REVIEW

# ELEMENTARY PROCESSES IN THE DEVELOPMENT
# OF THE ELECTRICAL BREAKDOWN OF LIQUIDS

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## ABSTRACT

A review is given of the elementary processes
which play a role in the initiation and the propa-
gation of electric breakdown processes in liquids.
The discussion is essentially limited to pure,
non-polar liquids subjected to step-impulse
voltages and to voltages which vary slowly in time
(dc, line-frequency ac). The topics treated
include: electrode processes, ionization in the
liquid phase, bubble formation, and evolution of
the breakdown phenomenon.

## INTRODUCTION

The investigation of electric breakdown phenomena in
liquids has been a continuing effort since the early
years of this century. An immense amount of informa-
tion (both published in journals and books and unpub-
lished, resting in the archives of industry or research
laboratories) has been accumulated - but our under-
standing of the phenomenon remains rudimentary when
compared to our state of knowledge with respect to the
breakdown of gases or solids. While theoretical con-
cepts have been developed for the latter two, which in-
corporate the physical elementary processes of charge
carrier generation and transport (e.g. for gases the
Townsend and streamer theory, and for solids the Landau-
Zener theory and the electrothermal breakdown theory),
a similar high level status of theoretical penetration
is missing for liquids. The main reasons for this poor
performance are the following:

(1) the understanding of the physical properties of the
liquid state is less well developed as compared to
gases and solids;

(2) the experimental information on liquid breakdown
accumulated in the literature to a large extent does
not lend itself suitable for generalization or as a
starting point for theoretical considerations. Hundreds
of papers and reports are for instance available on
transformer oil which actually is an ill-defined
heterogeneous system comprised of different liquids,
solid materials, and gases. From the measurements
point of view, many papers lack sufficiently well-
controlled experimental conditons so that the data can-
not be used as points of reference for theories;

(3) the number of liquids of possible interest to elec-
trical engineering applications is in the range of ten
to hundred and these liquids exhibit a wide spectrum
of physical and chemical properties.

Time and space preclude an extensive treatement of all
the various aspects of the breakdown phenomenon. Some
topics omitted here may be found in other talks of this
symposium or in some recent reviews of this field [1-3].
In this review we shall limit ourselves mainly to pure
non-polar liquids and we shall consider only two ex-
treme cases of voltage application: step-impulse vol-
tages and voltages which vary slowly in time (dc, line
frequency ac).

## ELECTRODE PROCESSES

The process of charge carrier generation under the
influence of a high electric field is best studied
with point to plane gaps, since the generation process
is confined to a small volume and the influence of
polarity can be analyzed. Not too many reports have
appeared in the literature. The classical work on this
subject has been carried out by Halpern and Gomer [4-6]
who investigated experimentally and theoretically the
field emission and field ionization process in various
liquids. Their contribution triggered several other
papers in which this type of investigation was extended
to other liquids [7-11]. A schematic presentation of
the physical situation at the metal needle is shown in
Fig. 1.
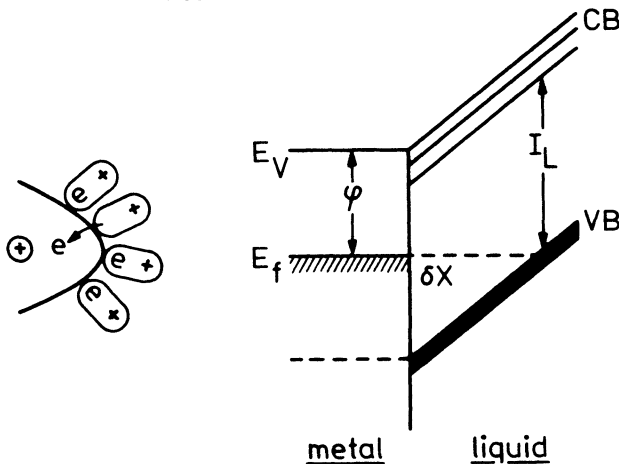
## Field emission
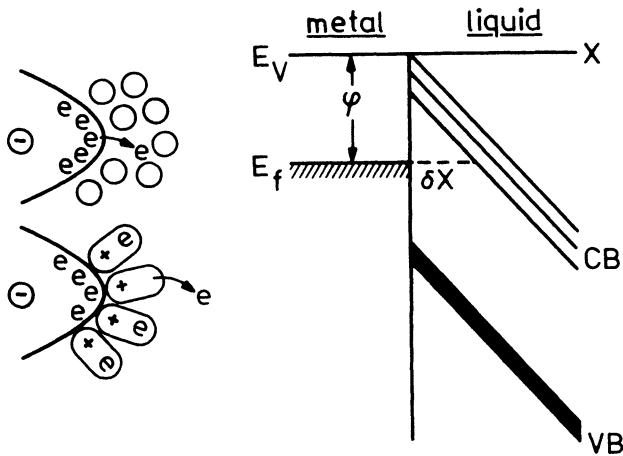


