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STUDY TO OBTAIN DESIGN DATA FOR REENTRY ECM ANTENNA SYSTEMS(U)

P.E. Bisbing, D.L. McMenarnin, P. Scherer

REENTRY SYSTEMS DEPARTMENT MISSILE AND SPACE DIVISION GENERAL ELECTRIC COMPANY P. O. BOX 8555, PHILA., PA. 19101

Contract No. F 19628-67-C-0210 Project No. 8671

Second Quarterly Technical Report

THIS DOCUMENT IS SUBJECT TO SPECIAL EXPORT CONTROLS AND EACH TRANS-MITTAL TO FOREIGN GOVERNMENTS OR FOREIGN NATIONALS MAY BE MADE ONLY WITH THE PRIOR APPROVAL OF AFCRL (CRDM), L.G. HANSCOM FIELD, BEDFORD, MASS. 01730

> CONTRACT MONITOR: WALTER ROTMAN MICROWAVE PHYSICS LABORATORY

GE Report No. 67527170

September 1967

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SEDFORD, MUSEACHUSETTS 01730

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ABSTRACT

This report presents survey material on the effects of the reentry environment on the voltage breakdown characteristics of antennas. Most of the important effects are fairly well understood, in that theoretical models exist and experimental data are available in sufficient quantity to allow predictions to be made with confidence. However, the effect of high gas temperature is not sufficiently understood, although recent experimental data have indicated a mechanism which may prove to be important in controlling breakdown. This mechanism is strongly dependent on viorational excitation and dissociation of the gas molecules. Predicting the vibrational excitation state in a hypersonic flow field is not presently possible in a detailed microscopic analysis, but an approximate solution is possible.

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SECTION 1 INTRODUCTION

The study of which this report is a part is concerned with the effects of the reentry environment of a slender hypersonic vehicle on the transmission of ECM signals. The most important aspect of this study is the effects of reentry on antenna breakdown. In response to technical direction, the effort during this reporting period was concentrated on a survey of reentry effects on antenna breakdown and included visits to the facilities of some of the workers in the field.

Part of the scope of effort involves fluid mechanics. It turns out that one of the most important, but least easily analyzed, effects of reentry on antenna breakdown is the effect of high air temperature in terms of vibrationally excited states of molecular constituents. As a result, and in response to direction, the fluid mechanics efforts were devoted to the initial phases of a review of vibrational excitation effects in a nonequilibrium flow field situation.

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SECTION 2

FLOW FIELD ANALYSIS

In accordance with the recommendations which were made subsequent to the first technical direction meeting, the flow field literature survey has been rescheduled to be completed by the end of the third contract quarter. Following the suggestions which were made at the meeting, it is intended that during this survey, special emphasis will be directed toward vibrational nonequilibrium effects on the flow field properties. Part of this literature survey has been completed and is reported below. Also reported below is the development of a relatively simple method which will be used to determine the extent of the effects of vibrational nonequilibrium on the flow field calculations which were presented in the first quarterly report.

2.1 FLOW FIELD LITERATURE SURVEY

During the course of the flow field survey a report entitled 'Interaction of Chemical Reaction With Vibration or Translation in Nonequilibrium Processes'' by E. Schwartz of GE/RSD^{36*} was reviewed and found to pertain directly to this survey. Most of the following material has been taken from this report.

When air passes through a shock the Maxwellian velocity distribution, disrupted by the highly nonequilibrium conditions in the shock, is restored within the time of a very few collisions¹, and the translational degrees of freedom of the gas are equilibrated almost instantaneously at the new, higher temperature.

The relaxation time for rotation is somewhat longer, about a dozen collisions² being required to bring the molecular rotation into equilibrium, i.e., to establish the Maxwell-Boltzmann distribution of rotational energy levels characteristic of the new translational temperation. The time required for this is still small enough to justify its neglect.

*References appear in Section 6.

The relaxation of vibration is much slower; for instance, the approximate number of collisions required to establish vibrational equilibrium for N_2 and O_2 at 5000 °C is 3000 and 200, respectively³. Vibrational disequilibrium must be taken into account in reducing shock tube data and in making accurate calculations of hypersonic flows.

Lastly, the slowest processes in reactive flows are the chemical reactions themselves. In earlier work these rates were assumed to be infinite; i. e., the concentrations of various species were obtained from equilibrium constants. But for high-speed flows this assumption is entirely inadequate. For instance, species concentrations calculated on the 2ssumption of chemical equilibrium may be orders of magnitude in error⁴. Thus, the concentrations of the various species must be found from a set of differential equations, one for each reaction considered. Because the Law of Equipartition of Energy is not applicable in nonequilibrium processes, the various energy modes are strongly coupled by the rates at which energy is stored or transferred. The rate "constants" which are used in the above-mentioned differential equations are particularly sensitive to these coupling effects.

1. A.

In all the studies reviewed below, effects of viscosity, heat conduction, and diffusion have been ignored. Except in the boundary layer and in the interior of the shock wave, the various gradients are small enough to justify this neglect of transport phenomena.

2.1.1 PERTURBATION OF MAXWELLIAN VELOCITY DISTRIBUTION BY CHEMICAL REACTION

It has long been recognized that any chemical reaction taking place at a finite rate must necessarily disturb the Maxwellian distribution of translational velocity. Since the reaction is brought about by the more energetic collisions, the reaction may deplete the high-energy tail of the velocity distribution. On the other hand, for reactions with high activation energy and low steric factors (low probability for reaction even for sufficiently energetic collisions), most collisions will not be reactive but will help maintain translational equilibrium, and the departure from the Maxwellian distribution should be negligible. A number of investigators, by making perturbation solutions of a suitably generalized Boltzmann equation, have made quantitative estimates of this interaction of chemical reaction and translational disequilibrium.

Prigogene and Xhrouet⁵ consider the initial rate of the reaction A + A = B + C for molecules of spherical symmetry and no internal degrees of freedom. The influence of B and C is ignored and the heat of reaction disregarded. It was also postulated that the cross section for reaction was small. The method of Chapman and Enskog⁶ was used for solving a modified Boltzmann equation with the velocity distribution taken as $f = f_0 (1 + \phi)$ where f_0 is the equilibrium (Maxwellian) distribution and ϕ , a perturbation. It was found that both ϕ and the ratio of the reaction rate to its value at equilibrium depend only on $\epsilon */kT$, where $\epsilon^* =$ activation energy. The quantitative results were very sensitive to the choice of the reaction cross section σ , a function of the relative molecular velocity; but the general conclusion was reached that when $\epsilon */kT > 5$ the perturbation of the velocity distribution and the deviation from equilibrium reaction rate are quite small and that the use of equilibrium theory in calculation of reaction rates was justified for reactions of the type considered.

According to References 7 and 8, the work of Curtiss⁹ is more general and his approach somewhat different, but his results are in essential agreement with those of Prigogene and Xhrouet.

Prigogene and Mahieu¹⁰ extend the work of Reference 5 by including the influence of heat of reaction r and find that it can perturb the Maxwellian distribution to an appreciable extent. They calculate the initial rate of the reaction $A_0 + B - A_1 + B$, where A_0 and A_1 differ only in electronic energy, and obtain the equation (for a particular choice of reaction cross section):

$$v/v_{o} = 1 + 1.2 \chi_{A_{o}} \chi_{B_{o}} / \epsilon^{*}$$
 (2.1.1-1)

where

v = reaction rate

v = equilibrium v (i.e., under assumption of Maxwellian distribution)

 χ = mole fraction

This shows that the reaction rate will be increased for exothermic reactions and that the order of the reaction is increased because of the presence of the term $\chi_A = \chi_B$.

