A Nonequilibrium Model for a Moderate Pressure Hydrogen Microwave Discharge Plasma

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ABSTRACT

This document describes a simple nonequilibrium energy exchange and chemical reaction model to be used in a computational fluid dynamics calculation for a hydrogen plasma excited by microwaves. The model takes into account the exchange between the electrons and excited states of molecular and atomic hydrogen. Specifically, electron-translation, electron-vibration, translation-vibration, ionization and dissociation are included. The model assumes three temperatures, translational/rotational, vibrational, and electron, each describing a Boltzmann distribution for its respective energy mode. The energy from the microwave source is coupled to the energy equation via a source term that depends on an effective electric field which must be calculated outside the present model. This electric field must be found by coupling the results of the fluid dynamics and kinetics solution with a solution to Maxwell's equations that includes the effects of the plasma permittivity. The solution to Maxwell's equations is not within the scope of this present paper.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$C_1$</td>
<td>mass fraction</td>
</tr>
<tr>
<td>$D_{ls}$</td>
<td>binary diffusion coefficient</td>
</tr>
<tr>
<td>$\mathbf{e}$</td>
<td>electric field vector</td>
</tr>
<tr>
<td>$e$</td>
<td>electron charge</td>
</tr>
<tr>
<td>$e$</td>
<td>total internal energy per unit mass</td>
</tr>
<tr>
<td>$e_v^*(T)$</td>
<td>equilibrium vibrational energy per unit mass evaluated at gas temperature</td>
</tr>
<tr>
<td>$E_e$</td>
<td>energy per unit volume of electrons</td>
</tr>
<tr>
<td>$e_e$</td>
<td>energy per unit mass of electrons</td>
</tr>
<tr>
<td>$E_{if}$</td>
<td>ionization energy for the $i^{th}$ species</td>
</tr>
<tr>
<td>$E_0$</td>
<td>threshold energy for a reaction</td>
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<tr>
<td>$E_v$</td>
<td>vibrational energy per unit volume</td>
</tr>
<tr>
<td>$e_v$</td>
<td>vibrational energy per unit mass</td>
</tr>
<tr>
<td>$f_s$</td>
<td>body force on species $s$</td>
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<td>$h_s^c$</td>
<td>enthalpy of formation of species $s$</td>
</tr>
<tr>
<td>$j$</td>
<td>vibrational quantum number</td>
</tr>
<tr>
<td>$k_b$</td>
<td>recombination rate coefficient</td>
</tr>
<tr>
<td>$k_{oj}$</td>
<td>rate coefficient for excitation of jth energy level by electrons</td>
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<tr>
<td>$k_{im}$</td>
<td>rate coefficient for ionization of molecules by electrons</td>
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<tr>
<td>$k_{ia}$</td>
<td>rate coefficient for ionization of atoms by electrons</td>
</tr>
<tr>
<td>$m$</td>
<td>mass of particle</td>
</tr>
</tbody>
</table>

* This work was done while Visiting Professor. Permanent address: EG3, NASA Johnson Space Center, Houston, Texas 77058.
Ms
nef
ns
p
pe
Q^{1e}_{e-V}
Q^{1v}_{e-V}
Q^{3d}_{e}
Q^{3d}_{e-d}
Q^{e}_{ex}
Q^{v}_{ex}
Q_{e}
q_{e}
Q_{e-V}
Q_{rad}
Q_{T-e}
Q_{T-v}
Q_{T-V_a}
q_v
T
T_e
T_v
u
V_e
V_s
W
W_e
W_s
x_j
X_s
Z_s
\delta_{ij}
\gamma
\lambda
\lambda_e
Greek

