

ternally, the internal surfaces being due to the existence of microvoids, impurities, and chemical additives. Therefore, the solid phase reaction should depend a great deal on the physical state of the propellant as well as the chemical nature. Of course, this argument does not preclude the fact that some of the bonds away from the surface can break; rather it implies that the activation energy for bond breaking at the surface must be lower than that away from the surface.

The abrupt change in the burning rate at certain pressures is shown to be due to the fact that discrete gas phase reactions occurring a few microns above the burning surface reach the surface at these pressures (Thompson and Suh⁹). The flame seems to appear when the concentration of reactants increases sufficiently because of the increased burning rate.

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Mobility of NO⁺ Ions in Air

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Nomenclature

e	= electron charge
f_j	= fractional concentration of the j species
k	= Boltzmann constant
m_j	= mass of particle of the j species
n	= total number density
n_0	= Loschmidt number
r_0	= nondimensionalizing length in the inverse power repulsive potential
r_{ij}	= interparticle separation
$A^{(1)}(\nu)$	= collision integral for an inverse power potential
$B(\nu)$	= collision integral correcting for a weak secondary potential
K_{ij}	= coefficient of the short-range inverse power repulsive potential
T	= temperature
α_j	= polarizability of the j species

μ_{ij}	= mobility of ion i in the j species
ν	= index of the inverse power repulsive potential
σ_{ij}	= hard sphere diameter
σ_{eff}	= effective hard sphere diameter of the inverse power potential
$\psi(r_{ij})$	= interparticle potential
$\Gamma(x)$	= gamma function
$\Omega_{ij}^{(1,1)}$	= collision integral characteristic of diffusion

Introduction

IN order to use the results of any theory of continuum electrostatic probe operation, it is necessary to possess a good knowledge of the mobility of the particular ions being collected. In air plasmas, the ions of most interest are NO⁺. In spite of the importance of this ion species, there are few experimental data available on its mobility at room temperature, and none at all at the higher plasma temperatures of interest in probe diagnostics. An alternative to direct measurement of the mobility is an accurate calculation from known or measured interparticle potential functions such as that based on the Chapman-Enskog theory, for example. This is the approach taken in this note, since reasonable hypotheses may be made regarding the interaction potential of NO⁺ and the air species.

In the first approximation of the Chapman-Enskog theory,¹ the mobility of an ion (subscript i) in a gas of neutral particles (subscript j) may be written

$$\mu_{ij} = \frac{3}{16} \left(\frac{m_i + m_j}{m_i m_j} \right) \frac{e}{n(1/\Omega_{ij}^{(1,1)})} \quad (1)$$

where $n = n_i + n_j$, and $\Omega_{ij}^{(1,1)}$ is the collision integral appropriate to diffusion.^{1,2} The collision integral depends in a complicated way on the interparticle potential and, for a given pair of particles, is a function of the temperature only. We shall assume the potential to be the sum of a short-range repulsive potential and an attractive polarization potential

$$\psi(r_{ij}) = \psi_{rep}(r_{ij}) + \psi_{att}(r_{ij}) \quad (2)$$

$$\psi_{rep}(r_{ij}) = K_{ij}(r_0/r_{ij})^\nu \quad (3)$$

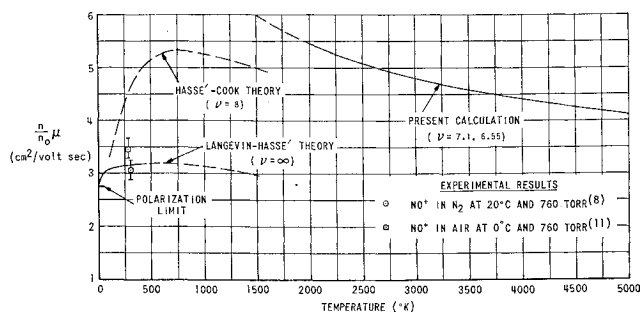
$$\psi_{att}(r_{ij}) = -\alpha_j e^2 / 2r_{ij}^4 \quad (4)$$

