DIELECTRIC BREAKDOWN IN SOLIDS

FINAL REPORT

Paul P. Budenstein

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A theoretical model of dielectric breakdown in solids has been proposed by Budenstein. In this model the breakdown process starts with the development of a critical local charge density. This density, in turn, causes chemical bonds to be broken and leads to the formation of a high density gaseous plasma, the conducting path for destructive breakdown. The present work explores the magnitude of the critical charge density by comparison of the bonding energies of the $H_2^{(+)}$, H_2, $H_2^{(-)}$ and $H_2^{(--)}$ molecules. An ab

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20. initio calculation of the ground state of the $H_2^{\eta(-)}$ molecule is performed and is the major contribution of this work. The implica- tions of this calculation on the breakdown problem and on other problems are discussed. (This calculation and its implications form the doctoral thesis of Jack M. Lloyd, Jr.)

DIELECTRIC BREAKDOWN IN SOLIDS

Paul P. Budenstein

Physics Department

Auburn University, Auburn, Alabama 36830

The goal of this study on dielectric breakdown in solids was to develop a theory of breakdown that was consistent with experimental evidence. The initial idea for the theory came during the summer of 1973 when the principal investigator was reviewing breakdown phenomena under nanosecond excitation(1). The proposed theory assumes that breakdown is initiated when a localized charge density reaches a critical value. Then chemical bonds are disrupted and atoms of the solid are freed to form a high-temperature, high-pressure gas. Electrons are assumed to be released during the bond breakage and later in reactions of the gaseous atoms. These cause further breakdown of the chemical bonds. Ultimately, through continuation of the above reactions and, possibly, through crack propagation, a gaseous channel grows in the dielectric until it bridges the electrodes. Only then does the high current of breakdown occur. Joule heating subsequent to the formation of the channel can cause further erosion of the solid.

If the above is essentially correct, then the fundamental issue of dielectric breakdown of solids is to properly characterize the conversion of the solid to the gas. During the academic year of 1973-1974, neither the principal investigator nor his graduate students were able to work on the breakdown problem. Thus an extension of time was requested to allow the work to be carried on during the 1974-1975 year. This request was generously granted. In the summer of 1974, the principal investigator again worked on the breakdown problem at the Guidance and Control Laboratory of the U. S. Army Missile Command, Redstone Arsenal, this time designing breakdown experiments employing a megavolt, nanosecond pulser with thick solid samples and also pursuing the implications of his proposed breakdown model. The latter have been summarized in a technical report (2) and in two conference presentations (3,4). In the fall of 1974, two graduate students (Jack Lloyd and James Knaur) undertook portions of the breakdown study.

Lloyd, a doctoral candidate with considerable experience with computers and a fairly good background in solid state theory, was given support funds under this contract to consider the theoretical question concerning the magnitude of the excess charge density required for bond disruption and

the energies of the released atoms. Knaur, using the megavolt, nanosecond pulser of the Guidance and Control Laboratories, set out to make more detailed observations of the electrical waveforms and light emissions than was previously possible. This work was done partially to provide certain engineering data needed by the Missile Command and partially to provide information pertinent to the breakdown mechanism. Basic support for Knaur's work has come from the Guidance and Control Laboratory, but a small portion of the funds of the current contract have been used to purchase specimen materials and, since Knaur's work is the basis for his M. S. thesis, Auburn University has contributed machine shop time to fabricate samples and fixtures. Also two spectrometers and associated equipment have been loaned by Auburn University for use at the test facility at Redstone Arsenal. During the summer of 1975 the principal investigator was provided with funds to work 20 days with Knaur at Redstone Arsenal.

A third graduate student, Aradhana Baruah, was added to the breakdown program in July of 1975 and given some financial aid from this contract. Her problem, which is to be her doctoral dissertation, is to make detailed calculations of the growth of the gaseous region using the chemical kinetics model described in Ref. 2. The chemical kinetics model involves generation of the gas from the solid, reactions in the high temperature gas, and heat conduction from the gas to the solid. From the model one obtains such information as the rate of growth of the gaseous region, its changing composition, and its temperature and pressure vs time. From the temperature, the degree of excitation of the gas can be inferred and hence its light emission spectrum. One of the major goals of these calculations is to delineate the material parameters that are important in the breakdown process. It is hoped that the calculations will ultimately lead to expressions for the thickness dependence and temperature dependence of the breakdown voltage.

