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ON THE THERMAL ENERGY TRANSFER BETWE FREE ELECTRONS AND MOLECULAR VIBRATION*

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ABSTRACT

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Thermally averaged probabilities for the electron de-excitation of the first vibrational level in N_2 are calculated from the discrete velocity-dependent collision cross-sections measured by other workers. The results are presented for the electron temperature range 1000° to 5000°K. Over this range the probability is found to have an empirical temperature dependence of the form $AT^{-1.8}\exp(T^{1/3})$, with $A = 1.58 \times 10^{-3}$. The probability increases from 10^{-4} at 1000°K to 10^{-2} at 5000°K. By comparison, the corresponding experimental probabilities for the de-excitation of N_2 vibration by nitrogen molecules are 10^{-8} at 1000°K and 3×10^{-4} at 5000°K. These figures imply that in some circumstances an electron concentration of only 1 in 3×10^6 could halve the normal nitrogen molecular relaxation time at 1000°K, and that a concentration of 1 in 6×10^3 could do so at 5000°K. Existing spectrum-line reversal measurements of N_2 vibrational relaxation carried out in nozzle-expansion flows in the presence of small amounts of easily ionized Na and Cr atoms are reviewed in the light of these findings. It is shown that the electron concentrations in these experiments were too low to have significantly influenced the relaxation measurements.

Author

The relative rates of degradation of electron kinetic energy to the translational, rotational and vibrational modes of N_2 are considered on the basis of the above calculations. From these considerations it is proposed that in many nonequilibrium molecular systems the kinetic electron temperature will be closely coupled to the vibrational temperature of the molecules. Some results of current expansion-flow experiments which support this proposed coupling process are briefly mentioned, and its possible importance in relation to the extent of chemical and ionization nonequilibrium in other expansion flows of shock-heated air in hypersonic nozzles and around re-entry vehicles is discussed. It is suggested that free electrons, although present perhaps in small quantities, could be important in energy-degradation processes in these systems. Other existing observations in N_2 plasmas which appear to support the proposed coupling mechanism are reviewed.

1. INTRODUCTION

The possible influence of free electrons on molecular vibration in thermal systems has apparently received little consideration, possibly because the effect of a light and unaccelerated electron on the motion of relatively massive nucleii would be expected to be very slight. Thus, unlike the very efficient processes of electronic excitation and ionization by electrons, the probability of vibrational excitation by these particles would be expected to be very small. However, recent studies of the energy transfer between a beam of

essentially mono-energetic electrons and various diatomic molecules by Schulz[1,2] and by Schulz and Dowell[3] reveal that large inelastic cross sections exist at much lower electron energies than those corresponding to the excitation of electronic states in these molecules. For example, for nitrogen[1,2] the total inelastic cross-section peaks at a value of $5.5 \times 10^{-16} cm^2$ at an energy of 2.3 eV, for carbon monoxide[1] the peak occurs at 1.7 eV, and for oxygen[3] the peak occurs with little or no activation energy. Schulz[2,3] has convincingly shown that the energy transfer process involved is the vibrational excitation of these molecules, occurring probably by way of a negative-ion state.

These cross sections for electron excitation of vibration are many orders of magnitude greater than those for direct vibrational excitation by way of the normal transfer of translational to vibrational energy between molecules. The measurements of Schulz[1,2] and Englehardt, Phelps and Risk[4] show that the cross section for de-excitation of the first vibrational level in N_2 by electrons rises from a value of $4 \times 10^{-19} cm^2$ at electron energies of 0.5 eV to a near-constant value of about $6 \times 10^{-17} cm^2$ at energies between 2 to 4 eV, and falls to about $10^{-19} cm^2$ again at 5 eV. By comparison, the corresponding theoretical values for de-excitation by nitrogen molecules are about $10^{-23} cm^2$ at a kinetic energy of 0.5 eV, $10^{-18} cm^2$ at 2 eV, and $3 \times 10^{-17} cm^2$ at 4 eV. These differences in the cross sections may be expected to produce an even more pronounced difference in thermally averaged cross sections, since the thermal energies of the vast majority of particles are well below 1 eV even for temperatures

as high as 5000°K. The contrast will be further enhanced since the gas-kinetic collision frequency for electron-molecule collisions is two orders greater than that for molecule-molecule collisions.

It is thus pertinent to consider to what extent the rate of relaxation of molecular vibrational energy may be effected by the presence of small amounts of ionization. The effect would be expected to be greatest for a gas such as nitrogen, which has a normally long relaxation time and an apparently large probability for electron de-excitation. Accordingly, a simple method for evaluating the thermally averaged transition probabilities for the de-excitation of the first vibrational level in N_2 by nitrogen molecules or electrons is presented in Sec. 2 of this paper. The probabilities for de-excitation by nitrogen molecules are first calculated using this method and these are shown to be in agreement with existing experimental data. Probabilities for N_2 vibrational de-excitation by electrons are then calculated and presented for the temperature range 1000° to 5000°K. The probability is found to increase from 1.4×10^{-4} at 1000°K to 9.6×10^{-3} at 5000°K. The probability for de-excitation by nitrogen molecules is considerably lower, as anticipated, and varies from 8×10^{-9} at 1000°K to 3×10^{-4} at 5000°K. Allowing for the higher electron collision frequency, these figures imply that in some circumstances an electron concentration of only 1 in 3×10^{6} could halve the normal N_2 relaxation time at 1000°K, and that a concentration of 1 in 6×10^{3} could do so at 5000°K.

The interpretation of existing spectrum-line reversal measure-

ments of N_2 vibrational relaxation in nozzle-expansion flows containing small amounts of easily ionized metal additives is examined on the basis of these calculations. It is shown in Sec. 3 that the interpretations are not affected by the more rapid predicted relaxation in the presence of electrons, since the levels of ionization in these experiments were sufficiently low to make the maximum possible electron influence insignificant.

The effect of the large vibrational-transfer probability on the electron temperature in a nonequilibrium system is examined in Sec. 4. From considerations of the interchange of electron kinetic energy with the translational, rotational and vibrational modes of nitrogen molecules, it is thus proposed that the kinetic electron temperature will be kept in close equilibrium with the vibrational temperature of the molecules in simple nonequilibrium systems. Some initial results of current spectrum-line reversal temperature measurements in Ar and Ar/N_2 expansion flows which support this conclusion are briefly mentioned.

Possible consequences of this proposed coupling between the electron-kinetic and molecular-vibrational temperature are then discussed in relation to the nonequilibrium properties of supersonic-expansion flows of air in hypersonic nozzles and around re-entry vehicles. It is suggested that the coupling could reduce the extent of chemical and ionization nonequilibrium in these expansion flows. Existing phenomena observed in N_2 plasmas are reviewed as possible evidence for the proposed coupling scheme, and its possible influence

in other similar environments is considered.

2. THERMALLY AVERAGED TRANSITION PROBABILITIES

2.1 Relaxation Theory

The Landau-Teller theory of vibrational relaxation, as formulated by Montroll and Schuler[5], shows that the over-all rate of collisional excitation of molecular vibration may be characterized by the rate at which the first excited vibrational level acquires energy from the translational modes of the colliding partners. This feature enables the expression for the relaxation of a harmonic oscillator to be written as

$$E_{T_v}(t) = E_T - \left[E_T - E_{T_v}(0)\right] \exp\left(-t/\tau\right), \qquad (1)$$

where $E_{T_v}(t)$ is the vibrational energy of the oscillator at the local vibrational temperature T_v, E_T is the energy which the oscillator would have at the local translational temperature T, and $E_{T_v}(0)$ is the vibrational energy at time $t = 0$. τ is the vibrational relaxation time for the collision process concerned and may be written as

$$\tau\left[1 - \exp\left(-\theta/T\right)\right] = \left[Z < P_{10}(T) >\right]^{-1}, \qquad (2)$$

where θ is the characteristic temperature of the oscillator, Z is the gas-kinetic collision frequency for momentum transfer, and $< P_{10}(T) >$ is the thermally averaged probability that a vibrational quantum will be transferred from the first excited vibrational level to the translational

modes of the colliding partners during a collision. As indicated, $\langle P_{10}(T) \rangle$ is a function of the translational temperature of these partners.

