CHAPTER II

MATHEMATICAL FORMULATION

II.1 Introduction

In this chapter the set of coupled partial differential equations that describes the dynamics of a high temperature flowfield are derived. This equation set is Navier-Stokes equations expanded so that it is applicable to a gas that is vibrationally and electronically excited, chemically reacting and weakly ionizing. The corresponding equation of state for this gas is also developed. The assumptions underlying the current description are discussed and its weaknesses and limitations are exposed. The models that represent the transfer of mass between different chemical species and the transfer of energy between different energy modes are discussed.

II.2 Basic Assumptions

The nonequilibrium flowfields that are of interest here are assumed to conform to some particular criteria. These conditions make the derivation of the governing equations feasible and are the basis for the entire solution technique.

The flowfields are assumed to be accurately described by a continuum formulation. Let us define the Knudsen number, Kn, to be the ratio of the mean-free-path associated with the flow conditions to the characteristic length scale of the body or of the flow itself. The continuum formulation requires that the Knudsen number be much less than one[1] so that there are a large number of molecules within a computational volume. This implies that there is little statistical variation at any point and as a result the continuum description of the viscous fluxes is consistent. A second requirement of this approach regards the treatment of the interaction between the gas and the surface of the body. It is assumed that there are a large enough number of collisions of the gas molecules with the wall so that there is no velocity or temperature slip at the wall. This condition is also satisfied with a small Knudsen number.

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[1] This requirement is usually met with $Kn < 0.1$ and flowfields for this Kn have been computed.

The thermal state of the gas is assumed to be described by separate and independent temperatures. The energy in the translational modes of all the heavy-particles, *i.e.* everything except the electrons, is assumed to be characterized by a single translational temperature. The rotational state of the diatomic molecules is taken to be equilibrated with this translational temperature. Thus, we have a single temperature, T, that characterizes the translational-rotational state of the gas. This assumption is reasonable at conditions within the continuum regime where, for air species rotational equilibration with translation takes typically five collisions because of the low characteristic temperature of rotation.

The energy contained in the vibrational modes of diatomic species s is assumed to be described by the vibrational temperature, T_{vs}, which is not a direct function of the rotational state of the gas. The vibrational state is assumed to conform to the harmonic oscillator description at all vibrational temperatures. This is equivalent to assuming that the rate of equilibration of the different vibrational quantum states to the vibrational temperature which characterizes species s is much greater than the equilibration rate of vibrational energy with the other energy modes. This is accurate at low vibrational levels, but becomes suspect at high vibrational temperatures where the vibrational states may be significantly non-harmonic. However, the energy contained in these states is negligibly small for the flowfields of interest in this study[2]. A second assumption implicit in the formulation of the vibrational state is that rotational-vibrational coupling is not appreciable. This becomes questionable at high temperatures, but the increased complexity associated with a more accurate treatment of the rotational states is thought not to be warranted for this work. Each diatomic species has been assumed to have a separate vibrational energy, and a corresponding vibrational temperature. The coupling between the vibrational states of the different molecules can be significant and thus vibration-vibration coupling must be included.

The translational energy of the free electrons is quantified by the electron temperature, T_e. The excited electronic states of the molecules are assumed to be in a Boltzmann distribution corresponding to the electron translational temperature. This implies that the temperature that characterizes the excited states of molecules is in equilibrium with

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[2] See Lee (1985)

the temperature of the free electrons. Because the electrons associated with the excited states of the molecules can change places with the free electrons with relative ease, they must have nearly identical temperatures. The Boltzmann description of the excited states is most accurate at low electron temperatures, but the energy contained in the highly excited, non-Boltzmann states is insignificant for the conditions of present interest (Park (1985b)).

The gas has been assumed to be weakly ionized, which implies that there the mass fraction of ions is less than one percent[3]. Although this assumption is not implemented explicitly in the derivation of the governing equations, however several terms that can have a significant influence in a highly ionized plasma have been ignored. This is a reasonable assumption because the flowfields of interest in this work are within this limitation. Further, more specific, assumptions are made and these will be discussed in conjunction with the derivation of the governing equations.

II.3 The Conservation Equations

The time-dependent equations that govern the motion of a gas mixture are derived in this section. First the individual species mass, momentum, and energy conservation equations are discussed and then these are combined to yield the complete equation set. This will make the underlying assumptions embodied in the governing equations evident.

The equations that describe the conservation of mass, momentum, and energy for the chemical species s of the gas may be written as follows. The species mass conservation is given by[4]

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x_j}\left(\rho_s u_{sj}\right) = w_s. \tag{2.3.1}$$

The species momentum conservation is written as

$$\frac{\partial}{\partial t}\left(\rho_s u_{si}\right) + \frac{\partial}{\partial x_j}\left(\rho_s u_{si} u_{sj} + p_s \delta_{ij} + \tau_{sij}\right) = N_s e Z_s \tilde{E}_i + P_{si}, \tag{2.3.2}$$

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[3] Weak ionization depends on having a small Coulomb cross-section relative to the electron-neutral cross-section (see Section II.7.2).

[4] See Lee (1985), Vincenti and Kruger (1965), and Appleton and Bray (1964).

and the species energy conservation as

$$\frac{\partial E_s}{\partial t} + \frac{\partial}{\partial x_j}\left((E_s + p_s)u_{sj} + u_{si}\tau_{sij} + q_{tsj}\right) = N_s e Z_s \tilde{E}_i u_{si} + Q_s, \qquad (2.3.3)$$

where u_{si} is the species velocity in the i direction. The terms appearing on the right-hand side of these equations, w_s, P_{si}, and Q_s, represent the mass, momentum, and energy transfer rates respectively. They describe the interaction of species s with the other chemical components of the mixture. The mass source term, w_s, is the rate of production of species s due to chemical reactions. P_{si} is the rate of momentum transfer between species s and the other molecules due to collisions and force-field interactions in the i direction. And Q_s represents the rate of energy transfer to and from the various energy modes of s due to interactions with other species. The quantity $\tilde{E}_i$ is the electric field in the i direction due to charge separation; it acts on ions and electrons only. τ_{sij} is the shear stress tensor and q_{tsj} is the total heat flux vector of species s. Each of these terms is modeled or eliminated as discussed below.

