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CLASS 1

PROGRESS IN THE FIELD OF ELECTRIC BREAKDOWN IN DIELECTRIC LIQUIDS

by

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SUMMARY

The electric breakdown of liquid dielectrics is a complicated process and there is no single theory that explains all the experimental results. Specific experimental conditions will be the determining factor as to which of the several mechanisms will be operative.

In commercial liquids there are the following important mechanisms: (a) thermal breakdown due to heat generated by ionic impurities (e. g., H_2O); (b) breakdown caused by suspended particles (order $\geq 1\mu$ in diameter); and (c) electrochemical breakdown wherein the passage of a current will cause electrode reactions which generate gaseous bubbles (e. g., H_2 and O_2 from H_2O). Under ideal laboratory conditions, the three preceding mechanisms can be more or less avoided and one can measure a relatively higher strength. This is done by giving especial attention to chemical and physical purification (filtering) of the sample, close control of the electrode surface polish and geometry, and the use of pulsed voltages. In this manner one can measure a breakdown strength which depends upon a particular variable, other variables being held constant. These values serve as a basis for the evaluation of the two principal mechanisms of liquid breakdown: electronic breakdown involving field-intensified ionization, and a cavitation or bubble mechanism.

One cannot completely rule out the existence of collisional ionization in liquids at or very close to the breakdown field strengths. However, the collective evidence definitely favors a cavitation (bubble) theory of breakdown. Measurements designed specifically to detect an alpha process (electron multiplication) at fields up to and including breakdown are needed for liquid dielectrics other than hexane.

KEY WORDS

dielectric breakdown, insulation liquid dielectrics breakdown

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PROGRESS IN THE FIELD OF ELECTRIC BREAKDOWN IN DIELECTRIC LIQUIDS

A. H. Sharbaugh

I. INTRODUCTION

For some fifty years the mechanism of electric breakdown in liquid insulation has been a subject of great interest for both theoretical as well as practical reasons. Over the years a number of promising hypotheses of breakdown have been advanced and it has been necessary to modify, and sometimes reject, interpretations of the breakdown data as additional experimental evidence has been accumulated.

In 1950, Dr. S. Whitehead(1) stated in the preface to his book on solid breakdown that he would not consider writing a companion book on liquid breakdown for fear that it would become simply "a compendium of unrelated facts."* Yet, in the ensuing twenty years we have seen substantial progress in this complex field of investigation, and we may now profitably review the important developments during this period.

Broadly speaking, workers in the field have been divided into two principal schools of thought. There are those who favor an electron multiplication theory of breakdown, analogous to the Townsend theory of breakdown in gases. According to this theory, breakdown will occur when an electron, on the average, makes a suitable number of ionizing collisions in its transit across the breakdown gap.

On the other hand, there are those who doubt the existence of collision ionization in liquids and favor the so-called "bubble mechanism" of breakdown. Specifically, my colleague, Dr. P. K. Watson, and I propose that a bubble of gas is formed by vaporization of liquid by local heating in the strong-field region at the tips of asperities on the cathode.(2) A bubble, so formed, will grow and breakdown will take place in the low-strength vapor within the bubble. This rapidly leads to rupture of the bulk liquid.

In this report, I shall first examine some of the difficulties which are encountered in the measurement and interpretation of breakdown phenomena in the liquid state. Comparisons and generalizations with breakdown in gases and solids will be made, wherever possible. The concept of the "intrinsic strength" of a liquid will be discussed, as well as the development of the very important experimental technique in which pulsed voltages are used in conduction and breakdown studies.

Following this, the chronological development of the two central ideas of breakdown mentioned above will be examined in the light of experimental results as they have been accumulated. The evidence for each will be presented and, finally, our reasons for preferring the bubble theory of breakdown will be discussed.

From a consideration of densities alone, we should expect liquid breakdown to resemble that for solids, and indeed the general magnitude of breakdown strengths of liquids and solids are of the same order. Evidence that field emission plays an important role in the breakdown of liquids has been adduced. On the other hand, in their absence of structure, liquids more nearly resemble gases. Amorphous solids, on this basis, would be expected to behave more like liquids than crystalline solids.

The potential difference at which breakdown occurs, divided by the dielectric thickness, is loosely referred to by such terms as the breakdown field strength, dielectric strength, electric strength, or intrinsic electric strength. The magnitude of such a strength will depend upon the composition and structure of the dielectric, but--in addition--will often be a function of a multiplicity of external variables such as the uniformity of the field, possible heating effects caused by long stress times, and the presence of gaseous discharges.

When breakdown is caused by a thermal runaway process, it is called a thermal breakdown. If it is induced by deterioration from a gaseous discharge, it is classed as a discharge-type of breakdown. This latter breakdown may arise from discharges in voids or bubbles in the dielectric under investigation. In the case of solids, it may occur in the ambient medium at the electrode edges. However, if certain precautions are observed during the measurement, the possibility of these two kinds of breakdown and the influence of other external variables may be substantially reduced and an electric strength that is more or less characteristic of the constituent atomic and molecular structure of the liquid may be measured. As we shall see, there is no such thing as an intrinsic strength in the strict at sense of the word. However, we can measure values which reflect the composition and properties of the liquid itself by holding external variables constant throughout the experiment. Until a more detailed understanding of the mechanism of breakdown is available, the precise influence of many of the variables cannot be evaluated. For example, some theories of breakdown in liquids predict a dependence on the composition of the electrodes; however, within the present limits of conventional measurement techniques (values reported by various investigators often differ by, say, 30 percent), these effects cannot be positively assessed. In solids, however, the electronic theories have all assumed that the breakdown strength is an intrinsic property of the solid.

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*This statement is all the more remarkable when it is realized that Dr. Whitehead had, indeed, written a book on liquid breakdown(62) some 25 years earlier!

Compared to gases the increased density of the liquid state, and higher electric strength, brings with it the complications of field emission. Field emission depends critically on electrode surface conditions. This, in turn, introduces a dependence on surface layers as they control emission and an area effect. The concept of mean free path for the electron in a liquid becomes unclear when we try to extrapolate our ideas of the kinetic theory of gases. The distance of free travel on acceleration in the field is highly restricted because of the high density of molecules.

Breakdown in solids usually occurs at even higher fields than liquids and these complications remain. On the other hand, the theory of the solid state has advanced in recent years with the impetus of semiconductor technology and science. Solids can be characterized as amorphous and/or crystalline with intermediate mixtures of each. The crystal structure and lattice parameters of simple cubic systems are well known and provide ideal specimens for study. On the other hand, the theory of the liquid state has lagged and this has hampered theoretical treatment of breakdown in liquids.

Several comprehensive reviews and books have appeared on this subject in the last decade (Refs. 22, 45, 52, 59, 60, 61). In Professor Adamczewski's comprehensive book(33) there are over three hundred references in the part on electrical conductivity and breakdown at high fields, most of which have been published in the last twenty years. This gives some idea of the task of condensing the activity in this field into a single report. Necessarily I have had to establish some sort of criterion for selection of subject matter. I will consider the research specifically concerned with highly purified organic liquids, and so, reluctantly have to omit much interesting and important work concerned with commercial insulation systems. I make no apology for a highly biased presentation. Having personally worked in this field for a number of years, I cannot avoid some prejudice; however, I will try to present objectively my reasons for preferring certain mechanisms of breakdown.

2. EXPERIMENTAL TECHNIQUES

The search for reproducible values to assign as breakdown strengths of liquids has been a long and tedious one. However, with increased attention given to sample purity, both chemical and physical, electrode preparation, and the use of microsecond pulse techniques, the values obtained by different investigators are now in fair agreement. It is still necessary to specify the electrode configuration and composition as well as the stress duration, and so, in the strict use of the word, it is not possible to speak of an "intrinsic electric" strength of a liquid as defined earlier.

The role of imperfections has become increasingly evident. For example, asperities or points on the cathode and suspended particles migrating to high stress regions of the gap may enhance the applied field to cause breakdown. Also, electrochemical processes, such as electrolysis of water or dissociation of the liquid by electron bombardment, may generate low-strength bubbles which lead to breakdown. Both imperfections, electrochemical deterioration, and suspended particles are commonly operative in the breakdown of commercial liquids. The suspended particles often cause low breakdown voltages in otherwise highly purified liquids and have long plagued workers' experiments in the field of liquid breakdown.

Liquid breakdown has some peculiar experimental difficulties which may not be present in solid or gas breakdown. For example, the usual decomposition products are solids (carbon) which remain in the breakdown path and tend to render spuriously low breakdowns thereafter. Thus, fresh liquid samples and electrodes surfaces (without pits) must be used for each breakdown. Figure 1 shows a typical breakdown cell used at the General Electric Laboratory: S, Sylphon bellows; C, Teflon polymer cup; B, stainless steel mount for electrode; W, glass windows; J, ball-socket joint; and M, microscope. There is also the possibility that minute suspended particles may be moved by electrical forces into the strong field region and give rise to spurious results. Elongated bodies, such as fibers, which tend to be hygroscopic, may align to bridge the electrodes. Such motions are not possible in solids. For these and various other causes the spread in breakdown values is generally much larger for liquids than for gases. A typical distribution of breakdown values in benzene and butyl benzene is shown in Fig. 2. Bubbles, of course, have no meaning in gas breakdown and, if formed, cannot move in solids.

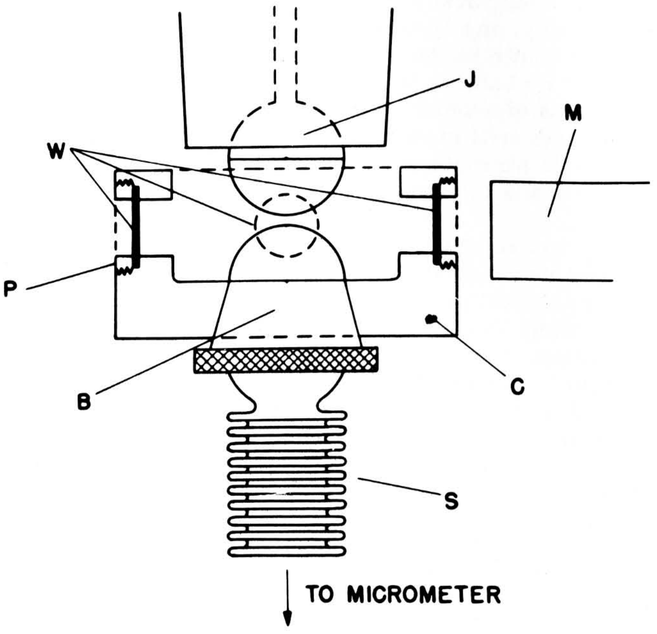

Fig. 1 Liquid breakdown cell.

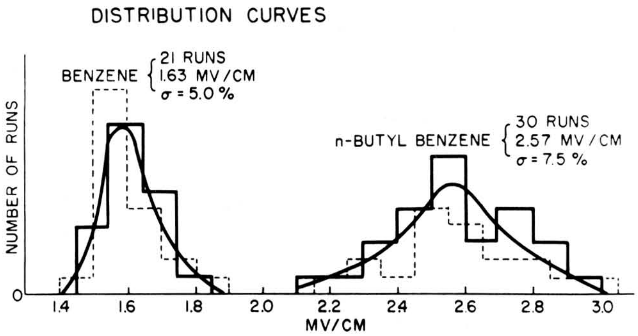

Fig. 2 Distribution of breakdown data for benzene and butyl benzene.