The status of the three efforts will be summarized here. Lloyd's work constitutes the major portion of this contract and is nearing completion. It will be his doctoral dissertation and should provide the basis for a substantial journal article. His thesis and the article will be submitted as the major documentation for this contract. Calculations for this work are just about completed and work on the final document is in progress.

Lloyd first attempted to modify the traditional approaches of band theory to analyze the effect of localized charge distributions on the realignment of energy levels. However, the problem soon became too complex and an alternate approach was sought. We decided the basic question was the alteration of chemical bonds by the addition of extra electrons and that this question could be attacked by examining bonding in simple molecular systems. The simplest molecule is the H_2 molecule. Theoretical solutions previously existed for the H_2^+ ion, the H_2 neutral molecule, and the H_2^- molecular ion; all of these are stable in the ground state. Lloyd has performed an <u>ab initio</u> calculation of the ground state of the H_2^{--} molecular ion. A valence-bond method similar to that used by Fischer-Hjalmers for the calculation of the ground state of the H_2^- ion was employed. Only 1s electronic basis functions were used, but with a choice of different exponents in the orbital wavefunctions for greater accuracy. Briefly, the method entails the use of the basis functions to form a wave function having the proper symmetry and then computing the state energy from the expression

$$E = \frac{\int \psi^* H \psi . dV}{\int \psi^* \psi \, dV}$$

The internuclear distance appears as a parameter in the wave function and also in the energy expression.

Lloyd is making his final calculations now and is plotting his results. With several terms still to be included, he obtains a non-bonding state at the internuclear separation corresponding to the equilibrium position of the neutral H_2 molecule. The energy should asymptotically approach that for two single H^- ions in the limit of infinite separation. The height of the curve at the point of maximum stability for the neutral system will give some indication of the degree of instability of the neutral system with respect to the addition of the two extra electrons. The curve will also allow estimation of the energy liberated per particle upon bond disruption.

Kinetics of cavity growth were formulted in Ref. 2 (see Appendix A, taken from Ref. 2), but the details of the model were not quantified. The first task toward quantification has been performed by Baruah. She has made a literature study of very fast reactions that take place at high temperatures and at high pressures to determine reasonable parameters for the rate equations, an appropriate equation of state for the cavity gas, and an internal energy function for the cavity gas. Equations 4a to 4d of Appendix A describe the rates of change of each of the constituents of the gas in the highly idealized model. Only four constituents are

assumed to exist: neutral atoms, positive ions, negative ions, and free electrons. Once the atoms and ions have been released from the wall, the reactions are taken to be ionization of neutrals, recombination, charge transfer from a negative ion to a positive ion, charge exchange between two neutrals, electron attachment to a neutral, and electron detachment from a negative ion. Three types of kinetic coefficients occur: wall release coefficients (α_+, α_-, α_o, α_e) that describe the portion of wall particles released as positive ions, negative ions, neutrals and electrons; first order kinetic coefficients (β_1 and β_2) which describe rates depending only on a single constituent's concentration; and second order coefficients (γ_1, γ_2, γ_3, and γ_4) which describe rates depending upon two concentrations.

We assume that the wall coefficients are temperature-independent and are determined by the reaction details when bond disruption occurs. The four wall coefficients are not independent since they obey the constraints of charge neutrality ($\alpha_+ = \alpha_- + \alpha_e$) and particle conservation ($1 = \alpha_+ + \alpha_- + \alpha_o$).