## Field ionization



*Fig. 1: Energetic conditions for field emission and ionization*

*Field emission.* When a negative voltage is applied to the needle, a steep rise of the current is observed once the voltage exceeds a certain critical value. This is followed by a more gradual rise of the current at higher values of the applied voltage. Fig. 2 shows an example for such injection currents in highly purified hydrocarbons. Halpern and Gomer attributed such a behavior to the field emission of electrons in the liquid. The emission of electrons from a metal under the influence of a high electric field is described by the Fowler-Nordheim-equation which relates the emitted current $i$ to the applied voltage $V$

$$\ln\left(\frac{i}{V^2}\right) = \ln\left(A\,\frac{\beta^2 K}{\psi}\right) - B\psi^{3/2}\,\frac{1}{\beta V} \tag{1}$$

with $F_e=\beta V$ the field strength at the emitter, $K,B$ are parameters slightly depending on $\psi$ and $F$, $\psi$ is the work function and $A$ the emitting area.

By plotting $\ln(i/V^2)$ as a function of $1/V$ straight lines were obtained for the range of voltages where the steep increase occurred [4,7]. At higher levels of the injection current deviations from Eq. 1 occur which are caused by space charge formation around the needle due to the finite velocity with which the electrons leave the region around the tip. For this range of voltages Halpern and Gomer derived under the assumption of concentric spherical electrodes

$$V = V_{vac} + 98\,\left(\frac{R}{\varepsilon\mu\alpha}\right)^{1/2} i^{1/2} \tag{2}$$

with $V_{vac}=F_e r_t$, $r_t$ the radius of the emitter and $\varepsilon$ the dielectric constant, $\mu$ the mobility of charge carriers, and $\alpha$ angle into which emission occurs. For the case that $v_d$ (drift velocity) is constant in the high field region near the tip Halpern and Gomer derived

$$V = (4i/\alpha\varepsilon v_d)\left[\ln\left(\frac{R}{r_t}\right) - 1\right] + V_{vac} \tag{3}$$

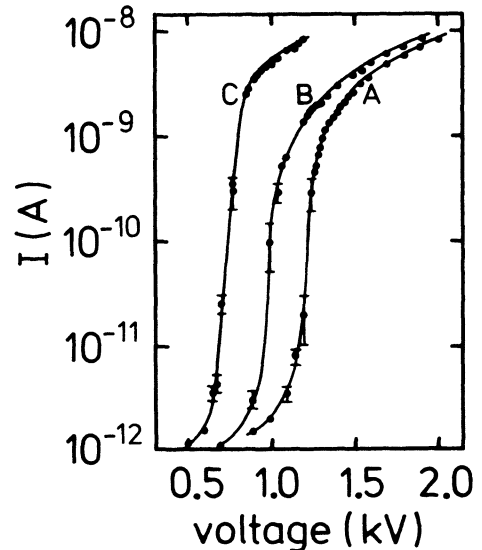with $R$ the radius of the outer sphere, $R>>r_t$.



*Fig. 2: Current-voltage dependence for the field emission case at 293 K; A: n-hexane; B: iso-octane; C: tetramethyl silane; (after reference 7)*

Field-emission controlled injection has been observed in a few liquids only since it requires careful purification of the samples in order to obtain a very low conductivity at low voltages and in order to prevent electron attachment to electro-negative molecules and the formation of ions with a much smaller mobility.

In most cases space-charge-limited injection currents according to Eq. 2 were observed. Sometimes the mobilities of the charge carriers derived from Eq. 2 agreed with values obtained from drift measurements, sometimes, however, differences were notices. Reasons may be due to insufficient purity or field dependent mobilities.