Present⁷ gives a simplified derivation of the results of Prigogene and Xhrouet using a more realistic reaction cross section. He finds that even for $\epsilon */kT$ as small as 5, the reaction rate is only 8 percent less than that predicted from equilibrium theory.

Mahan¹¹ points out that, since perturbation of the Maxwellian velocity distribution becomes important only for reactions of low activation energy at high temperatures, the most serious deviations from equilibrium reaction rate may be expected to occur in free radical combination reactions, where little or no activation energy is involved. He derives a collision cross section for radical combination reactions and then calculates ϕ and v/v_o in the manner of Prigogene. Mahan concludes that the equilibrium assumption is justified in photochemical systems where free radical concentrations are low but may not be valid in flames and detonations where radical concentrations may exceed 0.1 mole fraction.

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Ross and Mazur¹² present a formal perturbation solution of a Boltzmann-type equation for a bimolecular reaction $(A + B \neq C + D)$, in which the backward as well as the forward reaction is considered and the molecules may have internal degrees of freedom. They conclude that the usually assumed phenomenological rate expressions for chemical reactions (for example, $-dn_a/dt = k_f n n_b - k n n_c$ for the reaction $A + B \neq C + D$) are strictly valid only in the lowest order of the perturbation. Higher order perturbations show the rate "constants" to be a function of affinity and bence, implicitly, of the time.

2.1.2 PERTURIATION OF MAXWELL-BOLTZMANN DISTRIBUTION OF VIBRATIONAL LEVELS BY DISSOCIATION

Since a molecule in a state of high vibrational excitation is more likely to undergo dissociation on collision than one of lesser excitation (with the same translational energy), a dissociation reaction ($A_2 + M \stackrel{?}{=} A + A + M$) will disturb the Maxwell-Boltzmann (equilibrium) population of the vibrational levels; and the reaction rate will be smaller than that calculated on the basis of vibrational equilibrium. In order to study vibrational level populations and dissociation rates under nonequilibrium conditions, the investigators cited below consider a dilute solution of oscillators (diatomic molecules A_2) in an inert gas M which acts as a constant temperature heat bath (i.e., effects discussed in Section 2.1.1 need not be considered). The concentration of oscillators is so small that only collisions with the heat bath molecule need be taken into account. This leads to a set of N simultaneous linear rate equations in the χ_1 (t) (N = number of vibrational levels; χ_1 = fraction of oscillators in level i), whose coefficients are the probabilities per unit time of transition from one level to another or of dissociation from that level. This set of differential equations is known variously as the "master equation" or the "transport equations." Methods are available for their solution which do not require that the system be close to equilibrium, as do the perturbation methods of Section 2.1.1. It should be pointed out, however, that generally these methods involve finding the eigen values and eigen functions of very large matrices (order of matrix = number of vibrational levels), so that approximations are eventually introduced.

Montroll and Shuler⁸ consider a "ladder climbing" model in which transitions can take place only between nearest neighbor levels and dissociation only from the highest level N (dissociation consists of attainment of level N + 1). In the language of the theory of stochastic processes, this is the problem of a one dimension random walk with reflecting (level zero) and absorbing (level N + 1) barriers. The reciprocal of the "mean first passage time" for the N'th level serves as an average reaction rate.

The authors apply their general theory to the case of harmonic oscillators where the transition probabilities are given by the Landau Teller relations $P_{mn} = [(m + 1) \delta_{n-1, m} + m \delta_{n+1, m}]P_{10} = P_{nm}$, where P_{mn} is the probability per collision of transition from level n to level m, and δ_{nm} is the Kroneker delta. They find that the rate of chemical reaction is not much affected by deviation from vibrational equilibrium if the activation energy ϵ^* is larger than 10 kT.

 Kim^{13} gives a general mathematical treatment of a problem similar to that of Montroll and Shuler but in which transitions are allowed between any two levels (dissociation only from highest level). He calculates the mean first passage time for a truncated harmonic oscillator with an arbitrary initial distribution of the χ_i and with a Boltzmann initial distribution at a vibrational temperature \neq T and for a slightly anharmonic oscillator, where nearest neighbor and next-nearest neighbor transitions only are allowed.

Gans¹⁴ presents the formal solution for a set of equations prore general than that of Kim in that dissociation can take place from any state (not just the highest) and molecules may enter the system at any level.

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Shuler¹⁵, treating the same model for dissociation of a truncated harmonic oscillator as Montroll and Shuler, uses their general solution for the vibrational level distribution χ_i (t) in terms of Gottlieb polynomials. He specializes this to the cases of a Boltzmann and a delta function (χ_i (0) = δ_{ij}) initial distribution. Some numerical work for an initial Boltzmann distribution presented as a plot of $\ln \chi_n$ versus n shows very little perturbation of this distribution for $\epsilon */kT = 11$ (the largest value considered), the population of only the highest level (n = 10) being appreciably reduced. He also gives a figure showing the effect of dissociation on the role ation of a system of oscillators all of which are initially in the level n = 3, where the highest discrete level is n = 4. In this work the probability of dissociation, transition from level N to "level" N + 1, is taken as (N + 1) P_{i0}, i.e., as though N + 1 were the next vibrational level.

Nikitin¹⁶ treats a ladder model for dissociation of a harmonic oscillator similar to the above except that probability of dissociation P_{∞} is taken as a parameter. Necessary eigen values and eigen vectors are found by a perturbation method, and simple approximate expressions are derived for the reaction rate and the distribution χ_n (t) that hold after a certain induction time. They find that for small P_{∞}/P_{10} the distribution χ_n (t) differs little from the Boltzmann but for large P_{∞}/P_{10} the equilibrium distribution is disturbed, so that the probability of finding

a molecule in an upper level is close to zero. If, further, $P_{\infty}/P_{10} \gg \epsilon */kT$, the reaction rate is independent of P.

In a later paper¹⁷ Nikitin and Sokolov apply the above model and methods to an arbitrary oscillator. They obtain for the dissociation rate, after an induction time, an approximate equation in which the transition probal lities do not appear and the energy levels enter through Q, the vibrational partition function. Before confronting this dissociation rate with experimental results, the authors correct it for the influence of rotation on the effective dissociation energy and the influence of vibrational state on collision diameter and multiply by the electronic statistical weight. The equation can be extended to polyatomic molecules, and a table of experimental and calculated values of the ratio of pre-exponential factor to collision number shows excellent agreement for both diatomic and polyatomic molecules.

Nikitin and Sokolov point out that for an anharmonic oscillator dissociation leads to an essential perturbation of the Boltzmann distribution; because the energy levels become very close together near the dissociation limit (see Figure 1¹⁸), there are many levels in the energy range kT and hence many levels with depleted population. This conclusion is opposite to that which can be drawn from Shuler's paper for a truncated harmonic oscillator when $\epsilon^*/kT \gg 1$.

