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Ionization of NO at High Temperature

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Rate coefficients for ionization produced in collision of N and O atoms and the reverse dissociative recombination of NO^+ and electrons is redeveloped so as to provide the specific rate dependence on translational, vibrational, and free-electron temperatures. At equilibrium, the results compare favorably with experimental data over a wide range of temperature.

Nomenclature

a	= characteristic collision velocity for transition
b_m	= maximum collision miss distance
E	= electron collision energy
$\hbar$	= Planck constant/2π
I	= ionization energy of NO
K_{eq}	= equilibrium constant
k	= Boltzmann constant, also rate coefficient
k_{eq}	= equilibrium rate coefficient
n	= species concentration
P	= probability of transition
Q_M	= partition function for species M
$Q_M(T_e)$	= electronic partition function for species M at T_e
q	= probability of no transition at potential crossing
r, r_e	= distance between collision partners, electron distance
S	= collision cross section
T,T_e,T_v	= kinetic, free electron, and vibrational temperature
u	= electron collision velocity
$\bar{u}$	= root-mean-square velocity $(8kT_e/\pi m_e)^{1/2}$
v	= vibrational quantum number
x	= dimensionless collision energy E/kT
ε_i, g_i	= energy and degeneracy of electronic state i
θ	= characteristic vibrational temperature $\hbar\omega/k$
τ	= vibrational period $2\pi/\omega$
ω	= vibrational frequency in rad/s

Introduction

SPACE vehicles flying at high speed in the atmosphere excite a complex set of reactions ranging from vibrational excitation to dissociation, atom exchange, electronic excitation, ionization, and charge exchange. The rates of major reactions in high-temperature air were measured in the 1960s, generally in shock tubes, and Arrhenius-type equations fit to the data, at temperatures up to about 10,000 K.

However, rate coefficients are now needed at much higher temperature and lower density than formerly, for application to newer classes of space vehicles such as the aeroassisted orbit transfer vehicle. Temperatures up to 40,000 K are beyond the range that seems accessible to experiment, and at very high altitude shock heated gases are often not in thermal or chemical equilibrium. Theoretical models are needed that can extrapolate measured equilibrium rates both to higher temperature and to conditions where vibrational and electronic nonequilibrium occur.

In particular, production of NO^+ is one of the more important ionization reactions, but measurements are widely scattered and nonequilibrium effects are undetermined. The purpose of this paper is to develop rate expressions for ionization produced by collision between N and O atoms, and the reverse dissociative recombination of NO^+ and electrons, which will include the specific dependence of the rate coefficients on heavy particle temperature T, the vibration temperature T_v, and the electron temperature T_e. These expressions will apply to both nonequilibrium conditions and to high temperatures where experimental rates are presently unavailable.

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Ionization Reactions in Air

Collision between N and O atoms is one of the principal mechanisms leading to ionization in air

$$N + O \Leftrightarrow NO^+ + e \tag{1}$$

Numerous measurements of the rate coefficient have been made; generally the endothermic rate is observed and the exothermic rate is obtained by dividing the endothermic rate by the theoretical equilibrium constant.

Measured exothermic rates are of most interest because these have the best chance of providing the correct temperature dependencies; in the endothermic rate the temperature dependence of the pre-exponential factor is obscured by the domination of the exponential term. However, experiments performed to measure the endothermic rate are easier to set up in shock tubes and this was first done by Lin and Teare.[1] They deduced a $T^{-3/2}$ dependence for the exothermic rate, and chose the constant to agree with low temperature data of Doering and Mahan.[2]

$$k = \frac{1.8 \times 10^{21}}{T^{3/2}} \quad \text{cc/mol-s} \tag{2a}$$

Subsequent experiments[3–6] confirmed the low-temperature values rather well. However, with the exception of some results reported by Daiber,[7] measured high-temperature rates have generally been higher. Thompson[8] suggested that Eq. (2a) be increased about a factor of three, and Frohm and DeBoer[9] observed that a factor of two increase gives a better fit to Lin and Teare's original data. Results reported by Eckerman and Stern[10] and by Stein et al.[11] appear to confirm the higher values. The various rate coefficients proposed for the exothermic reaction are presented in Fig. 1.