In general, the average probability of vibrational energy transfer per collision is obtained by integrating the effective frequency of collisions resulting in energy transfer over all values of the relative kinetic energy of the colliding partners, and dividing by the total collision frequency. Thus,

$$\langle P_{10}(T) \rangle = \int_0^\infty P_{10}(\varepsilon)\, d[\bar{z}(\varepsilon)] \Big/ \int_0^\infty d[z(\varepsilon)] \quad , \tag{3}$$

where $P_{10}(\varepsilon)$ is the discrete transition probability, or the probability that a vibrational quantum will be transferred on collision between two particles having a relative kinetic energy ε , and $d[\bar{z}(\varepsilon)]$ is the frequency of molecular collisions having the energy ε ; the denominator is thus $\bar{z}$. From kinetic theory, the value of $d[\bar{z}(\varepsilon)]$ is given by

$$d[\bar{z}(\varepsilon)] = [x]\, Q_k \left(8\tilde{\pi} k T/\tilde{m}\right)^{1/2} \varepsilon\, (kT)^{-2} \exp\left(-\varepsilon/kT\right) d\varepsilon \quad , \tag{4}$$

where $[x]$ is the concentration of the de-exciting partners, which have a kinetic temperature T , Q_k is the elastic cross section, $\tilde{m}$ is the reduced mass of the colliding pair, and k is Boltzmann's constant. Since

$$\bar{z} = [x]\, Q_k \left(8\tilde{\pi} k T/\tilde{m}\right)^{1/2} \quad , \tag{5}$$

we thus write

$$\langle P_{10}(T)\rangle = (kT)^{-2} \int_0^\infty P_{10}(\varepsilon)\, \varepsilon \exp(-\varepsilon/kT)\, d\varepsilon \,. \qquad (6)$$

The value of $P_{10}(\varepsilon)$ for electrons is not available in closed form, so that in the present work the integral in Eq. (6) is evaluated by the approximate method outlined in the next two sections. Values of $\langle P_{10}(T)\rangle$ for de-excitation by nitrogen molecules are first calculated using this method, and compared with existing calculated and measured values.

2.2 Discrete Transition Probabilities

The discrete probabilities $P_{10}(\varepsilon)$ for the de-excitation of the first excited vibrational level in N_2 by electrons and by nitrogen molecules are plotted as a function of the relative kinetic energy ε of the colliding particles in Fig. 1.

Values of $P_{10}(\varepsilon)$ for N_2 de-excitation are taken from the theory of Rapp and Sharp,[6] who plot $P_{10}(\varepsilon)$ versus (molecular velocity)^2. The upper energy of 5 eV considered here is below the corresponding velocity at which Rapp and Sharp find deviations between their discrete probabilities and those calculated by the usual perturbation methods.

The values of $P_{10}(\varepsilon)$ for electron de-excitation are taken from Schulz[1,2] and Englehardt, Phelps and Risk.[4] They are derived by detailed balancing from measured values of the cross section $Q_{01}(\varepsilon)$ for excitation of the first vibrational level in N_2, obtained from observations using beams of essentially mono-energetic electrons. In

order to facilitate the comparison between the calculated values of $\langle P_{10}(T) \rangle$ for nitrogen molecules and electrons in the present study, the cross sections $Q_{10}(\varepsilon)$ derived from the above authors' measurements were transformed into effective probabilities by dividing by the cross section for momentum transfer between nitrogen molecules, $Q_K(N_2)$. (This artifice does not affect the final result since $Q_K(N_2)$ cancels out in the final determination of τ from Eq. (2).) Hence, for both electrons and N_2, $P_{10}(\varepsilon)$ is given by $Q_{10}(\varepsilon)/Q_K(N_2) \cdot Q_K(N_2)$ has been taken as 10^{-15}cm^2. As shown in Fig. 1, the experimental values of $Q_{01}(\varepsilon)$ for electrons have small periodic variations. These can be smoothed out as indicated in this figure without introducing any significant error into the calculations.

The most striking feature of the values of $P_{10}(\varepsilon)$ shown in Fig. 1 is that the electron probabilities are several orders of magnitude larger than those for N_2 molecules in the important thermal range 0 to 2 eV. The values of $\langle P_{10}(T) \rangle$ for electrons at temperatures up to 5000°K are thus expected to be much larger than those for N_2. This feature, together with the higher collision frequency for electron-molecule collisions, will make the relaxation time derived from Eq. (2) for electron collisions much smaller than that for N_2 collisions.

To facilitate the integration in Eq. (6) to obtain the thermally averaged probabilities, $\langle P_{10}(T) \rangle$, approximations to the $P_{10}(\varepsilon)$ curves are used. The electron probabilities can be approximated by

a linear dependence of $\ln P_{10}(\varepsilon)$ on ε over each of the ranges 0 to 1.7, 1.7 to 3.7, and 3.7 to 5.0 eV. The N_2 probabilities can likewise be approximated by a linear dependence over each of the ranges 0 to 1, 1 to 2, 2 to 3, and 3 to 5 eV. The discrete energy-dependent probabilities are thus written in the form

$$P_{10}(\varepsilon) = \exp(-a)\exp(b\varepsilon) \tag{7}$$

where a and b are constants in a particular energy range. The numerical value of these constants for the i th energy range, defined by $\varepsilon_{i,i+1}$, is given by the terms $a_{i,i+1}$ and $b_{i,i+1}$ listed in Table I.

2.3 Evaluation of $\langle P_{10}(T)\rangle$

Using the above approximation to $P_{10}(\varepsilon)$, the integration of Eq. (6) may be written as the summation

$$\langle P_{10}(T)\rangle = \sum_{i=0}^{i=N} \left(\frac{1}{kT}\right)^2 \exp\left(-a_{i,i+1}\right) \int_{\varepsilon_i}^{\varepsilon_{i+1}} \varepsilon \exp\left[\left(b_{i,i+1} - \frac{1}{kT}\right)\varepsilon\right] d\varepsilon , \tag{8}$$

where the summation is carried out to $N = 3$ for electrons and to $N = 4$ for N_2. Integrating Eq. (8) over each energy range gives

$$\langle P_{10}(T)\rangle = \sum_{i=0}^{i=N} \frac{1}{\beta_{i,i+1}^2} \exp\left(-a_{i,i+1}\right) \left[\left(\frac{\varepsilon\beta_{i,i+1}}{kT} - 1\right) \exp\left(\frac{\varepsilon\beta_{i,i+1}}{kT}\right)\right]_{\varepsilon_i}^{\varepsilon_{i+1}} \tag{9}$$

where $\beta_{i,i+1} = \left(b_{i,i+1} kT - 1\right)$.

Nitrogen Molecules

Using the above method, the values of $\langle P_{10}(T) \rangle$ for de-excitation by nitrogen molecules were calculated at T = 1000°, 1500°, 3000°, and 5000°K. The total average probabilities, as well as the contributions $\langle \Delta P_{10}(T) \rangle$ to these values from each individual energy range, are given in Table II. For comparison, the theoretical values of $\langle P_{10}(T) \rangle$ as obtained by Dickens and Ripamonti[7] and the measured values as obtained from various experimental studies of N_2 relaxation[8] are also listed. It is seen that the present calculated values agree better with the experimental probabilities than do the theoretical values of Ref. 7. This is because the analysis of Ref. 7 integrates the discrete transition probabilities over all collision energies, and thus includes the contribution from the higher energies where the value of $P_{10}(\varepsilon)$ (as given by the perturbation method) become greater than unity. The N_2 transition probabilities as calculated by the present approximate method would thus be expected to agree better with those which would be obtained from an exact calculation using the smaller values of $P_{10}(\varepsilon)$ proposed for the higher energies in Ref. 6. It is noted that for energies up to the value of 5 eV considered in the present work the values of $P_{10}(\varepsilon)$ used in both Refs. 6 and 7 are the same; in the present calculations the values from Ref. 6 were used because they are listed there in convenient form.

Electrons

The values of the thermally averaged probabilities for electron de-excitation at 1000°, 1500°, 3000°, and 5000°K as calculated from Eq. (9) are presented in Table III, together with the individual contributions from each energy range. It is seen that the contributions from the higher energy range 3.7 to 5 eV are quite negligible, thus permitting the cessation of the summation at 5 eV.

In Fig. 2, the values of $\left[<\Delta P_{10}(T)>\right]_{\mathcal{E}_{i,i+1}} \left(\mathcal{E}_{i,i+1}-\mathcal{E}_i\right)^{-1}$, or the contributions to the total thermally averaged probabilities per eV, are shown as a function of the relative energy of the colliding pairs. The area under each curve is the value of $<P_{10}(T)>$ for the temperature indicated on the curve. Several features are apparent from this figure. The greatest contribution to the electron probabilities comes from the lower range of particle energies, and in this range the electron probabilities exceed the corresponding N_2 probabilities by more than 100. The greatest contribution to the N_2 probabilities comes from the small fraction of high-energy particles which are far out in the tail of the indicated Boltzmann distributions. Thus, the region of particle energies which contributes most to the electron probabilities varies little as the temperature increases. In contrast, the position of the peak contributions to the N_2 probabilities shifts to high energies with increasing temperature. The magnitudes of the peak N_2 contributions also show a considerably greater variation with temperature than do the electron contributions. The temperature-dependence of the thermally averaged probabilities for electrons is thus much

weaker than that for N_2.