mass flux vector of species s
number density of species f
number density of species s
pressure
electron pressure
energy exchange rate per unit volume from electrons to excited singlet states
energy exchange rate per unit volume from electrons to vibrational ground electronic states via singlet state excitation
electron energy exchange rate per unit volume due to dissociation
electron energy loss rate per unit volume for excitation of triplet states
rate of exchange of energy to electrons per unit volume
rate of energy exchange per unit volume to vibration
rate of energy gain per unit volume from the electromagnetic field
electron energy flux vector
electron-vibration energy exchange rate per unit volume
radiative energy exchange with gas (usually a loss)
electron-translation energy exchange rate per unit volume
translation-vibration energy exchange rate per unit volume for molecule-molecule collisions
translation-vibration energy exchange rate per unit volume for atom-molecule collisions
vibrational energy flux vector
translational/rotational temperature
electron temperature
vibrational temperature
gas velocity
electron diffusion velocity
diffusion velocity of species s
molecular weight of mixture
molecular weight of electron
molecular weight of species s
jth component of position vector
mole fraction of species s
degree of ionization of species s
Kronecker delta
wall recombination probability
thermal conductivity
thermal conductivity for electrons
\( \lambda'_{e} \) thermal conductivity for electrons considering electrons only
\( \lambda_{v} \) thermal conductivity for vibrational energy
\( \lambda'_{v} \) thermal conductivity for vibrational energy considering only vibrating molecules
\( \mu \) viscosity
\( \nu_{c}(u) \) electron-heavy particle collision frequency at energy \( u \)
\( \nu^{**}_{er} \) heavy particle-electron momentum transfer collision frequency
\( \nu^{*}_{er} \) heavy particle-electron momentum transfer collision frequency weighted with electron energy
\( \theta \) energy loss rate per electron
\( \rho \) mass density of gas
\( \rho_{s} \) mass density of species \( s \)
\( \sigma \) cross section
\( \sigma_{er} \) electron-heavy particle momentum exchange cross section
\( \sigma_{r} \) real part of complex electrical conductivity
\( \tau \) shear stress tensor
\( \tau_{e-v} \) electron-vibration relaxation time
\( \tau_{v} \) translation-vibrational relaxation time
\( \tau_{v_{H_{2}-H_{2}}} \) translation-vibrational relaxation time \( H_{2}-H_{2} \)
\( \tau_{v_{ls}} \) vibrational relaxation time for pair \( l \) and \( s \)
\( \omega \) frequency of microwave
\( \omega_{s} \) rate of production per unit volume of species \( s \)

Subscripts and Superscripts

\( e \) electron
\( i \) ionization
\( r \) heavy particles
\( s \) species \( s \)
\( T \) translational
\( v \) vibrational

INTRODUCTION

Hydrogen plasmas with a few percent of methane and a trace of oxygen have been used to produce diamond films in the laboratory. The rates of deposition and etching of graphite and diamond on substrates are significantly affected by the concentrations of the various species and the energy states in which they exist. Likewise, the surface temperature and flow pattern in the reactor affect transport of reactive species to the surface. Therefore, a program to compute the chemistry, flow field, and energy states of a hydrogen plasma has been started. Eventually, the flow simulation must include the carbon containing species and oxygen, but for the present we have started with a pure hydrogen microwave generated plasma to be discussed in the present paper.
The subject of modeling the energy exchange between the various energy states in hydrogen plasmas has been developed over the last two or three decades with various degrees of complexity depending on the plasma conditions. Cross sections and reactions rates for electron-hydrogen collisions have been measured and calculated by a number of workers. These interactions involve dissociation, excitation, electron-vibration energy exchange, ionization and translational-vibrational energy exchange. The various paths of energy loss from electrons to the internal degrees of freedom of hydrogen and then to the translational/rotational degrees of freedom affect the ultimate conditions of the plasma and thus the possible chemical reactions both in the gas phase and on surfaces.

This paper defines equations and reactions for modeling experiments1 at the Laboratoire d'Ingénierie des Matériaux et des Hautes-Pressions at the Université Paris Nord, Villetaneuse, France. In these experiments a pressure level of about 4 kPa assures a reasonable rate of deposition. The plasma is established by a microwave system operating at about 500 watts. A schematic of the apparatus is given in Fig. 1. The plasma zone that is approximately hemispherical in shape exists next to the substrate surface. This surface is essentially immersed in a region of high electric field produced by a focused microwave antenna. The size and conditions of the plasma depend on the power coupled to this cavity as well as the electron and energy loss mechanisms in the plasma. These loss mechanisms include diffusion of electrons and excited species to the surface and out of the high microwave field zone, electron energy loss by collision with H2 to form vibrationally or electronically excited molecules, dissociation of the molecules, ionization of atoms and molecules, and electron-translation/rotation exchange. Forced and free convection also play a role in loss of electrons and other excited species from the plasma zone by removing electrons and other excited species from the active plasma zone.