It was recognized some years ago that the use of short pulses of voltages 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 of 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 technique, 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(3) 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 τ 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. (4) As shown in Fig. 3, the results obtained with the two techniques were quite different. First, the absolute magnitudes of the pulse currents were orders of magnitude greater than for d. c. ; and secondly, in the time range 10^{-2} to 10^{-6} seconds the magnitude of the pulse currents was 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.

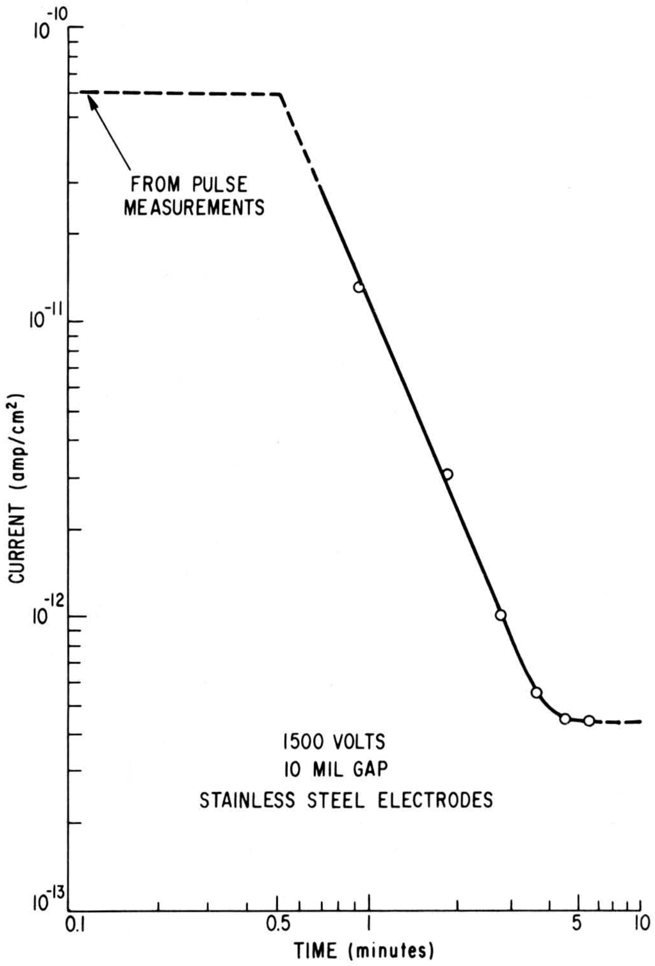

Fig. 3 A comparison of the magnitudes of conduction currents in n-hexane measured under d-c and pulsed conditions. Dashed line extrapolated from pulse measurements; solid line shows time dependence with d-c. After Watson and Sharbaugh. (4)

Macfadyen and Helliwell(5) 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 these circuit problems. The use of an oscilloscope to 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.

3. EXPERIMENTAL RESULTS

3.1 Low-field Conduction

At low field strenghts (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 ultraviolet 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,$^{(6)}$ and early workers may not have recognized the importance of these requirements. Forthermore, the use of radiation including wavelengths of less than 2000Å 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 (>3000Å) and thereby inject electrons from the cathode without the complication of charge generation in the body of the liquid itself. LeBlanc,$^{(7)}$ Inuishi,$^{(8)}$ and Morant (Ref. 6) have exploited this technique in recent years. Sletten$^{(9)}$ has called attention to the stabilization of currents in hexane by dissolved oxygen. The use of tunnel diodes to inject electrons into the liquid has been exploited by Silver and co-workers.$^{(10)}$ This avoids many of the problems mentioned above.

After an electron is injected into the liquid by some process, such as photo-injection or tunnel diode emission, 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.$^{(11)}$ 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$^{(7)}$ has reported upon an 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 (aluminum) by illumination with a high intensity pulse of ultraviolet light, the duration being short compared to the transit time of the electrons. The transient current produced in the external circuit followed closely the expected behavior; 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 Fig. 4.

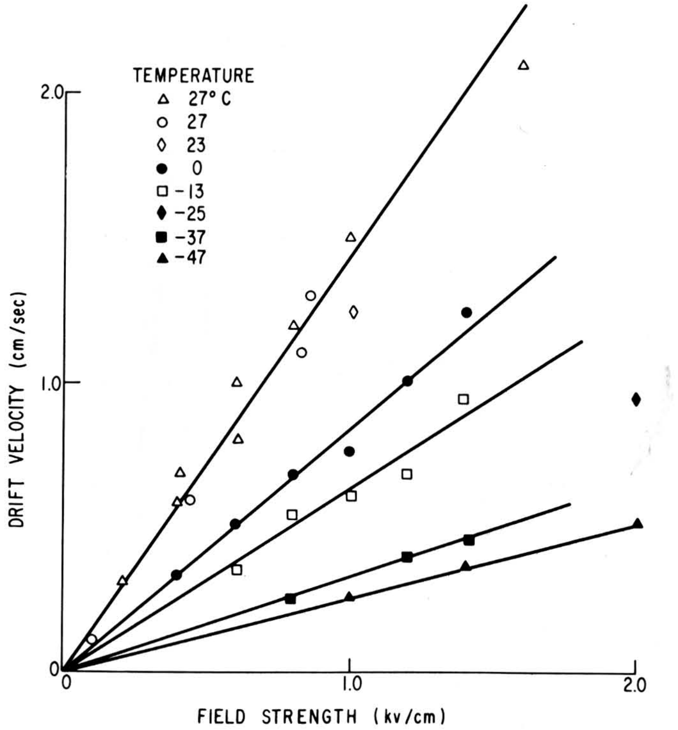

Fig. 4 The dependence of electron drift velocity upon field strength at various temperatures. Liquid n-hexane. After LeBlanc.$^{(7)}$

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 $1.4 \pm 0.1 \times 10^{-3}$ 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^2 V^{-1} sec^{-1}). As shown in Fig. 5 the drift mobility was found to change with the absolute temperature T according to the relation

$$\mu = \mu_0 \exp(-\Delta u/kT). \qquad (1)$$

Here $\mu_0 = 0.3 \pm 0.2$ cm^{2}V^{-1}sec^{-1} and $\Delta u = 0.14 \pm 0.02$ eV.

The product of mobility and liquid viscosity changed with temperature, indicating a violation of Walden's rule (see Fig. 5). LeBlanc points out that the small value of mobility and anomalous behavior with respect to Walden's rule 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 1.1 ± 0.2.

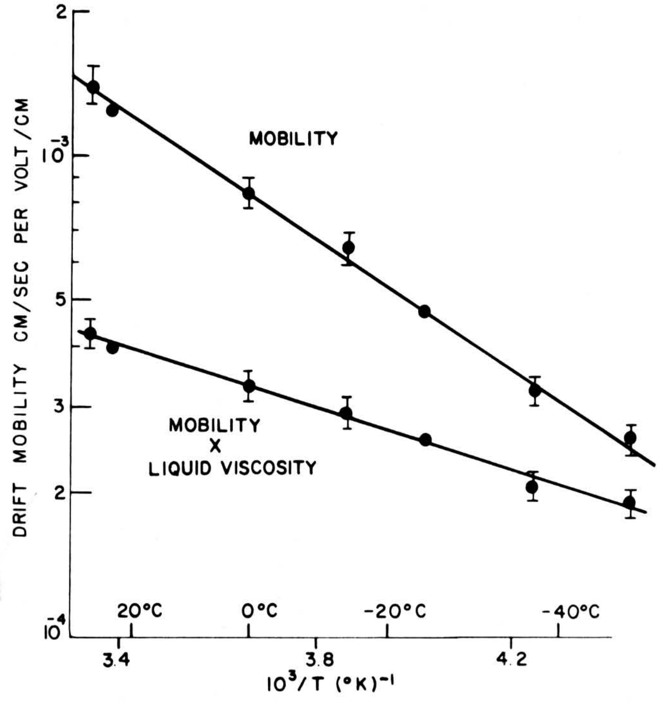

Fig. 5 The dependence of the drift mobility of electrons in n-hexane upon temperature (upper curve). The dependence of mobility times liquid upon temperature (lower curve). After LeBlanc.(7)

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 λ before being trapped. After a time τ the electron escapes from the trap and travels another free path before being trapped again. Since λ is much smaller than the total interelectrode distance, then the electron drift mobility will be given by

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

Here μ_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 λ/c in comparison to τ, and assuming that τ will decrease exponentially with increasing temperature, then Eq. (2) may be written in the form of Eq. (1). In this manner, the observed value of Δu is interpreted as being the average trapping energy, and the small value (0.14 eV) is an indication of relatively shallow traps. Assuming classical processes only, and square-well traps of radius a, LeBlanc gives the expression for the field dependence of mobility

$$\mu = \mu_0 \exp[\Delta u - Ea/kT] . \qquad (3)$$

In recent years, it has been found that motion of the dielectric liquid which is induced by momentum transfer of the charge carriers produces an apparent mobility that is greater than the true values. Gray and Lewis(65) report mobilities in hexane ranging between 1.2×10^{-4} and 2.4×10^{-3} cm^{2}V^{-1}sec^{-1} in a field of 1 kV cm^{-1} and ascribe the variation to this cause.

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 ϵ is the dielectric constant,(12) and Poisson's equation is written as

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

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 (Ref. 13). 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.(6) 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(69) 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(69) has experimentally demonstrated the existence of the postulated space-charge potential.

Another experimental approach for injecting electrons into dielectric liquids is by the use of tunnel diodes. Silver(10) and co-workers have shown a qualitative agreement of the transient behavior of carriers so injected into cyclohexane and a mobility $\mu \cong 2.5 \times 10^{-4}$ cm^2 V^{-1} sec^{-1} is derived from the current at infinite time and the transit time. His results yield an active area of the cathode to be almost exactly equal to the geometric area; such an estimate was not possible before the development of this transient technique. This method promises to be very useful in determining the electrical properties of dielectric liquids, in particular the transport properties of solvated electrons.

3.2 High-field Conduction

Chong and Inuishi(8) 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(7) 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 buildup of charge was observed directly on an oscilloscope. The transit time of the charge is then simply the time elapsed during the linearly rising portion of the charging curve. Chong and Inuishi generated photocurrents whose magnitude was about 10^{-9} amp cm^{-2} (about 10^3 larger than those used of LeBlanc). Apparently, this higher current was achieved by the use of high-intensity light pulses and a magnesium cathode.

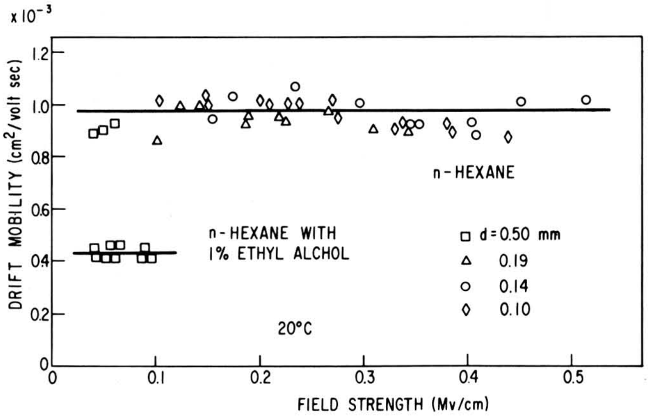

Fig. 6 The dependence of drift mobility upon field strength. After Chong and Inuishi.(8)

The results of Chong and Inuishi for the drift mobility of electrons in hexane are shown in Fig. 6, as a function of field strength. It will be noted that their value of 1.0×10^{-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 1.4×10^{-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 Eq. (1), Chong and Inuishi derived a value of $\Delta u = 0.16$ 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 fulfillment 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.(14)

A value of 0.45×10^{-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 percent 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 vs 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.