In general, it will be true that the repulsive potential will depend on a higher inverse power of the interparticle distance than the attractive potential (i.e. $\nu > 4$) so that the repulsive potential will dominate at high temperatures and the polarization potential should dominate at low temperatures. In the special case when the repulsive potential is represented by a hard sphere core ($\nu \rightarrow \infty$), the collision integral has been calculated by Langevin and later by Hassé. A function that for this case is closely related to $\Omega_{ij}^{(1,1)}$ is tabulated by McDaniel³ where references to the original calculations are listed. This calculation is useful at low temperatures where the exact form of the repulsive potential is least important. The form of the potential function Eqs. (2-4) is in fact suggested by the success of the Langevin-Hassé theory in predicting the mobility in many cases.³ It should be pointed out, however, that while this potential is assumed to be suitable for the interaction of NO⁺ and the air species, it may be inadequate in other cases where quadrupole and dipole-dipole (dispersion) forces interactions may contribute substantially to the attractive portion of the potential function.

The exact calculation of $\Omega_{ij}^{(1,1)}$ for potentials of the type given by Eqs. (2-4) is very complicated, except for special cases.^{1,2} Moreover, such a complete calculation is not warranted since the measured repulsive potentials on which it would be based are known only over restricted temperature ranges (e.g. Ref. 4). At high temperatures, where the attractive potential is weak compared to the repulsive potential, Chapman and Cowling² show that for the type of interparticle potential assumed here, the collision integral can be

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Figure 1 THE MOBILITY OF NO⁺ IN AIRFig. 1 The mobility of NO⁺ in air.

written

$$\Omega_{ij}^{(1,1)} = \Omega_{ij,rep}^{(1,1)} [1 - B(\nu) \psi_{att}(\sigma_{eff})/kT] \quad (5)$$

where

$$\Omega_{ij,rep}^{(1,1)} = [(\pi kT/2)(m_i + m_j)/m_i m_j]^{1/2} \sigma_{eff}^2 \quad (6)$$

$$\sigma_{eff}^2 = A^{(1)}(\nu) \{ \nu \psi_{rep}([kT]^{1/\nu}) \}^{2/\nu} \Gamma(3 - 2/\nu) \quad (7)$$

Here, $\Omega_{ij}^{(1,1)}$ is the collision integral for the inverse-power repulsive potential alone, and σ_{eff} is an effective hard sphere diameter defined in terms of an additional collision integral $A^{(1)}(\nu)$, which has been calculated for some values of ν .^{2,5} This result, Eq. (5), is similar to Sutherland's hypothesis⁶ and it introduces the new collision integral $B(\nu)$. Values of $A^{(1)}(\nu)$ and $B(\nu)$ for the interaction potential of NO⁺ with O₂ and N₂ have been calculated and are listed in Table 1. The mobility of an ion in a mixture of gases, when it is a minority species, is given by the Chapman-Enskog theory (also known as Blanc's law in the case of a binary mixture)

$$1/\mu_i = \sum_j f_j / \mu_{ij} \quad (8)$$

where f_j is the fractional concentration of the j species.

Low Temperature Mobility

At a temperature sufficiently low that polarization forces dominate, the Langevin-Hassé theory may be used, provided charge exchange and clustering effects are not important. Since the short range forces are of secondary importance, the effective hard sphere diameter may be estimated with sufficient accuracy from viscosity data measured in the temperature range of interest. The polarizability α_j is obtained from the dielectric constant of the gas. The dielectric constant for O₂ and N₂ and the viscosity of NO and O₂ up to 550°K and N₂ up to 1695°K were obtained from Ref. 7. The hard sphere diameter of NO⁺ is assumed to be the same as that of NO. The diameters are combined according to