Modeling of hydrogen plasmas and the study of energy exchange mechanisms have been done by several workers in other applications. Among them are the works of Gorse, et al.2, Gorse et al.,3 who applied their models to multicusp magnetic discharge plasma, and Loureiro and Ferreira,4 who applied their model to the positive column of a dc discharge. These applications are at sufficiently low temperature and pressure that it was necessary to account for the strong nonequilibrium associated with the electronic energy distribution function. Their distributions were expected to deviate from a Boltzmann distribution. In the present case the pressure and temperature are sufficiently high that the electron energy distribution function may be nearly Boltzmann, and the vibrational distribution function of H2 can expected to be Boltzmann also. However, it is expected that the temperatures describing these Boltzmann distributions for the various degrees of freedom are not the same, nor are they equal to the translational/rotational temperature. Validation of these expectations will await spectroscopic and other diagnostic measurements.

The model will be introduced into a finite difference solution of the Navier-Stokes equations set up for the geometry of the plasma reactor. In lieu of a solution of measurements of the electron temperature and density, It will also be necessary to couple the microwave power into the model via results from a solution of Maxwell's equations. This procedure must involve an iteration with the solution of the Navier-Stokes equations because there is a strong coupling between the loss mechanisms computed by the N-S solution and the energy coupled to the plasma from the microwave source. The electromagnetic field of the source and in the plasma depend strongly on plasma conditions.
HYDROGEN PLASMA ENERGY EXCHANGE MODEL

The Flow Equations

It is assumed that the microwave discharge plasma and the associated flow in the reactor can be described by the continuum Navier-Stokes equations in a form patterned after those presented for shock heated air by Lee. Since there are several modes of energy that are not strongly coupled we expect that it is necessary to account for three temperatures and thus use three energy equations. The vibrational distribution of the molecules is assumed to be describable by a vibrational temperature, the electrons and electronic excited states are assumed to be described by an electron-electronic temperature, (called electron temperature in subsequent paragraphs), and the heavy particle translation and rotation distribution can be described by a translational/rotational temperature. The chemical species are not assumed to be in equilibrium, but must be described by chemical kinetic relations. In addition to the momentum equations and continuity equation, whose forms are independent of the kinetic model, we have the set of species equations, one for each species. The three energy equations are electron, vibration, and total. These equations whose form is dependent on the kinetics, are given here. The time dependent form is given even though the problem is actually steady state because the solution technique may be a time relaxation scheme in which the parabolic coordinate is time. Otherwise, the steady state equations are elliptic, which makes the solution technique for the problem less flexible.

Species equation:

$$\frac{\partial \rho_s}{\partial t} + \nabla \cdot (\rho_s u + \rho_s V_s) = \omega_s$$  \hspace{1cm} (1)

Electron energy equation:

$$\frac{\partial E_e}{\partial t} + \nabla \cdot (E_e u) = -\nabla \cdot q_e + Q_{ex}^e - \nabla \cdot ((E_e + p_e)V_e)$$

- $\nabla \cdot (p_e u) - \epsilon_n u_e \cdot \mathbf{E} + Q_e$  \hspace{1cm} (2)

Vibrational energy equation:

$$\frac{\partial E_v}{\partial t} + \nabla \cdot (E_v u) = -\nabla \cdot q_v + Q_{ex}^v - \nabla \cdot \sum_{s=1}^{n} \rho_s e_v V_s$$  \hspace{1cm} (3)

Total energy equation:

$$\frac{\partial E}{\partial t} + \nabla \cdot (p u) = -\nabla \cdot q - \nabla \cdot (u p) + \nabla \cdot (u \cdot \tau) + \sum_{s=1}^{n} \rho_s u_s f_s + Q_e - Q_{rad}$$  \hspace{1cm} (4)

where, $\rho_s$ is the density of species $s$, $u$ is the mass averaged convection velocity. $\rho_s V_s$ is the diffusion mass flux of species $s$ given by

$$\rho_s V_s = \rho \frac{W_s}{W} \sum_{i=1}^{n} D_{ui} [\nabla C_i + C_i \nabla \ln(W)]$$  \hspace{1cm} (5)
where $W_s$ and $W$ are the molecular weights of species $s$ and the mixture, respectively, and $D_{ik}$ is the multicomponent diffusion coefficient for the $i,s$ pair of species, and $C_i$ is the species mass fraction $\rho_i/\rho$.