As mentioned in the introduction, 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 behavior at high fields by means of a Townsend model are prone to favor the existence of a multiplication, or "α-process," and some have published d-c conduction data which are consistent with this model.(15-17)

On the other hand, there are others who doubt the existence of an α-process in liquids and have measurements to support their point of view.(18, 19) As indicated earlier, most of these studies have been confined to fields less than about 25 percent of breakdown. House(15) and Green(18) 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 observed no catastrophic current increase up to a field of 1.06 MV cm^{-1} and set an upper limit of α equal to 2 at fields above 0.8 MV cm^{-1}, if it existed at all. House thought he had positive evidence at fields of 1.5 MV cm^{-1}. However, both of these investigations suffered from the use of spherical electrode geometry which makes the analysis of results very difficult since the area involved in field emission of the current increases when the voltage is increased at constant electrode separation.

Watson and Sharbaugh(2, 3) overcame this difficulty 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 Fig. 7, currents were measured over a wide range of fields (0.04 to 1.4 MV cm^{-1}) and at several gap widths in order to determine whether or not an α-process exists in the liquid. These authors concluded there was no evidence for multiplication at fields up to 1.2 MV cm^{-1}, but observed marginal indication of the beginning of the process at 1.3 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 αd equal to about 0.1.

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.

On the basis of test plots and the assumption of realistic emission parameters, these authors concluded 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. The authors calculate the active emitting area, 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 1.3 MV cm^{-1} the measured current density was 10^{-3} to 10^{-2} amp cm^{-2}; hence the local current density at the emitting points is computed to be about 1 amp cm^{-2}. Such a calculation assumes that the sum of all the local currents in linearly related to the local emission and this would only be true for the hypothetical case of identical emitting points.

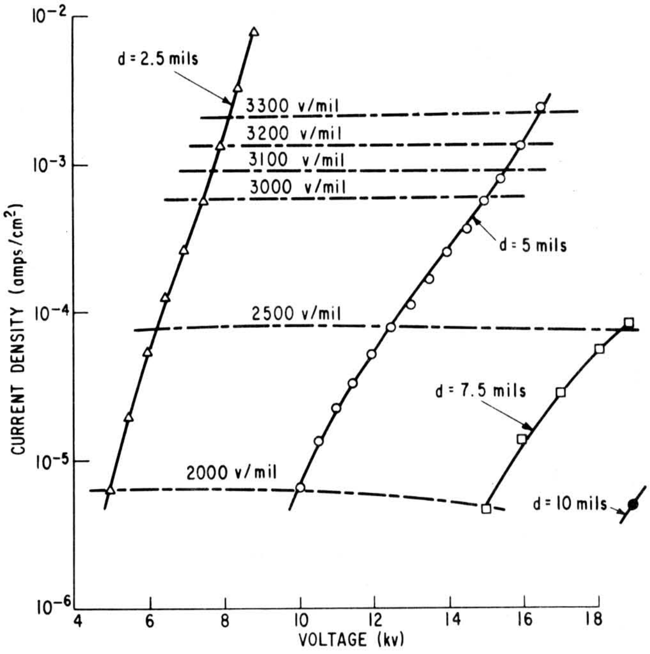

Fig. 7 The dependence of conduction current density upon voltage a different electrode separations (in n-hexane). Lines of constant field strength are shown as dashed lines. After Sharbaugh and Watson.(2)

3.3 Breakdown

3.31 Time Effects

When the breakdown strength of a liquid is measured as a function of pulse length, the strength is practically independent of the applied pulse lengths for rectangular pulses longer than a certain critical time, τ_c. For pulse lengths less than τ_c, the measured breakdown strength rises rapidly as shown in Fig. 8. The d-c values of electric strength of a given liquid are about two-thirds the long-time value measured with rectangular pulses. The value of τ_c increases with increasing gap width and is of the order of 1µ sec for 50µ (2 mil) gaps. The existence of a critical time has been verified for highly purified hydrocarbon liquids as well as commercial oils. Its value is primarily independent of molecular structure for a given homologous series (see Fig. 9) and does not change with increasing applied hydrostatic pressure up to 25 atm.(20)

Impulse breakdown strengths are normally measured by the successive application of a number of single pulses of short duration (microseconds) whose amplitudes are gradually increased. In this manner, the breakdown experiments were conducted which lead to the curve sketched in Fig. 9. These results suggest that only the formative time lag is involved and that there is no statistical time lag in these experiments. If, instead of the multiple pulse technique, a single pulse of relatively long duration (milliseconds) is applied, different time lags are observed and there is an indication of a statistical time lag.(21) The matter needs clarification.

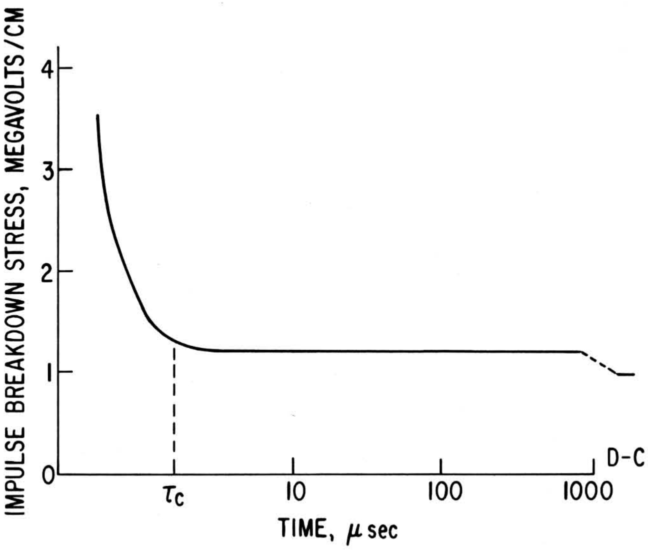

Fig. 8 Breakdown strength of liquids as a function of applied pulse length.

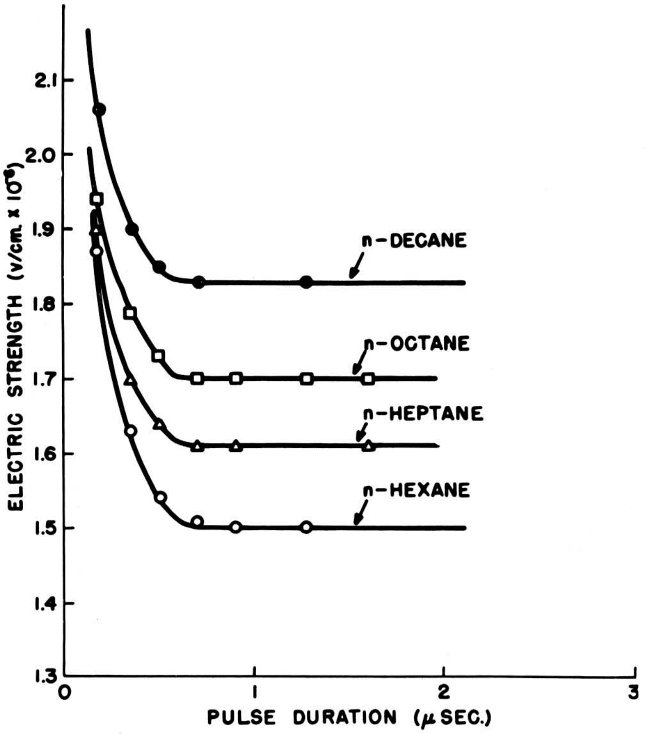

Fig. 9 Electric strength vs pulse duration for straight chain hydrocarbons. After Crowe.(11)

3.32 Dependence upon Molecular Structure

In Fig. 10 the electric strengths of members of three different homologous series of liquids are presented: the alkanes, the alkylbenzenes, and the dimethyl siloxanes. The strengths are plotted against bulk density, which increases regularly for the siloxanes and the alkanes, but is constant for the alkyl benzenes. It is clear that density alone is not the controlling factor because of the large variation in the electric strength of the alkyl benzenes. Branching of the hydrocarbon molecules leads to a lowering of the electric strength. The d-c strengths for the alkanes are seen to be about two-thirds of the values measured with pulse voltages. These data illustrate that it is relatively easy to obtain a relation between the breakdown strength and some physical property such as density or viscosity, but that it is much more difficult to ascertain what is the significant process which gives rise to this relationship.

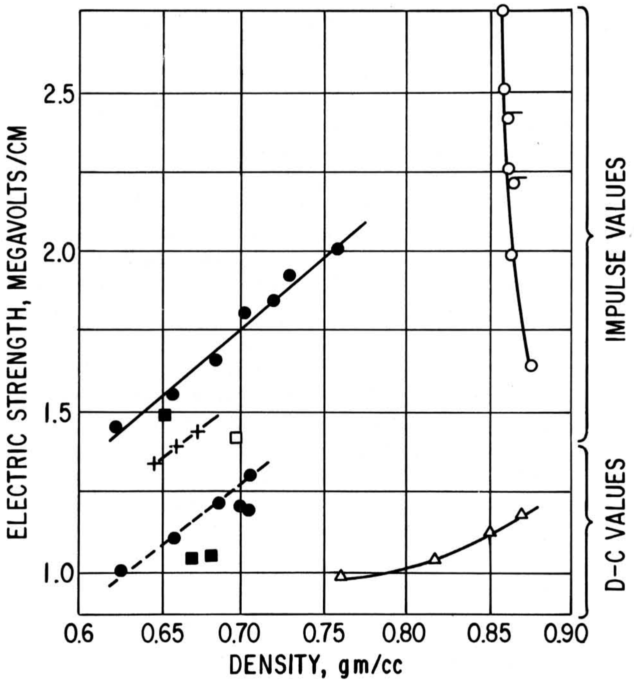

Fig. 10 Electric strengths of three homologous series of liquids as a function of density. From Sharbaugh et al. and Lewis.(22)

3.33 Electrode Effects

A conditioning effect in which the breakdown strength increases continuously with the first few breakdowns is often observed in liquid studies. Of course, if an excessive number of breakdowns are made on the same liquid sample without limiting the breakdown current, the strength will eventually decrease due to the formation of decomposition products. Sometimes, fresh liquid and electrodes are used for each breakdown in an effort to avoid these effects. Each successive spark during the conditioning period seems to remove the most prominent point or asperity on the electrode, and each breakdown occurs at a new spot on the electrode, avoiding the breakdown craters produced earlier.

If there is a distribution in the sizes of the asperities on the electrode surface and the most prominent of these initiates breakdown, then an increase in the area of the electrodes will lead to a greater probability of breakdown. This gives rise to an area effect, which has been studied extensively in commercial liquids(24, 25) and (to a lesser extent) in purified hydrocarbons.(23) As a consequence of the area effect, the modal values of breakdown strength as observed with flat electrodes having different areas, but at a constant gap, decrease approximately with the logarithm of the area (see Fig. 11). A few investigators have reported a correlation between liquid breakdown strength and the work function of the electrode material. Since the strengths are in the range where field emission is important, such a dependence is not unexpected. More often, investigators have failed to observe any correlation with vacuum work function of metal electrodes, and it is generally agreed that the electrodes are not likely to exhibit vacuum work functions because of surface layers arising from oxidation and adsorption of hydrocarbon films.