The β's and γ's, however, are assumed to depend on the gas temperature in the manner typical of chemical reactions, regardless of the kinetic order of the reactions:

$$\beta_i = A_i \, e^{-E_i/kT} \quad , \quad \gamma_i = A_i' \, e^{-E_i'/kT}$$

where A_i and A_i' are descriptive of collision frequencies and E_i and E_i' are activation energies. In the breakdown kinetics problem, very high rates of reaction are required because the time scale of growth of a conducting channel is 10^{-11} to 10^{-8} sec. The required reaction rate seems to be somewhat faster than that of explosive reactions. For explosive reactions, such as the detonation of TNT or EDNA, the kinetics are well-described by Eyring's surface corrosion theory in terms of a kinetic coefficient k_r

$$k_r = A' \, T_2 \exp(-\Delta H^*/kT) \quad ,$$

where A', T_2 and ΔH^* are constants for a given explosive system. This equation is of the Ahrennius type. The kinetic equation defining k_r is

$$dn/dt = k_r(4\pi r^2/s), \text{ where } 4\pi r^2/s \text{ is the}$$

number of molecules on the surface of a reacting grain of radius r and dn/dt describes the change in this number per unit time. Thus k_r can be thought of as the fractional change in the number of surface molecules per unit time. For explosive reactions, k_r is about 10^{11}/sec.

The equation of state for a highly dense, high temperature gas is a matter of conjecture. In explosive reactions, best results seem to be obtained by using equations that are perturbations of the ideal gas law. The gas that we wish to describe is both more dense and at a higher temperature than that of high power chemical explosions. Hence, it is plausible to use the ideal gas law as the equation of state as a start. Later, when a more sophisticated kinetics model is developed, the choice of equation of state will have to be re-examined.

An internal energy function is required because the kinetic coefficients are temperature dependent and the temperature depends both on the rate at which energy is added during dissociation and the heat transfer to the surroundings. In addition to translational kinetic energy for each specie, it is necessary to consider electronic excitation of the neutral atoms, positive ions and negative ions. The internal energy may be written

$$U = (n_+ + n_- + n_0 + n_e)(4\pi r^3/3)(1.5\ kT) + \left(\frac{\sum E_i e^{-E_i/kT}}{\sum e^{-E_i/kT}}\right)_{Positive\ ions}$$

$$+ \left(\frac{\sum E_i e^{-E_i/kT}}{\sum e^{-E_i/kT}}\right)_{Negative\ ions} + \left(\frac{\sum E_i e^{-E_i/kT}}{\sum e^{-E_i/kT}}\right)_{neutrals} + \sum Q_i$$

The term with the factor (1.5 kT) describes translational kinetic energy of neutrals, negative and positive ions, and electrons (assumed to be in thermal equilibrium) and the three summations describe the contributions of electronic excitations to the internal energies of neutrals, positive ions and negative ions. The remaining terms are descriptive of the heats of reaction.

This report is in the nature of an interim report. The main report for the contract will be Lloyd's thesis and article for publication. It is hoped that these will be ready by the end of this year. We appreciate the support of the Army Research Office and hope that the current effort makes a meaningful contribution to the understanding of dielectric breakdown in solids. We are particularly grateful for the continuing encouragement received from members of the Guidance and Control Laboratory, U. S. Army Missile Command, Redstone Arsenal.

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3. Paul P. Budenstein, "A Model of Electric Breakdown in Solids," pp. 135-136 in Extended Abstracts, 147th Meeting of the Electrochemical Society, May 11-16, 1975, Toronto, Canada.

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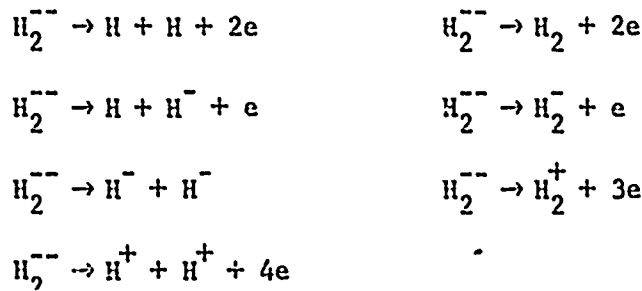
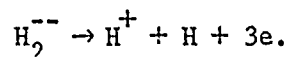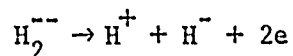## 2. Proposed Model of Dielectric Breakdown in Solids

a. Concepts of the Model

(1) Critical Charge Density. The basic assumption made is that breakdown occurs when the density of excess charge in an insulator in a local region containing many atoms attains a critical value. The source of this excess charge may be field emission from an electrode, charge multiplication by an avalanche process, charge injection at the surface of an ionized void, electron injection from an external accelerator, electrons produced by ionization processes associated with absorption of laser light, or some other means.