The above features are reflected in Fig. 3, which shows the variation of $\langle P_{10}(T) \rangle$ with temperature for electrons and for N_2 over the range 1000° to 5000°K. The electron probabilities are as calculated from Eq. (9), and the N_2 probabilities shown are the experimentally deduced values given in column (c) of Table II. It is seen that the probability of electron de-excitation is about 10,000 times greater than that for de-excitation by N_2 at 1000°K, but is only about 30 times greater at 5000°K. The influence of electrons on N_2 vibrational relaxation is thus expected to be largest in the 1000° to 3000°K range.

2.4 Temperature Dependence of Electron De-excitation

It is of interest to determine the empirical form of the temperature dependence shown by the four values of the thermally averaged electron probabilities plotted in Fig. 3. Over the range 1000° to 5000°K the empirical relation

$$\langle P_{10}(T) \rangle = 1.58 \times 10^{-3} T^{-1.8} \exp\left(T^{1/3}\right)$$

is found to provide an excellent fit to the calculated values. The curve drawn through the four calculated points in Fig. 3 is the plot of this expression.

Attempts were made to fit the calculated probabilities to an empirical temperature dependence of the form $T^{-n} \exp\left(-BT^{-1/3}\right)$, which holds for N_2 vibrational de-excitation by nitrogen molecules.[8] A satisfactory fit could not however be obtained. The dependence on the power of the temperature in the exponent was found to be very critical,

and the cube root dependence indicated is an exact one. It is thus of some interest that, although the probabilities for de-excitation by electrons and N_2 both feature an exponent in $T^{1/3}$, the signs in the exponent for the electrons are everywhere opposite to those in that for N_2. The pre-exponential temperature dependence is also greater for the electron probability. These two effects are opposed, and the over-all temperature dependence of electron de-excitation is consequently less pronounced than for de-excitation by nitrogen molecules.

A physical insight into these interesting differences might be obtained from a more sophisticated theoretical study of the electron-molecule interaction processes. Herzenberg and Mandl[9] have successfully derived the energy dependence of the discrete electron de-excitation probabilities observed in Ref. 2 from theoretical considerations of the lifetime of the postulated N_2^- state, and it would be interesting if their approach could be carried over to discuss also the thermal dependence.

3. THE INFLUENCE OF FREE ELECTRONS ON N_2 VIBRATIONAL RELAXATION

3.1 Dependence of N_2 Relaxation Time on Electron Mole Fraction

In the following analysis of the vibrational relaxation of a system of nitrogen molecules and electrons, it is stressed that the electron kinetic temperature is considered to be equal to the N_2 translational temperature. Although it is shown in Sec. 4 that the electron temperature is likely to be more closely associated with the N_2 vibrational temperature in some simple nonequilibrium systems, and that the electron

influence on relaxation is then expected to be greatly reduced, the equality of kinetic temperatures is used in order to determine the maximum possible electron influence on the relaxation measurements to be described in the Sec. 3.2.

The effective vibrational relaxation time τ for a mixture consisting of a mole fraction ϕ of electrons in N_2 may, for small ϕ, be written

$$1/\tau = (1-\phi)/\tau_{N_2} + \phi/\tau_e$$

where τ_{N_2} is the relaxation time for N_2-N_2 collisions and τ_e is the relaxation time for electron-N_2 collisions. If we define $\phi(a)$ to be the mole fraction of electrons required to reduce the effective relaxation time of the mixture to $1/a$th that for pure N_2 (when both the electrons and molecules have the same kinetic temperature), then the above expression gives $\phi(a) \approx (a-1)\tau_e/\tau_{N_2}$. From Eqs. (2) and (5) this relation becomes

$$\phi(a) = 6.25 \times 10^{-3} (a-1)\left[\langle P_{10}(T)\rangle\right]_{N_2} \Big/ \left[\langle P_{10}(T)\rangle\right]_e, \quad (10)$$

and it is noted that $Q_K(N_2)$ cancels out in Eq. (10).

The family of curves in Fig. 4 has been constructed by using the appropriate values for the thermally averaged transition probabilities from Fig. 3 in Eq. (10). From these curves it is seen that the influence of electrons increases rapidly as the temperature decreases, but for a particular value of ϕ appears to remain almost constant for temperatures above 5000°K. The reciprocal of ϕ is equivalent to the number of nitrogen molecules which one electron effectively replaces in the relaxation process. Thus, at 1000°K an electron concentration of only 1 in 3×10^6 could halve the normal N_2 relaxation

time, and at 5000°K a concentration of 1 in 6×10^3 could do so. At 1000°K, a tenfold increase of the electron concentration could reduce the relaxation time by 90%.

3.2 Spectrum-Line Reversal Measurements in N_2 Expansion Flows

One of the motives for the present analysis was to determine whether recent measurements[10] of the extent of vibrational nonequilibrium in supersonic-expansion flows of shock-heated N_2 could have been influenced by the free electrons, originating from the ionization of the metallic additives used in the spectrum-line reversal method[11] employed. In the experiments, sodium and chromium compounds were introduced into the N_2 test gas in a shock tube, and the excitation temperature of these atoms was measured by line-reversal in the expansion flow in a conical nozzle attached to the end of the tube. For reasons discussed elsewhere[10,11], these excitation temperatures are interpreted in terms of the N_2 vibrational temperature.[12] The measurements indicate that the N_2 molecules relax at an apparent rate which is fifteen times faster than that observed behind shock waves. Whilst several possible reasons were advanced in Ref. 10 to explain this phenomena, none can at present be considered conclusive.

The electron influence on the N_2 relaxation in these nozzle-expansion experiments could be significant for the following reason. The electron mole fraction is determined by the thermal state of the gas in the reflected shock wave, prior to expansion through the nozzle. During the expansion process the loss of electrons by ternary recombination is expected to be very slight because the ion concentrations are small and the expansion rates are high. The mole fraction

will thus be expected to be preserved at its high initial reflected-shock value, ϕ_o , throughout the expansion. This value will greatly exceed that corresponding to local equilibrium in the expansion.

The maximum effect of this on the relaxation process in the expansion can best be visualized by referring to Fig. 4. During the expansion the kinetic temperature and pressure fall very rapidly. Under nonionized conditions, this creates a sufficiently fast increase in the local vibrational relaxation time to cause the vibrational temperature to first lag behind the falling kinetic temperature, and then to freeze at a fixed value for the remainder of the expansion.[15] Under ionized conditions, and for equilibrated N_2 and electron kinetic temperatures, the local relaxation time at a particular value of the local kinetic temperature in the expansion will be reduced to the effective value given by a line ϕ_o = constant in Fig. 4. The relaxation time thus increases less rapidly, so that the vibrational temperature will tend to become frozen at a later stage in the expansion or, perhaps, will not freeze at all.

In the work of Ref. 10, the concentration of Cr metal additive used was varied from 0.1% to 0.003% and trace amounts of Na were also used. From the fact that the vibrational temperatures measured in the expansion were the same for each concentration, and additive, it was concluded that neither the additives or their derivatives were effecting the relaxation process. However, the possibility that the faster observed relaxation was due to the vibrational de-excitation by electrons, and that the effect of this was sufficiently great to be

relatively unchanged by the large variations in ϕ_o , should perhaps also be considered.

The calculation of each expected vibrational temperature distribution for the individual values of ϕ_o resulting from ionization of the Cr and Na additives is a formidable and lengthy task. Since only an indication of their possible effect is required the following simplification is used. The analysis of Ref. 16 shows that over a limited range of reservoir conditions the vibrational temperature will become frozen in a nozzle when the quantity $v\tau/x_o$ becomes approximately unity, where v and τ are respectively the local gas velocity and relaxation time in the expansion at a distance $x=x_o$ from the nozzle throat, and x_o is a geometrical parameter defined in Ref. 16. Figure 5 shows the variation of $v\tau$ for fully frozen flow in pure N_2 as a function of x for the expansion conditions shown in Fig. 6 of Ref. 10. It is seen from Fig. 5 that $v\tau$ increases very rapidly with x . From this curve, and from other similar ones based on the corresponding behavior for relaxation times which are 1/10, 1/15, and 1/20 τ , it is found empirically that the value $v\tau/x = 10$ predicts very well the value of x at which the vibrational temperature has fallen to within three-quarters of its final frozen value, as measured from the throat.[17] From the local values of the translational and vibrational temperatures appropriate to these values of x the interdependence of these temperatures for this expansion is obtained and found to be almost linear. The line $v\tau/x = 10$ drawn on Fig. 5 thus defines the freezing limit, and this

line and the above criteria are used below to estimate the influence of the electrons on the final level of the vibrational temperature.