Dunn and Lordi[12] measured the exothermic rate directly in expanding flow in a high-temperature shock tunnel, so their data is perhaps the most reliable indication of the temperature dependence of the rate coefficient at high temperature. They confirmed the same temperature dependence as Eq. (2a) but with a somewhat larger rate.

$$k = \frac{6.7 \pm 2.3 \times 10^{21}}{T^{3/2}} \quad \text{cc/mol-s} \tag{2b}$$

Extrapolation of this function to a lower temperature lies above most of the exothermic rate data there. Hansen[13] argued that at low temperature the relation should change to a $T^{-1/2}$ dependence due to the vibrational partition function that is involved in the equilibrium constant.

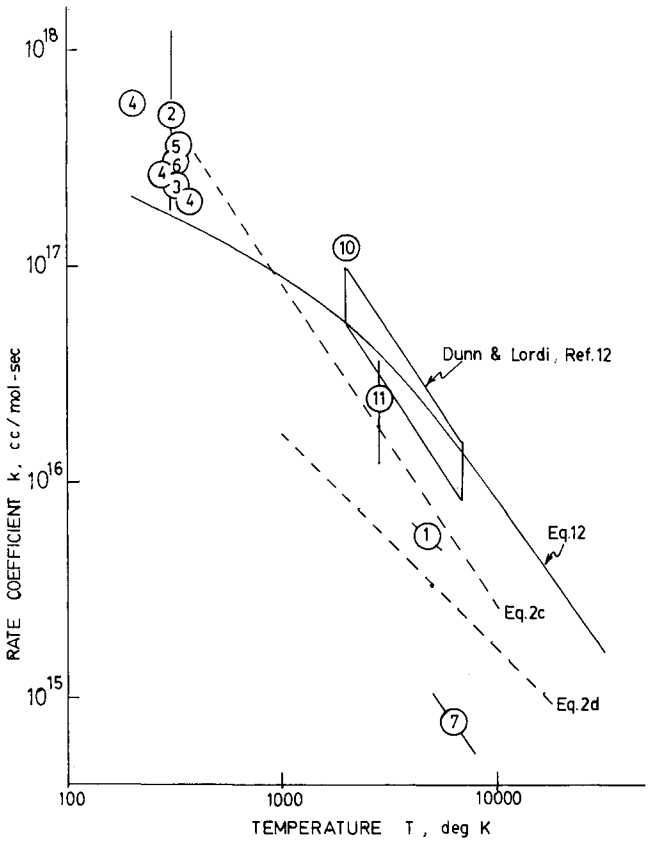

Fig. 1 Experimental and theoretical rate coefficients for dissociative electron recombination with NO^+ ions; 1) Lin and Teare,[9] 2) Doering and Mahan,[2] 3) VanLindt et al.,[3] 4) Gunton and Shaw,[4] 5) Weller and Biondi,[5] 6) Young and St. John,[6] 7) Daiber,[7] 10) Eckerman and Stern,[10] 11) Stein et al.,[11] and 12) Dunn and Lordi[12].

Two relations given in rate data reviews are shown by the dotted lines in Fig. 1. Bortner[14] reviewed the literature available before 1969 and recommended

$$k = \frac{(1.5 \pm 2.9) \times 10^{21}}{T^{3/2}} \quad \text{cc/mol-s} \qquad (2c)$$

while Blottner[15] chose a slightly different function which has been widely used in flowfield calculations.[16]

$$k = \frac{1.8 \times 10^{19}}{T} \quad \text{cc/mol-s} \qquad (2d)$$

Few measurements of $NO^+ + e$ dissociative recombination seem to have been made at high temperature since the 1960s, though work has continued on the reaction at low temperatures because of its importance in upper-atmosphere airglow. The low temperature rate has generally been determined using microwave heating of electrons[17–19] in glow discharges or from cross sections measured with merged beams of electrons and ions.[20] These measurements agree rather well with the earlier results, and have added some information about the dependence of the rate on electron temperature. The exothermic rates recommended for gas temperatures in the vicinity of a few hundred K are

$$k \approx 2.5 \times 10^{17} \left(\frac{300}{T_e}\right)^{\gamma} \quad \text{cc/mol-s} \qquad (2e)$$

where the values of the exponent γ range from 0.90 given by Alge et al.,[17] to 0.75 by Dulaney et al.,[18] and 0.85 by Torr et al.[19]