(2) Disruption of Chemical Bonds by Excess Charges. The effect of a charge density greater than critical on the solid is assumed to be disruption of chemical bonds. (Bowden and McLaren [25], in attempting to explain how a relatively small electric field (4.5×10^3 V/m) could initiate an explosive reaction in a single crystal of silver azide, hypothesized that a high local electron density led to the decomposition of the crystal. Subsequent work on silver azide has neither confirmed or disproven this hypothesis [26].)

The mechanism of bond disruption by an excess electron density can be visualized by considering the hydrogen molecule and its ions. An electron can be attached to H_2 to form a stable ion, H_2^-. The three-electron, two-nucleus system (H_2^-) will have a different set of electronic energy levels than the two-electron, two-nucleus system (H_2)[27,28]. (The bond length of H_2 is 0.746 Å, while it is estimated to be 1.65 Å in H_2^-. The H_2 molecule is probably best thought of with the two electrons shared by the two nuclei on an equal basis, while the H_2^- molecule is more like an H weakly coupled to an H^-.) The addition of still another electron to the system [$H_2^- + e \rightarrow H_2^{--}$ (unstable)] leads to a nonbonding situation. This nonbonding may occur with a variety of end products as illustrated in the following chemical reactions:

$$H_2^{--} \rightarrow H + H + 2e \qquad\qquad H_2^{--} \rightarrow H_2 + 2e$$

$$H_2^{--} \rightarrow H + H^- + e \qquad\qquad H_2^{--} \rightarrow H_2^- + e$$

$$H_2^{--} \rightarrow H^- + H^- \qquad\qquad H_2^{--} \rightarrow H_2^+ + 3e$$

$$H_2^{--} \rightarrow H^+ + H^+ + 4e$$

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$$H_2^{--} \rightarrow H^+ + H^- + 2e$$

$$H_2^{--} \rightarrow H^+ + H + 3e.$$

The reactions that dominate should be the ones most favorable energetically. These cannot be determined readily from calculations because of the number of particles involved. Note that it is possible to end up with an excess of electrons; i.e., more than 1 electron may be produced in the dissociation of H_2^{--}, whereas only one electron was added to H_2^- to form the unstable H_2^{--}.

(3) <u>Chain Reaction</u>. The third ingredient believed essential to the breakdown process is the chain reaction. A well-known example of a chain reaction is the explosive combination of H_2 and Cl_2 gases [29]. In the absence of light or an electric spark, this mixture is stable at STP. However, a flash of ultraviolet light or a spark will cause the formation of HCl with great rapidity, the reaction being strongly exothermic. The reaction scheme may be represented as follows:

$$H_2 + light \rightarrow H + H$$

$$H + Cl_2 \rightarrow HCl + Cl$$

$$Cl + H_2 \rightarrow HCl + H$$

$$H + Cl \rightarrow HCl + light.$$
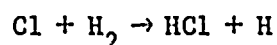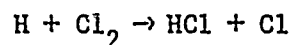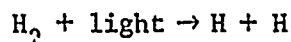
The reaction products in each case have the potential for causing further reactions; the total energy released is many times the initiating energy. The rate of reaction depends upon the concentrations of the reacting components, temperature, and pressure. These, in turn, depend on the processes of diffusion, loss through boundaries, heat dissipation, wall effects, competing reactions, etc.

In the breakdown problem, we assume that an electron density is created in a local region sufficient to disrupt chemical bonds. Atoms are thus freed from their positions in the solid and form a dense gas. The gas density is the same as that of the solid for an appreciable time. For breakdown to occur, we require that a chain reaction can take place inside the solid so that a gaseous cavity is created with the dissociation products. The reaction sequence as it might occur in crystalline sodium chloride will now be described; the general ideas are believed to be applicable for all types of chemical bonding.