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (9)$$

to obtain the effective hard sphere diameters listed in Table 1. For simplicity in the calculations, air has been assumed to be a binary mixture of 22.1% oxygen and 77.9% nitrogen. The calculated mobility is plotted in Fig. 1 up to a temperature of 1500°K, although the collision diameter estimates are valid only to 500°K. For comparison the figure also includes some measured mobilities. The measured mobility of NO⁺ in air at 0°C and 760 torr¹¹ is

$$\mu_{NO^+ - AIR} = 3.49 \pm 5\%, \text{ cm}^2/\text{v sec}$$

and the measured mobility of NO⁺ in N₂ at 20°C and 760 torr⁸ is

$$\mu_{NO^+ - N_2} = 3.3 \pm 0.2, \text{ cm}^2/\text{v sec}$$

The corresponding mobility calculated from the Langevin-

Table 1 Interaction potential data

	$\sigma_{ij}(\text{\AA})$	ν	$K_{ij}(\text{eV})$	Temp. range (°K)	$A^{(1)}(\nu)$	$B(\nu)$
NO-N ₂	3.01	7.1	426	1946-11820	0.3137	-0.164
NO-O ₂	3.12	6.55	281	2020-12520	0.3098	-0.183

Hassé theory is

$$\mu_{NO^+ - N_2} = 3.40, \text{ cm}^2/\text{v sec}$$

The good agreement may be viewed as evidence that charge-exchange effects are small, which is also to be expected in view of the large difference in the ionization potentials of NO and N₂. Young et al.⁸ also find that NO⁺ obeys Blanc's law in mixtures of N₂ and He, indicating a negligible amount of clustering.

High Temperature Mobility

Direct measurements of the short-range interaction potentials of NO⁺ are not available. However, effective spherically symmetric potentials of the form of Eq. (3) have been measured for the N₂-N₂, N₂-O₂, O₂-O₂ interactions⁹ using high energy neutral beams. These potentials may be used to estimate the interaction potentials for NO-N₂ and NO-O₂ by using the empirical combining principle

$$\psi_{ij} = (\psi_{ii}\psi_{jj})^{1/2} \quad (10)$$

It may be noted that the original potentials satisfy this rule among themselves.⁹ The potentials for the NO interactions are assumed to also apply to the NO⁺ ion (the ion may be expected to be slightly more compact than the neutral molecule judging by the interatomic bond length¹⁰). The characteristic parameters of the potentials are listed in Table 1, with the interparticle distance nondimensionalized by $r_0 = 10^{-8}$ cm. The temperature range of validity is taken as the interior range of the temperature ranges of the original measured potentials determined from the given span of interparticle separation distance by the formula $kT = \psi(r_{ij})$.

The mobility is calculated by Eqs. (5-8) and plotted in Fig. 1, assuming the same binary composition of air as that used for the low temperature calculation, i.e., neglecting the effects of dissociation. Further refinements in the calculation are not justified until better interaction potentials become available.

The qualitative variation of mobility in the intermediate temperature range is illustrated in Fig. 1 using the Hassé-Cook calculation for $\nu = 8$. The coefficient of the short-range Hassé-Cook potential has been evaluated to give the same value of potential as the NO-N₂ repulsive potential at 2000°K. The figure illustrates the fact that the maximum value of the mobility increases with decreasing ν (i.e. with increasing "softness" of the repulsive potential) for potentials of the form given by Eqs. (2-4). To correctly account for experimental measurements in this temperature range it will be necessary to include the quadrupole and dipole-dipole interactions, which act to reduce the value of the mobility.¹³

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Conductivity of an Impure, Nonequilibrium Plasma with Electrothermal Instabilities

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Introduction

IT is generally recognized that small amounts of impurity can have a significant effect on the conductivity of a plasma.^{1,2} This is particularly true for a nonequilibrium plasma, where the elevated electron temperature is determined principally by collisions between electrons and neutral atoms. A few tenths of a percent of molecular impurity can absorb a large proportion of the electron energy and lower the electron temperature.