The vibrational energy conservation equation for each diatomic species may be derived by considering the conservation of ε_{vs}, the vibrational energy per particle, as it is convected at a velocity u_{si}. If there is no conduction of vibrational energy or energy transfer, then we have simply

$$\frac{\partial \varepsilon_{vs}}{\partial t} + \frac{\partial}{\partial x_j}\left(\varepsilon_{vs} u_{sj}\right) = 0. \qquad (2.3.4)$$

The vibrational energy per particle is related to the vibrational energy per unit volume by the relation

$$E_{vs} = \rho_s e_{vs} = \rho_s \varepsilon_{vs} \frac{\hat{N}}{M_s}. \qquad (2.3.5)$$

If we multiply equation (2.3.4) by $\rho_s \hat{N}/M_s$, and use expression (2.3.5), we have the equation

$$\frac{\partial \rho_s e_{vs}}{\partial t} - e_{vs}\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x_j}\left(\rho_s e_{vs} u_{sj}\right) - e_{vs}\frac{\partial}{\partial x_j}\left(\rho_s u_{sj}\right) = 0. \qquad (2.3.6)$$

The vibrational energy conservation equation results by multiplying equation (2.3.1) by e_{vs} and adding it to equation (2.3.6), to get

$$\frac{\partial E_{vs}}{\partial t} + \frac{\partial}{\partial x_j}\left(E_{vs}u_{sj}\right) = -\frac{\partial q_{vsj}}{\partial x_j} + Q_{vs} + w_s e_{vs}, \tag{2.3.7}$$

where the vibrational heat conduction and energy transfer rate have also been included. The term $w_s e_{vs}$ in this equation results from the derivation and is due to the fact that vibrational energy is conserved on a per-particle basis, not on a volumetric basis. It represents the amount of vibrational energy that is added to or taken away from the vibrational energy due to the production or destruction of species s. Thus when a diatomic molecule dissociates, the vibrational energy associated with it must also be removed from the vibrational energy pool of that molecule. The same process is assumed to occur in reverse, namely that when a molecule is created, it is formed with the average vibrational energy of that species. We have not taken into account any preferential removal of vibrational energy due to dissociation with this approach. That is, the diatomic molecules that dissociate tend to be those in the highly excited vibrational levels. Thus they carry more than the average vibrational energy with them and a dissociation reaction suppresses the vibrational temperature[5]. However, as indicated by Park (1986, 1987), ignoring the effect of preferential removal is appropriate because the dissociation reaction rates that are available currently were computed without including this effect and this approach is consistent with the use of these rates.

In principle, the n component gas could be represented by solving equations (2.3.1–3) and (2.3.7) for each species. However, this would entail the solution of n momentum equations and the evaluation of the momentum exchange term P_{si}. This approach is not feasible for a two or three-dimensional flowfield with more than a few species. The problem may be simplified by assuming that the species velocities, u_{si}, are approximately the same size as the mass-averaged velocity, u_i, defined by

$$u_i = \sum_{s=1}^{n} \frac{\rho_s}{\rho} u_{si}, \qquad \rho = \sum_{s=1}^{n} \rho_s. \tag{2.3.8}$$

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[5] See Marrone and Treanor (1963), Treanor and Marrone (1962), and Park (1988).

Then we define the diffusion velocity, v_{si}, to be the difference between the species velocity and the mass-averaged velocity

$$v_{si} = u_{si} - u_i. \tag{2.3.9}$$

Expressed with these new variables, the species mass conservation equation, (2.3.1), becomes

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x_j}\big(\rho_s u_j\big) = -\frac{\partial}{\partial x_j}\big(\rho_s v_{sj}\big) + w_s. \tag{2.3.10}$$

The species momentum equation, (2.3.2), may be summed over all species to yield the mass-averaged momentum equation

$$\frac{\partial}{\partial t}\big(\rho u_i\big) + \frac{\partial}{\partial x_j}\big(\rho u_i u_j + p\delta_{ij}\big) = -\frac{\partial}{\partial x_j}\sum_{s=1}^{n}\rho_s v_{si}v_{sj} - \frac{\partial \tau_{ij}}{\partial x_j} + \sum_{s=1}^{n}eN_s Z_s \tilde{E}_i, \tag{2.3.11}$$

where the total pressure, p, and shear stress τ_{ij}, are defined as the sum of the species quantities. By making this summation, the inter-species momentum transfer terms, P_{si}, sum identically to zero, which is a significant simplification. However, the sum of the electric field induced forces is not zero due to the differing charge numbers on ions and electrons.

A similar summation may be made to the species energy equation, (2.3.3), to yield the total energy equation for the mixture

$$\begin{aligned}
\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j}\big((E+p)u_j\big) &= -\frac{\partial}{\partial x_j}\big(q_j + q_{vj} + q_{ej}\big) - \frac{\partial}{\partial x_j}\big(u_i \tau_{ij}\big) \\
&\quad - \frac{\partial}{\partial x_j}\sum_{s=1}^{n}v_{si}\big(h_s\delta_{ij} + \tau_{sij}\big) + \sum_{s=1}^{n}eN_s Z_s \tilde{E}_i\big(u_i + v_{si}\big).
\end{aligned} \tag{2.3.12}$$

The heat conduction vector has been expressed in component form, where each term is due to gradients in the different temperatures in the flowfield.

In addition to the total energy equation, we require an equation for each form of energy that is treated separately. In this case, we are using the approach where a vibrational

energy for each diatomic species and the electron energy are computed. Thus, for a gas with m diatomic species, we need to solve m vibrational energy equations, (2.3.7), which may be re-written as

$$\frac{\partial E_{vs}}{\partial t} + \frac{\partial}{\partial x_j}\left(E_{vs}u_j\right) = -\frac{\partial}{\partial x_j}\left(E_{vs}v_{sj}\right)$$
$$-\frac{\partial q_{vsj}}{\partial x_j} + Q_{T-vs} + Q_{v-vs} + Q_{e-vs} + w_s e_{vs}. \tag{2.3.13}$$

The various energy transfer mechanisms to the vibrational energy modes have been represented here. Q_{T-vs}, Q_{v-vs}, and Q_{e-vs} are respectively the rates of translation-vibration, vibration-vibration, and electron-vibration energy exchange. We have chosen to treat the vibrational energies separately instead of summing over the m diatomic species because it is not clear that the vibrational temperatures of each species are the same. In the limiting case where vibration-vibration coupling is very strong, the vibrational temperatures will be identical. However, the strength of this energy coupling was not known *a priori*, and with this method we are able to examine its effects.