Chromium Additive

The $\nu\tau$ curves in Fig. 5 for 0.01% and 0.1% Cr additive are found by determining the appropriate values of ϕ_o from Sahas' equation, namely $\phi_o = 8.1 \times 10^{-7}$ and 2.5×10^{-6}, and using these to obtain the reduced values of τ from Fig. 4 at each stage in the expansion. It is seen that the $\nu\tau$ curves are shifted relative to the pure N_2 curve to intercept the $\nu\tau/x = 10$ line at successively increasing values of x. From the values of the translational temperature corresponding to these values of x the final level of the predicted frozen vibrational temperature is obtained using the above mentioned linear dependence between these two temperatures. It is thus found that the influence of 0.01% Cr is negligible, while 0.1% could lower the final freezing level by 100°K.

Sodium Additive

Evaluation of the $\nu\tau$ curve for the Na additive is made difficult by the lack of a measured value for the Na concentration. However, an estimate of this quantity may be obtained from a comparison of the emission intensities of the Na and Cr resonance lines for similar conditions in the nozzle. These measurements were made with identical optical and electronic recording systems, and the ratio of the over-all amplification in each case is known. In each case the gas may be safely considered to have been optically thick for the

resonance radiation, so that the intensity of the resonance radiation would be proportional to the square root of the density of metal atoms. Using the appropriate values for the constants in the radiation relations listed on p. 239 of Ref. 11, a calculation gives the percentage Na additive to be 2×10^{-3} (allowing for ionization). The corresponding value of ϕ_o is 1×10^{-5}.

The $\nu\tau$ curve calculated for 0.002% Na is also shown in Fig. 5. It is found that the Na could produce a reduction of about 150°K in the level of the frozen vibrational temperature.

The effect of the Cr and Na additives in the work of Ref. 10 could result therefore in small reductions in the true frozen vibrational temperatures. However, these reductions would not be large enough to account for the difference of 900°K between the frozen vibrational temperature of 2800°K, calculated from the shock-wave measured relaxation times, and the lower vibrational temperature of 1900°K observed in the typical expansion flow considered here. It must therefore be concluded that ionization of the additives is not an explanation for this large difference. These results do indicate, however, that it is wise to use a minimum amount of metal additive in spectrum-line reversal measurements of relaxation processes.

4. THE COUPLING OF FREE ELECTRON AND VIBRATIONAL TEMPERATURES

It was assumed in Sec. 3 that the kinetic temperature of the electrons remained in equilibrium with that of the nitrogen molecules

during the nozzle-flow analyses. However, the actual level of the electron temperature under these conditions will be determined by the balance between the rates at which the electrons exchange their energy with the N_2 translational, rotational, and vibrational degrees of freedom. This level will lie closest to the effective temperature of the degree of freedom with which the exchange is most efficient.

4.1 Efficiency of Exchange of Electron Energy with N_2 Degrees of Freedom

N_2 Translation

The discrete loss of electron energy to the N_2 translational degree of freedom per collision can be shown to be $\lambda\varepsilon$, where ε is the electron energy and $\lambda = 2m/M$, m and M being the masses of the electron and molecule. The thermally averaged amount of energy $\langle\Delta\varepsilon_t\rangle$ transferred per collision may be written as

$$\langle\Delta\varepsilon_t\rangle = \int_0^\infty \lambda\varepsilon \cdot d[Z(\varepsilon)] \Big/ \int_0^\infty d[Z(\varepsilon)] \, .$$

From Eqs. (4) and (5) this may be evaluated to give $\langle\Delta\varepsilon_t\rangle = 2\lambda k T_e$, where T_e is the electron temperature.

N_2 Rotation

The discrete loss to the N_2 rotational degrees of freedom during electron-N_2 collisions has been examined theoretically by Gerjouy and Stein[18] and experimentally by Mentzoni and Row.[19] The analysis of Ref. 18 assumes that rotational excitation takes place by long-range quadrupole interaction, and indicates that over the range of electron energies from 0 to 0.5 eV the fractional loss of

electron kinetic energy per collision falls from 50λ to 10λ. These predictions are confirmed in Ref. 19 which shows that the loss to rotation varies as (electron temperature)$^{-3/2}$, and falls from 56λ at 300°K to 14λ at 735°K, tending to level off around 10λ at higher temperatures. For electron temperatures between 3000° and 5000°K, Formato and Gilardini[20] have found that the fractional energy loss to N_2 rotation per collision is 3.95×10^{-4}, which is again almost exactly 10λ. The average energy loss to rotation per collision can thus be written as $\langle \Delta\varepsilon_r \rangle = 10\lambda\bar{\varepsilon} = 15\lambda kT_e$ over the temperature range 1000° to 5000°K.

In nonequilibrium systems in which the degrees of freedom can be characterized by differing Boltzmann distributions it is usually safe to consider the translational and rotational modes to be in equilibrium. Hence, the exchange of electron energy with either mode has energetically the same result, so that the transfer to the rotational mode can be considered to operate in parallel with the transfer to the translational modes. The effective total loss of electron kinetic energy per collision to N_2 translation is thus $\langle \Delta\varepsilon_t + \Delta\varepsilon_r \rangle = 17\lambda kT_e = 6.15 \times 10^{-4} kT_e$. The number of electron - N_2 collisions, $n_{t,r}$, required for an electron to lose an amount of energy equal to one quantum of vibration, $k\theta$, to the N_2 translational modes is thus $1.63 \times 10^3 (\theta/T_e)$, where θ is the characteristic N_2 vibrational temperature.

N_2 Vibration

The number of collisions n_{v} which an electron requires in order to lose one quantum of vibrational energy to the N_2 vibrational mode is $1/\langle P_{10}(T)\rangle$, where this number is obtained from Fig. 3. The ratio $n_{t,r}/n_{v}$ may thus be written as $1.63 \times 10^3 (\theta/T_e) \langle P_{10}(T)\rangle$, and for T_e = 1000°, 3000°, and 5000°K this ratio is about 1, 5, and 11. Thus, at temperatures above about 1000°K, an electron exchanges energy more efficiently with the vibrational degree of freedom than with the translational and rotational degrees combined.

4.2 Relaxation of Electron Temperature in N_2

The above results indicate that in a thermal system of electrons and N_2, initially having an electron temperature below 1000°K and differing N_2 translational and vibrational temperatures, the electron temperature will relax to a value intermediate between the N_2 translational and vibrational temperatures. However, when the initial electron temperature is greater than 1000°K the electrons will relax to a temperature closer to the N_2 vibrational temperature. At electron temperatures above 3000°K the electrons will be in equilibrium with the vibrational temperature.

The rates with which the electron temperature relaxes will be fast. For N_2 at 1 atm pressure the effective electron collision frequency for N_2 vibrational transfer is $6 \times 10^7 \text{sec}^{-1}$ at an electron temperature of 1000°K, and $2.6 \times 10^9 \text{sec}^{-1}$ at 4000°K, using the transfer probabilities from Fig. 3. The electron relaxation times at

these temperatures will thus be around 2×10^{-8} and 4×10^{-10} sec. The electron relaxation time for transfer to the N_2 translational modes at 1000°K will also be around 2×10^{-8} sec at a pressure of 1 atm. The temperature assumed by the electrons in a nonequilibrium N_2 system will thus be attained almost instantaneously, and certainly long before the departure from vibrational equilibrium changes.

4.3 Electron Temperature in Supersonic Expansion Flows

The above considerations indicate that in nozzle-expansion flows similar to those discussed in Sec. 3.2 the electron temperature behind the reflected shock wave will be equal to the equilibrated N_2 translational and vibrational temperature in this reservoir region. They also indicate that, as the expansion proceeds, the electron temperature will quickly relax towards, and then follow, the N_2 vibrational temperature. Once this correspondence is obtained, the influence of the free electrons on the N_2 relaxation will be greatly decreased. Thus, any reduction in the N_2 relaxation time due to free electrons in the above expansions will be even smaller than that anticipated in Sec. 3.2.

Experimental evidence which supports these conclusions has been obtained in current spectrum-line reversal measurements of Na excitation temperatures in expansion flows of shock-heated Ar and Ar/N_2 mixtures, to be described fully in a subsequent publication.[21] The results show that for a typical expansion from a reservoir temperature of 4000°K the measured Na temperature is around 2600°K, whilst the Ar temperature at the measuring station

in this expansion is only 500°K. In the absence of other sources of Na excitation this high excitation temperature is interpreted as being due to free electrons, which are produced by Na ionization in the reservoir, and which are frozen at a high kinetic temperature ($\approx$ 3000°K) during the early stages of the expansion. The addition of 1% N_2 to this flow is found to reduce the measured Na excitation temperature to around 1900°K. This correlates very well with the frozen N_2 vibrational temperature expected for this expansion on the basis of the faster relaxation times observed in the earlier N_2 relaxation measurements[10] in the same nozzle. The thermodynamic effects of the 1% N_2 additive can be shown to be very slight.