The rate of production of species $s$ is $\omega_s$. $E_e$ and $E_v$ and $q_e$ and $q_v$ are the specific energies and energy fluxes of the electrons and vibrating molecules respectively. The total internal energy per unit mass is $e$. The energy per unit mass of electrons and of vibrational energy are denoted $e_e$ and $e_v$ respectively. The rates of exchange of energy per unit volume between the various modes and vibration is given by

$$Q_{ex}^V = Q_{T-V} + Q_{T-V,a} + Q_{e-V}^1 + Q_{e-V}$$

and the rate of exchange to the electrons is given by

$$Q_{ex}^e = Q_{T-e} - Q_{e-V} - Q_{e-V}^1 - Q_{e-V}^2 - \sum_i \frac{\partial n_{ef}}{\partial t} E_{if}$$

which exhibit the rate of exchange of energy per unit volume between the various modes designated by the subscripts. The energy loss by the electrons in exciting the singlet states is $Q_{e-V}^1$ and the energy gain by the vibrational states in this process is $Q_{e-V}^V$ and their difference accounts for the radiation loss from the singlet states of H$_2$ and contributes to $Q_{\text{rad}}$. The energy lost by electron in exciting the triplet electronic levels which lead to dissociation is $Q_{e-d}^3$. The last term in (7) is the rate of energy loss per unit volume by electrons ionizing the $f$th species, in the present case forming H$_2^+$ and H$^+$. The shear stress tensor is denoted $\tau$

$$\tau_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \mu_b \delta_{ij} \frac{\partial u_k}{\partial x_k}$$

The external forces are denoted $f_s$.

The viscosity and bulk viscosity are respectively $\mu$ and $\mu_b$. The heat flux vectors can be expressed by

$$q = -\lambda \nabla T - \lambda_e \nabla T_e - \lambda_v \nabla T_v + \sum \rho_s \delta_s c_s V_s$$

$$q_e = -\lambda_e \nabla T_e$$

$$q_v = -\lambda_v \nabla T_v$$
The thermal conductivities of the gas, the electrons, and the vibrational energy are, respectively \( \lambda \), \( \lambda_e \) and \( \lambda_v \), while the modified vibrational and electron thermal conductivities \( \lambda'_v \) and \( \lambda'_e \) are defined by Lee\(^5\).

Electrostatic forces are the only ones that may be present due to induced electric fields. This force can be expressed by

\[
\rho_s \mathbf{f}_s = n_s e Z_s \mathbf{E}
\]

where \( \mathbf{E} \) is the time averaged induced electric field, which is likely to be zero in the continuum regime for usual conditions of microwave plasmas, except in regions of strong gradients. The electric field can be computed by the Langmuir and Tonks formula

\[
\mathbf{E} = -\frac{1}{n_e e} \nabla n_e
\]

The microwave source pumps energy into the electrons through an electric-magnetic wave that penetrates the plasma. This e-m heating depends on the time averaged electric field which depends on the plasma conditions as well as the electromagnetic and geometrical characteristics of the source. Thus as mentioned in the introduction the fluids problem is coupled to the electromagnetic problem. In the present treatment of the plasma it will be necessary to solve the problem iteratively by calculating \( \mathbf{Q}_e(x) \) by assuming a distribution of the mean electric field in the plasma zone, then updating its value by solving Maxwell's equations with the resultant plasma conditions from the solution to the fluids equations. An alternative to solving Maxwell's equations is to use measured electron temperature and density distributions when computing \( \mathbf{Q}_e(x) \). However, measuring these quantities is difficult, particularly without resorting to Langmuir probes which could perturb the plasma.