*Field ionization.* In these experiments the needle is positive and electron emission from the liquid in the metal occurs. Halpern and Gomer [5] reported on field

ionization currents of some cryogenic liquids, Schmidt and Schnabel [8,11] found field ionization of some aromatic liquids (benzene etc.), Dotoku et al. [7] reported on n-hexane, and Rabe et al. [13] investigated silicon oils. The voltage and hence the electric field strength required for saturated hydrocarbons is usually higher than for field emission. Aromatic liquids show a similar $i$-$V$-dependence as in the field emission case (cf. 11). While in the field emission case the work function $\psi$ of the metal is a controlling factor (Eq. 1) in the case of field ionization the difference $I_1$-$\psi$ is the dominating quantity ($I_1$ ionization potential of the molecules or atoms in the liquid). Halpern and Gomer [5] obtained for the ionization current under the assumption of tunneling from non-interacting individual atoms or molecules

$$i \alpha \frac{(I_1 - \psi)\, \mu_f^{1/2}}{(I_1^{1/2} - \psi^{1/2})} \exp\left(-A' \frac{\psi^{1/2}\,(I_1 - \psi)}{F}\right) \qquad (4)$$

with $\mu_f$ the Fermi energy of the molecules, and $A'$ a constant.

For $I_1 \approx 2\psi$ field emission and field ionization currents become comparable. In the case of aromatics it may be possible that emission of electrons occurs directly from a molecule rather than from the metal point in the case of field emission [12]. The influence of increasing aromatic content on the carrier generation at the positive point in silicone oils was amply demonstrated in the work of Rabe et al. (cf. Fig. 5 of Ref. 13). As in the field emission case at higher injection levels SCL currents are observed (cf. Eq. 2). Completely different conditions are met in LHe. The ionization potential is $I(\text{LHe}) \approx 25.6$ eV which means that a very high field should be necessary to ionize He-atoms in the liquid phase. In the experiment it was observed [5,14] that the voltage had to exceed a threshold voltage upon which the current jumped to a high value which decreased only moderately when the voltage was lowered below this threshold. Only at much lower values of the voltage the injection stopped. We may assign this behavior to the fact that a high voltage is necessary to start the field ionization process. Once carriers are being injected, Joule heating leads to the formation of a gas bubble in which, also at lower voltages, a micro discharge is maintained. Generally, it must be assumed that at higher levels of the injection currents the dissipated energy leads to the formation of a gas bubble around the needle. Physical evidence comes also from the observation of corona light.

*Corona light.* Hickson and McClintock [15] and Metzler and Schmidt [16] assumed that the energy dissipated by the carriers near the needle is correlated to the bubble size. Photographic evaluation of the corona spot yielded radii of the order of 0.1 mm in hydrocarbons. Time resolved measurements of injection currents and light emission indicated impulse emission in the field emission case for LAr and LXe [17]. A very sophisticated experiment was carried out by McClintock et al. [18], who measured the angular distribution of the field emission and ionization currents in LHe. They found that the emission pattern was away from the axis of the needle, which supports the idea of micro gas bubbles as current sources. A similar conclusion can be drawn from photographs of the light emission in LAr and LXe obtained by Arii [17] in this laboratory.

*Parallel-plate geometry.* The dominating role of charge carrier injection from the electrodes was also verified in measurements of the current density as a function of applied voltage for propylene carbonate [19] and liquid sulfur [20] (Figs. 3 and 4). Above a certain voltage, a steep increase of the current with voltage is observed which in the case of PC was attributed to electrochemical charge carrier generation at the electrodes. The same process seems to take place in LS, although the authors assign this rise to electron avalanches.
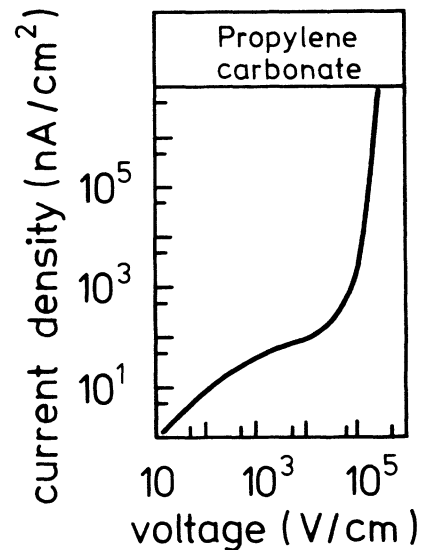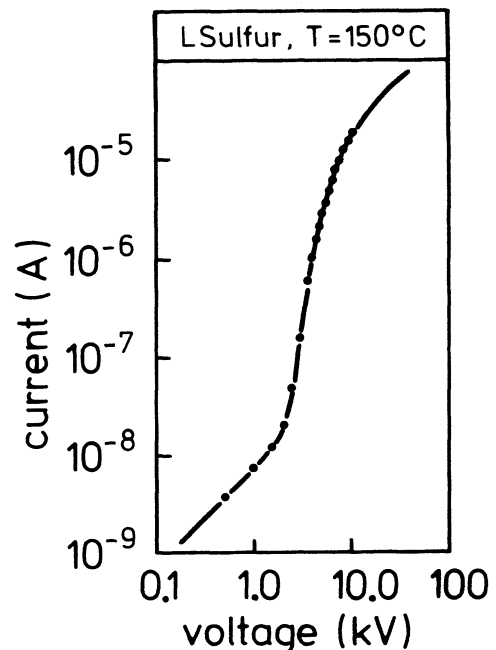