The conductivity of a two-temperature, nonequilibrium plasma is also affected by fluctuations in the electron density, usually referred to as electrothermal instabilities. When the Hall parameter exceeds a certain critical value, oscillations in the local electron density and current density occur, reducing the effective conductivity.^{3,4}

The purpose of this paper is to discuss the combined effect of impurities and fluctuations on the conductivity of a nonequilibrium plasma.

Plasma Specification

A steady-state, seeded plasma is assumed to be flowing perpendicular to a uniform magnetic field. The Hall current is assumed to be zero, so that the electric current is perpendicular to both the magnetic field and the gas velocity. Except for electron density, the properties of the plasma are uniform. The bulk gas total temperature is 2000°K, while the electron temperature is determined from a balance between Joule heating and the losses from collisions between electrons and the heavy species. For simplicity, radiation

and thermal conduction are neglected. The average electron density is determined from the Saha equation. The bulk gas total pressure is 2×10^5 Newtons per square meter and the magnetic field strength is one tesla. The argon is seeded with $\frac{1}{10}\%$ cesium.

The analysis of the electron density fluctuations follows Solbes.³ In that paper a uniform plasma consisting of a neutral carrier and a partially ionized seed is assumed to be present in a uniform magnetic field. A quasi-linear plane wave instability is analyzed and expressions for the effective conductivity of the plasma presented. The analysis in this paper uses the equations in Ref. 3 with only slight modification to include an impurity in the neutral carrier gas. The number density of the carrier is replaced by the sum of the number densities of the carrier and impurity. The electron-atom collision cross section is replaced by an average cross section based on the relative number density of carrier and impurity. The molecular weight of the carrier gas is replaced by an average molecular weight based on the mass fraction of carrier and impurity.

The only impurity discussed in this paper is carbon monoxide. It is a fairly common impurity and absorbs an appreciable amount of energy in a collision with an electron.⁵ The effect of other impurities is qualitatively the same as that presented in this paper.

Discussion and Results

The electron temperature of the plasma is dependent on the current density and therefore on the electric field in the plasma. The external circuit, connected through the electrodes, controls the electric field and determines the state of the plasma. The effect of this external circuit is introduced through a dimensionless load parameter, K , defined as $K \equiv -E/UB$ where E is the electric field in the plasma, U is the gas velocity, and B is the magnetic field strength. The output power density is then given by $P_D = -JE = K(1 - K)\sigma U^2 B^2$.

The variation of power density with load parameter is shown in Fig. 1. The Mach number is 0.5. Curve *a* shows the power density variation when no impurity is present and the density fluctuations are neglected. This curve represents the ideal output with nonequilibrium conductivity. The electron temperature varies inversely with the load parameter, from about 3100°K at $K = 0$ down to the gas temperature at $K = 1$.

When the instability analysis by Solbes³ is included in the calculation, the power density variation follows curve *b*. Curves *a* and *b* are identical until the load parameter K reaches 0.2. Then the plasma becomes unstable and local oscillations reduce the conductivity. No impurity is present in curve *b*.

Curve *c* shows the reduced power density when $\frac{1}{10}\%$ impurity is added to the carrier gas. Density fluctuations are neglected and only the effects of the impurity included. The carbon monoxide impurity has a large inelastic collision cross section and energy is quickly transferred from the electrons to the impurity molecules. The result is a lower electron temperature and a drop in plasma conductivity. The addition of the impurity reduces the power density by a factor of one half.

The effect of both $\frac{1}{10}\%$ impurity and density fluctuations is shown on curve *d*. Since the generated voltage ($U \times B$) is constant, the drop in conductivity caused by the density fluctuations reduces the Joule heating available to the electrons. This energy loss also lowers the electron temperature. The combination of these two nonlinear effects, the impurity and the density fluctuations, lowers the electron temperature more than the sum of the two effects acting singly. The maximum value of power density is about one eighth that of curve *a* and about one fifth that of the impurity alone (curve *c*). For comparison the power density at equilibrium con-

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