Modeling Energy Exchange Between Modes

Energy exchange between the electrons, vibration, translation/rotation, and dissociation is accounted for by the terms \( \mathbf{Q}_t-v \), \( \mathbf{Q}_v-e \), \( \mathbf{Q}_t-e \), \( \mathbf{Q}_e-v \), and \( \mathbf{Q}_e-d \), which will be defined in this section.

**Translation-Vibration Relaxation (Molecules).**

One could calculate the \( T-v \) exchange for molecules by summing over all rate probabilities as shown in Cacciatore, et al.\(^6\), and basing the rates on the data of Billing and Fisher\(^7\) and the method of Audibert, et al.\(^8\) but we shall adopt some of the modeling methods of Lee\(^5\) who applied Landau-Teller type relations for vibration-translation relaxation to mixtures of nitrogen and oxygen. The energy exchange rate is given by

\[
\mathbf{Q}_{t-v} = (\rho_{H_2} + \rho_{H_2^+}) \frac{e_v^*(T) - e_v}{\tau_v} \left( \frac{e_v^*(T) - e_v}{e_v^*(T) - e_v} \right)^{s-1}
\]

where \( e_v^*(T) \) is the equilibrium specific vibrational energy at the translational temperature, \( e_v \) is the vibrational energy of the flow, and \( \tau_v \) is the relaxation time for \( T-v \) relaxation. The subscript \( o \)
indicates the initial value \((t = 0)\) of the energy and \(s \geq 1\) is an exponent that takes the value determined by a fit of the relaxation with exact solutions of the relaxation rate. Lee has given the general form for relaxation of species \(1\) in a mixture.

\[
\tau_{vl} = \sum_{s \geq 1} \frac{X_s}{\tau_{vl,s}} \tag{15}
\]

The \(\tau_{vl,s}\) values can be determined from either the Millican and White or Kiefer and Lutz correlations. Audibert, et al. have shown that the Kiefer and Lutz correlations agree with their higher temperature results over a fairly broad temperature range of interest here. The Kiefer and Lutz correlation is

\[
\tau_{H_2H_2} p = 3.9 \times 10^{-10} \exp \left( \frac{100}{3/\sqrt{T}} \right) \text{ atm-s} \tag{16}
\]

For now we use only the one expression since there are no other molecules in the system. The rate of energy exchange between translational and vibrational modes is

\[
Q_{T-v} = \rho_{H_2} \frac{\partial e_v}{\partial t} = \rho_{H_2} \frac{e_v^*(T) - e_v}{\tau_{H_2H_2}_v} \tag{17}
\]

where \(e_v^*(T)\) is the equilibrium vibrational energy per unit mass evaluated at the translational temperature and \(e_v\) is the vibrational energy per unit mass.

**Translation-Vibration Relaxation (Atoms)**

The relaxation scheme for atoms exchanging translational energy with molecules involves significant quenching of hydrogen molecule vibrational states. The rates are given in the appendix of Gorse, et al. The relaxation expression is of the same form as equation (14) and the two terms are additive. There are two principle mechanisms that transfer energy from vibration to translation when H atoms collide with \(H_2\) molecules. The first is an exchange of energy without any chemical rearrangement of the molecule. The other involves the exchange of an atom by first forming a complex of three atoms, which immediately split apart, transferring vibrational energy in the process. Rates for these two reaction paths are given in Ref. 3. There are rates for many combinations of initial and final vibrational energy, but since the ground state dominates at low temperatures we only consider transitions involving the ground state and the first excited vibrational state of \(H_2\). We have included the transition 1,0 for the two paths in Table 2. The energy transfer expression for this exchange is given by

\[
Q_{T-V,v}= (k_{T-V,v,d} + k_{T-V,v,dr}) n_{H_2} n_H E_v \tag{18}
\]

where \(k_{T-V,v,d}\) and \(k_{T-V,v,dr}\) are the direct and exchange energy transfer rates respectively and \(E_v\) is the energy of the \(v=1\) state. If conditions are such that additional vibrational states are important, these
rates can be easily added, weighting them with the relative populations determined by the vibrational temperature and summing.