Fig. 3: *Current-voltage dependence (after [19,20])*



Fig. 4: *Current-voltage dependence (after [19,20]*

*Electrode surface conditions.* The state of the electrode surface plays an important role in the initiation of the breakdown via the injection process. Coletti et al. [21] investigated the breakdown of LHe and found a reduction of the breakdown strength with increase of the electrode surface from 17 MV/m with 6787 mm$^2$ area to 11.7 MV/m with 12054 mm$^2$ area. Yoshino [29] applying impulse voltages to a point to plane gap in LHe found that in the case of the positive point the breakdown voltage depended on the material of the plane, while this was not the case for the negative point. He concluded that breakdown of LHe always originates from the cathode. Olivier [22] carried out a very elaborate and tedious experiment on the first ac breakdown voltage of highly polished sphere-sphere gaps in LHe. Several different materials were used and up to 17 spark gaps could be cooled down at the same time. The breakdown of the virgin gap yielded the highest voltage independent of the electrode material. For a number of test gaps the location of the spark pit was determined optically. It correlated with the calculated field strength at that point. Most breakdown events originated from areas where the computed surface field strength was lower than at the rotary axis. In these experiments the voltage was raised rather slowly, so that the gradual development of thermal processes may have obscured any influence of the work function.

In order to compare the importance of charge carrier generation at the electrodes to ionization processes in the bulk liquid, we should like to discuss the ionization process in the liquid phase in some more detail.

## THE IONIZATION PROCESS IN THE LIQUID PHASE

One of the basic quantities in the ionization process is the ionization potential $I$. In the liquid phase modifications occur due to the electron affinity of the liquid and due to the polarization energy of the positive ion. $I_1$ is then given by

$$I_1 = I_g + V_o + P_+ \tag{5}$$

with $I_g$ the ionization potential in the gas.

Direct measurements of $I_1$ have recently become feasible and a compilation of data is given in Table 1. Generally, a reduction of the ionization potential of the order of 1 to 1.5 eV in the molecular liquids and 2 to 3 eV in the atomic liquids occurs.

There is probably no reduction at all in the case of LHe since the gain in polarization energy will be cancelled by the large value of $V_o{\sim}1$ eV of the electron affinity. In order to produce collisional ionization, electrons have to obtain a mean energy of several electron volts. For the molecular liquids it is difficult to see how such an energy can be accumulated since the mean free paths are $\leq$ = 10 nm and many energy sinks as e.g. vibration, electronic excitations are available at subionization energies. In the liquified rare gases it should be easier to obtain higher mean electron energies since only elastic losses occur until the first electronically excited state becomes accessible (7 eV for instance in the case of Xe). Usually the cross sections for all these processes are very large, so that the energy losses are concentrated in space, possibly leading to gas bubble formation before collisional ionization sets in. Evidence for collisional ionization so far has been observed in LXe only [24].