In certain special studies where aqueous electrolyte solutions have been used as electrodes (see Fig. 12), the amount of emission has been controlled by changing the strength of the solution. In this case, good correlation with theory is found.(26)

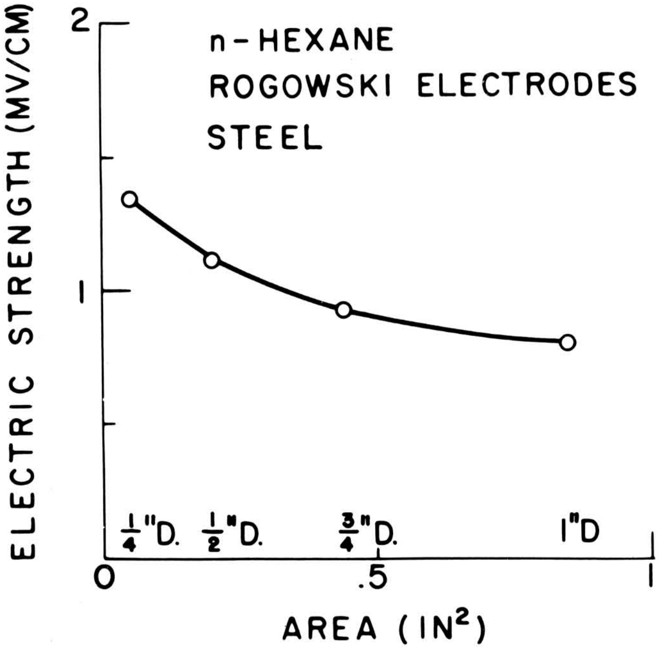

Fig. 11 Area effect on electric strength of n-hexane. Flat stainless steel electrodes. Electrode separation = 2 mils. After Sharbaugh et al.(23)

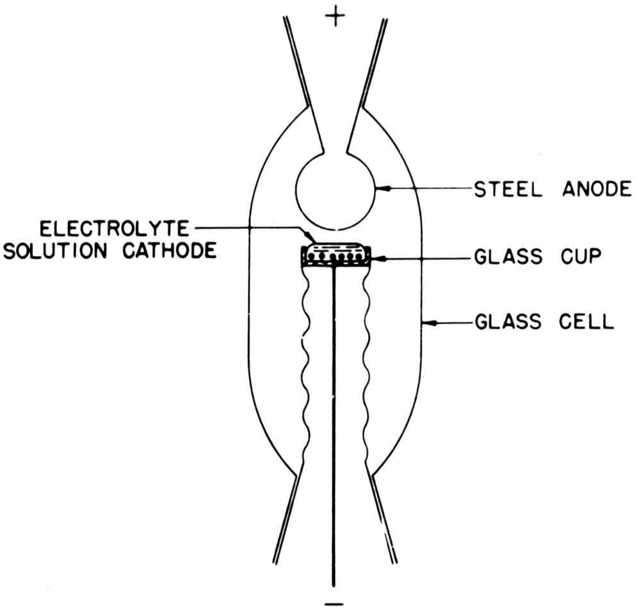

Fig. 12 Experimental breakdown cell using aqueous-electrolyte solution as an electrode. After Bragg, Sharbaugh, and Crowe.(26)

When flat electrodes are used, the electric strength of hydrocarbon liquids and carefully filtered insulating oils is nearly independent of the spacing of the electrodes.(23-25) Thus, the effect of the volume of liquid under stress is small, if it exists at all. This dependence has been studied over a large range of spacings, ranging from a few mils to about 1/4 inch. However, insulating oils that contain suspended particles larger than about 0.1 mil average diameter will show a volume effect--i.e., E_b will decrease with increasing δ. Unless a special filtration procedure is employed, all liquid samples will contain such particles.

One of the major pieces of evidence used in favor of the electronic theory of breakdown of liquids is the gap dependence of breakdown strength, shown in Fig. 13 from the data of Sharbaugh, Bragg, and Crowe.(27) A plausible explanation of the phenomenon was that for an electron avalanche mechanism of breakdown, the multiplication factor αd must reach a certain critical size, as in certain types of gas breakdown. By assuming a reasonable exponential dependence of the multiplication coefficient α 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 (Fig. 14) does not fit into this picture, and later work suggests an entirely different interpretation of these observations. The measurements of Sharbaugh et al.(23) 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 produce 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 Fig. 13 would lie on a common curve when strength is plotted against the product ad, as shown in Fig. 14. The most 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. (22)

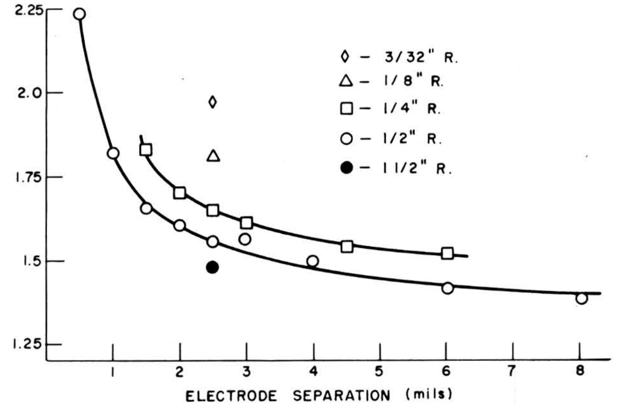

Fig. 13 Electric strength of n-hexane as a function of electrode separation. After Sharbaugh, Bragg, and Crowe. (27)

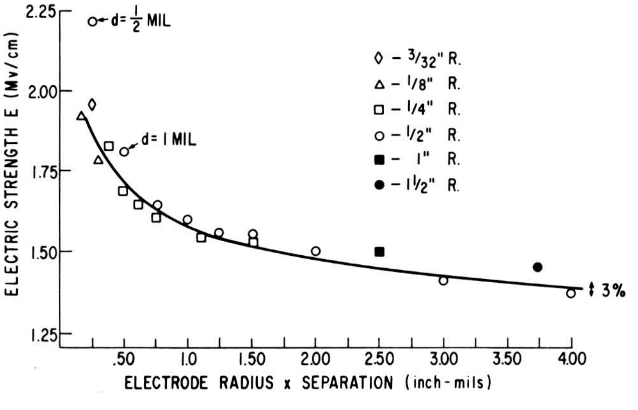

Fig. 14 Electric strength of n-hexane as a function of electrode radius times separation. After Sharbaugh, Cox, Crowe, and Auer. (23)

The electronic theory of breakdown, as generally understood, predicts the presence of an electron multiplication process or α-process in the liquid. Indeed, some estimates, such as those of Goodwin and Macfadyen(16) give values of αd, as high as 10 at breakdown, but pulse measurements (Section 3.2) have not been able to detect an α-process in n-hexane, even at fields as high as 1.2 MV cm^{-1}. However, the observation of light emission from liquids 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 α-process at the highest fields studied and this sets an upper limit on αd of about 0.1 at 1.3 MV cm^{-1}.

3.34 Pressure

The density increase of a liquid due to normal applied hydrostatic pressures is so small that no change in electric strength arising from it would be expected. However, depending on the experimental conditions, the observed breakdown strengths usually exhibit, to a greater or lesser extent, some kind of dependence on pressure. For example, the results may depend upon the gas content of the liquid, the amount of gas adsorbed on the electrodes, or the state of equilibration of the liquid with the gas above it in the cell. The nature of the dissolved gas may also effect the strength; it has been shown that dissolved air (oxygen) will raise the strength of hydrocarbon liquids as well as transformer oil.

Kao and Higham(20) 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 subatmospheric results were also included. A range of pulse widths from 0.5 to 1 msec was used. The results are shown in Fig. 15.

The initial slopes of the curves, near atmospheric pressure, vary somewhat but are of the order of 5 percent increase in strength per atmosphere; this is almost one-third of the effect reported by Edwards(28) for benzene at subatmospheric pressures.

In a later investigation of pressure dependence, Kao and McMath(64) measured the breakdown strength of hexane with linearly rising voltages in the manosecond range with different amounts of hydrostatic pressure. They found that at fields greater than 4 MV $cm^{-1}usec^{-1}$ indeed the pressure dependence disappeared.

This is direct experimental evidence that the "bubble" mechanism does not have time to be operative and that an electronic mechanism takes over.

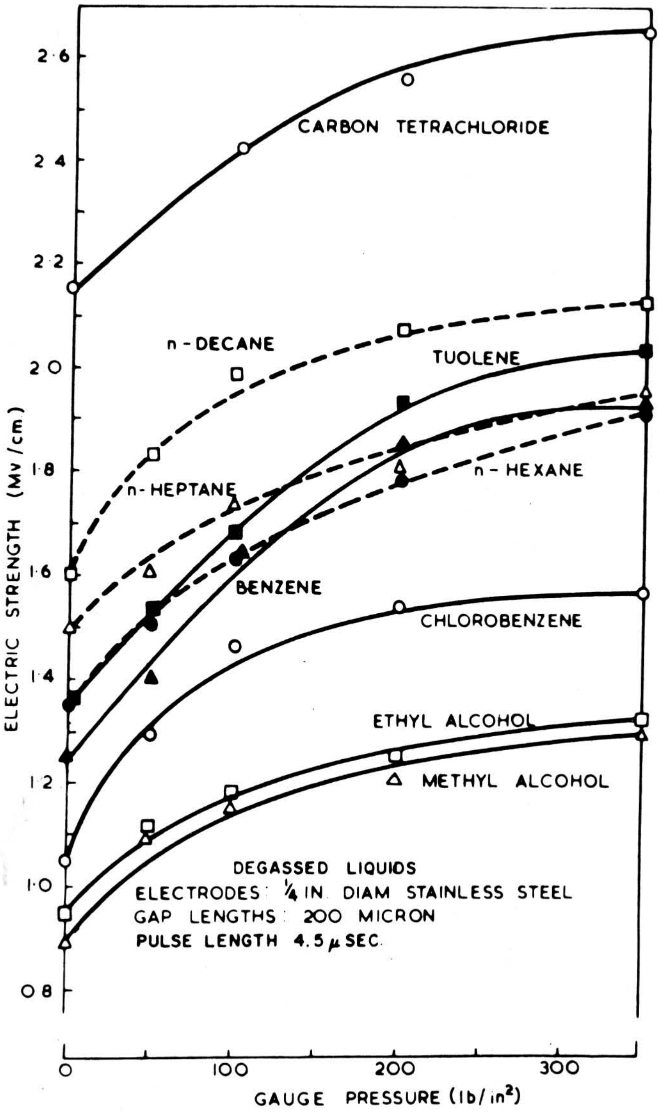

Fig. 15 The dependence of the electric strength of some organic liquids upon applied pressure. After Kao and Higham.(20)

3.35 Temperature

A dependence of the electric strength upon temperature has been observed in liquids for both d-c and pulsed voltages (see Fig. 16). There is a rather slow change centered around room temperature, terminating in a rapid decrease near the boiling point. Below room temperature, a considerable rise in strength occurs. The effect is not one of density alone, for the results show the same general character after a correction has been made for the density change. A temperature dependence is complicated by possible changes in cathode emission, gas content, and viscosity. The final drop near the boiling point is very likely connected with bubble formation.