Theoretical understanding of the reaction improved when Bardsley[21] first proposed that transitions occur at a crossing of potentials for the molecular complex and the bound ion (in this case the N-O repulsive potential with the NO^+ vibrational potential). Bardsley showed that the electron is captured in vibrationally excited Rydberg states which are diabatic and not subject to the noncrossing rules that exist between adiabatic states. Multichannel quantum defect theory applied by Sun and Nakamura[22] produced rate coefficients about three times smaller than those given by Eq. (2e), but their theoretical exponent $\gamma = 0.82$ is in reasonable accord with experiment. A summary of work on low-temperature dissociative recombination up to 1988 is given in a collection of papers edited by Mitchell and Graham.[23] Figure 1 indicates that uncertainty remains regarding the best expressions to use for the dissociative recombination reaction of Eq. (1). Also, the results are for purely equilibrium conditions, except for a few experiments indicating a dependence on electron temperature.[17–19]

Simplified Model for Dissociative Electron Recombination

Schematic potentials for collision of an electron with an NO^+ ion are drawn in three-dimensional representation in Fig. 2. Potentials for the N + O repulsion and for the NO^+ attractive well, when the free electron is at infinity, are shown in the U vs r plane, where r is the separation between nuclear centers. Sun and Nakamura[22] identified several states of the excited N + O complex which cross the NO^+ potential near its minimum. For simplicity, this multiplicity of channels is idealized as a single effective repulsive N + O potential that is presumed to cross somewhere near the ion's potential minimum; then the activation energy for endothermic reaction is the change in zero point chemical energy and the activation energy for exothermic reaction vanishes, which seems to correspond with observations.

The electron approaching the ion with kinetic energy E is accelerated as it falls into the Coulomb potential, but eventually it slows as it interacts with the ion's bound electrons. This opens the possibility for transition to the N + O system if the vibrational configuration of the ion is nearly at the potential crossing point r_o. Of course, electrons behave as quantum waves rather than classical particles, but except for misrepresenting features like glory and rainbow effects, a classical treatment is expected to cut through the average of the quantum results.

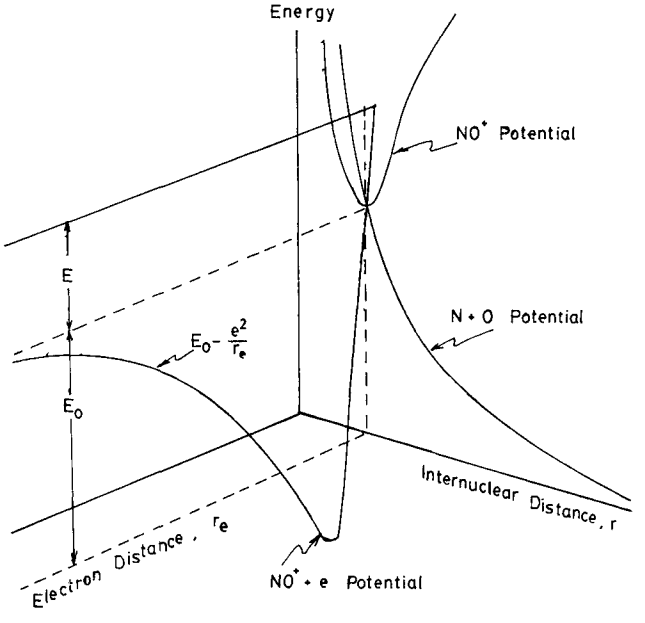

Fig. 2 Diagram of schematic potential surfaces for E, NO^+, and N+O systems.