The above observations indicate that electron-kinetic energy has been rapidly degraded to vibrational energy of the nitrogen molecules in the early stages of the expansion, and that the electron-kinetic and N_2 vibrational temperatures are thus equilibrated during the remainder of the nozzle flow.

Although these results do not directly prove the proposed coupling between the free electron and N_2 vibrational temperatures, they do however indicate that the electron temperature in these expansions is very much reduced in the presence of nitrogen molecules. On this basis, it appears worthwhile to examine some of the possible consequences which a reduction in the electron temperature by this coupling process could have in similar expansion-flow systems. These possibilities are briefly mentioned below.

Chemical Aspects of Hypersonic Air-Expansions

In the hypersonic expansions of shock-heated air in high-temperature shock-tunnel facilities, an exceedingly complex combination of possible chemical reactions can act both to promote the recombination of atoms and of ions and to quench vibrationally excited species. The effective temperature of the expanding gas is not readily defined, and the application of temperature-dependent reaction rates -- which are in the main determined in other environments -- to such systems is, at best, a hazardous procedure; several workers have discussed these nonequilibrium aspects at length.[22,23] Any possible simplification of this picture is thus of advantage.

For expansions of air from typical reflected-shock conditions of 7000°K and 200 atm, the predominant initial species are N_2, O, and NO, and the electron mole fraction is 1.6×10^{-4}. The present analysis would suggest that for these conditions the free electron temperature will keep in equilibrium with the vibrational temperature of the predominant N_2 constituent during the expansion. If the vibrational temperature of the other molecular species present are to some extent coupled to the N_2 vibration (such as by way of the efficient electron -N_2 and electron -O_2, Ref. 3, vibrational energy transfers), it is possible that the over-all extent of vibrational nonequilibrium will be reduced. This could have two important effects. First, the electron temperature would be reduced, and this could produce an enhancement of the rate of ion recombination. Second,

since the majority of atom recombinations are expected to take place into the upper vibrational levels of the molecule formed, the more rapid rate of vibrational de-excitation would act to promote the rate of atom recombination.

Re-entry Expansion-Flow and Wake Phenomena

The concentration of electrons in the bow-shock and expansion-flow regions around a re-entering vehicle is sufficiently high to make radio communication with the vehicle very difficult. The present analysis suggests that the electron temperature in the low-density gases of the expansion region, and in the wake, will be maintained at the high nonequilibrium level of the vibrational temperature of these gases. It is thus conceivable that by introducing into the expansion region small amounts of polyatomic gases such as water or methane, which have a rapid catalyzing effect on vibrational relaxation, the over-all vibrational temperature could be reduced and the electron temperature consequently lowered. Since the radio attenuation is dependent on both the temperature and density of free electrons an increased transmission could result. The possibility of seeding the expansion flow with material to cool or neutralize the re-entry plasma has been discussed by Huber and Nelson[24], who consider that this might be achieved by an appropriate selection of ablation products.

In after-body flows and in the simulated wakes produced in hypersonic test facilities, including ballistic ranges, it is perhaps of interest to note that temperature measurements using the

spectrum-line reversal method are, in this respect, thus likely to yield the effective temperature of the equilibrated electron-kinetic and N_2-vibrational degrees of freedom.

4.4 Electron Temperature in Nitrogen Plasmas

The preceding sections have been concerned with systems in which the amount of kinetic electron energy degraded to N_2 vibrational energy is small, so that the proposed coupling produces little or no direct change in the vibrational energy. For example, in a mole of N_2 initially having a vibrational temperature of 3000°K, and containing an electron mole fraction of 10^{-4} at a temperature of 6000°K, the energy in vibration is 1.2×10^3 cal whilst the electron kinetic energy is only 3 cal. However, in a N_2 plasma where the electrons are continually receiving energy from an applied field, the transfer of energy from the accelerated electrons to the molecules would be expected to quickly raise the energy in N_2 vibration. Since it has been shown [5, 25] that a given distribution of molecular vibrational energy quickly relaxes to a Boltzmann distribution under the influence of vibrational exchange processes, the proposed coupling mechanism would suggest that the electron energies in a N_2 plasma might also conform to a similar Boltzmann distribution. The electron and N_2 vibrational temperature in the plasma would then be equal, the term temperature then being a meaningful concept.

In the above respects, several interesting phenomena which

tend to further support the coupling scheme proposed in the present paper have been observed of late in nitrogen plasmas. There are also other ionized regimes in which the process would appear to be of possible consequence. These aspects are briefly discussed below in the light that they may be considered worthy of future closer examination.

Pulsed Discharges and Plasma Jets

Formato and Gilardini[26] measured the electron temperature in the afterglow of a pulsed d.c. discharge in nitrogen, and found that the electron temperature decayed very slowly, remaining at a high temperature even at post-discharge times longer than 100μsec. These times are stated to be much longer than the electron thermalization time observed in a similar discharge in helium. They concluded that an explanation for this was the generation of new electrons in the N_2 afterglow, the source of these possibly being ionizing collisions between certain metastable nitrogen molecules excited during the discharge. However, the results of the present paper suggest that the N_2 would be excited to a high vibrational temperature in the discharge by collisions with energetic electrons. It may be possible that the observed slow decay could be due to the slow relaxation of the N_2 vibrational temperature, to which the electron temperature would be coupled, during the post-discharge period.

A rough indication of the possibility of this explanation may be obtained as follows. The pressure of N_2 used in the experiments was between 1 and 2 mmHg, and the N_2 translational temperature in

the afterglow may be assumed to be that of the room. The N_2 vibrational relaxation time[8] for de-excitation by nitrogen molecules would be about 10^5 sec under these conditions. However, the calculations of Sec. 4.2 show that in the absence of N_2 vibration the electron temperature would decay by transfer to the N_2 rotational and translational modes in about 10^{-5} sec at the pressures used. In the presence of N_2 vibration the decay of the coupled electron and vibrational temperatures would be expected to be much longer than this value, but considerably shorter than the above normal N_2 relaxation time. For example, for an electron temperature of 1000°K and an electron concentration as large as 1%, the N_2 relaxation time for de-excitation by electrons is about 1 msec. The coupled temperatures at post-discharge times of 100μsec would thus still be expected to be high.

A similar correlation might be expected between the free electron and N_2 vibrational temperatures in the expansion of a N_2-bearing gas in an arc-heated plasma jet. A spectroscopic measurement of the N_2 vibrational temperature would then yield the electron temperature, which would be expected to be frozen at a high value in the expansion.

Microwave Discharges and Convective Flows

In possible support of the proposal that the N_2 vibrational temperature in a plasma may be expected to be high, it is of interest to note that Bass[27] recently reported observations which suggest

that N_2 in the ground electronic state may be excited to vibrational levels as high as $v'' = 20$, with apparently more than 10% of the molecules in levels greater than $v'' = 8$, in the convective flow of N_2 from a microwave discharge region. He suggests that the vibrationally excited N_2 may be involved in the mechanism of excitation of the pink N_2 afterglow observed in the same region. His observations show that the pink afterglow decays over a distance corresponding to a time of about 20 msec beyond the discharge.

In accordance with Bass' suggestion, and the conclusions of the present paper, it may further be possible that the decay of the pink afterglow is due to the quenching of the vibrationally excited N_2 by electrons in the post-discharge region. The N_2 pressures used were around 5 mm, and the observed decay time would not disagree with the relaxation estimates indicated in the preceding sub-section.

Degradation of Electron Energy at High Altitude

The present analysis would indicate that at high altitudes, where the electron temperature can be greater than the kinetic temperature of the air, the electrons will exchange their energy more efficiently with N_2 vibration than with rotation or translation. This suggests that the very efficient conversion of the electron energy into vibrational excitation of N_2 may be an important step in the degradation of this energy. The production of vibrationally excited N_2 by electron impact in these regions has also been considered by Dalgarno,[28] who concludes that for altitudes below about 250 km the slowing of fast electrons occurs more rapidly through vibrational

excitation than through any other process, including elastic collisions with ambient electrons. Since the loss of the resulting N_2 vibrational excitation would be inhibited by the long vibrational relaxation time at the pressures involved, it is possible that the N_2 vibrational temperature is not too different from the electron temperature at these altitudes.