3.36 Comparison of Breakdown Strengths of Liquid and High Density Vapor Near the Critical Region

The breakdown strengths of hydrocarbon gases at low pressures increase regularly with density in accord with the Townsend mechanism as has been shown by Devins and Crowe,(29) and also Heylen and Lewis.(30) Using this fact, one can extrapolate the strength of a low density vapor to somewhat higher densities; if, however, this extrapolation is carried into the high-pressure, high-field region, anomalously large strengths are predicted. As an example, an extrapolation of this type has been made for hexane up to densities corresponding to the liquid, using a formula that is based on the Townsend criterion for breakdown. The result of this extrapolation is shown as the dotted curve in Fig. 17; for comparison, point X shows a typical observed value of the strength of the liquid. As may be seen, the liquid strength is appreciably different from the calculated curve, but this is not surprising in view of the extent of the extrapolation; however, the magnitude of the disparity between the two sets of results is an intriguing one, and the primary aim of an investigation by Watson and Sharbaugh was to bridge the gap between these two extremes: the low pressure gas, and the liquid results.

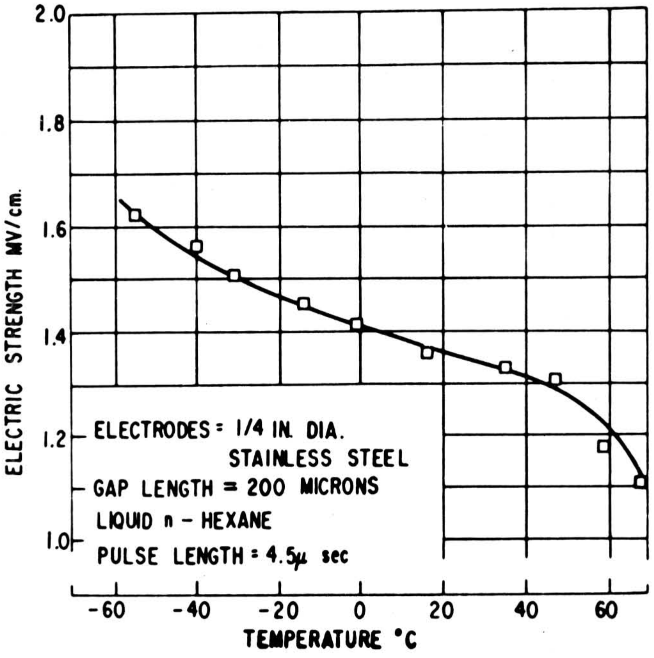

Fig. 16 Temperature dependence of the electric strength of n-hexane. After Kao and Higham.(20)

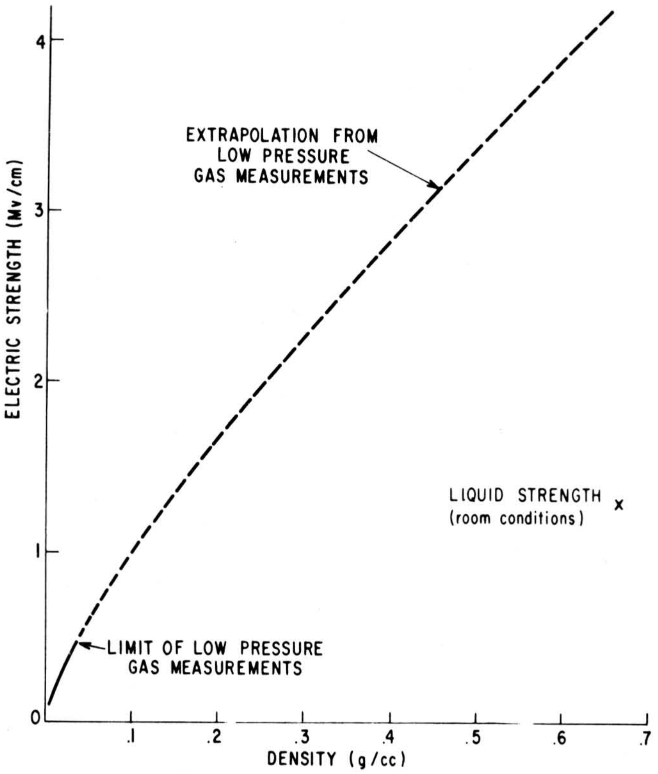

Fig. 17 Extrapolated electric strength of n-hexane vapor as a function of density.

To be more specific, experiments were designed: (1) to determine the course of breakdown strength as a function of density in both liquid and vapor phases; (2) to determine whether there is a difference between the strength of the liquid and of the vapor at the same density, i. e., to find out whether there is a singularity corresponding to the change of phase; and (3) to use these results in an attempt to distinguish between the various possible mechanisms of breakdown in liquids and high density gases.

When making measurements in a vapor at temperatures below critical, there is a limit to the pressure one may attain and still remain in the vapor; above the critical pressure, one passes into the liquid phase. At temperatures above critical--as is well known--one remains in the vapor phase at all pressures.

One of the few materials with a readily accessible critical point is carbon dioxide, and some years ago Young(31) measured the breakdown strength of carbon dioxide in the critical region. No difference was reported between vapor and liquid near the critical point--though little experimental data were presented in this region. It was desirable to conduct a more extensive series of breakdown measurements up to and beyond the critical region, though it was recognized that high-voltage breakdown measurements in the critical region of hexane would raise many experimental problems. Hexane was chosen for study because of the large accumulation of breakdown data on liquid and gaseous hydrocarbons.

In order to examine the effect of the change of phase, Watson and Sharbaugh made measurements in both liquid and vapor in the immediate vicinity of the critical point, where a relatively small change in temperature would change the phase without altering the density. The cell was filled with vapor just above critical temperature; the system was then closed off and allowed to cool slowly to condense the vapor. The level of the liquid was maintained above the electrodes, and ample time was allowed for equilibration as the temperature was lowered.

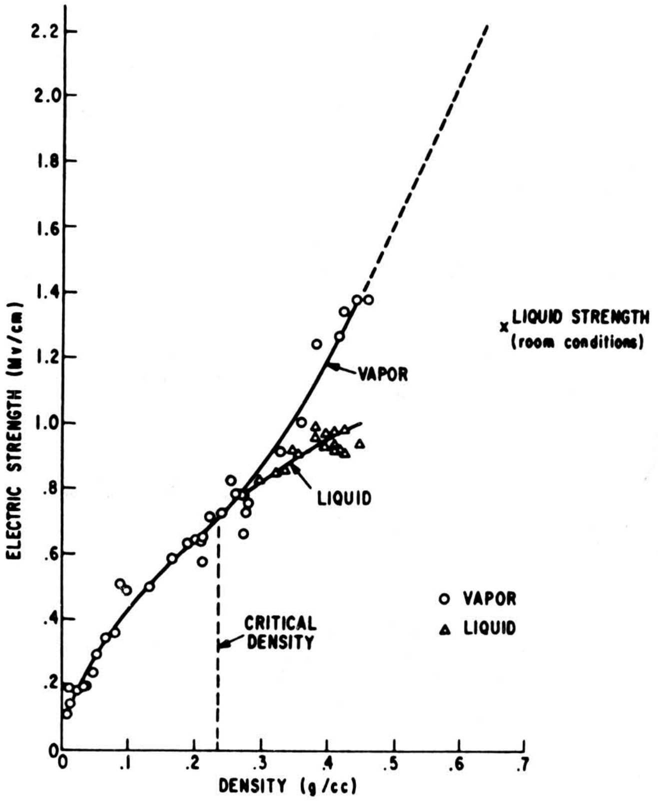

Fig. 18 Electric strength of n-hexane in the critical region. After Sharbaugh and Watson.(70)

The liquid results obtained near the critical point are plotted in Fig. 18. As shown, the breakdown strengths of the liquid are significantly lower than those of the vapor when compared at the same density. We also note that the values converge as one approaches the critical point where the strengths of vapor and liquid are identical. It is only at the critical point that liquid and vapor are at the same temperature and pressure, so that an exact comparison is only possible there. In the liquid phase we are dealing with hexane which is in equilibrium with its saturated vapor, so that temperature and pressure are not independent; for example, at a liquid temperature of 200°C, the pressure of the liquid is fixed at 250 psi by the pressure of the vapor in equilibrium with the liquid.

In the liquid at temperatures near the critical point, visual observations indicated that the liquid was highly turbulent and was often a seething mass of bubbles. These violent density fluctuations are a well-known phenomenon in the critical region; they are due to the rapid change of thermodynamic properties with temperature and the fact that the heat of vaporization vanishes at the critical point. In spite of the constant presence of bubbles in the liquid, its strength was remarkably constant; one typical set of fifteen breakdowns at $T/T_c = 0.99$ had a coefficient of variation of only 2.4%.

4. THEORIES

4.1 Electronic Theory of Breakdown

As indicated above, several early workers 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(31) proposed this mechanism for the breakdown of carbon dioxide at high pressures, and Goodwin and Macfadyen(16) applied the concept to liquids. Since then, others(30, 32, 33, 45) have modified and extended the model.

We consider first the mechanism of emission from an electrode into a liquid. 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, as described by the Schottky equation. 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, van der Boogaart, and Erne(34) and Swan and Lewis(35) on liquid nitrogen at a temperature of 65°K give breakdown strengths in the range of 1.6 to 2.0 MV cm^{-1}. These are virtually the same as the values measured by Sharbaugh and Watson(36) on high-pressure nitrogen gas at room temperature. Also, when the breakdown strength of hexane vapor above the critical temperature (approximately 500°K) is extrapolated to a density equal to the liquid phase at room temperature, one obtains a value that is of the order of, or greater than, the liquid breakdown strength (see Fig. 17).

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. 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(37-39) 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

$$eE\lambda = ch\nu \qquad (5)$$

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

Equation (5) was proposed originally by von Hippel (Ref. 40) for ionic crystals; it has been applied to liquids by a number of authors(32, 27, 41, 42, 33, 45) and Lewis has re-examined the hypothesis in detail.(71) 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 Eq. (5), and so it has been possible to relate breakdown strength to molecular structure.

The infrared spectra of the hydrocarbon liquids suggest that the various groups CH, CH_2, and CH_3 behave independently, so that one may analyze a molecule in terms of its component groups, each acting as an independent collision center. Thus, the mean free path of the electron λ is given by

$$\lambda^{-1} = N \sum n_i Q_i \qquad (6)$$

where N is the number of molecules per cubic centimeter, and n_i is the number of groups having cross section Q_i. Combining Eq. (5) and (6) and expanding the summation term for the n-alkanes, C_nH_{2n+2},

$$EN^{-1} = k\,(n_2Q_2 + 2Q_3)\ . \qquad (7)$$

The suffixes refer to the CH_2 and CH_3 groups, respectively, and the constant k includes $h\nu$ and c. This equation suggests that a plot of EN^{-1} vs n_2 should yield a straight line and, as shown in Fig. 19, 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.