The dynamics of the electron translational energy, E_e, are computed with the solution of the electron energy equation which is a species energy equation, (2.3.3), applied to electrons. This may be written as

$$\frac{\partial E_e}{\partial t} + \frac{\partial}{\partial x_j}\left((E_e + p_e)u_j\right) = -\frac{\partial}{\partial x_j}\left((E_e + p_e)v_{ej}\right) - \frac{\partial q_{ej}}{\partial x_j}$$
$$-\frac{\partial}{\partial x_j}\left((u_i + v_{ei})\tau_{eij}\right) - N_e e \tilde{E}_i(u_i + v_{ei}) + Q_{T-e} - \sum_{s=1}^{m} Q_{e-vs} + w_e e_e. \tag{2.3.14}$$

Where Q_{T-e} is the translation-electron energy exchange rate. We should note that the transport of electron energy is fundamentally different than that of vibrational energy. The vibrational energy of a species is convected at the local velocity u_i, whereas the electron energy convection speed is also a function of the local electron pressure, p_e.

These differential equations describe the flow of an n species, the first m of which are diatomic, ionized gas. The solution of these equations yields the dynamics of the conserved

flow variables $\rho_1 \ldots \rho_n$, ρu_i, $E_{v1} \ldots E_{vm}$, E_e, and E. With the equations of state, the non-conserved variables may be determined as will be described below. The models that have been used to describe the energy transfer rates will be discussed.

II.4 Simplifications to the Conservation Equations

Some minor simplifications to the governing equations may be made which make it possible to determine an algebraic expression for the electric field. Consider the species momentum equation, (2.3.2), applied to electrons

$$\frac{\partial}{\partial t}\left(\rho_e u_{ei}\right) + \frac{\partial}{\partial x_j}\left(\rho_e u_{ei} u_{ej} + p_e \delta_{ij}\right) = -\frac{\partial \tau_{eij}}{\partial x_j} - eN_e \tilde{E}_i + P_{ei}. \tag{2.4.1}$$

If we take the ratio of the dynamic pressure of the electron gas to the electron pressure and assume that the electron speed and temperature are about the same as the bulk gas, we have

$$\frac{\rho_e u_e^2}{p_e} = \frac{M_e u_e^2}{RT_e} \simeq \frac{M_e u^2}{RT} \simeq \frac{M_e}{M}\mathcal{M}^2. \tag{2.4.2}$$

The ratio M_e/M is of the order of 10^{-6} and for conditions of interest the square of the Mach number will be of the order of 10^3 at most. Therefore we can neglect the electron dynamic pressure relative to the electron pressure. The electron shear-stress is also small relative to the electron pressure, and because we are solving for a steady-state, we may neglect the time derivative of the momentum. The momentum transfer rate due to inter-species collisions, P_{ei}, is assumed to be small for electrons due to their small collision cross-section. Therefore, by neglecting these terms, the electric field may be expressed as

$$\tilde{E}_i \simeq -\frac{1}{N_e e}\frac{\partial p_e}{\partial x_i}. \tag{2.4.3}$$

This expression for the electric field may be inserted in the mass-averaged momentum equation, (2.3.11), and the total energy equation, (2.3.12). This simplification eases the solution considerably because the electric field is fundamentally represented by a set of electro-dynamic equations[6].

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[6] See Appleton and Bray (1964).

The electron energy equation (2.3.14) may also be simplified with the use of this expression. A further modification to this expression is required to make the equation set diagonalizable, which is necessary for its numerical solution, as will be seen in the following chapter. Namely, the term $\frac{\partial}{\partial x_j} p_e u_j$ must be moved to the right-hand side and treated as a viscous term, taking the equation set out of conservation-law form. Then (2.3.14) becomes

$$
\frac{\partial E_e}{\partial t} + \frac{\partial}{\partial x_j}\left(E_e u_j\right) = -\frac{\partial}{\partial x_j}\left(E_e v_{ej}\right) - p_e \frac{\partial}{\partial x_j}\left(u_j + v_{ej}\right) - \frac{\partial q_{ej}}{\partial x_j}
$$
$$
+ Q_{T-e} - \sum_{s=1}^{m} Q_{e-vs} + w_e e_e,
$$
(2.4.4)

where we have assumed that the electron shear stresses are negligible. The final assumption is that the terms which involve the square of diffusion velocities or are products of species shear-stresses and diffusion velocities are considered to be negligible. This alters (2.3.11) and (2.3.12), the final form of which will be given in Section II.10.

II.5 Equations of State

The relationship between the conserved quantities and the non-conserved quantities such as pressure and temperature are derived in this section. The total energy, E, is made up of the separate components of energy which may be written as

$$
E = \sum_{s\neq e}^{n} \rho_s c_{vs} T + \frac{1}{2}\sum_{s\neq e}^{n}\rho_s u_i u_i + \sum_{s=1}^{m} E_{vs} + E_e + \sum_{s\neq e}^{n}\rho_s h_s^{\circ} + \sum_{s\neq e}^{n}\rho_s e_{\mathrm{els}}.
$$
(2.5.1)

This expression may be inverted to yield the energy in the translational-rotational modes, and consequently T. The constants of specific heat at constant volume, c_{vs}, are the sum of the specific heat of translation, $c_{vtr\,s}$, and the specific heat of rotation, $c_{vrot\,s}$. These are given by

$$
c_{vtr\,s} = \frac{3}{2}\frac{R}{M_s},
$$
$$
c_{vrot\,s} = \begin{cases} \frac{R}{M_s}, & \text{for } s = 1, m; \\ 0, & \text{otherwise.} \end{cases}
$$
(2.5.2)

