving rise to gaseous products; (4) heat generated by conduction currents in impurities causing vaporization of liquid; (5) local vaporization of liquid due to energy input at tips of asperities on the cathode.

Once a bubble has been formed, it will tend to be distorted from its spherical shape by the electrostatic forces, as can be seen from the principal of minimum potential energy. The total energy stored in a dielectric containing a cavity of volume $v$ is given by[86]

$$W = \frac{1}{8\pi}\int_v (\epsilon_1 - \epsilon_2) E_2 E_0 \, dv \qquad \ldots(18)$$

Here $v$ is the volume of the bubble, $E_0$ is the applied field strength, $E_2$ is the field strength inside the bubble, $\epsilon_1$ and $\epsilon_2$ are the dielectric constants of liquid and bubble, respectively. From equation (18) it can be shown that the stored energy decreases when an initially spherical bubble is distorted into a prolate spheroid with its major axis in the direction of the field. A bubble will, therefore, tend to elongate in the direction of the field, the work being done at the expense of the stored energy in the electrostatic field.

In order to solve the equation for breakdown, Kao makes the assumptions that the volume of the bubble remains constant during its elongation and that breakdown occurs when the voltage drop along the bubble is equal to the minimum in the Paschen's law curve for the gas in the bubble. He concludes that breakdown will occur at a field given by

$$E_0 = \frac{1}{(\epsilon_1 - \epsilon_2)}\left\{\frac{24\pi\sigma(2\epsilon_1+\epsilon_2)}{r}\left[\frac{\pi}{4}\sqrt{\left(\frac{V_b}{2rE_0}\right)} - 1\right]\right\}^{1/2} \qquad \ldots(19)$$

where $\sigma$ is the surface tension of the liquid, and $r$ is the initial radius of the bubble. This equation indicates that the critical electric strength required for breakdown

of the liquid depends upon the initial size of the bubble, which is affected by the external pressure and temperature, in accordance with the ideal gas laws. Fitting equation (19) to the experimental results at atmospheric pressure, Kao's model gives the type of behaviour shown in Figure 27. The theory does not attempt to deal with the vital step of the production of the initial bubble; moreover, it is dubious if the condition of constant volume is a valid one.

A thermal mechanism of breakdown under pulse conditions has been proposed by Watson and Sharbaugh.[38] This is based upon the observation that the currents flowing in *n*-hexane at fields in the vicinity of breakdown are extremely large (see Section 3). There are indications that the currents originate at microscopic points on the surface, and that local current densities may possibly be in excess of 1 $A\,cm^{-2}$.

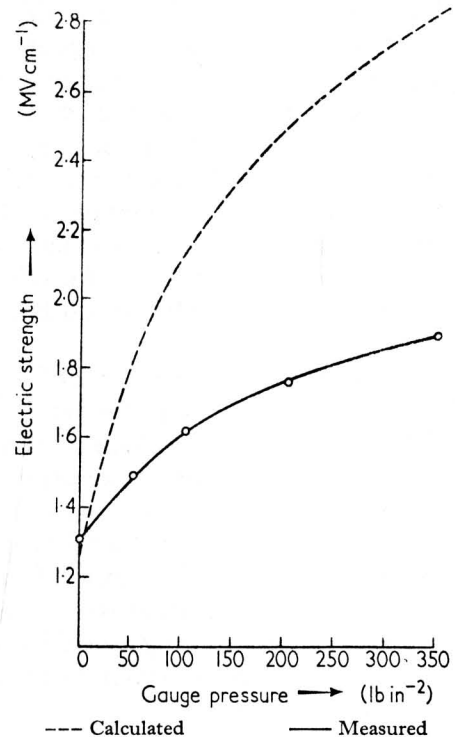



Figure 27. *Breakdown strength of n-hexane as a function of pressure. After Kao*[85]

Because of this large current density and the high local field, the energy input to the liquid may even be in excess of $10^7\,W\,cm^{-3}$, which could lead to the formation of a vapour bubble in a few microseconds. Once a bubble has formed, breakdown of the liquid should follow rapidly: for example, the bubble may expand until it reaches a critical length[85] or until it bridges the gap; in either case the spark will pass through the low strength vapour. Several early workers, including Whitehead,[25] had considered thermal breakdown processes in liquids, but until recently such a mechanism was thought to be impossible with applied fields of only a few microseconds duration.