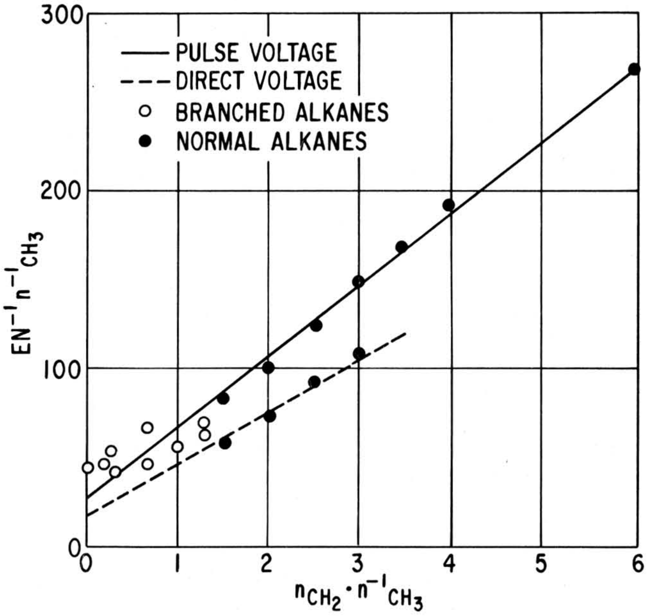

Fig. 19 Test plot of electric strength as a function of molecular structure for the liquid alkanes. After Lewis.(71)

The measurements on the alkyl benzenes by Sharbaugh, Crowe, and Cox(43) can also be fitted by a model of this type, although the resulting cross sections kQ_2 and kQ_3 are considerably larger (about 100 percent) than estimated from the alkanes. On the other hand, the estimate for kQ_3 obtained from measurements on a series of methyl silicones(44) 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 in the analysis made by Lewis, and this casts some doubt on the validity of associating the electron energy loss with the C—H bond vibrations.

Adamczewski(33) 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 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 $h_0(n-1)$, where 2r is the mean distance between molecular axes, h_0 is the C—C bond length projected on to the axis of the molecule, and n is the number of carbon atoms in the backbone of the molecule.

From a consideration of the molecular structure of hydrocarbon liquids r is taken to be 2.5Å ± 0.1Å and the axial projection of a C—C bond distance to be $h_0 = 1.54 \sin 55° = 1.23$Å. From these values the active cross section of a single molecule may be computed, viz:

$$Q = 2rh_0(n-1) = Q_0(n-1) \qquad (8)$$

where $Q_0 = 2rh_0$ and is constant for the whole series of straight-chain saturated hydrocarbons. The active cross section per cm^3 will be:

$$S = Qp = Q_0(n-1)\frac{\rho}{M}N = A(n-1)\frac{\rho}{M} \qquad (9)$$

since the number of molecules per cm^3 is equal to $p = (\rho/M)N$, where ρ is the density, M is the molecular weight of the liquid, N is Avogadro's number and $A = 2rh_0N$ which is constant for the whole series of the liquids. In each collision an electron loses an amount of energy equal to $E_0 = h\nu = 0.11$ eV. ν is taken to be the stretching frequency for a C—C bond.

The breakdown criterion is based on the assumption that the energy gained by the electron on its mean free path λ due to the work done L by an electric field E ($L = eE\lambda$) is not less than the energy which retards the electron on this path

$$eE\lambda = E_0 = h\nu. \qquad (10)$$

Since

$$A(n-1)\frac{\rho}{M} = \frac{1}{\lambda}, \qquad (11)$$

we obtain

$$eE = h\nu A(n-1)\frac{\rho}{M}. \qquad (12)$$

Equation (12) has precisely the same form as those given by Lewis, but the expression for the mean free path (11) is characteristic of Adamczewski's assumptions. The final equation for breakdown stress in terms of the parameters characterizing a given liquid (ρ, M, n) has the following form:

$$E = E_{bd} = \frac{h\nu}{e}A(n-1)\frac{\rho}{M} = B(n-1)\frac{\rho}{M} = BZ, \qquad (13)$$

where

$A = 2rh_0N$, $B = A(h\nu/e)$, $Z = (n-1)\rho/M$.

From the Eq. (13) we can see that for straight-chain saturated hydrocarbons E_{bd} should be a linear function of $(n-1)\rho/M$. Figure 20 (bottom curve) shows the graph illustrating the relationship in Eq. (13) for ten saturated hydrocarbons. The experimental results are seen to be in very good agreement with the straight line passing through the origin.

Some difficulties arose in the extension to the liquid alkyl benzenes. Here Adamczewski arbitrarily assumed that the length of the molecule is determined by the number of C—C bonds along the molecule with only two bonds being counted for the benzene ring, the other bonds of the ring simply increasing the transverse cross section of the molecule. The length of branched benzene molecule is thus (n-4) where n is the total number of carbon atoms in the molecule. The expression for electrical breakdown stress for normal aromatic compounds can therefore be written in the form:

$$E_{bd} = B_2(n-4)\frac{\rho}{M},$$

where B_2 is a new constant and the other symbols have the same meanings as before.

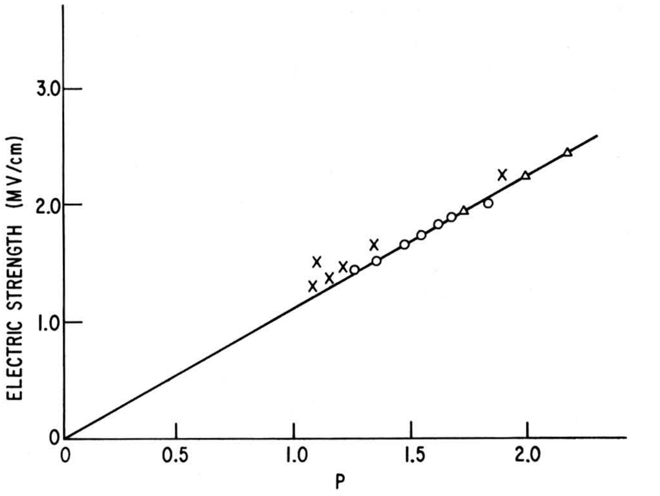

Fig. 20 Test plot for the Adamczewski equation for breakdown strength. Experimental values from Sharbaugh, Crowe, and Cox.(43) o, x: Straight chain; Δ, branched.

Table I shows a striking agreement between theoretical and experimental results for both branched and unbranched molecules. Adamczewski states that his theory can explain the dependence on temperature and pressure through the density variation with these parameters. Comparison of experiment with his theory is not at all convincing in the case of temperature. Furthermore, there is about 50% increase in the breakdown strength of hexane with the application of 25 atm hydrostatic pressure, and yet there is negligible change in density.

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(16) associated the critical time lag τ_c (Section 3.31) with the movement of positive ions in the liquid. Crowe(11) was led to postulate a trapped electron model and identified τ_c with the transit time of the charge carrier. He inferred a carrier mobility which was fairly close to that measured later by LeBlanc(7) (Section 3.1). However, Crowe's conclusions were largely based upon a linear dependence of τ_c on gap width, and there is some evidence against this.(20)

TABLE I

Comparison of Adamczewski Breakdown Theory with Experiment

Breakdown stresses for hydrocarbons liquids–

n	Liquid	M	ρ	E 10^6 v cm Experimental	E 10^6 v cm Theoretical
	Saturated hydrocarbons C_nH_{n+2}				
5	Pentane, C_5H_{12}	72·14	0·627	1·44	1·44
6	Hexane, C_6H_{14}	86·17	0·659	1·56	1·57
7	Heptane, C_7H_{16}	100·19	0·6838	1·66	1·68
8	Octane, C_8H_{18}	114·22	0·703	1·79	1·77
9	Nonane, C_9H_{20}	128·25	0·717	1·84	1·85
10	Decane, $C_{10}H_{22}$	142·27	0·730	1·92	1·91
14	Tetradecane, $C_{14}H_{30}$	198·37	0·762	2·00	2·08
6	*iso*Hexane, C_6H_{14}	86·17	—	—	—
6	2-Methylpentane	—	0·654	1·49	1·44
6	2,2-Dimethylbutane	—	0·649	1·33	1·21
6	2,3-Dimethylbutane	—	0·662	1·38	1·21
7	*iso*Heptane, C_7H_{16}	100·19	0·673	1·44	1·44
7	2,4-Dimethylpentane	—	—	—	—
8	*iso*-Octane, C_8H_{18}	114·22	0·692	1·40	1·44
8	2,2,4-Trimethylpentane	—	—	—	—
	Aromatic hydrocarbons				
6	Benzene, C_6H_6	78	0·879	1·63	1·56
7	Toluene, C_7H_8	92	0·866	1·99	1·98
8	Ethylbenzene, C_8H_{10}	106	0·867	2·26	2·28
9	*n*-Propylbenzene, C_9H_{12}	120	0·862	2·50	2·53
9	*i*-Propylbenzene, C_9H_{12}	120	0·864	2·38	2·18
10	*n*-Butylbenzene, $C_{10}H_{14}$	134	0·862	2·75	2·73
10	*i*-Butylbenzene, $C_{10}H_{14}$	134	0·867	2·22	2·44

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(21) and others(47, 48) 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 present a statistical function f(E) which gives the mean rate of breakdown events in a liquid under stress E. They consider this function to be the product of I and W, where I is the mean rate of a localized burst of emission from the cathode and W is the probability that one of these bursts will lead to a complete breakdown. This relates the breakdown to cathode and liquid functions, respectively. This theory leads to a time dependence of pulse breakdown strengths which approaches the d-c value at long times. More recent extensions of this approach lead to a time dependence which agrees better with the pulse breakdown characteristics which are substantially independent of time in the 1 to 20 μsec range of pulse lengths. (46-48)

Since the formative time as well as I and W (see above) are all field-dependent, it is difficult to test these models. Furthermore, the observed increase in the time lag with electrode spacing is pretty convincing evidence that the time lag is substantially formative and not statistical.

Watson(49) has noted that the high-field currents which are observed in liquids under microsecond pulse conditions are 1 to 10 mA cm^{-2} of cathode area. Assuming a value for electron mobility of the order of $10^{-3} cm^2 V^{-1} sec^{-1}$, 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(20) find virtually no change in critical time lag in going from atmospheric pressure to 25 atm, despite the very marked increase in breakdown strength. The experimental observation of random fluctuation of the time lags certainly indicates there is some statistical process involved; but it seems unlikely that this process involves the chance appearance of a starting electron.

4.2 Field Distortion in the Liquid

In the discussion to this point we have tacitly assumed that the field everywhere in the gap at breakdown is essentially equal to that applied. This is, of course, only true, provided that the currents just prior to breakdown are sufficiently low that space-charge distortion of the field does not occur. As we have seen in Fig. 7, prebreakdown currents in liquids may reach rather high values, and some attempt must be made to allow for space-charge distortion. If the current is largely electronic due to field emission from the cathode, the field at the anode will be enhanced while that at the cathode will be reduced. Since field emission is strongly field-dependent, the current will tend to limit itself owing to the reduction in cathode field. At the same time, the increase in anode field may cause breakdown in the region near the anode; this will occur at a lower applied field than would be the case in the absence of space charge. It will be apparent, therefore, that if a critical field, E_c is required for breakdown of the liquid, then the applied field necessary to cause breakdown, E_b, will depend on the work function of the cathode. If the work function is very high, so that little space-charge distortion occurs up to E_c, then E_b will be equal to E_c, and essentially independent of work function over a range of values. On the other hand, for very low work-function cathodes, the current will become space-charge-limited; E_b will be lower than E_c, and again will be independent of work function over a range of values. It may be shown theoretically(42) that, under these conditions, E_b is equal to $2/3\ E_c$. Referring to Fig. 21, curve a is the characteristic for a low work-function cathode. The current follows this line until it intersects the space-charge-limited characteristic (dashed line) after which it becomes space-charge-limited and breakdown ensues when the applied field is $2/3\ E_c$ due to enhancement at the anode. Curve c corresponds to a high work-function case where $E_b = E_c$. For intermediate values of work functions, $2/3\ E_c < E_b < E_c$. This theory has been verified experimentally for benzene for cathodes whose negative ion work function was varied by different concentrations of electrolytes dissolved in water. The space-charge-limited plateau was not observed for more viscous insulating liquids where the mobility of the ions was too small to permit build-up of the space charge within the applied pulse length (several μsec).