The vibrational temperature of species s is determined by inverting the expression for the vibrational energy contained in a harmonic oscillator at the temperature T_{vs}

$$E_{v_s} = \rho_s \frac{R}{M_s} \frac{\theta_{vs}}{e^{\theta_{vs}/T_{vs}} - 1},$$ (2.5.3)

where θ_{vs} is the characteristic temperature of vibration. The electron temperature is determined by inverting the relation between the electron energy E_e and the energy contained in the electron thermal and kinetic energy

$$E_e = \rho_e c_{ve} T_e + \frac{1}{2} \rho_e u_i u_i.$$ (2.5.4)

The electronic excitation energy of the molecules which is characterized by T_e has been included in the total energy and not in the free electron translational energy. This implies that the electronic energy is grouped with the heavy-particle energy modes and that the free electrons tend to assume their temperature independently. This approach is different than that taken by Lee (1985), however without further evidence, one approach is as valid as the other.

The total pressure is the sum of the partial pressures,

$$p = \sum_{s \neq e}^{n} \rho_s \frac{R}{M_s} T + p_e,$$ (2.5.5)

and the electron pressure is given by

$$p_e = \rho_e \frac{R}{M_e} T_e.$$ (2.5.6)

The enthalpy per unit mass, h_s, is defined to be

$$h_s = c_{vs} T + \frac{p_s}{\rho_s} + e_{vs} + h_s^\circ + e_{els}.$$ (2.5.7)

The expression for the energy contained in the excited electron states comes from the assumption that they are in a Boltzmann distribution governed by the electron translational temperature, T_e (Lee (1985)). This yields

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$$e_{\mathrm{els}} = \frac{R}{M_s} \frac{\sum_{i=1}^{\infty} g_{is}\theta_{\mathrm{el}\,is} \exp(-\theta_{\mathrm{el}\,is}/T_e)}{\sum_{i=0}^{\infty} g_{is} \exp(-\theta_{\mathrm{el}\,is}/T_e)}, \tag{2.5.8}$$

where g_{is} is the degeneracy of state i and $\theta_{\mathrm{el}\,is}$ is the excitation energy of that state. In this study only the terms in the sum up to $i=1$ are included. These constants are listed in Appendix A.

II.6 Shear Stresses, Heat Fluxes, and Diffusion Velocities

The shear stresses are assumed to be proportional to the first derivative of the mass-averaged velocities and the Stokes assumption for the bulk viscosity is made. Therefore the expression for the shear stress tensor is

$$\tau_{ij} = -\mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \lambda\frac{\partial u_k}{\partial x_k}\delta_{ij}, \qquad \lambda = -\frac{2}{3}\mu \tag{2.6.1}$$

And the heat conduction vectors are are assumed to be given by the Fourier heat law

$$\begin{aligned}
q_j &= -\kappa\frac{\partial T}{\partial x_j}, \\
q_{vsj} &= -\kappa_{vs}\frac{\partial T_{vs}}{\partial x_j},
\end{aligned} \tag{2.6.2}$$

The flux of electron energy, q_{ej}, has been taken as zero in this work, in part because the conductivity of electron temperature is not well known. This assumption is reasonable because the proportion of electron energy in the total energy is very small. The assumptions of a linear relation between the shear stress and the velocity gradients and between the heat fluxes and the gradients of temperature are suspect as hypersonic Mach numbers. A more accurate description is a topic of current and future research[7] and has not been included in this work.

A viscosity model for reacting air developed by Blottner *et al.* (1971) is used to determine the species viscosity, μ_s. The model uses three constants for a curve fit and yields

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[7] See Fiscko and Chapman (1988).

$$\mu_s = 0.1 \exp\left[(A_s \ln T + B_s) \ln T + C_s\right], \quad \text{(in kg/m\,s)} \qquad (2.6.3)$$

where A_s, B_s, and C_s are found in Appendix A. The curve fits for the viscosity are appropriate for temperatures up to $10,000\,\text{K}$ and for weak ionization. The region of a flowfield where viscous effects are important is in the boundary layer which for most flows is below this temperature and for the cases that have been computed in this study, the flowfield is less than one percent ionized. Thus the viscosity formulation is adequate.

The conductivity of the translational-rotational and vibrational temperatures for each species may be derived from an Eucken relation[8]. With this formulation, it is assumed that the transport of translational energy involves correlation with the velocity, but the transport of internal energy (rotational and vibrational) involves no correlation. The result is that

$$\kappa_s = \mu_s\left(\frac{5}{2}c_{vtr\,s} + c_{vrot\,s}\right) \qquad \kappa_{vs} = \mu_s c_{vvib\,s} \qquad (2.6.4)$$

The total viscosity and conductivity of the gas are then calculated using Wilke's semi-empirical mixing rule (Wilke (1950)).

$$\mu = \sum_s \frac{X_s \mu_s}{\phi_s}, \qquad \kappa = \sum_s \frac{X_s \kappa_s}{\phi_s},$$

where

$$X_s = \frac{c_s M}{M_s}, \qquad M = \left(\sum_s \frac{c_s}{M_s}\right)^{-1}, \qquad (2.6.5)$$

$$\phi_s = \sum_{r \neq e} X_r \left[1 + \sqrt{\frac{\mu_s}{\mu_r}}\left(\frac{M_r}{M_s}\right)^{1/4}\right]^2 \left[\sqrt{8\left(1 + \frac{M_s}{M_r}\right)}\right]^{-1}.$$

If we assume that the diffusive fluxes due to pressure and temperature gradients are negligible, then the diffusion velocity of each component of the gas mixture is proportional

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[8] See Vincenti and Kruger (1965), pp. 15–21.

to the gradient of the mass concentration. With the additional assumption of binary diffusion where species s diffuses into a mixture of similar particles, we have

$$\rho_s v_{sj} = -\rho \mathcal{D}_s \frac{\partial c_s}{\partial x_j}. \tag{2.6.6}$$