Table 1: Ionization energies of non-polar liquids (determined by VUV photo conductivity experiments)

| liquid | T [K] | $I_g$ (eV) | $I_1$ (eV) | | $V_o$ (eV) | $P_+$ (eV) |
|---|---|---|---|---|---|---|
| xenon | 161 | 12.08 | 9.2 | a | -0.67 | -2.21 |
| krypton | 121 | 13.93 | 11.55 | b | -0.42 | -1.96 |
| neo-pentane | 296 | 10.35 | 8.8 | c | -0.39 | -1.02 |
| tetramethyl silane | 296 | 9.73 | 8.1 | c | -0.57 | -1.12 |
| n-hexane | 295 | 10.18 | 8.6 | d | +0.06 | -1.54 |
| c-hexane | 295 | 9.88 | 8.4 | d | 0.0 | -1.46 |
| neo-hexane | 295 | 10.06 | 8.5 | d | -0.25 | -1.32 |
| iso-octane | 295 | 9.86 | 8.3 | d | -0.16 | -1.33 |
| tridecane | 296 | 10.05 | 9.25 | e | +0.21 | -1.01 |
| 3-methyl-pentane | 296 | 9.9 | 8.9 | e | 0.0 | -1.0 |

references: a-U.Asaf and I.T. Steinberger, Phys. Rev. B10, 4464 (1974); b-R.Reiniger, U. Asaf, P. Laporte, V. Saile and I.T. Steinberger, to be published; c-H. Böttcher and W.F. Schmidt, J. Electrostatics 12, 153 (1982); d-J. Casanovas, R. Grob, D. Delacroix, J.P. Guelfucci and D. Blanc, J. Chem. Phys. 75, 4661 (1981); e-H. Böttcher and W.F. Schmidt, to be published. $V_o$-values from A.O. Allen, NSRDS-NBS 58.

## BUBBLE FORMATION

The process of bubble formation in liquids has been discussed in connection with bubble chambers [25]. The sudden heating of a small volume of liquid leads to a fast outward motion of the molecules. The process has to be considered as adiabatic. A region of low density is created which we will call a bubble. This bubble expands and the pressure inside the bubble falls until this pressure is equal to the hydrostatic pressure of the liquid and the surface pressure of the bubble. Energetic considerations show that most of the energy goes into surface energy and into vaporization. Nucleation and expansion amount to less than 7% of the total energy necessary for bubble generation. Similar conditions may prevail when a step impulse voltage leads to rapid carriers injection and energy dissipation near the electrode.

## EVOLUTION OF BREAKDOWN

*Theoretical considerations.* After the formation of a gas bubble has occurred at one electrode, its expansion towards the counter electrode initiates the final stage of the breakdown. A zeroth-order theory which treats this process in the point to plane gap was presented by Watson [26] based on earlier work by Thomas [27]. Watson assumed that the cavity around the tip would be filled with a plasma which would make the surface equipotential with the electrode. This way he could calculate the electrostatic pressure which tends to expand the cavity. The conservation of energy law led to an equation for the dependence of the cavity radius on the time

$$R^2 = V t (2\varepsilon\varepsilon_0/3\rho)^{1/2} \tag{6}$$

with $V$ the applied voltage, $\varepsilon$ the relative dielectric constant, and $\rho$ the density. Taking data from Schlieren-photographs obtained by Farazmand [26], Watson indeed found the dependence of $R$ on $t$ within experimental error (Fig. 5). Perturbations occurring at the surface during the expansion could be rationalized by invoking Raleigh-Taylor instabilities. The numerical comparison with experimental data yielded gratifying agreement.
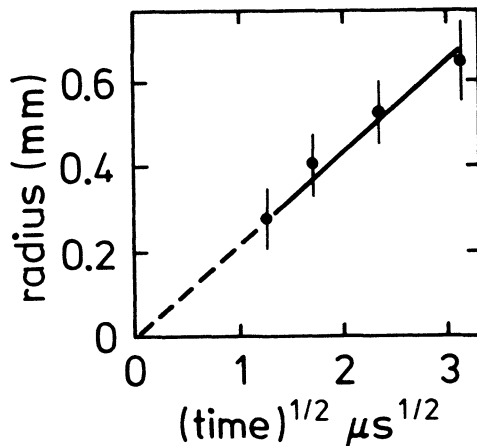
Fig. 5: *Dependence of bubble cavity radius on time (after Ref. [26])*

Another theoretical approach stems from Kao [28] who assumed that filamentary injection of electrons takes place at asperities and that one filament in which the current density is much larger becomes the leading filament. In this filament enough heat is produced, vaporization takes place and a gaseous discharge channel is formed.