Eyring and collaborators¹⁹ give a formal solution to a set of transport equations which is more general than that used by Kim in that molecules can be injected at any level and less general than those of Gans in that only the N + 1 level is absorbing. An explicit solution is then given for the case of equally spaced levels where only nearest neighbor transitions are allowed and the transition probability $P_{k+1,k}$ is independent of the level K (for the harmonic oscillator $P_{k+1,k}$ is proportional to K + 1). If all the molecules are initially in the lowest state, and no new molecules are injected into the system, it is found that when $\epsilon^*/kT \gg 1$ the ratio of reaction rate k (reciprocal of mean first passage time) to the equilibrium rate k_e is given by $k/k_e = 1 - e^{-\delta/kT}$, where δ is the spacing between energy levels. (It was also assumed that $\delta/2kT > 3/N + 1$ or $\epsilon^*/kT > 6$). This identical result was obtained by Montrose and Shuler for the truncated harmonic oscillator when N $\gg 1$.

Again, let all molecules be initially in the lowest level and let molecules be injected into this level at a constant rate. After sufficient time, a steady state will be set up, and the authors find that the ratio of steady state to the equilibrium reaction rate is also given by $k_{ss}/k_e = 1-e^{-\delta/kT}$.

2.1.3 SOME TREATMENTS OF NONEQUILIBRIUM REACTIVE FLOW

The methods for treatment of reactive flows in several papers are described below in the order of the completeness with which the authors consider various nonequilibrium processes.

2.1.3.1 Finite Reaction Rates Only

Lick²⁰ assumes that both rotation and vibration are in equilibrium with translation and that the approach to local thermodynamic equilibrium is governed by the dissociation and recombination rates in the reactions $O_2 + M = O + O + M$ and $N_2 + M = N + N + M$.

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A

Dissociation rates k_d are calculated by Logan's mcdification of simple collision theory²¹, in which molecules in different vibrational levels are considered separate species and the probability of dissociation by a sufficiently energetic collision is the same for all levels. Recombination rates k_r are calculated from $k_d/k_r = K_e$ where K_e is the equilibrium constant. The use of this equation is consistent with the assumption of vibrational equilibrium, but its use is not justified where vibrational equilibrium does not hold^{17,22,23}

2.1.3.2 Finite Reaction Rate Flus Vibrational Relaxation

An earlier paper of Lick's²⁴ is very similar to the above. Here, however, vibration is not assumed to be in equilibrium with translation, and the vibrational energy is calculated from the Landau Teller equation¹ for the relaxation of a set of harmonic oscillators: $dE_v/dt = \bar{E}_v - E_v/\tau$ where \bar{E}_v is the equilibrium vibrational energy at the temperature T.

2.1.3.3 Interaction of Dissociation and Vibration (First Model)

Duff and Davidson²⁵ consider the coupling between vibrational excitation and chemical reaction by adopting the following model: The O_2 molecules (or N_2) are considered to consist of two classes:

 0_2^1 - those in the ground vibrational state

 0_0^* - all those in excited vibrational states

Dissociation was assumed to take place only from excited states and the following reactions assumed to occur:

 $0_{2}^{1} + M \neq 0_{2}^{*} + M$ $N_{2}^{1} \neq M \neq N_{2}^{*} + M$ $N_{2}^{1} + M \neq N_{2}^{*} + M$ $N_{2}^{1} \neq M \neq N_{2}^{*} + M$ $N_{2}^{*} + M \neq 0 + 2 + M$ $N_{2}^{*} + M \neq 0 + 2 + M$ $N_{2}^{*} + M \neq N + N + M$ $N_{2}^{*} \neq N + N + M$ $N + N_{2}^{1} \neq N + N$ $O + N_{2}^{1} \neq N + N$

 $NO + M \neq N + O + M$

Numerous kinetic assumptions had to be made in the use of these equations.

ŝ

The O_2^* (and N_2^*) is assumed to be in equilibrium with the translational heat bath; i.e., the relative population of the excited vibrational levels are given by a Boltzmann distribution at the translational temperature. This assumption was made for convenience in calculation; it avoids the introduction of a vibrational temperature.

The necessary thermodynamic functions for the two classes of molecules are obtained by splitting the partition function of the harmonic oscillator into a part corresponding to the ground state and a part corresponding to all the excited states.

The authors are completely aware of the limitations of this model. They conclude from initial calculations made with the model that the vibrational excitation reactions had no clearly significant effects at shock strengths up to M = 15 and assumed zero vibrational relaxation times in their further calculations.

2.1.3.4 Interaction of Dissociation and Vibration (Second Model)

A more sophisticated model for the interaction of dissociation and vibration has been introduced by Hammerling, Teare, and Kivel²² and subsequently used by other authors^{4, 26}. Their method is based on the assumption that dissociations can take place from any vibrational level and that t' \circ efficiency of collision in producing dissociation from a given level is the same for all levels. The dissociation rate is then taken to be proportional to the sum over all levels of the product of the probability of being a level and the fraction of molecules having translational energy D $-E_{0}$ or greater:

1

(2.1.3-1)

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$$k_{d}(t) = \sum_{0}^{N-1} X_{n} e^{-(D_{0}-E_{n})/kT}$$

where

- $X_n =$ fraction of melecules in n'th level
- N = total number of vibrational states
- D_{o} = dissociation energy

 $E_n = energy of n'th level$

T = local heat bath temperature

To use this formula requires knowledge of the X_n under conditions of vibrational nonequilibrium. For this purpose the authors make use of the results of Montroll and Shuier²⁷, who showed that for a dilute solution of harmonic oscillators in a constant temperature heat bath, an initial Boltzmann distribution will relax to a final Boltzmann distribution through a continuous sequence of Boltzmann distributions characterized by a parameter T_{ν} , the so called "vibrational temperature." In fact, Bazley, Montroll, and Rubin²⁸ show this to be nearly true also for anharmonic oscillators with a Morse potential. They present the following equation for the ratio of instantaneous to equilibrium dissociation rate:

$$\frac{\mathbf{k}_{d}(\mathbf{t})}{(\mathbf{k}_{d})_{eq}} = \frac{1}{N} \frac{1-e}{\begin{pmatrix}\theta_{v}-\theta\\e&-1\end{pmatrix}} \frac{\theta_{v}-1}{e^{\theta}-1}$$

(2.1.3 - 2)

where

$$\theta = hc\omega / kT$$

$$\theta_{\rm v} = {\rm h} \omega_{\rm e} / {\rm k} {\rm T}_{\rm v}$$

 ω = vibration constant

 θ_{v} can be obtained from the equation for the vibrational energy relaxation of harmonic oscillators:

$$d\epsilon/dt = \frac{(\epsilon)_{eq} - \epsilon}{\tau}$$

(2.1.3-3)

where

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 ϵ = average vibrational energy per modecule

= vibrational relaxation time

and the relations

$$(\epsilon)_{eq} = hc\omega_{e}/(e^{\theta} - 1)$$
(2.1.3-4)
$$\epsilon = hc\omega_{e}/(e^{\theta} - 1)$$
(2.1.3-5)