The diffusion coefficient, $\mathcal{D}_s$, is derived by assuming a constant Lewis number, $\mathcal{L}e$, which by definition is given by

$$\mathcal{L}e = \frac{\mathcal{D}\rho c_p}{\kappa}. \tag{2.6.7}$$

The uncharged particles all have the same $\mathcal{D}$, but the diffusion coefficient for ions is assumed to be doubled (*i.e.* the ambipolar diffusion assumption holds) because of the existence of an electric field. The diffusion velocity of electrons is computed using

$$\mathcal{D}_e = M_e \frac{\sum_{s=\text{ions}} \mathcal{D}_s \rho_s / M_s}{\sum_{s=\text{ions}} \rho_s}, \tag{2.6.8}$$

which is derived from Lee (1985). This is a simplified model of the diffusion coefficients. A more accurate model would be similar to the one developed by Blottner *et al.* (1971) which computes the multi-component diffusion coefficients using curve fits. However, it is both computationally and memory intensive and it was assumed that the increased cost of the more accurate model was not justified. In principle however, this model could be implemented and the pressure and temperature driven diffusive fluxes could be treated without difficulty.

II.7 Energy Exchange Mechanisms

The energy exchange mechanisms that appear on the right hand side of equations (2.3.13) and (2.3.14) must be modeled. The models that have been proposed are simplifications of the complicated energy exchange processes that occur on a molecular level. This phenomenologic treatment has inadequacies because it does not fully embody the physics of molecular interactions. The models that have been previously published are outlined below and new models for vibration-vibration and electron-vibration energy exchanges are derived.

II.7.1 Translation-Vibration Energy Exchanges

The rate of energy exchange between vibrational and translational modes has been discussed extensively[9]. The rate of change in the population of the vibrational states at low temperatures is described well by the Landau-Teller formulation where it is assumed that the vibrational level of a molecule can change by only one quantum level at a time (Vincenti and Kruger (1965)). The resulting energy exchange rate is

$$Q_{T-v\,s_{L-T}} = \rho_s \frac{e_{vs}^*(T) - e_{vs}}{<\tau_{s_{L-T}}>}. \tag{2.7.1}$$

Where $e_{vs}^*(T)$ is the vibrational energy per unit mass of species s evaluated at the local translational-rotational temperature and $<\tau_{s_{L-T}}>$ is the molar averaged Landau-Teller relaxation time given by Lee (1985).

$$<\tau_{s_{L-T}}> = \frac{\sum_r X_r}{\sum_r X_r/\tau_{sr_{L-T}}}, \quad \text{for } r \neq e. \tag{2.7.2}$$

An expression developed by Millikan and White (1963) yields the Landau-Teller inter-species relaxation times, $\tau_{sr_{L-T}}$, in seconds using the function

$$\begin{aligned}
\tau_{sr_{L-T}} &= \frac{1}{p} \exp\left[A_{sr}(T^{-1/3} - 0.015\mu_{sr}^{1/4}) - 18.42\right], \quad p \text{ in atm}, \\
A_{sr} &= 1.16 \times 10^{-3} \mu_{sr}^{1/2} \theta_{vs}^{4/3}, \\
\mu_{sr} &= M_s M_r/(M_s + M_r).
\end{aligned} \tag{2.7.3}$$

However, at high vibrational temperatures the vibrational ladder climbing process due to heavy particle collisions is diffusive in nature[10]. Park (1987) proposes an empirical bridging function between the Landau-Teller and diffusive rates of the form

$$Q_{T-v\,s} = \rho_s \frac{e_{vs}^*(T) - e_{vs}}{<\tau_{s_{L-T}}>} \left| \frac{T_{\text{shk}} - T_{vs}}{T_{\text{shk}} - T_{vs\,\text{shk}}} \right|^{S_s - 1}, \tag{2.7.4}$$

where the exponent, S_s, has the form

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[9] See Millikan and White (1963), Park (1985b, 1986, 1987), and Parker (1959).
[10] See Park (1985b, 1986, 1987), and Keck and Carrier (1965).

$$S_s = 3.5 \exp(-\theta_s/T_{\text{shk}}). \tag{2.7.5}$$

The quantities T_{shk} and $T_{vs\,\text{shk}}$ are the translational-rotational and species vibrational temperatures evaluated just behind the bow shock wave. At low temperatures, the relaxation is governed by the Landau-Teller rate, and at high temperatures, by the slower diffusive rate. The characteristic temperatures, θ_s, for use in calculating the exponent, S_s, are assumed to be as given in Appendix A. It should be noted that the diffusive relaxation depends on the post-shock temperature for each fluid element. Thus for a general location in the flowfield, the streamline that passes through that point should be traced back to the shock wave where T_{shk} and $T_{vs\,\text{shk}}$ are evaluated. This process is not easy to generalize, and as an approximation for the two-dimensional flowfields discussed here, the post-shock translational-rotational temperature at each point was evaluated at the nearest shock wave location. For the flowfields of interest this approximation is reasonable near the nose, however an efficient technique that follows the streamline back to the shock wave is needed to correctly implement this procedure. The post-shock vibrational temperature was simply taken to be the free-stream temperature.

A second modification to the translational-vibrational relaxation rate is made to account for the limiting collision cross-section at high temperature. The Landau-Teller rate expression from Millikan and White yields a relaxation rate that is unrealistically large at high temperatures due to an overprediction of the collision cross-section. The addition of the limiting cross-section rate corrects this inaccuracy. As suggested by Park (1985b), a new relaxation time, τ_{vs}, that is the sum of the Landau-Teller relaxation time and the collision limited relaxation time, τ_{cs}, corrects this inadequacy. Thus if we use equation (2.7.4) with this new rate, we have the final form of the energy exchange mechanism

$$Q_{T-v\,s} = \rho_s \frac{e_{vs}^*(T) - e_{vs}}{\tau_{vs}} \left| \frac{T_{\text{shk}} - T_{vs}}{T_{\text{shk}} - T_{vs\,\text{shk}}} \right|^{S_s - 1}, \tag{2.7.6}$$
$$\tau_{vs} = <\tau_{s_{\text{L-T}}}> + \tau_{cs},$$

where

$$\tau_{cs} = \frac{1}{c_s \sigma_v N_s}. \tag{2.7.7}$$

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c_s is the average molecular speed of species s, $c_s = \sqrt{8RT/\pi M_s}$ and N_s is the number density of the colliding particles. The expression for the limiting collision cross-section, σ_v, is assumed to be as given by (Park (1985b))

$$\sigma_v = 10^{-21}(50,000/T)^2 \quad \text{m}^2. \tag{2.7.8}$$

This expression was originally developed for nitrogen, but has been applied to the other diatomic molecules because an alternative is not available and nitrogen is the primary diatomic molecule in the flowfields of interest.