It is quite possible that both mechanisms may be operative with the Watson model being applicable to step-impulse conditions while the Kao model would apply to the dc case. During the investigation of the chemical decomposition of silicon oil by sparks we noticed that continuous injection currents were superimposed by short discharge pulses (cf. Fig. 3 of [13]).

*Time to breakdown measurements.* Time lags to breakdown measured with short (100 ns) voltage pulses were characterized by a distribution encompassing a formative time lag $t_f$ and a statistical time lag $t_s$. An example obtained with LAr is shown in Fig. 6. Both time lags decrease with increasing applied electric field strength but only $t_f$ increases with gap separation. The formative time lag has been correlated to the movement of injected charge carriers across the gap [29]. Attempts have been made to estimate carrier mobilities [29,30]. The values obtained must not be compared to the usual low field mobilities [23], furthermore, it is possible that the formative time lag describes the expansion of the discharge channel. The statistical time lag would then reflect the charge carrier injection. Since field emission or ionization are instantaneous, we have to assume that $t_s$ reflects fluctuations in energy dissipation and bubble nucleation near the emitter. The influence of the charge carrier supply on $t_s$ and $t_f$ is demonstrated by data obtained for silicon oil with and without scratched electrodes as shown in Fig. 7. Although the experimental details are somewhat complicated, it is quite apparent that a scratched surface yields more carriers which leads to a shorter $t_s$ and due to the increase of the rate of energy dissipation to a shorter $t_f$.

The influence of the injection current on the time to breakdown was demonstrated by Goto and Aso [32] for LHe. The geometry of the gap was sphere-plane. By variation of a resistor in series with the gap they demonstrated the influence of the magnitude of the injection current

on the formative time lag. This led them to postulate that the formative time lag should be determined by the time it takes to vaporize a certain liquid volume. At the same time also $t_s$ was shortened by the greater injection current.
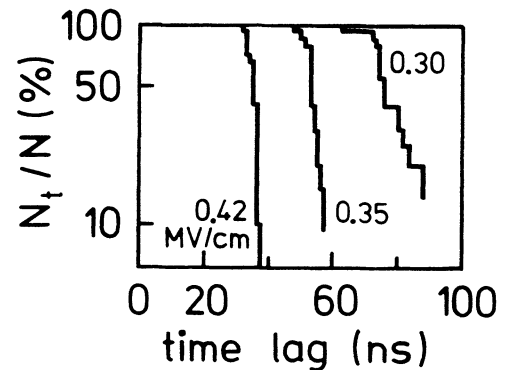


Fig. 6: *Time to breakdown data for LAr; parallel plate geometry (after ref. 29)*
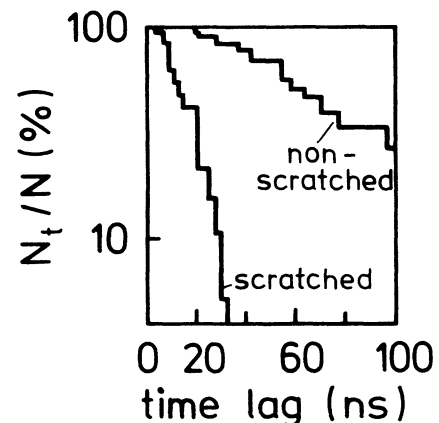


Fig. 7: *Time to breakdown data for dimethyl silicone oil; parallel plate geometry (after ref. 31)*

## SIMPLIFIED UNIVERSAL PICTURE
## OF LIQUID BREAKDOWN

For the sake of disucssion let us identify four stages in the development of the breakdown process which are shown schematically in the following chart:

1: ELECTRONIC STAGE

| | |
|---|---|
| Electric charge carrier generation at metal electrodes by field emission or field ionization. Formation of a space charge region. | *i-U-curves* *Fowler-Nordheim-equation:* work function of electrode, state of electrode surface. *Halpern-Gomer tunnel-equ.:* ionization potential $I_1$. *SCL currents:* drift velocity. |

### 2: ELECTRO-THERMAL STAGE

| | |
|---|---|
| Temperature rise due to frictional motion of charge carriers; formation of low density regions at points of largest energy dissipation; corona light emission; expansion of low density region towards counter electrode; surface instabilities. | Schlieren photographs, corona light *Heat-flow equation:* thermal conductivity. *Vollmer-equ. for bubble formation:* surface tension, heat of vaporization. *Thomas-Watson-model:* liquid density, applied voltage. |

### 3: GAS DISCHARGE STAGE

| | |
|---|---|
| Formation of a gaseous discharge channel from cathode to anode; light emission; high temperatures; rupture of molecular bonds; formation of radicals and ions. | *i(t),* high speed photography, light analysis *Spark-laws* |

### 4: PHYSICO-CHEMICAL STAGE

| | |
|---|---|
| Extinguishing of the discharge; temperature decrease; recombination of ions and radicals; formation of molecular products. | Gas-analysis *Chemical kinetics* |

In the left hand column a description of the elementary processes taking place is given while in the right hand column the experimental evidence and the theoretical treatment are summarized.