2.1.3.5 Incorporation of Effect of Dissociation on Vibrational Energy

Dissociation does not take place at an equal rate from all levels; highly excited molecules having vibrational energies close to D_o are most easily dissociated. It is clear, therefore, that the dissociation process reduces the average energy remaining in the molecules. Treanor and Marrone²⁹ adopt the method of Hammerling, Teare, and Kivel but take this effect into account. They assume that dissociation does not appreciably perturb the Boltzmann distribution of the vibrational levels but modify the equation for relaxation of vibrational energy to include loss of energy by dissociation and gain by recombination:

$$\frac{d\epsilon}{dt} = \frac{(\epsilon)_{eq} - \epsilon}{\tau} - \frac{\left[\overline{E}\left(T, T_{v}\right) - \epsilon\right]}{\left[X\right]} \left(\frac{d\left[X\right]}{dt}\right)_{f} + \frac{\left[\overline{G}\left(T\right) - \epsilon\right]}{\left[X\right]} \left(\frac{d\left[X\right]}{dt}\right)_{r} \quad (2.1.3-6)$$

where

 $\begin{bmatrix} X \end{bmatrix} = number density of molecules \\f, r = forward (dissociation), rearward (recombination) \\\overline{E}(T, T_v) = average energy lost from vibration in a single dissociation$ $\overline{G}(T) = average energy gained by vibration in a single recombination$

From the assumptions concerning dissociation made above (Section 2.1.3.4), it can be shown that for a truncated harmonic oscillator

$$\overline{E}(T, T_{v}) = \omega \left\{ e^{\left[\frac{\omega}{k} \left(\frac{1}{T_{v}} - \frac{1}{T}\right)\right]} - 1 \right\} - N\omega \left\{ e^{\frac{N\omega}{k} \left[\frac{1}{T_{v}} - \frac{1}{T}\right]} - 1 \right\}$$
(2.1.3-7)

At equilibrium $d\epsilon / dt \rightarrow 0$, $T \rightarrow T$, $\epsilon \rightarrow (\epsilon)_{eq}$, and $(d [X]/dt)_r \rightarrow (d [X]/dt)_f$ it follows that

$$\overline{\mathbf{F}} (\mathbf{T}) = \lim_{\mathbf{V}} \overline{\mathbf{T}} \quad \overline{\mathbf{E}} (\mathbf{T}, \mathbf{T}_{\mathbf{V}})$$

$$= \frac{1}{2} (\mathbf{N} - 1) \omega$$
(2.1.3-8)

Calculations made by the authors, using the method of Hammerling, Teare, and Kivel without modification, of the temperature distribution behind a normal shock in oxygen or in nitrogen show that the vibrational temperature T_v overshoots the translational temperature T at the higher flow speeds (a similar result for O_2 was obtained in Reference 4). Incorporation of the modified vibrational relaxation equation results in higher translational and lower vibrational temperatures, completely eliminating the vibrational temperature overshoot.

2.1.4 DISCUSSION

As mentioned above, Montroll and Shuler's work on the relaxation of a system of harmonic oscillators²⁷, upon which Hammerling <u>et. al.</u> based the assumption of a Maxwell-Boltzmann distribution of vibrational levels at all times, assumes that the oscillators are contained in a large excess of inert gas that acts as a constant temperature heat bath. Although this condition holds for many shock tube studies, where the gas under investigation is mixed with a much larger amount of argon, it will not hold for the flow of air about a reentry body. Even here, however, if the temperature is not too high, the large excess of unexcited oscillators may be considered as serving as the heat bath for the small fraction of excited oscillators²⁷. Of course, the heat bath temperature is far from constant in hypersonic flows.

The essential point, however, is that Reference 27 treats relaxation only; dissociation was not included. And it can be concluded from the material of Section 2.1.2 that for anharmonic oscillators (real molecules) dissociation may deplete the population of upper levels and thus considerably perturb the Maxwell-Boltzmann distribution. The equation used for dissociation rate is based on the assumption that the efficiency of sufficiently energetic collisions in producing dissociation from a given vibrational level is the same for all levels. This assumption was made in the absence of specific knowledge of these efficiencies, but actually it is not consistent with the well-known difficulty of converting translational energy into vibrational energy³⁰. That the probability of transfer of translational energy varies inversely as the energy to be transferred is shown by the anharmonic (Morse) oscillator calculations of Heaps and Herzberg³¹, Pritchard²³, and Bauer and Cummings³².

The situation for transitions between bound states should also hold for transitions from bound states to the continuum (i. e., dissociation) and suggests that the efficiency of collisions in producing dissociation and the rate of dissociation from any but the highest levels will be insignificant. There is very little available in the way of calculations against which to check this conclusion; however, some crude calculations based on Pritchard's work²³ show that the three highest states make about equal contributions to the total dissociation rate, the contributions of others being negligible. In calculating matrix elements for the collisional perturbation potential, Pritchard uses the wave function for the highest bound state (M = 14) in lieu of the wave function for the continuum.

A much more complete and general analysis of dissociation rates from various vibration levels has been made by Herzfeld³³. He proceeds from his work on relaxation¹ and extends some results of Lennard-Jones and Strachan³⁴ and Strachan³⁵ in order to calculate matrix elements involving wave functions for the continuum. Herzfeld's final result is only formal in that there still remains to be carried out the integration of a series (finite) of complicated terms involving gamma functions of complex arguments; but he shows how approximate calculations can be made for dissociation from the ground state and from states near the top of the Morse curve. Numerical work on O₂ in Herzfeld's paper shows that only the uppermost four or five levels contribute to the dissociation rate. Although, as is evident from the above, the assumptions underlying the model of Hammerling <u>et. al.</u> may deviate considerably from reality, the model was forced to give correct results at equilibrium and hence reasonable approximations near equilibrium. This was accomplished by using it for calculating not absolute reaction rate but the ratio of dissociation rate under (vibrational) nonequilibrium to the equilibrium rate.

It would be possible to construct a somewhat more realistic model in which dissociation takes place only from a few highest levels, perhaps with the additional assumption of equal probability of dissociation from any of these levels under sufficiently energetic collisions. This would require calculation of the time history of the population of these levels as well as the time history of the total vibrational energy. These quantities could be obtained by setting up a ladder model incorporating dissociation from several upper states, calculating transition and dissociation rates from Herzfeld's work, and solving the resulting very numerous transport equations by the matrix methods of the references given in Section 2.1.3.

On the condition that the coupled vibrational-dissociational problem need be considered only for the ground electronic state (which is certainly questionable for hypersonic shock layer applications), this type of solution should be possible for simple systems such as oxygen, which has between 21 and 53 vibrational states in the ground electronic state, or nitrogen, which has between 30 and 70 vibrational states in the ground electronic state. For air, however, with the addition of between 25 and 60 vibrational states for nitric oxide (which comes to a total of between 76 and 183 vibrational states that must be accounted for) this type of solution becomes almost impossible. Considering this plus the fact that as yet there is no method available to account for vibrational interaction in reactives such as:

| NO | + | 0 | # | 0 ₂ | + | N |
|----------------|---|---|---|----------------|----|----|
| ^N 2 | + | 0 | # | NO | + | N |
| 2NO | | | # | N ₂ | +' | 02 |

leads to the conclusion that this type of solution for the air system is, indeed, at present impossible.

Subsequent to Treanor and Marrone's work²⁹, Marrone³⁷ published the development of a preferential model for vibration dissociation coupling which provides for variable probability of dissociation from different vibrational levels in the form

$$F(v) = exp - [D - \epsilon(v)]/kV$$
 (2.1.4-1)

where v denotes the vibrational level; D, the dissociation energy from the ground (v = O) level; ϵ (v), the energy of the vibrational level; k, Boltzmann's constant; and V, an arbitrary parameter. The energy levels are obtained from

$$\epsilon$$
 (v) = ω_{e} (v + 1/2) - ω_{e} X_e (v + 1/2)² + ω_{e} Y_e (v + 1/2)³ (2.1.4-2)

in which the coefficients are determined from spectroscopic data. A Boltzmann distribution is used for the vibrational level populations. Although certainly limited by this last condition as by the use of an arbitrary parameter to prescribe transition probabilities, Marrone's preferential model for coupled vibration-dissociation is the best available at present.