Because of the Coulomb attraction, a large cross section leads to encounters close enough to permit transition. The square of the maximum miss distance b_m, which allows the electron to come within some distance r^* needed for transition (the order of a Bohr radius), varies nearly inversely with electron collision energy.

$$\left(\frac{b_m}{r^*}\right)^2 = 1 + \frac{e^2}{r^*E} \approx \frac{e^2}{r^*E} \tag{3}$$

The Landau-Zener relation[24,25] for the probability of transition at a potential crossing, or near crossing, is

$$P = 2q(1 - q) \tag{4}$$

where q is the probability that no transition occurs at the crossing either during the incoming or outgoing portion of the trajectory. This factor can be expressed[26]

$$q = e^{-a/u} \tag{5}$$

where u is the velocity with which the system crosses the reaction zone and a is a characteristic velocity that depends on the interaction between the potentials and the difference in their gradients at that point. Although the Landau-Zener expression is known to increase somewhat too rapidly above threshold and to fall off too gradually in the high energy region, as $1/E^{1/2}$ rather than $1/E$, it does seem to give reasonable values and shapes for reaction cross sections near the peak, and its limits are valid. Thus the model is assumed to give a somewhat realistic functional dependence of rate coefficient on temperature.

Electron velocities are typically on the order of 100 times larger than heavy particle velocities in the gas, so for most collisions the transition probabilities are expected to be small enough that the total probability of transition given by Eq. (4) is approximately inversely proportional to the electron's velocity

$$P = 2e^{-a/u}(1 - e^{-a/u}) \approx \frac{2a}{u} = \frac{\text{const}}{E^{1/2}} \tag{6}$$

Although this approximation is invalid at very low collision energies, those collisions are weighted lightly by the Boltzmann distribution, at least at high electron temperature. Equations (3) and (6) combine to give a relation for the total cross section inversely proportional to the 3/2 power of electron kinetic energy

$$S \propto Pb_m^2 \propto \frac{1}{E^{3/2}} = \frac{1}{(kT_e)^{3/2}x^{3/2}} \tag{7}$$

where x is the dimensionless energy E/kT_e. The rate coefficient for transition is[26]

$$k = \bar{u}\int_0^\infty Sxe^{-x}\,dx \propto \frac{1}{T_e}\int_0^\infty \frac{e^{-x}\,dx}{x^{1/2}} = \frac{\text{const}}{T_e} \tag{8}$$

Equation (8) gives the dependence of the rate coefficient for a favorable vibrational configuration of the NO^+ ion. The probability p_v that an ion in vibrational state v is within a small region δ near the bottom of its potential well, and thus within the reaction zone, is

$$p_v = \frac{\delta}{\tau u_v} = \left(\frac{\mu}{2v\hbar\omega}\right)^{1/2}\frac{\delta}{\tau} \tag{9}$$

where τ is $2\pi/\omega$, the period of vibration. The overall rate coefficient is obtained by summing the coefficients for each state v weighted by the probability that the ion is in the vth vibrational state

$$k \propto \frac{1}{Q_v T_e}\sum_v \frac{e^{-v\theta/T_v}}{(v\theta)^{1/2}} \approx \frac{1}{Q_v T_e}\frac{(\pi T_v)^{1/2}}{\theta} \tag{10}$$

If the crossing were to occur at the second vibrational level, where at least two of the crossings apparently do occur,[22] the summation would merely start at the second level, but the functional relation would remain the same. Approximating Q_v with the harmonic oscillator partition function

$$k \propto \frac{T_v^{1/2}}{T_e}(1-e^{-\theta/T_v}) \xrightarrow{T_v>\theta} \frac{\text{const}}{T_e T_v^{1/2}} \xrightarrow{T_e=T_v=T} \frac{\text{const}}{T^{3/2}} \tag{11}$$

Thus at high temperature the overall dissociative recombination rate is predicted to vary inversely with electron temperature and the square root of the vibrational temperature. Although some of the low-temperature experiments[17–19] and Sun and Nakamura's multichannel quantum defect theory[22] suggest a slightly weaker variation with electron temperature, the above results are not greatly different and they preserve the rate which has been accepted for full equilibrium. The constant is chosen so that at high-temperature equilibrium the value will match Dunn and Lordi's result,[12] Eq.(2b). Then the recommended rate coefficient for dissociative electron recombination with NO^+ for use over a wide range of temperature is

$$k = 3.0\times 10^{18}\frac{T_v^{1/2}}{T_e}(1-e^{-3420/T_v}) \quad \text{cc/mol-s} \tag{12}$$

Equation (12) is a relatively simple expression which includes the effect of nonequilibrium electron and vibrational temperatures.