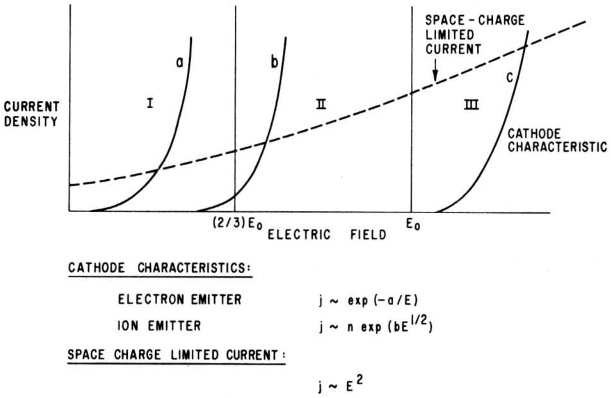

Fig. 21 Current-field characteristics for breakdown in liquids. Solid lines a, b, c for low, medium, high cathode work functions. Dashed line is space-charge-limited current $i \alpha E^2$.

If appreciable collisional ionization does occur prior to breakdown, it may be necessary to consider space-charge distortion due to positive ions present in the gap. In contrast to the above type of distortion, this would cause an increase in field at the cathode and reduction of field at the anode. Since an enhancement of the field at the cathode will increase field emission of electrons, this could generate more positive ions and lead to a runaway process. The conditions for such a runaway process have been worked out semiquantitatively, and the value for α required has been calculated to be $\approx 10^4$. Although the mechanism seems plausible, such a high value for α is inconsistent with recent measurements.

Swan(50, 45) attributes greater importance to field distortion at the cathode than have previous workers and assumes a smaller effect of collision ionization which, according to him, may only appear at very high fields of the order of 1.2 MV/cm. He also assumes that the product αd varies between 0.1

and 1 and is not, as other workers assumed before (for example, Goodwin and Macfadyen), about 100. For small electrode spacings, Swan's theory predicts an increase in the electric strength. The lowering of the d-c breakdown strengths due to dissolved oxygen is explained by the formation of a compact layer of negative oxygen ions near the anode which gives rise to a few additional ionizing collisions. Swan points out that while his mathematical condition for instability represents breakdown, it does not explain the final development of the discharge. He suggests that the pressure dependence may be due to an alteration of the gas in equilibrium at the electrode surfaces, which in turn could change the emission or the space charges.

4.3 Cavitation (Bubble) Theories

4.31 Kao's Theory

The work of Kao and Higham(20) 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(51, 63) has recently put forward a mathematical model for a bubble mechanism of breakdown. 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; and (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 principle of minimum potential energy. The total energy stored in a dielectric containing a cavity of volume v is given by

$$W = \frac{1}{8\pi} \int_{v} (\varepsilon_1 - \varepsilon_2)\, E_2 E_0 \, dv.$$

Here v is the volume of the bubble, E_0 is the applied field strength, E_2 is the field strength inside the bubble, and ε_1 and ε_2 are the dielectric constants of liquid and bubble, respectively. From this equation 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

$$E_0 = \frac{1}{(\varepsilon_1 - \varepsilon_2)} \left\{ \frac{24\pi\sigma(2\varepsilon_1 + \varepsilon_2)}{r} \left[\frac{\pi}{4} \sqrt{\left(\frac{V_b}{2rE_0}\right) - 1} \right] \right\}^{1/2}$$

where σ 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 the theoretical equation to the experimental results at atmospheric pressure, Kao's model predicts a breakdown 50% larger than he measured for hexane at 25 atm. 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.

4.32 Watson and Sharbaugh Theory(3, 52)

We examined in Section 4.1 the evidence for applying the von Hippel criterion for solid-breakdown to liquid-breakdown. While this approach is moderately successful in describing some experimental observations, there is one point upon which this theory appears to be at complete odds with experiment: viz., that the electric strength of a liquid should increase with pressure. It is not easy to see how a pressure change could appreciably alter the mean free path of an electron in a nearly incompressible liquid. Such a pressure dependence does, however, suggest strongly that there is a change of phase (formation of a bubble) during some step in the breakdown process. Once a vapor bubble has formed, breakdown would be expected to follow rapidly; for example, the bubble may expand until it reaches a critical length, or until it bridges the gap.

The idea of a thermal mechanism for liquid breakdown in which a vapor bubble is formed was suggested at least 40 years ago. However, until the recent observation of large current densities near breakdown, it was thought to be impossible to generate such a bubble with applied fields of only a few microseconds' duration. A rough calculation of this energy may be instructive.

Let us first estimate the expected heat input W to 1 cm^3 of hexane liquid per microsecond of applied pulse. The breakdown field E_b is about 1.6 MV cm^{-1}

and field enhancement at tips of asperities may be of the order of 5. The current density j_{local} in the same region of the liquid has been deduced in Section 3.2 to be of the order of 1 to 10 amp cm^{-2}. Thus,

$$W = E_{local}\, j_{local} \tag{14}$$

and

$$W = 20\ cal/cm^3/\mu sec \text{ or } 40\ cal/g/\mu sec.$$

Now, the heat required, ΔH, to raise the temperature of m grams of liquid from ambient T_a to the boiling point T_b and vaporize it, is:

$$\Delta H = m\,[c_p(T_b - T_a) + l_b] \tag{15}$$

where c_p is the average specific heat and l_b is the latent heat of vaporization. Inserting reasonable values for hexane,

$$\Delta H = (1)\,[0.6(40) + 80] = 100\ cal/g.$$

Thus, for applied pulse lengths of several microseconds' duration, the necessary energy input is available to cause the generation of a bubble at the tip of an asperity.

In order to put this model on a quantitative basis, it is necessary to relate ΔH to the applied field. In this connection, the current vs voltage characteristics shown in Fig. 7 imply a very strong (about ninth power) dependence of energy input upon field. If this relation is used directly in Eq. (14), poor agreement with breakdown data is obtained, and it is difficult at first sight to reconcile the theory with experimental fact. However, there are two phenomena which help to alleviate the difficulty. In the first place, it is probable that the motion of the liquid under stress may have to be taken into account; and second, it is possible that, at high fields, the current from the most strongly emitting points on the cathode is space-charge-limited. Both of these phenomena would have the effect of reducing the field dependence of the local energy input. Specifically, space-charge emitted currents are known to be of the form $I = cV^N$, where N is in the range 1.5 to 2.

Thus, the local energy input has the form

$$\Delta H = AE^{n}{}_{\tau}$$

which may be equated to the value of ΔH given in Eq. (15) to give a criterion for thermal breakdown:

$$AE^{n}{}_{\tau} = m[c_p(T_b - T_a) + l_b]\,. \tag{16}$$

The thermal 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 Eq. (16) the dependence of strength on pressure can be calculated. Comparing the calculated strengths with the experimental results(20) at constant pulse width, it is found that the same basic equation can be fitted to the observed pressure dependence for all the liquids which have been examined. These include hexane, heptane, decane, benzene, and toluene. In most cases, n = 3/2 in Eq. (16) gives the best fit, as shown in Fig. 22 for hexane.

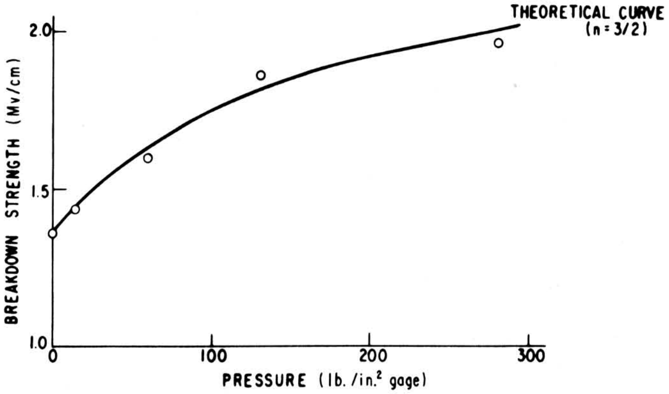

Fig. 22 Pressure dependence of the breakdown strength of n-hexane. After Sharbaugh and Watson (Ref. 52). Experimental data--Kao and Higham.(20)

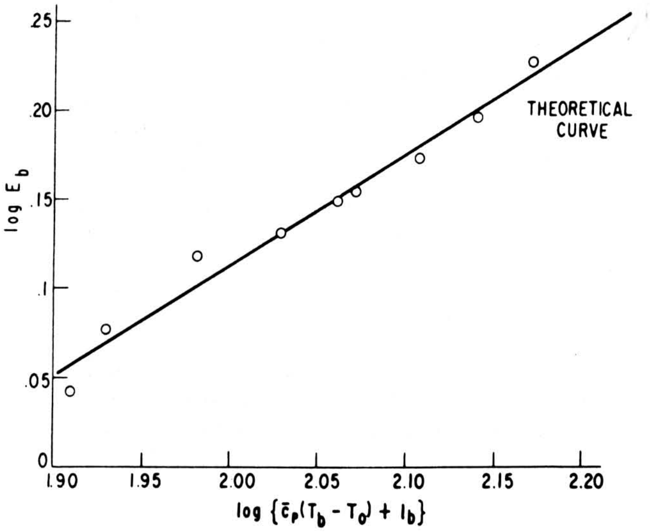

Fig. 23 Temperature dependence of the breakdown strength of n-hexane. Theory of Watson and Sharbaugh. Experimental data--Kao and Higham.(20)

The effect of ambient temperature T_a on breakdown strength can also be fitted to the model through the use of Eq. (16). Calculations again yield values of n which are about 3/2 and comparison of theory and experiment(20) is shown in Fig. 23.

The thermal mechanism may also explain the dependence of breakdown strength on thermal properties since, within a given homologous series, the thermal properties c_p and l_b increase with chain length. If we set n = 3/2 in Eq. (16) it is easily shown that $E_b^{3/2}$ should be linear with $(T_b - T_a)$ (see Fig. 24). As an example, the n-alkanes show this dependence; however, the branched alkanes show some scatter about the straight chain results and the alkyl benzene homologs require a different value of n in Eq. (16). The reason for these anomolies may well be in the differences between the conduction currents in these various liquids: unfortunately, hexane is the only liquid in which currents have been measured under pulsed conditions up to breakdown fields.

From the measurements described in Section 3.36, we have found that the breakdown strength of liquid hexane is significantly lower than that of the vapor, but the values converge as one approaches the critical point. We have also noted that the strengths of vapor and liquid are identical if compared at the same temperature and pressure, and this is only possible at the critical point.