Further progress in this field may be achieved by carefully controlled experiments (incorporating simultaneous electrical and optical measurements) on selected liquids with specific thermodynamic properties.

## ACKNOWLEDGMENT

## REFERENCES

[1] A. H. Sharbaugh, J. C. Devins and S. J. Rzad, IEEE Trans. EI-13, 249 (1978).

[2] Special Issue of the "US/Japan Seminar on El. Cond. Breakdown in Diel.", IEEE Trans. EI-15, 312 (1980).

[3] E. O. Forster, J. Electrostatics Vol. 12, 1 (1982).

[4] B. Halpern and R. Gomer, J. Chem. Phys. 51, 1031 (1969).

[5] B. Halpern and R. Gomer, J. Chem. Phys. 51, 1048 (1969).

[6] R. Gomer, Acc. Chem. Res. 5, 41 (1972).

[7] K. Dotoku, H. Yamada, S. Sakamoto, S. Noda and H. Yoshida, J. Chem. Phys. 69, 1121 (1978).

[8] W. F. Schmidt and W. Schnabel, Ber. Bunsen Ges. physik. Chemie 75, 654 (1971).

[9] P.V.E. McClintock, Phys. Lett. 29A, 453 (1969).

[10] B. L. Henson, Phys. Letters 33A, 91 (1970).

[11] W. Schnabel and W. F. Schmidt, J. Polym. Sci., Symp. No. 42, 273 (1973).

[12] R. Gomer, "Field Emission and Field Ionization", Harvard University Press, Cambridge (1961).

[13] J. G. Rabe, W. F. Schmidt and W. Klein, J. Electrostatics 7, 253 (1979).

[14] V. A. Goncharov and V. I. Levitov, Izvest. Akad. Nauk SSSR, Energetika i Transport, Vol. 12, 145 (1974).

[15] A. Hickson and P.V.E. McClintock, Phys. Letters 34A, 424 (1971).

[16] H. Metzler and W. F. Schmidt, J. Phys. D9, L199 (1976).

[17] K. Arii and W. F. Schmidt, to be published.

[18] P.V.E. McClintock and H. Read-Forrest, Cryogenics 13, 371 (1973).

[19] S. Theoleyre and R. Tobazéon, IEEE Int. Symp. El. Ins. Philadelphia, June 1982.

[20] J. M. Proud and J. J. Auburn, Appl. Phys. Lett. 27, 265 (1975).

[21] G. Coletti, P. Girdinio, G. Liberti and G. Molinari, J. Electrostatics 12, 297 (1982).

[22] Ch. Olivier, J. Electrostatics 12, 291 (1982).

[23] W. F. Schmidt, Can. J. Chem. 55, 2197 (1977).

[24] S. E. Derenzo, T. S. Mast and H. Zaklad, Phys. Rev. A9, 2582 (1974).

[25] A. G. Tenner, Nucl. Instrum. Methods 22, 1 (1963).

[26] P. K. Watson, 1981 Annu. Rep. Conf. El. Insul. Diel. Phenom., p. 370.

[27] W.R.L. Thomas, 1973 Annu. Rep. Conf. El. Insul. Diel. Phenom., p. 130.

[28] K. C. Kao, IEEE Trans. EI-11, 121 (1976).

[29] K. Yoshino, p. 186 of reference 2.

[30] K. Arii, I. Kitani, and M. Kawamura, J. Phys. D12, 787 (1979).

[31] K. Arii, K. Hayashi, I. Kitani and Y. Inuishi, Proc. 5th Int. Conf. Cond. Breakdown Diel. Liquids, p. 163, Delft University Press (1975).

[32] Y. Goto and T. Aso, Record of Electrical and Communication Engineering Conversation (Japan) 45, No 1, 40 (1976).