Within solid sodium chloride, the sodium and chlorine atoms exist as ions, Na^+ and Cl^-, respectively. These might be converted to gas atoms having different states of ionization, such as Na^o_{gas}, Na^+_{gas}, Cl^-_{gas}, Cl^o_{gas}, and Cl^+_{gas}, through the reactions:

1) $Na^+_{solid} + e \rightarrow Na^o_{solid} + Q_1$

2) $Na^o_{solid} + Q_2 \rightarrow Na^o_{gas}$

3) $Na^o_{gas} + Q_3 \rightarrow Na^+_{gas} + e$

4) $Cl^-_{solid} \rightarrow Cl^-_{gas} + Q_4$

5) $Cl^-_{gas} + Q_5 \rightarrow Cl^o_{gas} + e$

6) $Cl^o_{gas} + Q_6 \rightarrow Cl^+_{gas} + e.$

Reactions 3), 5), and 6) occur in the gaseous state and are activated by collisions among the particles of the gas. The entire reaction scheme must be highly exothermic if the chain reaction is to be vigorous.

The above reaction scheme is depicted in a two-dimensional format in Figure 1. Figure 1a shows a region with a single extra electron. This might stay trapped for an appreciable time, but would not cause lattice disruption. In Figure 1b, the electron density is increased so that the ionic charges on several nearest-neighbor sodium atoms are neutralized as indicated in reaction step 1) (note the five central sodium atoms in the figure). Because of their thermal energies, the neutralized sodium atoms [reaction step 2)] can move with ease from their former equilibrium positions (Figure 1c). The neutral sodium atoms experience only slight binding energy to their former equilibrium positions. [Reaction step 2) should occur more readily at high temperatures, suggesting that the breakdown strength should decrease with increasing temperature.] The movement of the sodium atoms removes the constraints on the adjacent Cl^- atoms. Figure 1d shows the system after the Cl^- atoms have moved, through their mutual repulsion, from their equilibrium positions [reaction step 4)]. In so doing they lose some potential energy and gain kinetic energy; thus, by subsequent collisions, they heat up the gas created by the atoms that have left their equilibrium positions. Figures 1e and 1f show how the electron density in the gas can be built up through further collisions [reaction steps 3), 5), and 6)]. Finally, in Figure 1g, the second stage of the chain reaction is depicted after the excess electron density has caused more sodium atoms to be freed from the solid matrix.

(a) SOLID NaCl SHOWING AN ISOLATED TRAPPED ELECTRON ON ONE Na+.

(b) ELECTRONS ATTACHED TO 5 NEAREST Na ATOMS PRODUCING Na⁰.

(c) Na⁰ ATOMS MOVE FROM LATTICE SITES.

(d) Cl⁻ ATOMS, THROUGH MUTUAL REPULSION, MOVE APART.

(e) Cl⁻ ATOMS RANDOMIZED.

(f) EXCESS ELECTRONS PRODUCED BY COLLISIONS COLLISIONS.