2.1.5 SUPERPOSITIONAL METHOD FOR INVESTIGATING VIBRATIONAL NONEQUILIBRIUM Landau and Teller²³ have shown that the Master Equation for a system of harmonic oscillators reduces to the familiar vibrational relaxation equation:

$$\frac{\mathrm{d}\epsilon_{\mathrm{v}}}{\mathrm{d}t} = \frac{1}{\tau} \left(\epsilon_{\mathrm{v}_{\infty}} - \epsilon_{\mathrm{v}}\right)$$
(2.1.5-1)

where τ denotes the relaxation time of the system; $\epsilon_{v_{\infty}}$, the equilibrium vibrational energy; and ϵ_v the vibrational energy at time t. For the harmonic oscillator

$$\epsilon_{v} = R \theta_{v} / (e^{\frac{\theta_{v}}{T_{v}}} - 1)$$
(2.1.5-2)

$$\epsilon_{v_{\infty}} = R \theta_{v} / (e^{v_{v} / T} - 1)$$
(2.1.5-3)

in which R is the universal gas constant, θ_v is the characteristic vibrational temperature; T, the kinetic or gas temperature; and T_v , the vibrational temperature. For applications in which the relaxation time and the equilibrium vibrational energy are implicit functions of time, the general solution of equation 1 is:

$$\epsilon_{\rm v} = \left[\int^{t} \frac{\epsilon_{\rm v\infty}}{\tau} \exp\left(\int^{t^*} \frac{dt^{**}}{\tau}\right) dt^* + {\rm const}\right] \exp\left[-\int^{t^*} \frac{dt^{**}}{\tau}\right] (2.1.5-4)$$

where t* and t** are dummy variables for time. Applying the boundary condition at t = 0, $\epsilon_v = \epsilon_v$ allows the integrals to be put into the definite form:

$$\epsilon_{v} = \left[\int_{0}^{t} \frac{\epsilon_{vo} - \epsilon_{vo}}{\tau} \exp\left(\int_{0}^{t} \frac{dt^{**}}{\tau}\right) dt^{*}\right] \exp\left(-\int_{0}^{t} \frac{dt^{*}}{\tau}\right) + \epsilon_{vo} \qquad (2.1.5-5)$$

For steady flow the distance along a streamline, s, and the ordered velocity, V, are related by

$$\frac{ds}{dt} = V$$
 (2.1.5-6)

so that the integrals in Equation 2.1.5-6 may be transformed into:

$$\epsilon_{\mathbf{v}} = \left[\int_{0}^{\mathbf{s}} \frac{\epsilon_{\mathbf{v}_{\infty}} - \epsilon_{\mathbf{v}_{\infty}}}{\mathbf{v}_{\tau}} \exp\left(\int_{0}^{\mathbf{s}^{*}} \frac{\mathrm{d}\mathbf{s}^{**}}{\mathbf{v}_{\tau}}\right) \mathrm{d}\mathbf{s}^{*}\right] \exp\left(-\int_{0}^{\mathbf{s}} \frac{\mathrm{d}\mathbf{s}^{*}}{\mathbf{v}_{\tau}}\right) + \epsilon_{\mathbf{v}_{0}} \quad (2.1.5-7)$$

Using Equations 2.1.5-2 and 2.1.5-3 the vibrational energy may be rewritten as:

$$\frac{\epsilon_{v}}{R\theta_{v}} = \left\{ \int_{0}^{S} \frac{1}{v\tau} \left[\frac{1}{\exp\left(\frac{\theta_{v}}{T}\right) - 1} - \frac{1}{\exp\left(\frac{\theta_{v}}{T}\right) - 1} \right] \exp\left(\int_{0}^{S^{*}} \frac{\mathrm{d}s^{**}}{v\tau}\right) \right\} \exp\left(-\int_{0}^{S} \frac{\mathrm{d}s^{*}}{v\tau}\right) + \frac{1}{\exp\left(\frac{\theta_{v}}{T_{v0}}\right) - 1} \qquad (2.1.5-8)$$

and the local vibrational temperature along the streamline is given by

$$T_{v} = \theta_{v} / \ln \left(1 + R \theta_{v} / \epsilon_{v} \right)$$

$$(2.1.5-9)$$

By superimposing the solution of Equations 2.1.5-8 and 2.1.5-9 over the thermal equilibrium calcu¹ations presented in the first quarter report, the relative importance of the vibrational nonequilibrium problem can be assessed.

2.2 FUTURE FLOW FIELD WORK

3

The literature survey will be completed and presented in the third quarter report.

The results of the superimposed vibrational nonequilibrium calculations obtained by the method described above and a critique on the relative importance of this problem will be included in the third quarter report.

Shock layer stagnation line profiles from the coupled influscid-boundary layer chemical nonequilibrium solution as well as any nonequilibrium boundary layer results which may be available will be reported at the end of the third quarter.

1

SECTION 3

REENTRY EFFECTS ON ANTENNA BREAKDOWN

The subject of this section is the effects of reentry on voltage breakdown of antennas, with emphasis on the reentry environment associated with slender cone bodies at hypersonic speeds. The discussion will depend entirely on ideas and data taken from written reports and verbal communications with a number of researchers in the field, in the manner of a survey of present knowledge.

For conical vehicle re-entry, three distinct flow field regions may be important in antenna breakdown: the ambient free stream, the inviscid shock layer, and the boundary layer. With the exception of relatively high altitudes where these regions are not necessarily distinct, the reentry environmental effects on breakdown will be different for each of the three regions. In fact, most workers assume that a convenient separation can be made such that the effects of each region can be treated independently. At any rate, the different basic processes which control breakdown can be identified for each of the three flow field regions, for example, as done by Reilly³⁹ and numerous other authors.

The free stream ahead of the shock layer is characterized essentially only by the fact that the air is moving relative to the transmitting antenna. The effects of altitude on the state or composition of the ambient air probably are not significant in breakdown; and even if they were, it would be a relatively simple task to account for them. Hence, the only important effect in the free stream is convection.

The inviscid flow region is characterized by a state of elevated temperature and increased particle number density rolative to the free stream. On a slender conical vehicle, ionization is probably insignificant in this region, but the detailed thermodynamic state and chemical composition of the shock heated air may be quite important. At any rate, the effects of the inviscid flow region are felt in terms of convection, increased air density, and elevated temperature.

The boundary layer is characterized by even higher temperatures produced by viscous dissipation. The presence of significant levels of thermal ionization is thus probable. Particle number density and convection are not now so easy to generalize because of the strong gradients of these quantities which exist here. In addition, the presence of chemical contamination of the air by products of ablation will be important. Thus, convection, sumber density, temperature, ionization, and chemical additives, all in the context of strong gradients, must be considered in the boundary layer.

3.1 CONVECTION EFFECTS

The period of time in which a given volume element of air comes under the influence of the field of an antenna mounted on a reentry body is on the order of other characteristic times for breakdown. Hence, convective effects on antenna breakdown are important during reentry.