Ionization Due to N + O Collision

The equilibrium constant relates the equilibrium endothermic rate for ionization due to collision between atoms to the equilibrium exothermic rate for dissociative recombination. Neglecting the upper electronic states and treating the diatomic species as rigidly rotating harmonic oscillators, the approximation for the equilibrium constant is

$$K_{eq} = \frac{Q_{NO^+}Q_e}{Q_N Q_O} = 1.22\times 10^{-8}\frac{T}{1-e^{-3420/T}}e^{-32400/T} \tag{13}$$

and the expression for the equilibrium endothermic rate coefficient which corresponds to Eq. (12) is

$$k = 3.66\times 10^{10}T^{1/2}e^{-32400/T} \quad \text{cc/mol-s} \tag{14}$$

This is functionally the same as proposed by Blottner,[15] though about four times larger.

The effect of nonequilibrium electronic energy on this rate coefficient can be estimated in the manner previously used for the effect of vibrational nonequilibrium on dissociation.[27] The overall rate coefficient is the sum which includes ionization transitions from all pairs of excited states i and j

$$k = \sum_i\sum_j\left(\frac{n_i}{n}\right)_N\left(\frac{n_j}{n}\right)_O k_{ij} \tag{15}$$

The rate coefficients k_{ij} are assumed to take the Arrhenius form

$$k_{ij} = \bar{u}Se^{-(I-\varepsilon_i-\varepsilon_j)/kT} \tag{16}$$

No doubt the effective cross section S will increase somewhat in the higher excited states, but that variation is assumed to be relatively minor and the cross section factor is treated as a constant that can be removed from the summation. For a distribution characterized by the temperature T_e, the fraction of each specie that occurs in excited state i with the degeneracy g_i and the electronic energy ε_i is

$$\left(\frac{n_i}{n}\right) = \frac{g_i e^{-\varepsilon_i/kT_e}}{Q(T_e)}; \quad Q(T_e) = \sum_i g_i e^{-\varepsilon_i/kT_e} \tag{17}$$

Then the overall rate coefficient can be expressed

$$k = \bar{u}Se^{-I/kT}\frac{Q_N(T^*)}{Q_N(T_e)}\frac{Q_O(T^*)}{Q_O(T_e)} \tag{18a}$$

where $Q_M(T^*)$ is the electronic partition function for the specie M at the fictitious temperature T^*

$$\frac{1}{T^*} = \frac{1}{T_e} - \frac{1}{T} \tag{18b}$$

In this approximation the ratio of the rate coefficient k to the equilibrium coefficient k_{eq}, is

$$\frac{k}{k_{eq}} = \frac{Q_N(T)\,Q_O(T)}{Q_N(T_e)\,Q_O(T_e)}\frac{Q_N(T^*)\,Q_O(T^*)}{\left(\sum_i g_i\right)_N\left(\sum_j g_j\right)_O} \tag{19a}$$

In the limits as T_e approaches T, T^* becomes infinite and the ratio becomes unity, while as T_e vanishes the fictitious temperature T^* approaches T_e and the ratio approaches a finite limit less than unity.

$$\frac{k}{k_{eq}} \xrightarrow{T_e \to 0} \frac{Q_N(T)\,Q_O(T)}{\left(\sum_i g_i\right)_N\left(\sum_j g_j\right)_O} \tag{19b}$$

To apply these approximations to N and O atoms, the electronic partition functions are truncated at energy levels where ε_i/k goes beyond 100,000 K, which should suffice for temperatures up to at least 15,000 K.

$$\begin{aligned} Q_N(T) &\approx 4 + 10e^{-27700/T} + 6e^{-48600/T} \\ Q_O(T) &\approx 5 + 3e^{-228/T} + e^{-326/T} + 5e^{-22800/T} + e^{-48600/T} \end{aligned} \tag{20}$$

In this case the limit of Eq. (19b) is about

$$\frac{k}{k_{eq}} \xrightarrow[T_e \ll T < 5000\,\mathrm{K}]{} \approx \frac{(4)\,(5+3+1)}{(20)\,(15)} = 0.12 \tag{19c}$$

Figure 3 shows the ratio k/k_{eq} calculated from these approximations for N and O atoms. Curves are shown as a function of temperature for ratios T_e/T of 0.95, 0.9, 0.8, 0.7, 0.5, and 0.1. The latter curve for T_e/T equal to 0.1 is close to the limit of Eq. (19b). These factors multiplied by the equilibrium rate coefficient of Eq. (14) provide an estimate for the endothermic rate coefficient when electronic temperature is not in equilibrium with the kinetic temperature of the gas.