II.7.2 Translation-Electron Energy Exchanges

The energy transfer rate between the heavy-particle and electron translational modes, Q_{T-e}, is given by an expression derived from Lee (1985)

$$Q_{T-e} = 3R\rho_e(T - T_e)\sqrt{\frac{8RT_e}{\pi M_e}}\sum_{r\neq e}\frac{\rho_r\hat{N}}{M_r^2}\sigma_{er}, \tag{2.7.9}$$

where σ_{er}, $r \neq$ ions, are the collision cross-sections for electron-neutral interactions. The functional form of these parameters is not well known and for this work a constant σ_{er} equal to $10^{-20}\,\mathrm{m}^2$ was assumed. For the case of electron-ion interactions the effective Coulomb cross-section is given by (Lee (1985))

$$\sigma_{e,\mathrm{ions}} = \frac{8\pi}{27}\frac{e^4}{k^2T_e^2}\ln\left[1 + \frac{9k^3T_e^3}{4\pi N_ee^6}\right]. \tag{2.7.10}$$

The excitation of the electron energy due to this form of energy transfer is fairly weak except at high temperatures. Thus, this mechanism causes a heating of the electron translational modes just behind the shock wave where the difference $(T - T_e)$ is large.

II.7.3 Electron-Vibration Energy Exchanges

The coupling of the electron energy with the vibrational energy of diatomic nitrogen is strong, but between the other vibrational states it is negligibly weak (Lee (1986)). The rate of energy transfer between electron translational modes and nitrogen vibrational modes, Q_{e-vs}, is assumed to be of the form,

$$Q_{e-vs} = N_e\frac{\varepsilon_{vs}^*(T_e) - \varepsilon_{vs}}{\tau_{es}}, \quad \text{for } s = \mathrm{N}_2, \tag{2.7.11}$$

where ε_{vs} is the vibrational energy per particle. Thus the rate of energy transfer between electron translational and vibrational modes is proportional to the number of electrons and the difference in the two energy levels. The energy per particle can be related to the energy per mass by

$$\varepsilon_{vs} = \frac{e_{vs}M_s}{\hat{N}}. \tag{2.7.12}$$

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Therefore the energy transfer rate may be written as

$$Q_{e-v\,s} = \rho_e \frac{M_s}{M_e} \frac{e^*_{vs}(T_e) - e_{vs}}{\tau_{es}}, \quad \text{for } s = N_2, \tag{2.7.13}$$

where the expression for the electron number density has been substituted.

Lee (1986) derived an expression for the rate of electron-vibration energy transfer, τ_{es}, by solving the system of master equations that accounts for transitions of multiple levels. τ_{es} was curve-fit to the results of Lee using two quadratics in the logarithm (base 10) of the electron temperature. This expression is

$$\log(p_e\tau_{es}) = \begin{cases} 7.50(\log T_e)^2 - 57.0 \log T_e + 98.70, & \text{for } T_e < 7000\,\text{K}; \\ 2.36(\log T_e)^2 - 17.9 \log T_e + 24.35, & \text{for } T_e > 7000\,\text{K}, \end{cases} \tag{2.7.14}$$

where p_e is in atmospheres and the resulting τ_{es} is in seconds. A plot of this function is given in Figure 2.1, which shows that the relaxation time is smallest at about $T_e = 7000\,\text{K}$ and increases rapidly on either side of this temperature. The very small relaxation time near 7000 K is due to a strong resonance between the electron and vibrational modes. Lee's model may be inadequate for electron temperatures away from this resonance, however this model was used in this work because it is probably better than a simple model based on a constant collision cross-section.

II.7.4 Vibration-Vibration Energy Exchanges

In a mixture of diatomic gases that have been thermally excited, the vibrational temperature of each constituent relaxes toward the translational temperature at a finite rate. However, as one species becomes vibrationally excited, it tends to transfer its vibrational energy to the other species in vibration-vibration $(v-v)$ energy exchanges which tend to drive the separate vibrational temperatures together. A rate of vibrational energy transfer between species can be derived from kinetic theory and experimentally determined probabilities of vibrational energy exchange during a collision.

The rate of vibrational energy transfer from species s to r is the product of the probability of a $v-v$ exchange, the number of collisions, and the average energy transferred. This may be written as

$$Q_{v-v\,sr} = P_{sr} \cdot Z_{sr} \cdot \varepsilon_{vr}, \tag{2.7.15}$$

where, P_{sr} is the probability of r transferring its vibrational energy to s, Z_{sr} is the number of $s-r$ collisions per unit time and volume, and ε_{vr} is the average vibrational energy per species r particle. From kinetic theory, Z_{sr} is given by

$$Z_{sr} = \sqrt{\frac{8kT}{\pi\mu_{sr}}}\sigma_{sr}N_sN_r, \tag{2.7.16}$$

where μ_{sr} is the reduced mass and σ_{sr} is the collision cross-section. The average vibrational energy is

$$\varepsilon_{vr} = \frac{R\theta_{vr}}{\hat{N}\left(e^{\theta_{vr}/T_{vr}} - 1\right)} = \frac{E_{vr}M_r}{\rho_r}. \tag{2.7.17}$$

Combining the three preceeding expressions, we have

$$Q_{v-v\,sr} = P_{sr}\sigma_{sr}\sqrt{\frac{8RT}{\pi\mu_{sr}}}\frac{\rho_s}{M_s}\hat{N}E_{vr}. \tag{2.7.18}$$