Two methods of treating convection appear in the literature of reentry breakdown. One approach, used by Reilly ³⁹, Chown⁴⁰, and Margenau⁴¹, solves the problem in the same way as that used in the pulse breakdown analysis of Gould and Roberts⁴². A particle in the frame of reference of the gas is subject to the high field region of the antenna for a finite time τ .

$$\tau = L/v \tag{3.1-1}$$

where v is the velocity and L is the length of the high field region parallel to the velocity vector of the flow. This has the effect of adding a term v_v to the equation for the ionization frequency.

$$v_{\rm v} = \frac{1}{\tau} \ln \left(n_{\rm c} / n_{\rm o} \right)$$
 (3.1-2)

where n_c is the critical electron density and n_o is the initial electron density. The effect of this added term is to increase the ionization frequency required for breakdown and hence to raise the breakdown field above that required for breakdown in the absence of convection.

The second method of analyzing convection effects, used by Romig⁴³, Fante⁴⁴, and Covert⁴⁵, is based on a generalized treatment of the electron continuity equation:

$$\nabla \cdot \Gamma + \frac{\partial n}{\partial t} = \frac{dn}{dt}$$
(3.1-3)

where Γ is the electron flux vector, n is the electron density, and t is time. The electron flux is written in terms of both diffusion and convection.

$$\Gamma = nv - \nabla D n$$

where D is the diffusion coefficient. Under the assumption of incompressible flow, the continuity equation becomes

$$\nabla^2 Dn - v \cdot \nabla n + \gamma n = \frac{\partial n}{\partial t}$$
(3.1-5)

where v is the net ionization frequency. For the case of constant D, an approximate solution has been obtained by Chown⁴⁶ using an effective diffusion length Λ .

$$\frac{1}{\Lambda^2} = \frac{1}{\Lambda_0^2} + \left(\frac{v}{2D}\right)^2$$
(3.1-6)

where Λ_0 is the characteristic diffusion length in the absence of flow. (It should be pointed out that the latter result is equivalent to the results of more rigorous analyses by Romig⁴³. Fante⁴⁴, and Covert⁴⁵.) The additional term in the equation for the breakdown ionization frequency is now of the form

 $v_v = \frac{v^2}{4D}$

(3.1-7)

3.2 GAS DENSITY EFFECTS

In voltage breakdown experiments under standard laboratory conditions, the practice is to express the state of the gas being tested in terms of pressure, since this is a directly measurable quantity. However, pressures in the reentry induced shock layer are often orders of magnitude higher than in the free stream. Also, because of increased gas temperature, shock layer density is not generally the same as in the free stream. MacDonald⁴⁷ has noted that the physically important parameter for breakdown is the gas density rather than pressure, since it is the number of gas particles per unit volume which determines the rates for all the processes which control breakdown. Thus the use of either the free stream pressure or the shock layer pressure in predicting breakdown at a given altitude would give erroneous results. The distribution of gas density in the high field intensity region is the correct determining factor.

In order to give a quantity which is commensurable with the classically used parameter of pressure, most authors define a reduced pressure p* Reilly³⁹ defines the reduced pressure in terms of the gas number density N in particles per cubic centimeter.

$$p^* = \frac{N}{3.5 \times 10^{16}} \text{ torr}$$
(3.2-1)

Light and Taylor⁴⁸ define the reduced pressure in an equivalent way in terms of temperature T in $^{\circ}$ K:

$$p^* = \frac{273}{T}p$$
 (3.2-2)

where p is the local pressure. These corrections have the effect of shifting the curve of breakdown field versus altitude about 30,000 feet higher in altitude at velocities of the order of 22,000 ft/sec, according to MacDonald⁴⁷.

These effects have been observed in reentry flight experiments. Bisbing⁴⁹ showed that the observed period of breakdown of a slot antenna on a conical vehicle agreed with laboratory data in cold air when the air density corresponding to the inviscid flow region was used as the independent variable. Also, Nanevicz⁵⁰ showed that when the VHF breakdown data from Nike-Cajun flights is corrected for local density, it agrees roughly with laboratory measurements in cold air.

3.3 HIGH TEMPERATURE EFFECTS

The effects of elevated gas temperature on voltage breakdown have been investigated in terms of dc breakdown at a relatively early date⁵¹. It was found that up to temperatures of 1400° K no deviation from cold gas results could be observed⁵². The investigation of this phenomenon by the use of a shock tube in order to produce higher temperatures was carried out by Sharbaugh <u>et. al.</u> for nitrogen⁵³. These investigators found that significant departures from cold gas value. Their analysis of this effect was based on a theory⁵⁴ of space-charge alteration of the field by ionization in the shock tube, although certain anomalies were present, which they ascribed to ionization relaxation in the shock tube. The same investigators carried out further experiments in both nitrogen and air, in which the electron density was also measured⁵⁵. These data showed an apparent correlation between the reduction in breakdown voltage and the electron density.

Notwithstanding the fact that dc breakdown is affected by surface phenomena and spacecharge effects, it may be that the above results provide an indication of effects of temperature on basic processes of gaseous breakdown. In fact, it is apparent that they are in qualitative agreement with more recent work on effects of high gas temperature on microwave breakdown^{56,57,48}. Light and Taylor⁴⁸ have attempted to explain the lowering of the breakdown field at high temperatures in terms of the effect of vibrationally excited states of oxygen. In their analysis of the data, they postulated that the curve of ionization frequency versus field strength is shifted to lower field strength values by the mechanisms associated with electron heating. The mechanism which they use to explain the data is inelastic collisions between electrons and oxygen molecules. When the oxygen is vibrationally excited in high temperature air, the electrons are more easily heated by the electric field due to the lack of important electron energy transfer to ground state molecules. A formula for this effect is postulated as follows.

$$\frac{v_i}{p^*} = F\left[\frac{\eta(T_o)}{\eta(T, p^*)} \left(\frac{E_e}{p^*}\right)^2\right]$$
(3.3-1)

where v_i is the net ionization frequency, p* is reduced pressure, T is temperature, T_o is 273^oK, and E_e is effective field. The effect of oxygen excitation is placed in the form

$$\frac{\eta (\mathbf{T}, \mathbf{p}^*)}{\eta (\mathbf{T}_0)} = \left(1 - e^{-\frac{\Delta}{\mathbf{k}\mathbf{T}}}\right) \frac{\mathbf{X} (\mathbf{T}, \mathbf{p}^*)}{\mathbf{X} (\mathbf{T}_0)}$$
(3.3-2)

where Δ is the minimum energy required to excite a vibrational state (0.2 ev for oxygen), k is Boltzmann's constant, and X is the mole fraction of oxygen molecules.

The equations of Light and Taylor predict that the amount of molecular oxygen prese..t would have a strong effect on the ionization frequency as a function of gas temperature. However Thompson⁵⁷, in an arc channel experiment, observed no apparent difference between pure nitrogen and mixtures of nitrogen and oxygen. This result would tend to place the hypothesis of Light and Taylor in doubt, except that the arc channel experiment is probably more sensitive to influences from other phenomena. At any rate, the hypothesis that oxygen excitation alone is important is an obvict s oversimplification in that the absence of oxygen would certainly require some other mechanism of electron energy transfer to dominate. Note also that in the equation of Light and Taylor oxygen dissociation has a much greater effect in terms of temperature than does excitation, since dissociation itself is a strong function of temperature. Aside from the effects of ionization, which are discussed elsewhere, various authors have identified other possibly important effects of high temperature on breakdown. Reilly³⁹ suggests that molecular excitation promotes ionization by effectively lowering the energy required to ionize the molecule. Epstein⁵⁸ suggests that the gas composition is important in terms of the presence of nitric oxide, which ionizes more readily than cold air. Epstein also notes that attachment and detachment rates increase with increasing air temperature.