For CFD computations where huge numbers of grid points in the flow must be considered, the algorithm used for the rate coefficient should be as simple as possible consistent with the needs for accuracy. Algorithms that provide rate coefficients within a factor of two are sufficiently accurate for many purposes. A totally empirical algorithm that fits the results of Fig. 3 within a factor of two may be as useful as the more complex algorithm of Eq. (19a).

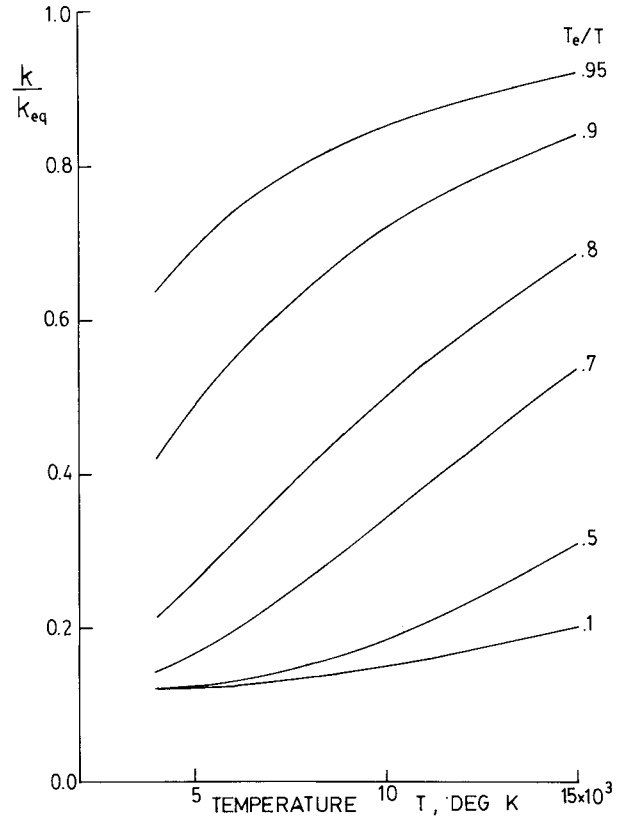

Fig. 3 Effect of nonequilibrium electron temperature on the ionization rate for N + O atom collisions.

$$\frac{k}{k_{eq}} \approx 0.15 + 0.85\left(\frac{T_e}{T}\right)^6 \tag{20}$$

Concluding Remarks

Simple functional relations have been developed for dissociative electron recombination with the NO^+ ion and for ionization produced in N + O collisions. At full equilibrium all the temperatures equate with the heavy particle kinetic temperature, in which case the dissociative recombination rate coefficient varies inversely with $T^{1/2}$ at low temperatures and inversely with $T^{3/2}$ when temperatures are high compared with the characteristic vibrational temperature $\hbar\omega/k$. This relation agrees more or less with most of the experimental determinations made at both normal and high temperatures, whereas the simple $T^{-3/2}$ variation that has often been used when making flowfield calculations does not describe the observations over the entire range of temperatures quite as well. The pre-exponential factor for the N + O ionization rate at equilibrium is predicted to vary as $T^{1/2}$ as is generally assumed.

Since many flow regions around the new generation of space vehicles will involve highly nonequilibrium vibrational and electron energy distributions, an expression is required which incorporates the specific variation of the rate coefficient with the nonequilibrium temperatures that describe these distributions. The present model merely provides functional relations, but by anchoring the results to experimental measurements, the need for quantitative expressions which include the dependence on translational, vibrational, and electron temperatures is addressed in an approximate manner. It has been kept in mind that if an expression for the rate coefficient is to be useful in computational fluid mechanics applications, where huge numbers of grid points in the flow must be considered, that expression must be as simple as possible consistent with the need for accuracy.

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