**Electron-Translation Exchange**

The form of the electron-translation energy transfer rate $Q_{T-e}$ is taken from Lee\(^5\) with relaxation coefficients calculated from the momentum exchange cross section data of Buckman and Phelps.\(^{12}\) The momentum exchange collision frequency is determined from integrals of the cross sections over the electron velocity distribution function

$$v_{er}^{**} = \frac{n_r}{n_e} \int \sigma_{er} c_e f_e \, dc_e$$

or the energy averaged collision frequency

$$v_{er}^* = \frac{m_e n_r}{3 n_e k T_e} \int \sigma_{er} c_e^3 f_e \, dc_e$$

These collision frequencies, written in terms of a Boltzmann energy distribution function, can be simplified to

$$\frac{v_{er}^{**}[1/s]}{n[cm^{-3}]} = \frac{6.69 \times 10^7}{T_e[eV]^{3/2}} \int \sigma_{er}[cm^2]E[eV]\exp(-E/T_e) \, dE$$

and

$$\frac{v_{er}^*[1/s]}{n[cm^{-3}]} = \frac{4.46 \times 10^7}{T_e[eV]^{5/2}} \int \sigma_{er}[cm^2]E[eV]^2\exp(-E/T_e) \, dE$$

These collision frequencies are plotted against electron temperature in Fig. 2. Polynomial curve fits of the results are given in the figure and in Table 2.

The elastic collision transfer term $Q_{T-e}$ is given by Sutton and Sherman\(^{13}\) by the relation

$$Q_{T-e} = \frac{m_e^2}{m_T} \left(1 - \frac{T_r}{T_e}\right) \int \sigma_{er} c_e^3 f_e \, dc_e$$

$$- m_e n_r (u_e - u_r) \cdot u_g \int \sigma_{er} c_e f_e \, dc_e$$

Lee\(^7\) expressed this in terms of the collision frequencies as

$$Q_{T-e} = 2 m_e n_e \sum_r \frac{v_{er}^*}{m_T} \left(\frac{3}{2}k T_r - \frac{3}{2}k T_e\right)$$

where a term involving the relative velocity (diffusion) between electrons and heavy particles has been neglected because of the assumption of zero current in the plasma. For a simple gas like
hydrogen only two species, H₂ and H are considered because the ionization level is very small. Since the collision cross sections for momentum exchange were obtained for a mixture of H₂ and H, an average cross section was obtained in the determination of the cross sections, thus we will only consider equation (24) as having one term with \( m_f \) equal to the mean mass.

**Electron-Vibration Exchange**

As indicated in Table 1 there are two paths to vibrational exchange with electrons. The first is direct vibration excitation and deexcitation in a given electronic state—in particular, the ground state. The second is vibrational excitation via electronic excitation of excited electronic singlet states followed subsequently by a radiative transition to a vibrationally excited ground state. Cross sections for these reactions are given in Ref. 12. The rate coefficients for these reactions are calculated by integrating the cross sections over the electron energy distribution function.

\[
 k_{oj}(T_e) [\text{cm}^3/\text{s}] = 6.70 \times 10^7 T_e^{-3/2} \int_{E_o}^{\infty} \sigma_{oj}(E) \exp(-E/T_e) \, dE
\]

(25)

where the energy \( E \) and the temperature are in electron-Volts. \( E_o \) is the threshold energy of the exchange, and \( \sigma_{oj} \) is in \( \text{cm}^2 \).

The relaxation time \( \tau_{e-V} \) is determined following the procedure developed in the appendix of Ref. 5.

\[
 \tau_{e-V} = \frac{1}{n_e (1 - \exp(-\theta_v/T_e))^2 \frac{1}{2} \int_{j=1}^{j=3} k_{oj} \, dj}
\]

(26)

It has been assumed that the vibrational levels are closely spaced so the integral in (26) well represents a sum over levels. This may not be the case for H₂, but we will use it until the error is determined to be too large. The form of \( k_{oj} \) for the first three vibrational levels \( (j=1-3) \) are very similar in shape. Therefore, an approximation was made that the integral in (26) could be done semi-analytically by fitting the maxima of the \( k_{oj} \) to a simple function of the form

\[
 k_{oj}^{\text{max}} = 3.39 \times 10^{-8} \exp(-2.401j)
\]