3.4 IONIZATION EFFECTS

A significant amount of thermal ionization is known to exist in the shock-heated air surrounding a reentry vehicle⁵⁹. The resulting high initial electron density n_0 which exists before the electric field is turned on may influence the rates of several of the electron production/ loss mechanisms. The following discussion explores three possible changes in the breakdown process due to high initial electron density as considered in the literature.

The first and probably most important effect of large electron densities is to change diffusion from a free to an ambipolar process. That is, with the buildup of a sizable electron space charge, the electron and molecular diffusion processes become inextricably linked. The result is to slow down the diffusion of electrons to the molecular rate and thereby correspondingly reduce diffusion as an electron loss mechanism (lowering the breakdown field). Allis and Rose⁶⁰ have indicated that the transition from free to ambipolar diffusion begins where the Debye length becomes comparable to the diffusion length. If we make the approximation that the diffusion length is approximately half the applied wavelength, then we must consider ambipolar diffusion for electron densities greater than about 10⁶ electrons/cm³ for signal frequencies on the order of 100 megahertz. Such electron densities clearly occur throughout reentry in at least some part of the flow field⁵⁹ and therefore require some modification of the diffusion coefficient. Whitmer and MacDonald⁶¹ have indicated that the free diffusion coefficient D is related to the ambipolar diffusion coefficient D_g by the equation D_g = $2 D \mu_{+}/\mu_{-}$ where μ_{\perp} and μ_{\perp} are the mobilities of ions and electrons respectively. They show from measurements of mobilities that the ratio D/D_a is approximately 40 in air. Now, using MacDonald's 47 expression for free diffusion in terms of the effective applied field,

 $DP = (29 + 0.9 E_e/P) 10^4$ torr cm²/sec, approximate values for purely free or purely ambipolar diffusion may be had. Chown et. al. ⁴⁰ suggest that the highly nonuniform electron density in the flow field of a reentering vehicle makes it extremely difficult to determine whether diffusion will be free or ambipolar or essentially a combination of the two. In addition, the fact that the transition from free to ambipolar diffusion may take place over several orders of magnitude change in electron density⁶⁰ makes it desirable to define an effective diffusion coefficient D_e which will take into account both processes. Bachynski et. al. ⁶² have defined such an effective diffusion coefficient $D_e = D_a [1 + \mu_- (N-n)/(\mu_+N + \mu_-n)]$ (where N and n are the ion and electron number densities respectively) which can easily be established from the flow field properties.

The second effect of high initial electron densities N_0 is to shorten the time required to reach critical electron density $(n = 1.24 \times 10^{-8} f^2)$, where f is the signal frequency) and considerably reduce the breakdown field strength. For vhf signals on the order of 100 megahertz, the critical density is about 10^8 electrons/cm³, which may easily occur purely from thermal generation during parts of a hypersonic flight⁵⁹. Chown et. al.⁴⁰ state that although the details of propagation in such an overdense plasma are not well understood, there is experimental evidence to suggest that once the electric field is turned on the plasma will grow in thickness such that the fields penetrating beyond it are just below the levels required to maintain the discharge under the existing local conditions of pressure, frequency, etc. In determining the practibility of ECM system designs, then, it will be important to establish over what portion of the trajectory it can be expected that the transmission will be thermally blacked out (independent of field strength) and just how much the propagated signal will be degraded by the overdense plasma.

Finally, we would like to consider the effect of high electron density on the recombination loss rate. Chown <u>et.</u> <u>al.</u> 40 remark that there is considerable uncertainty as to the lower limit of electron density above which recombination is important, especially in high-temperature air. They note that predictions have ranged anywhere from 10^9 to 10^{12} electrons/cm³ and above.

Reilly³⁹ considers the dissociative and the two body electron-ion recombination rates as reported by Brown⁶⁵, Massey and Burhop⁶³ over a sange of electron densities from 10^6 to 10^{12} /cm at NTP. He shows that the two-body dissociative recombination rate remains several orders of magnitude below the rate of two-body attachment for electron densities ranging up to 10^{12} /cm³, and therefore two-body recombination can be considered negligible at NTP. (For electron densities greater than 10^{12} /cm³, thermal blackout will be the predominant effect.) He likewise concluder that since the three-body rate of recombination and attachment are an order of magnitude slower than two-body recombination at NTP, they can be safely ignored. For high-temperature air, Reilly quotes the results of Lin and Tear⁶⁴, giving two-body recombination a T $_{e}^{-3/2}$ dependence, and the work of Massey and Burhop⁶³, which shows a $T_{e}^{-5/2}$ dependence for the three-body rate. Assuming these inverse temperature dependencies, he concludes that two-body attachment dominates both two- and three-body recombination for electron energies above 1 ev and electron densities below 10^{12} /cm³ 39.

3.5 EFFECTS OF CHEMICAL ADDITIVES

The effects of chemical additives in the boundary layer are important because of the natural effects of ablation as well as in terms of artificial breakdown alleviation techniques. In fact, most of the work done on this subject appears to be motivated by the search for alleviation / methods.

Thompson⁶⁷ has measured the effects of CO, CF_4 , and SF_6 on electron density and antenna breakdown in an arc channel. The first two of these materials are products of ablation for carbon and Teflon heat shields, respectively; and the last is a popular electrophilic quenchant candidate. Twenty percent by volume of each of these materials was added to the flow, and experiments were conducted at temperatures between 3000° and 5000° K. Carbon monoxide was found to have no effect on either electron density or breakdown. CF_4 reduced the electron density by a factor of 2 to 3 and increased the breakdown power by a factor of 3. SF_6 reduced the electron density by more than a factor of 3 and increased the breakdown power by a factor of 2. The authors attribute the breakdown alleviation by the fluorides to the additional electron attachment provided by fluorine and fluoride radicals. Space Sciences, Inc. of Waltham, Massachusetts, has been conducting analytical and experimental studies on alleviation of plasma sheath and antenna breakdown effects. They have been evaluating materials for the ability to reduce electron concentration and to increase breakdown power level in thermal plasmas. The primary alleviation mechanism studied is attachment of electrons by electronegative gases. The plasma simulation facility used in these studies is an argon arc jet. Conditions simulated include atmospheric pressure down to 13 torr and temperatures of 3000° K to 5000° K. Diagnostics are conducted by means of K-band transmission through the test section. Additives tested include SF₆, BF₃, N₂, Freon 116, air, and argon.

Space Sciences has concluded that materials which are good attachers in glow discharges often do not work in thermal plasmas because of dissociation. A figure of merit for attachers would appear to depend on the molecular weight, the electron attachment cross section (including its energy dependence), and the resistance to thermal dissociation. Highly electron negative materials have higher attachment cross sections in the molecular form than in the atomic form. Survival lifetimes of molecular additives in thermal plasmas are thus important in determining their effectiveness as plasma alleviative substances.

The ideal additive material for alleviation of both ionization and breakdown is pictured by Space Sciences as one made up of "giant molecules," which would actually be extremely small solid particles or liquid drops. These particles would have maximum survival times as well as providing surface recombination as a mechanism for electron removal. Refractory solids would have to be avoided because of thermionic emission and Saka-) angmuir ionization.