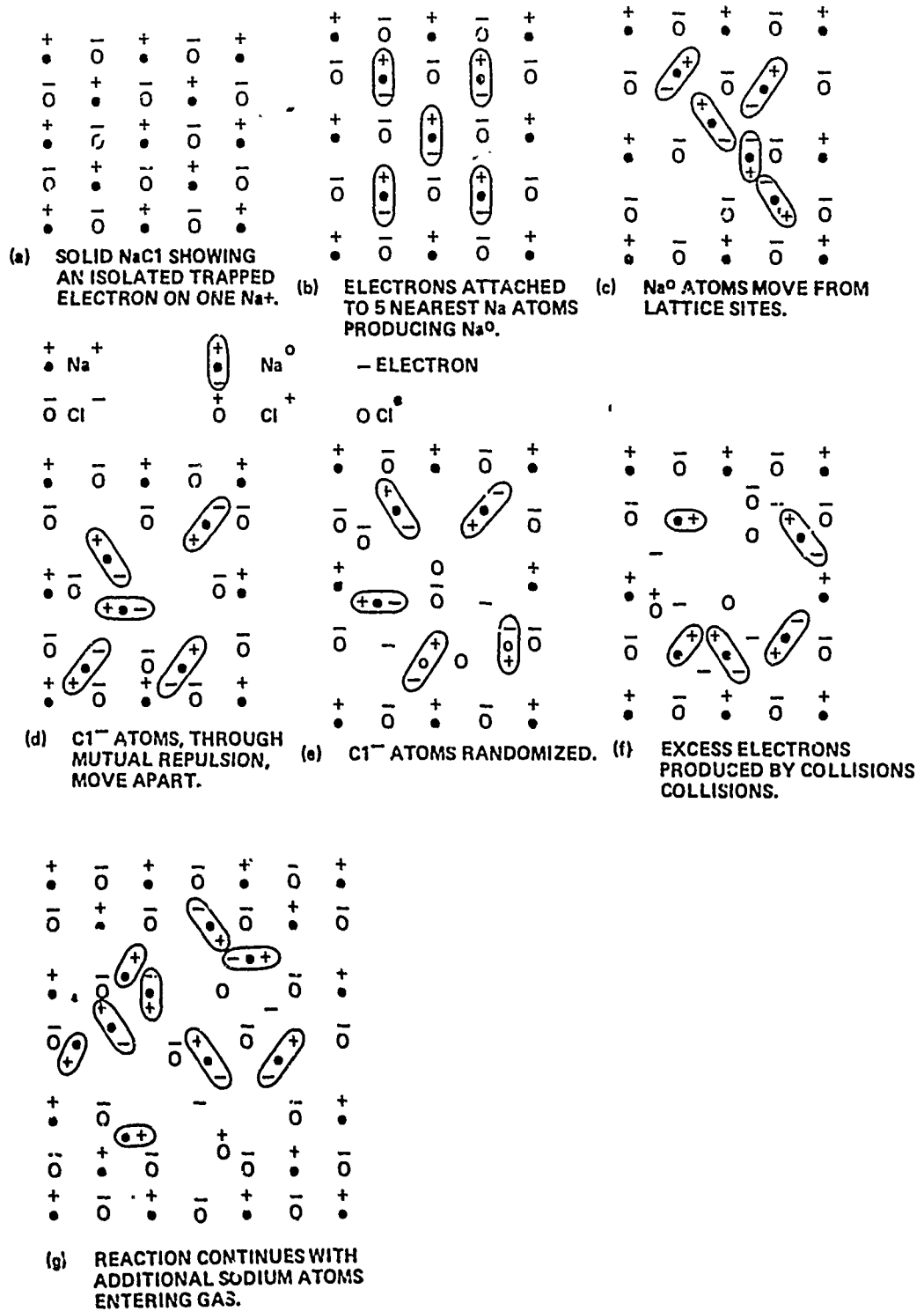(g) REACTION CONTINUES WITH ADDITIONAL SODIUM ATOMS ENTERING GAS.

Figure 1. Schematic description of the bond disruption and chain reaction in NaCl.

Note that the reaction sequence has the capability of releasing more electrons than were needed for initiation and hence has the potential for a chain reaction. The nature of the mechanism is believed to be quite general: nonbonding should occur whenever the local density of electrons is made too high, regardless of the detailed nature of the chemical bond.

(4) Establishment of a Gaseous Conducting Channel. The result of the chain reaction is the conversion of the solid in a local region to a partially ionized gas. As the chain reaction proceeds, a gaseous cavity is formed within the solid. The reactions must take place with great rapidity because sufficient energy must be continually added to the gas to compensate for heat transfer to the surrounding medium. As the size of the cavity increases, the medium about the cavity is subjected to very high stresses and cracks will start to form. As they form, new surface area is exposed and the chain reaction spreads to this, thus maintaining the high pressure.

(5) Completion of the Channel. We assume that the breakdown conduction current starts when a gaseous channel bridges the electrodes. The currents prior to this are associated with high field prebreakdown conduction mechanisms; these are assumed incidental to breakdown except as they give rise to a high local space charge density that can initiate the chain reaction. If the gaseous channel cannot completely bridge the electrodes during the time in which the voltage is applied, then the system experiences a "partial breakdown", one in which damage has occurred without completion of the conducting path. If the gaseous channel does bridge the electrodes, conduction through the channel begins since the gas is ionized. As conduction proceeds, further erosion of the walls can occur because of the high electron density and the heating of the plasma by the external circuit. Experimentally, the conductivity of the system in the breakdown region changes by a factor of about 10 [10] in a time of about 10 nsec, measured from the observed beginning of the gaseous channels to the onset of breakdown conduction [5,30].