These results corroborate the Watson-Sharbaugh model of the electric breakdown of liquids. As described above, liquid breakdown normally involves the formation of a low-density vapor bubble which then constitutes the weakest electrical link in the gap. This leads one to expect that liquid and vapor will have the same strength at the critical point, since the two phases become indistinguishable in this region. In the liquid at higher densities (i. e., lower temperatures and pressures) lower density gas bubbles can be formed, and these constitute a region of lower strength. However, as the temperature is lowered, the latent heat of vaporization increases, so that it is more difficult to form these bubbles. Because of these two opposing trends, it is not immediately evident what course the liquid strength should take as one progresses along a saturated liquid line from the critical point to room temperature.

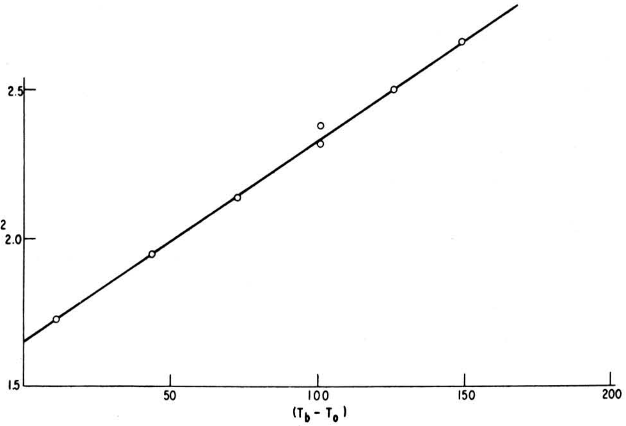

Fig. 24 Relation between boiling point and breakdown strength for n-alkanes. Watson and Sharbaugh theory--solid line. Experimental data--Kao and Higham. (20)

4.33 Krasucki's Theory

Another bubble theory of electrical breakdown of liquids has recently been developed by Krasucki. (53) His theoretical considerations are based on experiments with a very viscous liquid (hexachlorodiphenyl). The viscosity of the liquid at 17.5°C is 6 x 10^6P and it decreases rapidly with increasing temperature so that at, say, 75°C it is only 2P. The liquid was carefully filtered and degassed. The electrodes were stainless steel spheres of 5 mm diameter. Each measurement was made with newly polished electrodes and with a fresh quantity of purified liquid. The electrode gap was 3 1/2 mils. Negative 10/50 μsec impulses were used for breakdown strength measurements, and the times to breakdown were measured using direct voltages with the rise time of 10 μsec.

Krasucki measured the dependence of breakdown strength (E_b) on temperature and showed that E_b decreased from 5 MV/cm at about 20°C to about 1 MV/cm at 75°C. At a constant stress of 1.3 MV/cm, the times to breakdown decreased from 10 seconds at about 16°C to 10^{-5} seconds at about 60°C and was proportional to the viscosity throughout the entire temperature range.

Krasucki observed through a microscope the development of the breakdown event. Even at relatively slow speeds (16 frames/sec) his film records showed that, prior to breakdown, a bubble of vapor formed in the liquid and moved towards the anode. Apparently, the vapor bubble formed between the electrodes at a point of maximum field concentration which, in Krasucki's liquid was at the surface of a particle impurity resting on the electrode surface. Krasucki investigated the time rate of growth of such a bubble and showed that, in liquids with viscosities like n-hexane, breakdown due to formation and growth of vapor bubble should occur in times of about 0.14 μsec.

Krasucki analyzed the conditions for vapor bubble formation in highly stressed liquids and derived from first principles an expression for the breakdown strength E_b of a liquid. He showed that his equation predicts qualitatively the values of E_b for n-hexane at room temperature, the decrease of E_b for n-hexane with increasing temperature, the increase of E_b for n-hexane with increasing hydrostatic pressure, and the increase of E_b of aliphatic hydrocarbons with increasing molecular weight. The absolute value which is calculated is quite sensitive to the diameter of the particles which nucleate the breakdown. The assumption of two constant sizes of particles (rather unlikely in practice) of 200Å and 500Å diameter permitted bracketing of the experimental results. It would be interesting to compute the expected variations with a more realistic distribution of particle sizes.

4.34 Suspended Particle Theory of Kok

It is well known that the presence of minute particles gives rise to drastic lowering of the measured electric strength of liquids, and Kok$^{(54)}$ has 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 continuous 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 η. Kok and Corbey$^{(55)}$ derive a criterion for breakdown for short stress times,

$$t_b g^4 r^7 (E_b^2 - E_0^2)^2 N^2 = \eta^2 \times \text{constant}. \qquad (17)$$

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 neighborhood of the initiating electrode surface irregularity and is equal to 3 for an asperity of hemispherical shape. The time dependence expressed by Eq. (17) is tested by plotting the pulse breakdown measurements of Watson and Higham$^{(56)}$ for transformer oil and the breakdown values of Crowe, Sharbaugh, and Bragg$^{(32)}$ for hexane. There is a fair fit to the predicted linear plot of E_b^2 vs $1/t_b$, where t_b is taken to be the applied pulse length in breakdown studies.

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

$$(g^2 - 1)\, r^3 E_0^2 = 2kT$$

where r is the particle radius and kT is the thermal energy in ergs. For $g^2 = 9$, this becomes

$$r^3 E_0^2 = 1/4\, kT \qquad (18)$$

and the long time breakdown strength is proportional to $r^{-3/2}$. The observed limiting value for long applied pulses for transformer oil$^{(56)}$ is about 1.5 MV cm^{-1}, which according to the above equation, yields a particle diameter of about 20Å. The same value of particle diameter is derived from pulse measurements on hexane$^{(32)}$ 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, Eq. (18) predicts an increase of electric strength with an increase in temperature, which is contrary to experimental fact.

In another paper,$^{(57)}$ 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 1µ radius for which the calculated and measured breakdown strenghts are in the range 10 to 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 aluminum particles of 2.5µ 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 has shown that particles of the order of 1µ radius often lead to breakdown in the range of 100 to 500 kV cm^{-1}, and this is about four decades higher in strength than the theory of Kok and Corbey would predict. Edwards$^{(58)}$ has reported strengths even higher than this when 1µ 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.

5. SUMMARY

Breakdown of liquid dielectrics is a complicated process and there is no single theory that expalins all the experimental results. Specific experimental conditions will be the determining factor as to which of the several mechanisms will be operative.

In commercial liquids there are the following important mechanisms: (a) thermal breakdown due to heat generated by ionic impurities (e. g., H_2O); (b) breakdown caused by suspended particles (order ≥ 1µ in diameter); and (c) electrochemical breakdown wherein the passage of a current will cause electrode reactions which generate gaseous bubbles, e. g., H_2 and O_2 from H_2O.

It is now possible to measure a breakdown strength which depends upon a particular variable, other variables being held constant. This is done by giving especial attention to chemical and physical purification (filtering) of the sample, close control of the electrode surface polish and geometry, and the use of pulsed voltages. Under these antiseptic laboratory conditions, the three above mechanisms (which usually result in low values of breakdown) can be more or less avoided and one can measure a relatively high strength. These values can be reproduced by different investigators and serve as a basis for evaluation of theories of breakdown. Using these precautions, the following observations have been made and the evidence for the two principal mechanisms of breakdown are summarized.

5.1 Evidence in Favor of an Electronic Theory

1. Emission of light under high stress(37-39) is direct evidence for the existence of electrons with energies >2.5 eV which are probably high enough to cause ionization of liquid.

2. Light emission has been observed in the vicinity of the cathode by many investigators under high prebreakdown stresses.(66) One investigator(39) has noted an absence of pressure dependence of these light pulses, and concluded from this that the light did not come from discharges in bubbles.

3. One investigator(15) made current measurements at one gap with increasing electric field (approaching 1.5 MV cm^{-1}) and concluded that these might be a small values of αd. Spherical electrodes and the absence of a study at constant field negate any positive conclusions.

4. The use of the von Hippel criterion(33, 71) for breakdown along with the assumption that the energy losses largely arise through excitation of intramolecular vibration (C—C, or C—H) has been successfully used. This theory has predicted the observed dependence of E_b of simple homologous series, including branched structures.

5. Using the criterion of a critical avalanche size, the observed dependence of E_b upon gap spacing was predicted.(27) This was shown later(23) to be due probably to the variation of spherical electrode area with spacing and so nullifies this as supporting evidence.

5.2 Negative Evidence for Electronic Theory

1. The theory is not consistent with the observed pressure dependence. It is hard to see how modest pressure (25 atm) could appreciably alter the mean free path of an electron in a nearly incompressible liquid and yet this pressure increase causes the breakdown strength to rise about 50%.

2. The magnitudes of molecular scattering cross sections Q derived from breakdown strength of branched molecules do not increase regularly in Q_{CH}, Q_{CH_2}, Q_{CH_3} as would be expected.

3. A systematic search(2) for αd up to 1.2 MV cm^{-1} with flat electrodes and at constant fields revealed $\alpha d = 0$ and possibly $\alpha d \leq 0.1$ at 1.3 MV cm^{-1}. Values of 20 or more are expected on the basis of extrapolation from gas breakdown.

4. High-field current measurements(8) show linear growth of induced charge with constant field and constant injected charge. An exponential growth would be expected if there were electron multiplication.

5.3 Evidence for a Cavitation (Bubble) Theory

1. Predicts the observed pressure dependence and two theories(52, 53, 68) give nearly quantitative agreement when fitted at one point.

2. For viscous liquids (hexachlorodiphenyl), direct microscopic observation of breakdown shows the formation and growth of a bubble.(53)

3. For viscous liquids, the time to breakdown was directly proportional to the viscosity when the latter was changed over five orders of magnitude by temperature change.(53)

4. When the time of application of the field is too short for the vapor bubble to grow to its critical size, then the measured breakdown strength is higher than that for d-c stresses.(53)

5. There is a considerable prebreakdown evidence using both photography and image intensifier techniques for the formation and growth of a "bubble" in nonviscous liquids (hexane).(67, 72-74)

6. There have been measured extremely large values of pulse current density at fields near breakdown, which could give rise to sufficient heat input to vaporize a bubble of liquid in times as short as a few microseconds.(3)

7. Continuity of breakdown strength has been observed in passing from liquid to vapor at the critical temperature.(70)

8. Theory predicts the observed dependence on molecular weight of straight chain compounds through the change in boiling point or viscosity and surface tension.(52, 53)

9. Theory predicts the observed dependence on temperature through the variation of surface tension on temperature or the amount of heat required to raise to the boiling point.(52, 53)

10. Theory predicts the observed pressure dependence through the elevation of the boiling point with increased pressure or the ease with which a point of zero pressure may be formed in the liquid (Refs. 52, 53).

11. At very short times of application of the field (nanoseconds) the pressure dependence disappears and the strength increases markedly.(64)

5.4 Negative Evidence for Cavitation (Bubble) Theory

1. One bubble theory does not predict the lower strengths observed for hydrocarbon liquids with branched molecular structures.(52)

Although one cannot rule out the existence of collisional ionization in liquids (at or very close to the breakdown field strengths), the evidence, both direct and indirect, definitely favors a cavitation (bubble) theory of breakdown. Measurements designed specifically to detect an alpha process at fields up to, and including, breakdown are needed for liquid dielectrics other than hexane.

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