SUMMARY

The probability for the de-excitation of N_2 vibrational energy by thermal electrons has been calculated from measured values of the discrete velocity-dependent collision cross-sections obtained by other workers. The thermally averaged probabilities have been presented for electron temperatures from 1000° to 5000°K, and their temperature dependence over this range evaluated empirically. These probabilities have been compared to measured values of the probability for N_2 vibrational de-excitation by nitrogen molecules. The electron probabilities are shown to be much larger than the latter values, and are relatively insensitive to temperature change over the range 1000° to 5000°K. The possible effect of electrons on previous spectrum-line reversal measurements of N_2 vibrational relaxation in expansion flows has been investigated, and it is concluded that the electron concentration in these experiments was too low for the electrons to have significantly influenced the relaxation measurements.

It has been suggested that because of the large electron

probabilities, the free electron and N_2 vibrational temperatures are likely to be coupled in thermal systems. Current experimental results in expansion flows which support this conclusion have been mentioned, and it is suggested that in other expansion flows containing molecular nitrogen the free electron temperature is likely to be degraded to, and closely identified with, the vibrational temperature of the nitrogen molecules.

As a further consequence of the proposed coupling, it is suggested that the N_2 vibrational temperature in a plasma may be elevated to the free-electron temperature which, as a result, conforms to that for a Boltzmann distribution of electron energies. On this basis, it is considered possible that the electron and vibrational temperatures will relax together during the plasma decay. Experimental evidence which tends to support these conclusions has been mentioned.

ACKNOWLEDGEMENTS

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TABLES

Table I: Values of the constants a and b used in the approximation to the discrete transition probability, $P_{10}(\varepsilon)$, in Eq. (7).

Nitrogen				Electrons			
ε_i eV	ε_{i+1} eV	$a_{i,i+1}$	$b_{i,i+1}$	ε_i eV	ε_{i+1} eV	$a_{i,i+1}$	$b_{i,i+1}$
0	1	23.0	12.2	0	1.7	9.70	4.13
1	2	13.8	3.59	1.7	3.7	1.70	0.56
2	3	10.8	2.07	3.7	5.0	-13.2	-4.57
3	5	7.8	1.01	---	---	-----	-----

Table II: Comparison of calculated and experimental values of the thermally averaged N_2 vibrational transition probabilities, $\langle P_{10}(T)\rangle$, for de-excitation by nitrogen molecules. $\langle \Delta P_{10}(T)\rangle$ is the contribution to $\langle P_{10}(T)\rangle$ over the indicated energy ranges.

Nitrogen Kinetic Temperature °K	$\langle \Delta P_{10}(T)\rangle \times 10^6$				$\langle P_{10}(T)\rangle \times 10^6$		
	0-1eV	1-2eV	2-3eV	3-5eV	(a)	(b)	(c)
1000	0.006	0.005	-----	----	0.011	0.077	0.008
1500	0.10	0.30	0.006	----	0.40	0.92	0.11
3000	0.68	15.9	9.55	1.50	29.3	46	19
5000	0.99	32.6	148	113	295	463	280

(a) as calculated from Eq. (9) of present work.

(b) as calculated in closed form.[7]

(c) as obtained from experimental studies.[8]

Table III: Values of the thermally-averaged N_2 vibrational transition probabilities, $\langle P_{10}(T) \rangle$, as calculated for de-excitation by electrons from Eq. (9). $\langle \Delta P_{10}(T) \rangle$ is the contribution to $\langle P_{10}(T) \rangle$ over the indicated energy ranges.

Electron Kinetic Temperature °K	$\langle \Delta P_{10}(T) \rangle \times 10^6$			$\langle P_{10}(T) \rangle$
	0-1.7eV	1.7-3.7eV	3.7-5.0eV	$\times 10^6$
1000	140	0.003	0	140
1500	283	2	0	285
3000	1690	650	0.12	2340
5000	4430	5150	13	9590

FIGURE CAPTIONS

Figure 1. Discrete transition probabilities, $P_{10}(\varepsilon)$, for collisional de-excitation of the first excited vibrational level in N_2 by electrons and by nitrogen molecules.
- - - - Experimental values for electron de-excitation from Refs. 1, 2 and 4.
—— Theoretical values for nitrogen de-excitation from Ref. 6.

Figure 2. Energy-dependence of the contributions $[<\Delta P_{10}(T)>]_{\varepsilon_{i,i+1}} (\varepsilon_{i+1}-\varepsilon_i)^{-1}$, to the total thermally averaged transition probabilities, at various kinetic temperatures, for collisional de-excitation of N_2 vibration by electrons and by nitrogen molecules. The contributions for electrons and nitrogen are indicated ——— and – – – – respectively, and the curves - - - - illustrate a Boltzmann distribution of energies at 3000° and 5000°K.

Figure 3. Temperature dependence of thermally averaged transition probabilities, $<P_{10}(T)>$, for collisional de-excitation of N_2 vibration by electrons and nitrogen molecules. The values for electrons are as calculated in the present paper, and the values for nitrogen are experimental ones.[8]

Figure 4. Electron mole fraction ϕ required to reduce the N_2 vibrational relaxation time to 1/a th of its normal value at various temperatures, for a gas in which the free electron temperature is equal to the N_2 translational temperature.

Figure 5. Variation of "vibrational relaxation length", $\nu\tau$, with distance x from nozzle throat for supersonic-expansion flows of pure N_2, and N_2 containing small amounts of Na and Cr metal additives. The increase in the value of x at the intersection of the straight line and the various curves indicates the maximum influence of the free electrons from the additives on the location of vibrational freezing in the nozzle. The expansion conditions are given in Ref. 10, Fig. 6.

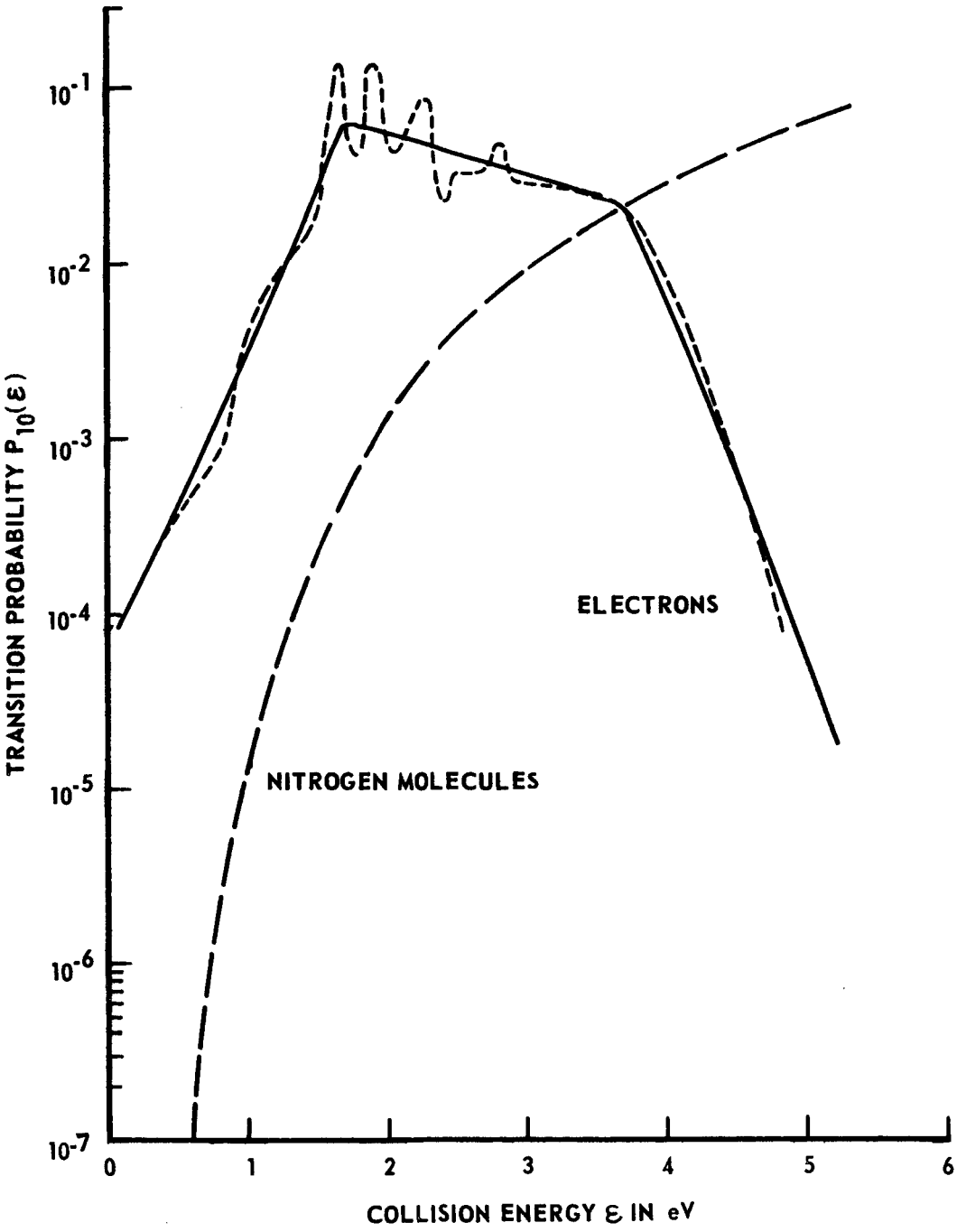
TRANSITION PROBABILITY $P_{10}(\varepsilon)$
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
ELECTRONS
NITROGEN MOLECULES
0
1
2
3
4
5
6
COLLISION ENERGY ε IN eV