b. Simplified Theory for the Growth of a Gaseous Channel

The reaction kinetics of real systems depend on the detailed reactions present. As was shown for the hypothesized reactions for breakdown in NaCl, many reactions are possible during the dissociation and recombination processes associated with creation of the gaseous channel. In a dielectric that is chemically complex, many more dissociative and recombinatorial processes would be involved. However, one of the significant features of dielectric breakdown is that the breakdown fields for homogeneous specimens of different materials are remarkably similar. Thus it becomes plausible to think in terms of a model having highly simplified chemical kinetics. Such a model will be outlined in this section. The solutions for this model, which depend on the treatment of the heat flow problem and detailed assumptions on kinetic coefficients have not yet been explored.

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We assume that the critical density of charge necessary for initiating the chain reaction is present; the proposed theory is intended to describe the growth of the gaseous cavity. The rate of reaction wherein the solid is converted to gas is assumed to depend upon the electron density n_e in the gas and on the wall area of the cavity. For each molecule removed from the solid, some neutral atoms, positive ions, negative ions, and electrons are added to the gas. Each material will have its own peculiar distribution of these reaction products. Also, there is some total energy released, partially as kinetic energy of the individual particles and partially as electron excitation, when a molecule of the solid is converted to the gaseous phase. In our simplified model, we describe the breakup without identifying the atomic species present. When an average molecule breaks away from the solid, we will say that a certain number of neutrals, positive ions, negative ions, and electrons are added to the gas. Atomic and ionic species will not be further differentiated; i.e., an atom of sodium in the gas will be treated the same as an atom of chlorine in the gas, a positive sodium ion the same as a positive chlorine ion, etc. For purposes of describing the gas, we will assume its mass density is the same as that of the solid and the average volume per atom in the gas is the same as the average volume (volume of a molecule in the solid/No. of atoms in one molecule) of an atom in the solid.

We define wall generation coefficients for describing the dissociation at the cavity walls as follows:

1) α_+ = fraction of wall atoms released as positive ions

2) α_- = fraction of wall atoms released as negative ions

3) α_o = fraction of wall atoms released as neutrals

4) α_e = fraction of the number of wall atoms of electrons released at the wall.

The wall generation coefficients are assumed to be independent of the gas parameters. For simplicity the ions are assumed to be singly ionized.

The gas (neutrals, positive ions, negative ions, and electrons) is a dynamic system. Particles are added continuously and the volume of gas increases as the solid is eroded. At any instant the cavity gas will be assumed to be sufficiently close to equilibrium values that there is meaning to speaking of temperature, pressure, and particle concentrations as system parameters. Since there is heat flow from the cavity gas while the cavity is growing, the temperature and pressure will vary with time. Thus the densities of neutrals, positive ions, negative ions, and electrons (n, n_+, n_-, and n_e, respectively) will

vary through the processes of recombination, electron attachment and

detachment, and ionization within the gas. The volume processes and their kinetic coefficients are as follows:

1) Ionization of neutrals, kinetic coefficient β_1

$$\text{neutral} \rightarrow (+ \text{ion}) + \text{electron}$$

2) Recombination, kinetic coefficient γ_1

$$(+ \text{ion}) + \text{electron} \rightarrow \text{neutral}$$

3) Charge transfer from a negative ion to a positive ion, kinetic coefficient γ_2

$$(- \text{ion}) + (+ \text{ion}) \rightarrow 2 \text{ neutrals}$$

4) Charge exchange between two neutrals, kinetic coefficient γ_3

$$\text{neutral} + \text{neutral} \rightarrow (+ \text{ion}) + (- \text{ion})$$

5) Electron attachment to a neutral, kinetic coefficient γ_4

$$\text{electron} + \text{neutral} \rightarrow (- \text{ion})$$

6) Electron detachment from a negative ion, kinetic coefficient β_2

$$(- \text{ion}) \rightarrow \text{electron} + \text{neutral}.$$

The kinetic coefficients are functions of temperature and pressure.