MIT Aerophysics Laboratory has been conducting experiments in a wind tunnel under the direction of E.E. Covert⁴⁵. In this experiment a supersonic arc jet is blown over the nose

of a cone model in a Mach 4 wind tunnel. Breakdown of an X-band slot on the cone was determined under conditions of injection of SF_6 . They have observed that the electron density was reduced by an order of magnitude, but that the breakdown was unaffected unless the additive was injected immediately in front of the antenna. Good results were also obtained with Teflon products.

3.6 EFFECTS OF GRADIENTS

As noted above, the boundary layer surrounding a slender cone vehicle in hypersonic flight has strong gradients of density, temperature, velocity, and electron density. In addition, the entire flow field is highly nonuniform, with large changes in properties in passing from one region to another. Thus the importance of these nonuniformities must be evaluated before the breakdown analysis can be simplified.

Fante⁴⁴ has analyzed the situation of nonuniform media in terms of two problems. In the first problem he treated the effect of an ambipolar diffusion layer and an outer free diffusion layer covering an aperture antenna. The results of this calculation show that even a small ambipolar diffusion layer can drastically reduce the breakdown field strength. The second problem considered is that of a hemispherical region in which the field, and hence the ionization frequency, is zero outside of an inner hemisphere. Although both of these problems illustrate the importance of considering nonuniform conditions, they were both done using locally homogeneous media in the analysis. Nevertheless, Fante points out how to solve the more general problem in terms of a generalized electron continuity equation,

$$\frac{\partial \mathbf{n}}{\partial t} = \nabla \cdot (\nabla \mathbf{D}_{\mathbf{n}} - \mathbf{n} \nabla) + (\nabla_{\mathbf{i}} - \nabla_{\mathbf{a}}) \mathbf{n}$$
(3.6-1)

where n is the electron density, D is the diffusion coefficient, V is the velocity vector, v_i is the ionization frequency, and v_a is the attachment frequency.

In general, it can be seen from the effects of reentry that several factors contribute to spatial nonuniformity of different terms in the continuity equation. The flow velocity is obviously nonuniform in space as determined by the flow field properties. The diffusion coefficient will have gradients due to particle number density gradients and ionization gradients (transition to ambipolar diffusion in high electron density regions). If the effective field is included in the formula for the diffusion coefficient, gradients will also be due to field nonuniformity. The frequencies of ionization and attachment have spatial gradients contributed by variations in particle number density, field intensity, and also air temperature. Profiles of chemical additives which are distributed in the flow field would conceivably contribute to gradients in both the diffusion coefficient (molecular weight effect) and the ionization and attachment frequencies. Finally, the ionization gradients would affect pulse breakdown in terms of the spatial variation of initial electron density, although this effect is probably not very important.

SECTION 4

METHODS OF ANALYSIS OF BREAKDOWN

Generally speaking there are two methods of analysis which can be used to predict antenna breakdown: the kinetic theory method and the phenomenological theory. In the kinetic theory approach an attempt is made to solve the Boltzmann equation for the electron distribution function, using data on collision cross section.

The phenomenological method of predicting breakdown has been widely used by various authors in classical breakdown theory. Essentially this method is a collection of extrapolation formulas based on the best fit of reasonable phenomenological ideas to existing basic data. This method starts with the electron continuity equation, which can be derived from the Boltzmann equation. The various terms in this equation are then treated as simple functions of the proper variables of the problem, and experimental data are used to determine the arbitrary constants in these equations.

The question of which approach is best suited for predicting the effects of reentry on antenna breakdown is very important. Some subsidiary issues need to be settled before this question can be answered. The following are important questions:

- a. Is there some essential feature of reentry effects on breakdown that will make the phenomenological analysis impossible to apply?
- b. What makes the kinetic theory approach disfavored in the classical theory and will this factor work against it in the reentry case?

Most investigators of xeentry effects have tried to analyze the situation by extending the phenomenological theory. No essential difficulty has yet been encountered except for lack of basic data. A possible difficulty is that the number of new effects may be too great to use this approach; however, the same difficulty would have a much worse effect on the practicality of the kinetic theory method. The reason the kinetic theory approach is not favored classically is that closed form solutions have been obtained only in very simple cases where the electron collision frequency is a simple function of velocity. However, Carleton and Megill⁶⁶ have successfully coded the Boltzmann equation for solution by a digital computer for the case of a weakly ionized air without ionization, attachment, or recombination reactions. Thus the kinetic theory is a useful approach when colligion cross-section data are available and a numerical solution using a digital computer is desirable.

M. Epstein and C. J. Lenander of Aerospace Corporation have adapted the program of Carleton and Megill to the solution of the Boltzmann equation in the breakdown problem. The program includes the effects on the electron distribution function of elastic collisions with nitrogen and oxygen molecules and inelastic collisions including rotational, vibrational, and electronic excitation. It requires 30 seconds to 1 minute on a CPC computer, per case. The solution of the diffusion equation by a variational method is an important part of the calculation. If the effects of the effective field concept are included in the uncertainty, the predicted breakdown conditions are within the scatter of MacDonald's data at all pressures, although the predictions do not agree with generally accepted phenomenological theory at low pressures (below 10 torr). All work so far has been applicable to cold air breakdown. It remains to be seen whether this program will give good predictions of re-entry effects.

SECTION 5

CONCLUSION

Most of the effects of the reentry environment on voltage breakdown of antennas are fairly well understood, and theoretical models exist in the literature for practically all these phenomena. One important exception, in which the effect is not sufficiently well understood, is in the area of high gas temperature. Basic data have been obtained recently on this effect, and an interpretation has been made in terms of the effects of molecular vibrational excitation on the ionization frequency. This explanation is fundamentally contingent on the effect of the presence of excited vibrational states of the gas particles on the rate of electron heating in the electric field.

In view of the apparent role of molecular excitation in the effect of high gas temperature on antenna breakdown, the problem of predicting the excitation levels for various flow field constituents becomes very important. Not only would the nonequilibrium vibrational excitation of flow field gases be an important part of the prediction of breakdown, but also the interpretation of experimental data on high temperature breakdown would hinge on a specification of the vibrational state of the test gas. Thus the solution of the problem of vibrational excitation is important in deriving theoretical models from experimental data as well as in applying such models to reentry breakdown predictions, although dissociation may be more important than vibration in terms of temperature effect on breakdown.

Based on an extensive, but as yet incomplete, literature survey on the effects of vibrational nonequilibrium in shock layer applications, the following provisional conclusions may be drawn:

a. An analysis on a microscopic scale which would provide the nonequilibrium distributions of vibrational energy level populations during the simultaneous relaxation of vibration and discociation is, at present, not possible for the air system.

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b. On the condition that the vibrational energy levels are populated according to a continuous sequence of Boltzmann distributions, a macroscopic analysis which offers an approximate solution to the coupled vibration-dissociation-recombination relaxation problem is possible for the air system and is, in fact, available.

SECTION 6

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voltage breakdown characteristics of antennas. Most of the important effects are fairly well understood in that theoretical models exist and experimental data are available in sufficient quantity to allow predictions to be made with confidence. However, the effect of high gas temperature is not sufficiently understood, although recent experimental data have indicated a mechanism which may prove to be important in controlling breakdown. This mechanism is strongly dependent on vibrational excitation and dissociation of the gas molecules. The problem of predicting the vibrational excitation state in a hypersonic flow field is not presently possible in a detailed microscopic analysis, but an approximate solution is possible.

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