(27)

which can be integrated analytically. The peak values are shown in Fig. 3. A polynomial curve fit of the result is shown in the figure. The relative rate coefficient function was integrated numerically to obtain a constant factor. The resulting relaxation time \( \tau_{e-V} \) as function of electron energy is given in Fig. 4. The loss rate of energy is obtained from the relaxation time by the relation

\[
 Q_{e-V} = \rho_{H_2} \frac{\partial e_v}{\partial t} = \rho_{H_2} \frac{e_v^{**}(T_e) - e_v}{\tau_{e-V}} \left( \frac{e_v(T) - e_v}{e_v(T_o) - e_{vo}} \right) \text{s}^{-1}
\]

(28)

where \( e_v^{**}(T_e) \) is the equilibrium vibrational energy evaluated at the electron temperature (the driving energy) and \( e_v \) is the current vibrational energy.

The excitation of vibrational energy via the second process (process no. 3 in the Table 1) that involves the singlet states leads to a loss of energy by the electrons since the plasma is optically thin.
It results in a gain by the vibrational states of the ground electronic state. A negligible amount of this radiation is absorbed by the plasma and thus the process is not reversed.

The loss rate by the electrons is then given by

$$Q_{e-V}^{le} = n_e n \sum_{m} E_m k_{1m}$$

(29)

The gain by the vibrational energy is similar, being

$$Q_{e-V}^{lv} = n_e n \sum_{m} (E_m - E_{m\nu}) k_{1m}$$

(30)

where $k_{3m}$ are the rate coefficients for the excitation of the ground electronic state of $H_2$ to the $m^{th}$ singlet excited state and $E_m$ is the energy per molecule required to excite the molecule and $E_{m\nu}$ is the mean vibrational energy of the final state to which the molecule radiates. The radiative energy loss due to this process is the difference between these terms

$$Q_{rad,1} = Q_{e-V}^{le} - Q_{e-V}^{lv}$$

(31)

**Electronic state excitation by Electrons**

Electrons may lose energy via excitation of electronic states if atoms or molecules. This has already be addressed for excitation of singlet and triplet states of $H_2$ which leads to vibrational excitation and dissociation respectively. Atomic hydrogen may also be excited by electron collisions. Rates for these reactions can be found from data in Janev, et al.\textsuperscript{15} Excitation of the $n=3$ state of $H$ via the reaction

$$e + H \rightarrow e + H(n=3)$$

(32)

and

$$e + H_2 \rightarrow e + H(n=3) + H$$

(33)

are given in Table 2. This leads to radiation from the $n=3$ to the $n=2$ state which should be included in the term $Q_{rad}$. Due to resonance of the $n=2$ state, we will neglect radiation cascading from it, so that the radiative energy loss rate is given by

$$Q_{rad,n=3} = n_e (k_{n=3,a} n_{H^+} + k_{n=3,m} n_{H_2}) E_{3,2}$$

**Energy Absorbed from Microwave Electromagnetic Field**

The energy absorbed by the plasma from the electromagnetic field can be obtained by the technique of Ferreira, Moisan, and Zakrzewski\textsuperscript{16}. In a global sense the power absorbed is exactly equal to the energy lost by electrons to the other particles and to the walls of the container. Losses are due to electron collisions with the other species and the wall. In their book\textsuperscript{15} the energy loss rate per electron in the plasma is given by

$$\theta_L = \frac{2m_e}{m} <v_e(E)E> + \sum_n <v_n(E)> E_{0n} + <v_i(E)> E_{0i}$$

(34)
where the brackets "< >" denote averages over the electron energy distribution function. The threshold energies for excitation and ionization are \( E_{On} \) and \( E_{Oi} \), respectively. The plasma will be in steady state when the power absorbed by the plasma \( n_e \theta_A \) equals the power lost by the electrons \( n_e \theta_L \). The local absorbed power is given by

\[
Q_e(x) = n_e \theta_A = \sigma_r (E \cdot E)_{\text{rms}} 
\]

where \( \sigma_r \) is the real part of the complex electric conductivity

\[
\sigma_r = \frac{2 \varepsilon^2}{3 \pi m_e} \int_0^\infty \frac{V_c(E)}{V_c^2(E) + \omega_e^2} u^{2/3} dF_0 \, dE 
\]

\( F_0 \) is the local electron energy distribution function and \( V_c(E) = n_0 \sigma_{cr}(E) \sqrt{2E/m_e} \) is the collision frequency for electrons of energy \( u \). The relations given in equations (35) and (36) can be used to compute the source term \( Q_e(x) \) in the energy equations given the rms value of the electric field.