The thermal breakdown criterion of Watson and Sharbaugh[89] is based upon the energy $\Delta H$ needed to boil the liquid, that is,

$$\Delta H = m[c_p(T_b - T_0) + l_b] \quad \ldots (20)$$

where $m$ is the amount of liquid evaporated, $c_p$ is the average specific heat of the liquid at constant pressure over the range from ambient temperature $T_0$ to the boiling point $T_b$, and $l_b$ is the latent heat of vaporization at the boiling point.

In order to put the model on a quantitative basis it is necessary to relate $\Delta H$ to the applied field. In this connection, the experimental current versus voltage characteristics shown in Figures 9 and 10 imply a very strong dependence of energy input on field. Specifically, the data in Figure 9 show a fifth power relationship between current and field, while those in Figure 10 obey a still higher, ninth power, law. Using these relations directly in equation (20), poor agreement with breakdown data is obtained, and, at first sight, it is difficult to reconcile the theory with experimental fact. However, there are two phenomena which help to resolve the discrepancy. In the first place, it appears probable that the motion of liquid under stress may have to be taken into account; as the liquid near an asperity heats up, its dielectric constant falls, and thus it experiences a force driving it from the region of highest stress. We may therefore define a 'residence time', $\tau_r$, for the liquid in the region of highest stress. This motion would tend to limit the temperature rise of the 'hot spot' near the asperity, and has the effect of reducing the field dependence of the local temperature rise. An effect of this type may explain some features of the photographs of Hakim and Higham,[68] as shown in Plates I and II.

Secondly, it is possible that, at high fields, the current from the most strongly emitting asperities on the cathode is space charge limited.[31,38] In this case, the relationship between local current and applied voltage is given by one of the well known space charge equations (the appropriate choice depending upon the local conditions, which are not known exactly). That is, we may either use the quadratic space charge equation, $I = bV^2/d^3$, or some other similar equation, in which current is related to voltage by a relationship of empirical form $I = cV^N$ where $N$ is in the range 1·5 to 2. The important point is that as one approaches breakdown fields, the current from the most highly emitting asperities is not necessarily as strong a function of voltage as appears from the measurement of total current.

Thus the local energy input has the form

$$\Delta H = AE^n\tau_r \quad \ldots (21)$$

where $\tau_r$ is the residence time of the liquid in the high field region near an asperity, and may well be equal to the critical time lag $\tau_c$ (see Figure 13). For applied pulse lengths longer than $\tau_r$, the strength should be independent of pulse width, and for pulses shorter than $\tau_r$, the strength should rise rapidly with decreasing pulse width.

The thermal breakdown model exhibits a marked pressure dependence of breakdown strength; as pressure on the liquid is increased, its boiling point $T_b$ increases in a known fashion, and from equation (20), the dependence of strength on pressure can be calculated. Comparing the formula with the experimental results at constant pulse width, it is found that the same basic equation can be fitted to the observed pressure dependence of strength for all the liquids examined.

These include hexane, heptane, decane, and benzene. In most cases, $n = 3/2$ in equation (21) gives the best fit, as shown in Figure 28. The effect of ambient temperature on breakdown strength can also be fitted to the model, and calculations again yield values of $n$ which are about 3/2.

The thermal breakdown model of Watson and Sharbaugh[89] may also explain the dependence of breakdown strength on molecular structure, since within a given homologous series, the thermal properties $c_p$ and $l_b$ increase with chain length. As an example, for the $n$-alkanes equations (20) and (21) predict the observed dependence of breakdown strength on chain length; however, the branched alkanes show some scatter about the straight chain results and the alkyl benzene

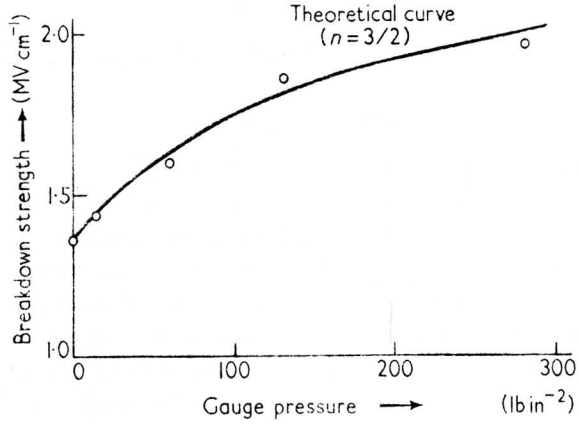



Figure 28. *Breakdown strength of n-hexane as a function of pressure. After Watson and Sharbaugh*[89]

homologues require a different value of $n$ in equation (21). The reason for these anomalies may well lie in the differences between the conduction currents in these various liquids; unfortunately, hexane is the only liquid in which currents have been measured under pulse conditions up to breakdown fields.