The same energy exchange process occurs in reverse, therefore

$$Q_{v-v\,s} = Q_{v-v\,sr} - Q_{v-v\,rs}, \tag{2.7.19}$$
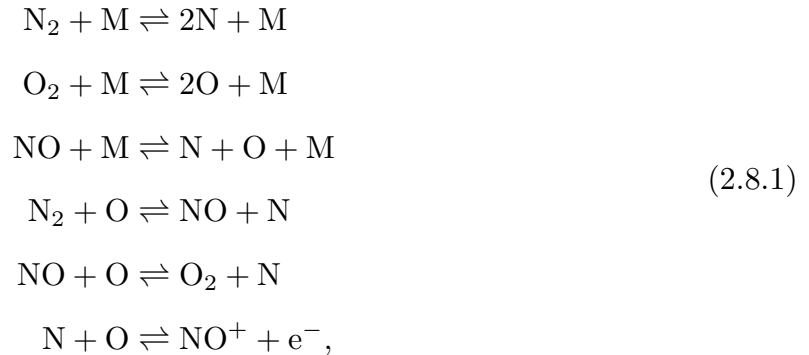
which may be generalized to m diatomic species as

$$Q_{v-v\,s} = \sum_{r\neq s}^{m}\left[\hat{N}\sigma_{sr}\sqrt{\frac{8RT}{\pi\mu_{sr}}}\left(P_{sr}\frac{\rho_s}{M_s}E_{vr} - P_{rs}\frac{\rho_r}{M_r}E_{vs}\right)\right]. \tag{2.7.20}$$

The probabilities of an exchange have been measured for several different molecules (Taylor $et\ al.$ (1966)). For temperatures of interest (above $2000\,\mathrm{K}$), the P_{sr} are typically of the order of 10^{-2}, and for this work have been assumed to be constant at that value. The collision cross-sections for this process are computed with the expression $\sigma_{sr} = d_sd_r$, where d_s are the collision diameters. They were assumed to be the same as those used to calculate the P_{sr} by Taylor, and are listed in Appendix A.

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II.8 Chemical Source Terms

The chemical source terms are derived from the reactions that occur between the components of the gas. As the reactions occur, molecules of one species are created from other species, *i.e.* a mass transfer process between species takes place. This is represented by the terms w_s on the right-hand side of the species mass conservation equation, (2.3.10). The expressions for these mass transfer rates are derived below and the treatment of the reaction rates is discussed.

For high temperature ionized air there are seven primary constituents, which may be ordered as follows, N_2, O_2, NO, NO^+, N, O, and e^-. The most important chemical reactions between these species are

$$N_2 + M \rightleftharpoons 2N + M$$

$$O_2 + M \rightleftharpoons 2O + M$$

$$NO + M \rightleftharpoons N + O + M$$

$$N_2 + O \rightleftharpoons NO + N$$

$$NO + O \rightleftharpoons O_2 + N$$

$$N + O \rightleftharpoons NO^+ + e^-,$$

$$(2.8.1)$$

where M represents a generic particle that acts as a collision partner in the reaction and is not altered. The first three are dissociation reactions, the fourth and fifth are exchange reactions and the last is an associative ionization reaction. Each reaction is governed by forward and backward reaction rate coefficients, k_{f_m} and k_{b_m}, respectively. The six reactions may be written in order in terms of the reaction rates as

$$\mathcal{R}_1 = \sum_m \left[-k_{f_{1m}} \frac{\rho_{N_2}}{M_{N_2}} \frac{\rho_m}{M_m} + k_{b_{1m}} \frac{\rho_N}{M_N} \frac{\rho_N}{M_N} \frac{\rho_m}{M_m} \right]$$

$$\mathcal{R}_2 = \sum_m \left[-k_{f_{2m}} \frac{\rho_{O_2}}{M_{O_2}} \frac{\rho_m}{M_m} + k_{b_{2m}} \frac{\rho_O}{M_O} \frac{\rho_O}{M_O} \frac{\rho_m}{M_m} \right]$$

$$\mathcal{R}_3 = \sum_m \left[-k_{f_{3m}} \frac{\rho_{NO}}{M_{NO}} \frac{\rho_m}{M_m} + k_{b_{3m}} \frac{\rho_N}{M_N} \frac{\rho_O}{M_O} \frac{\rho_m}{M_m} \right] \quad (2.8.2)$$

$$\mathcal{R}_4 = -k_{f_4} \frac{\rho_{N_2}}{M_{N_2}} \frac{\rho_O}{M_O} + k_{b_4} \frac{\rho_{NO}}{M_{NO}} \frac{\rho_N}{M_N}$$

$$\mathcal{R}_5 = -k_{f_5} \frac{\rho_{NO}}{M_{NO}} \frac{\rho_O}{M_O} + k_{b_5} \frac{\rho_{O_2}}{M_{O_2}} \frac{\rho_N}{M_N}$$

$$\mathcal{R}_6 = -k_{f_6} \frac{\rho_N}{M_N} \frac{\rho_O}{M_O} + k_{b_6} \frac{\rho_{NO^+}}{M_{NO^+}} \frac{\rho_e}{M_e}.$$

Thus the source terms that represent the inter-species mass transfer rates may be constructed as

$$w_{N_2} = M_{N_2}(\mathcal{R}_1 + \mathcal{R}_4)$$

$$w_{O_2} = M_{O_2}(\mathcal{R}_2 - \mathcal{R}_5)$$

$$w_{NO} = M_{NO}(\mathcal{R}_3 - \mathcal{R}_4 + \mathcal{R}_5)$$

$$w_{NO^+} = -M_{NO^+}\mathcal{R}_6 \quad (2.8.3)$$

$$w_N = M_N(-2\mathcal{R}_1 - \mathcal{R}_3 - \mathcal{R}_4 - \mathcal{R}_5 + \mathcal{R}_6)$$

$$w_O = M_O(-2\mathcal{R}_2 - \mathcal{R}_3 + \mathcal{R}_4 + \mathcal{R}_5 + \mathcal{R}_6)$$

$$w_e = -M_e\mathcal{R}_6.$$

We should note that the sum of the mass transfer rates is identically zero and that elemental conservation holds, as required.