The equations that determine the state of the cavity system are taken to be the following:

1) Charge neutrality condition

$$n_e + n_- = n_+$$

2) Constancy of density of solid and gas

$$n_+ + n_- + n = a_v \quad , \quad \text{where } a_v = \text{number of atoms per unit volume of the solid}$$

3) Rate of growth of the cavity:

a) The dielectric is assumed isotropic and the cavity spherical. The electron density is taken to be uniform at all points on the surface of the cavity. The number of particles added to the cavity per unit time is assumed proportional to the electron density in the cavity and the wall area; that is,

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$$d(a_v V)/dt = kn_e 4\pi r^2$$

where V is the volume of the cavity, r is the cavity radius, and k is a proportionality constant.

b) The proportionality constant is assumed to be independent of the gas parameters. n_e is one of the dependent variables of the system and its value as a function of time is part of the solution. Thus, using $V=(4/3)\pi r^3$, the above equation can be integrated to obtain r at any time t. The result is

$$r = (k/a_v) \int_0^t n_e(t)\, dt \quad .$$

4) Rate equations:

a) Positive ions

$$dn_+/dt = \alpha_+ kn_e 4\pi r^2 + \beta_1 n + \gamma_3 n^2 - \gamma_1 n_+ n_e - \gamma_2 n_+ n_-$$

b) Negative ions

$$dn_-/dt = \alpha_- kn_e 4\pi r^2 + \gamma_4 n_e n + \gamma_3 n^2 - \beta_2 n_- - \gamma_2 n_+ n_-$$

c) Neutrals

$$dn/dt = \alpha_o kn_e 4\pi r^2 + \gamma_1 n_+ n_e + \gamma_2 n_+ n_- + \beta_2 n_-$$
$$- \gamma_4 n_e n - \beta_1 n - \gamma_3 n^2$$

d) Electrons

$$dn_e/dt = \alpha_e kn_e 4\pi r^2 + \beta_2 n_- + \beta_1 n - \gamma_1 n_+ n_e - \gamma_4 n n_e$$

5) Heat flow from cavity to surroundings:

a) The temperature of the cavity changes according to the balance between the energy added due to the wall reactions and the energy conducting into the surrounding medium. The heat capacity of the cavity gas becomes strongly temperature-dependent when the temperature is high enough to excite electrons and produce ionization.

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$$kn_e 4\pi r^2 \epsilon_a = c(T) \, M \, dT/dt + dQ/dt \quad ,$$

where ϵ_a is the average energy released into the gas per atom converted to gas at the walls, $c(T)$ is the specific heat capacity of the gas, M is the mass of gas in the cavity at time t, T is the temperature of the cavity gas, and dQ/dt is a negative quantity, the heat flow from the gas to the surrounding medium.

b) The heat flow from the gas to the surroundings is determined by solving the heat conduction equation for the spherically symmetric system with the heat flow to the surrounding medium equal to dQ/dt in the above equation. The heat conduction equation for spherical symmetry is

$$\frac{\partial T}{\partial t} = \varkappa \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \right] \quad .$$

c) The temperature at the cavity surface is the same as that inside the cavity. (A detailed solution using the heat conduction equation is probably unattainable, but a simplified "law of cooling," such as Newton's law of cooling, might work adequately.)

The initial conditions are:

at $t = 0$, $\quad r = 0$, $n_+ = 0$, $n_- = 0$, $n = 0$, $n_e = (n_e)_{CRIT}$.

Here, $(n_e)_{CRIT}$ is the charge density necessary to initiate the chain reaction.

The method of solution is numerical integration. First, reasonable values must be chosen for the coefficients. The temperature dependence of the β's and γ's and $c(T)$ are required. The constraint equations,

$$n_e + n_- = n_+ \quad \text{and} \quad n_+ + n_- + n = a_v \quad ,$$

can be used to eliminate two of the four dependent variables in two of the rate equations. Thus, we might eliminate n_+ and n_- in the rate equations for n_e and n. The n_e and n rate equations would have to be solved simultaneously with the cavity size equation and the heat flow equations. Ultimately, the solution would give the cavity temperature as a function of time, the cavity radius as a function of time, $n_e(t)$ and $n(t)$. With these quantities and using the constraint conditions in the rate equations for n_+ and n_-, each of these equations can be expressed in terms of one dependent variable and functions of time and numerically integrated.

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