### 6.3. Suspended Particle Theory

It is well known that the presence of minute particles gives rise to drastic lowering of the measured electric strength of liquids, and Kok and Corbey[87] have attempted to treat this effect quantitatively. The particles are assumed to be polarizable spheres whose dielectric constant is larger than the liquid; as a result they experience an electrical force causing them to move in the direction of increasing electric stress. With parallel-plate or other uniform field electrodes, movement of particles is presumed to be initiated by surface irregularities on the electrode which give rise to a local field gradient. An accumulation of particles continues in this manner and tends to form a bridge across the gap which leads to breakdown. The movement of particles by the electrical force is opposed by diffusion and the viscous drag of the liquid. This introduces a dependence of the breakdown strength on time, concentration of particles $N$, their radii $r$, and the liquid viscosity $\eta$. Kok and Corbey derive a criterion for breakdown for short stress times

$$t_b g^4 r^7 (E_b^2 - E_0^2)^2 N^2 = \eta^2 \times \text{constant} \qquad \ldots (22)$$

Here $E_b$ is the breakdown strength, $E_0$ is the long time breakdown strength, and $t_b$ is the time required for breakdown; $g$ is the enhancement factor of the applied field in the neighbourhood of the initiating electrode surface irregularity and is equal to 3 for an asperity of hemispherical shape. The time dependence expressed by equation (22) is tested by plotting the pulse breakdown measurements of Watson and Higham[43] for transformer oil and the breakdown values of Crowe, Sharbaugh, and Bragg[45] for hexane. There is a fair fit to the predicted linear plot of $E_b^2$ versus $1/t_b$, where $t_b$ is taken to be the applied pulse length in breakdown studies.

For long times of application of the field, the theory of Kok and Corbey predicts that

$$(g^2-1)r^3E_0^2 = 2\mathbf{k}T$$

where $r$ is the particle radius and $\mathbf{k}T$ is the thermal energy in ergs. For $g^2 = 9$, this becomes

$$r^3E_0^2 = \tfrac{1}{4}\mathbf{k}T \qquad \ldots(23)$$

and the long time breakdown strength is proportional to $r^{-3/2}$. The observed limiting value for long applied pulses for transformer oil[43] is about $1 \cdot 5$ MV cm$^{-1}$, which according to the above equation, yields a particle diameter of about 20 Å. The same value of particle diameter is derived from pulse measurements on hexane[45] which, they point out, is comparable with the molecular dimensions of many simple organic compounds. In this way the original macroscopic concept is extended to particles of molecular dimensions, and a theoretical upper limit for breakdown strengths is established. It is difficult to reconcile this theory with the experimentally observed increase of breakdown strength with chain length for the *n*-alkanes. Furthermore, equation (23) predicts an increase of electric strength with an increase in temperature, which is contrary to experimental fact.

In another paper,[88] Kok and Corbey test their theory by comparing calculated and observed breakdown values of liquids having particles of known size in colloidal suspension. Of the three sets of experimental data which are discussed, two involve water suspensions of particles of the order 1 micron radius for which the calculated and measured breakdown strengths are in the range 10–100 V cm$^{-1}$. These breakdown field strengths are many decades lower than those commonly measured for insulating liquids and it seems likely that different breakdown mechanisms are involved. Another colloidal suspension consisted of gasoline with aluminium particles of $2 \cdot 5$ microns radius in suspension. A breakdown strength of 4 kV cm$^{-1}$ was measured, whereas the theory would have predicted a strength of about 10 V cm$^{-1}$ for this particular size. Furthermore, the theory of Kok and Corbey requires that a fivefold decrease in particle size should increase the strength by a factor of eleven, and only a threefold increase was measured.

Experience with studies made with highly purified hexane[49] has shown that particles of the order of 1 micron radius often lead to breakdown in the range of 100–500 kV cm$^{-1}$, and this is about four decades higher in strength than the theory of Kok and Corbey would predict. Edwards[50] has reported strengths even higher than this when 1 micron particles were present in hydrocarbon liquids. Evidently there is little quantitative evidence in support of this theory, though there is no doubt that particles often initiate breakdown in insulating liquids.

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