The forward and backward reaction rates of reaction m have the functional form

$$k_{f_m}(\bar{T}) = C_{f_m} \bar{T}^{\eta_m} \exp(-\theta_m/\bar{T}),$$

$$k_{b_m}(\bar{T}) = \frac{k_{f_m}(\bar{T})}{K_{\mathrm{eq}_m}(\bar{T})}, \quad (2.8.4)$$

where the constants C_{f_m}, η_m, and θ_m and the expression for K_{eq_m} are experimentally determined. As discussed by Park (1985a, 1986, 1987), the reaction rates will be a function of different temperatures depending on the type of reaction. Take, for example, the first

three reactions where the impacting particle, M, is a heavy species (*i.e.* not an electron). The forward reaction rate will be a function of the vibrational excitation of the diatomic molecule and the translational temperature of the impacting heavy particle. Thus we can postulate an average temperature that governs this reaction rate to be (Park (1987))

$$k_{f_{lm}} = k_{f_{lm}}(\bar{T}), \quad \bar{T} = \sqrt{TT_{vl}}, \quad \text{for } l = 1, 3 \quad \text{and } m = 1, 6. \tag{2.8.5}$$

However, the backward reaction rates will depend only on the translational temperature of the impacting particles,

$$k_{b_{lm}} = k_{b_{lm}}(T), \quad \text{for } l = 1, 3 \quad \text{and } m = 1, 6. \tag{2.8.6}$$

For the case where the impacting particle is an electron, the forward rate will depend on the average of the vibrational temperature and the electron translational temperature,

$$k_{f_{l7}} = k_{f_{l7}}(\bar{T}), \quad \bar{T} = \sqrt{T_{vl}T_e}, \quad \text{for } l = 1, 3. \tag{2.8.7}$$

Similarly, the backward reaction rate is governed by an average temperature

$$k_{b_{l7}} = k_{b_{l7}}(\bar{T}), \quad \bar{T} = \sqrt{TT_e}, \quad \text{for } l = 1, 3. \tag{2.8.8}$$

The forward and backward rates of reactions 4 and 5 will depend only on the relative speed of the impacting molecules, which implies that $\bar{T} = T$. The forward rate of reaction 6 will also be governed by the translational temperature of the impacting atoms. However, its backward reaction rate will depend on the vibrational temperature of the NO^+ and translational temperature of the electrons,

$$k_{b_6} = k_{b_6}(\bar{T}), \quad \bar{T} = \sqrt{T_{NO^+}T_e}. \tag{2.8.9}$$

The magnitudes of the published reaction rate coefficients vary greatly, especially at high temperatures. However, the use of the two temperature rate model tends to lower the effective temperature and decrease the variation. The forward reaction rates for the first

five reactions were taken from Park (1985a). The coefficients for the sixth reaction came from Wray (from Bussing and Eberhardt (1987)). The expressions for the equilibrium constants, K_{eq_m}, were taken from Park (1985a). These data are listed in Appendix A.

II.9 Boundary Conditions

The boundary conditions for the problem are as follows. The free-stream is supersonic so that all flow variables are fixed on the boundary outside of the bow shock wave. The outflow is also supersonic or within the boundary layer and, therefore, we can impose a zero-gradient exit condition. The wall boundaries are specified by assuming either an adiabatic or fixed-wall temperature, a no-slip velocity condition, and a zero normal gradient of pressure at the wall. In the results presented below the wall was assumed to be fully non-catalytic, which implies that the normal gradient of each species mass concentration is zero at the wall. The wall was considered to be adiabatic for the electron temperature.

II.10 Summary of Governing Equations

The governing differential equations are summarized in this section. For the case of interest, there is one mass conservation equation for each of the n chemical species. These equations may be written as

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x_j}\left(\rho_s u_j\right) = -\frac{\partial}{\partial x_j}\left(\rho_s v_{sj}\right) + w_s. \tag{2.10.1}$$

There are d momentum conservation equations, where d is the spatial dimension of the problem.

$$\frac{\partial}{\partial t}\left(\rho u_i\right) + \frac{\partial}{\partial x_j}\left(\rho u_i u_j + p \delta_{ij}\right) = -\frac{\partial \tau_{ij}}{\partial x_j} - \sum_{s=1}^{n} \frac{N_s}{N_e} Z_s \frac{\partial p_e}{\partial x_i}. \tag{2.10.2}$$

The conservation of vibrational energy for each of the m diatomic species is represented as

$$\begin{aligned}
\frac{\partial E_{vs}}{\partial t} + \frac{\partial}{\partial x_j}\left(E_{vs} u_j\right) = &-\frac{\partial}{\partial x_j}\left(E_{vs} v_{sj}\right) \\
&- \frac{\partial q_{vsj}}{\partial x_j} + Q_{T-vs} + Q_{v-vs} + Q_{e-vs} + w_s e_{vs}.
\end{aligned} \tag{2.10.3}$$

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The electron energy is conserved according to the equation

$$\frac{\partial E_e}{\partial t} + \frac{\partial}{\partial x_j}\left(E_e u_j\right) = -\frac{\partial}{\partial x_j}\left(E_e v_{ej}\right) - p_e \frac{\partial u_j}{\partial x_j} - \frac{\partial q_{ej}}{\partial x_j} + Q_{T-e} - \sum_{s=1}^{m} Q_{e-vs} + w_e e_e. \quad (2.10.4)$$

And finally the conservation of total energy is represented by

$$\begin{aligned}
\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j}\left((E+p)u_j\right) &= -\frac{\partial}{\partial x_j}\left(q_j + q_{vj} + q_{ej}\right) - \frac{\partial}{\partial x_j}\left(u_i \tau_{ij}\right) \\
&\quad - \sum_{s=1}^{n} \frac{\partial}{\partial x_j} v_{sj} h_s - \sum_{s=1}^{n} \frac{N_s}{N_e} Z_s \frac{\partial p_e}{\partial x_i} u_i.
\end{aligned} \quad (2.10.5)$$

Thus the flowfield is represented with $n+d+m+2$ coupled differential equations. These equations have been written with the inviscid fluxes on the left-hand side and the viscous fluxes and source terms on the right-hand side. The solution technique that was used to solve these equations is discussed in the next chapter.

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