Figure 1

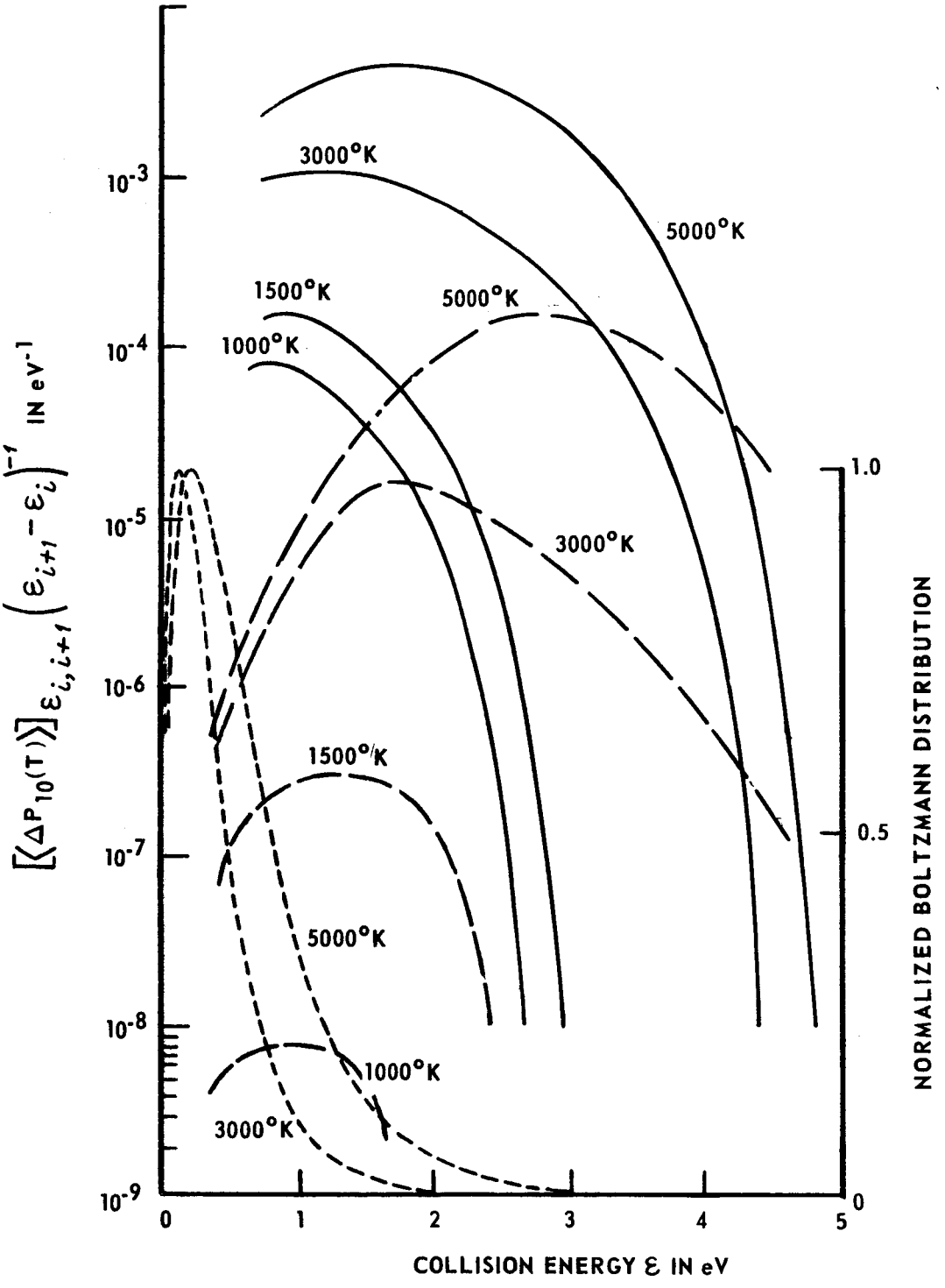
3000°K
5000°K
1500°K
5000°K
1000°K
3000°K
1500°K
5000°K
1000°K
3000°K
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
$[\langle \Delta P_{10}(T) \rangle]_{\varepsilon_i, \varepsilon_{i+1}} \left(\varepsilon_{i+1} - \varepsilon_i\right)^{-1}$ IN eV^{-1}
0
1
2
3
4
5
COLLISION ENERGY ε IN eV
1.0
0.5
0
NORMALIZED BOLTZMANN DISTRIBUTION

Figure 2

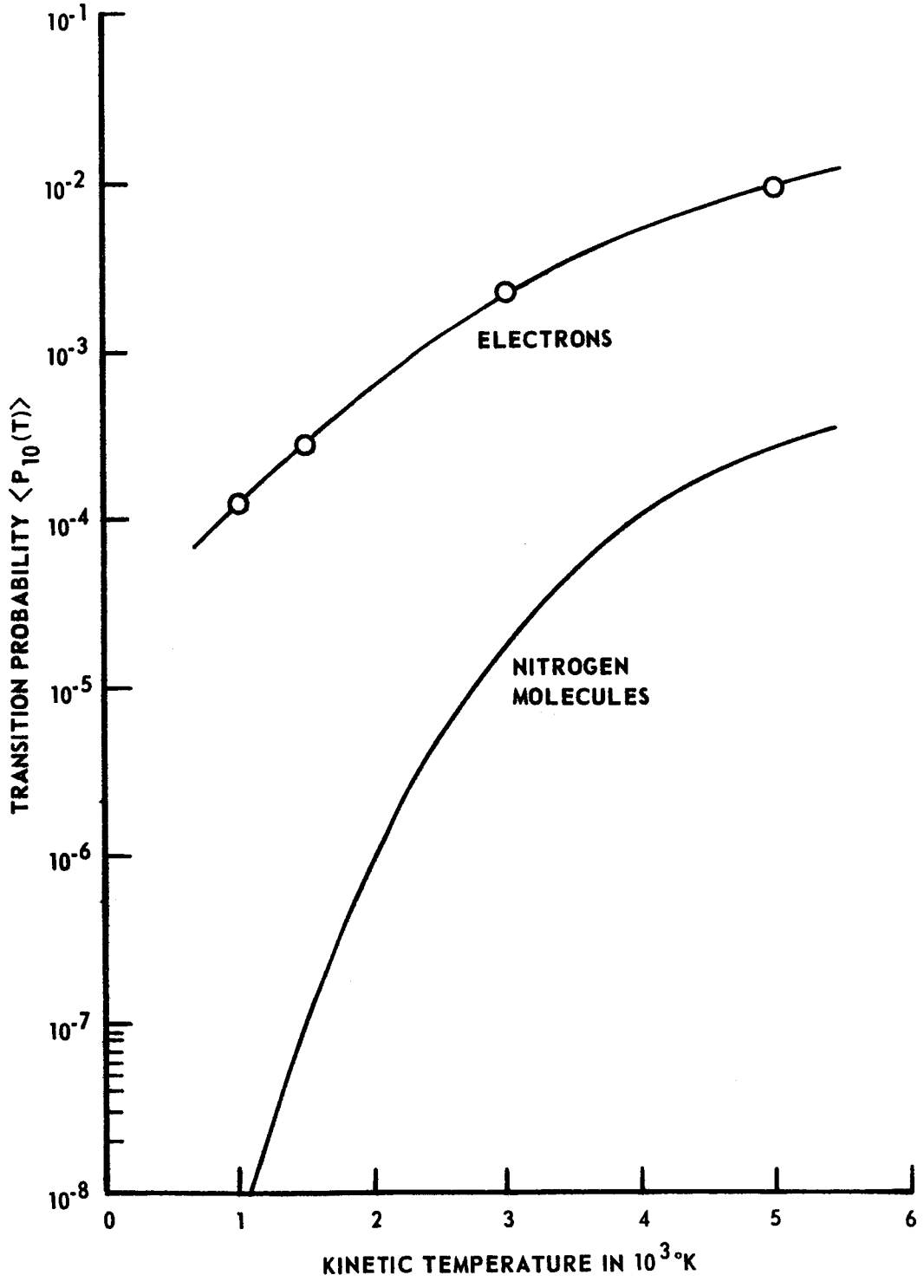
TRANSITION PROBABILITY $\langle P_{10}(T) \rangle$
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
ELECTRONS
NITROGEN
MOLECULES
0
1
2
3
4
5
6
KINETIC TEMPERATURE IN 10^3°K

Figure 3

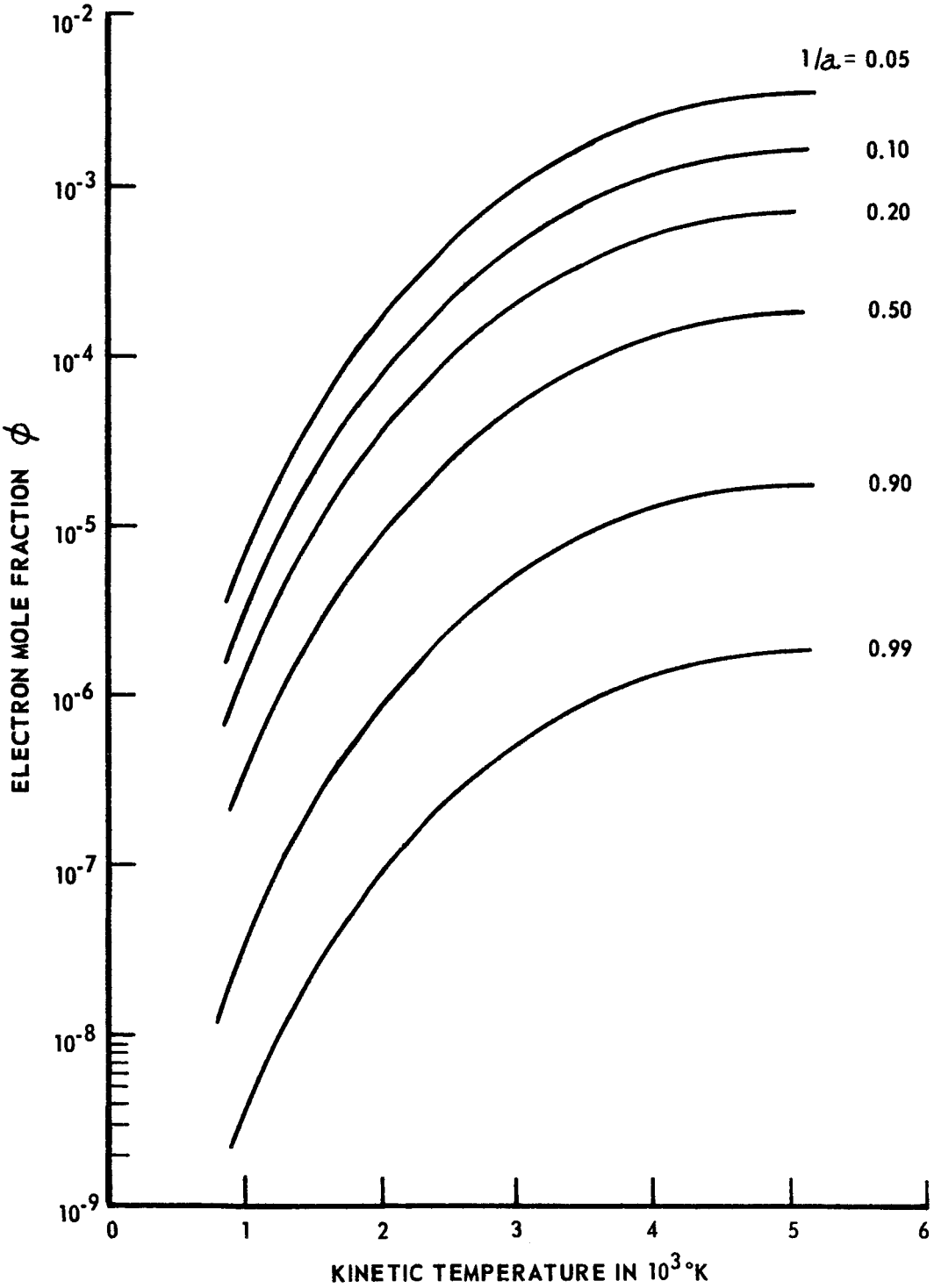
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
ELECTRON MOLE FRACTION ϕ
1/a = 0.05
0.10
0.20
0.50
0.90
0.99
0
1
2
3
4
5
6
KINETIC TEMPERATURE IN 10^3 °K

Figure 4

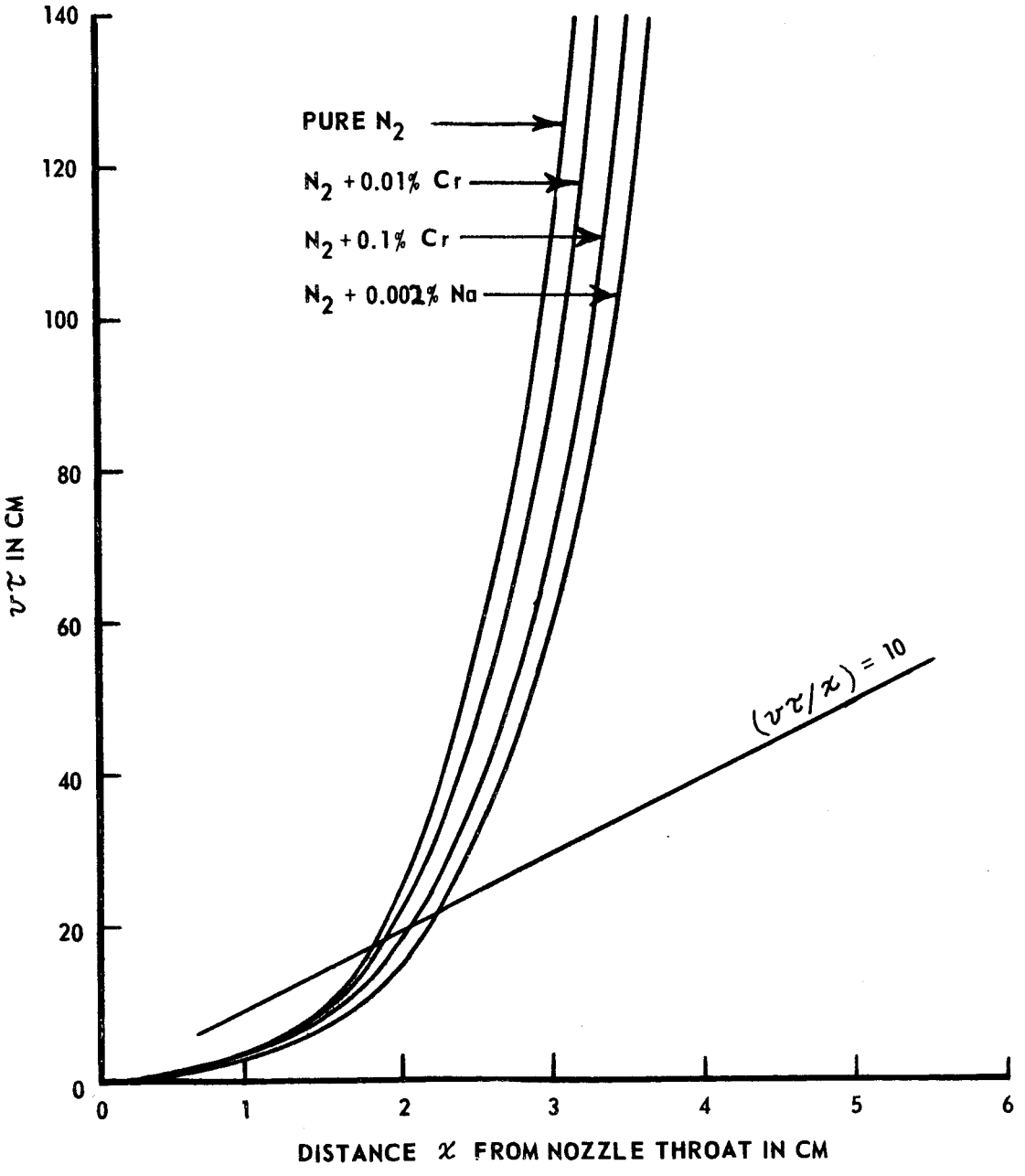
140
120
100
80
60
40
20
0
0
1
2
3
4
5
6
PURE N_2
N_2 + 0.01% Cr
N_2 + 0.1% Cr
N_2 + 0.001% Na
$(v\tau/x) = 10$
$v\tau$ IN CM
DISTANCE x FROM NOZZLE THROAT IN CM

Figure 5