The electric field must be found from a solution of Maxwell's equations. If the electron density and temperature distributions are known then one can compute the local value of the energy loss rate \( \theta_L \), hence \( Q_e(x) \) without having to solve Maxwell's equations. In that case one must assume that \( \theta_L = \theta_A \) locally. However, this leaves the problem of boundaries where there may be loss of electrons by convection or diffusion.

CHEMICAL REACTION MODEL

The gas phase chemical reactions that are assumed in this model fall in two basic categories. First are those that involve reactions with electrons, e.g., dissociation and ionization, while the other category includes the recombination of ions and atoms.

Electron and Ion Chemistry

The reactions for electron and ion chemistry are summarized here as

\[
e + H_2(v) \rightarrow e + H_2^* \rightarrow e + 2H \quad k_d \quad (37)
\]

\[
e + H_2(v) \rightarrow e + H_2^* \rightarrow e + H + H^* \quad k_d^* \quad (38)
\]

\[
e + H_2(v) \rightarrow e + H_2^+ + e \quad k_{i2} \quad (39)
\]

\[
e + H \rightarrow e + H^+ + e \quad k_{i1} \quad (40)
\]

\[
2e + H^+ \rightarrow e + H \quad k_{r1} \quad (41)
\]

\[
2e + H_2^+ \rightarrow e + H_2 \quad k_{r2} \quad (42)
\]
e + H⁺ → hv + H \hspace{1cm} k_{r1} \quad (43)

2e + H₂⁺(v) → e + H + H \hspace{1cm} k_{drv} \quad (44)

e + H₂⁺ → hv + H₂ \hspace{1cm} k_{r2} \quad (45)

The reaction rates for dissociation (37) and ionization (39) are calculated from cross section data from Ref. 12 by integration over the electron energy distribution function that is assumed to be Boltzmannian at an electron temperature Tₑ. Excitation of the triplet states of H₂, particularly the b₃Σ⁺, c₃Πᵤ, a₃Σ⁺, and d₃Π states, lead to dissociation. These reactions are denoted by reaction (37). Dissociation rate coefficients computed from the cross sections of Ref. 12 using equation (25) are given in Fig. 5, along with an Arrhenius curve fit.

A plot and curve fit of the ionization rate coefficient for H₂ are given in Fig. 6, where the cross sections were obtained from Ref. 12. Although the cross sections were obtained and presented as functions of \( 1 \ell/\theta \) where a Boltzmann distribution did not obtain, we have assumed that the Boltzmann distribution of electrons is the case here and we have used the cross sections of Ref. 12 directly.

For sufficiently energetic electrons and with H₂ molecule in excited states a dissociation as indicated by (38) can result in the production of an excited atom. Cross sections and rate coefficients for these reactions have been calculated by Celiberto, et al.\(^{17}\) For the present, these reactions shall not be incorporated into the model. However, it may be necessary to account for these reactions for diagnostic purposes because the other path for excitation of H atoms, direct excitation of H atoms by electron impact, may not be the only significant path of excitation of the Hα and Hβ lines, from which we may estimate the electron temperature.

The reverse (recombination and deionization) reactions are denoted by reactions (41)-(44). The rate of ionization is evaluated at the electron temperature Tₑ. Recombination of hydrogen atomic ions can follow two paths, one is three body recombination as indicated by (42), whereas the other is radiative recombination as indicated in (43). The rate of three body recombination depends on the energy level in which the H-atom is found, thus on the kinetics of the problem and the electron density and temperature. For sufficiently high electron temperature and low electron density the recombination coefficient is fairly insensitive to the electron density because it is dominated by radiative recombination. Radiation trapping of the Lyman-α line can affect the rate of recombination since the number density of the ground and excited states of the atoms may be affected. Drawin and Emard\(^{18}\) have solved the master equations, taking into account both three body recombination and radiative recombination with radiative absorption. Their results show a dependence on electron density in lower temperature and higher density regimes. Their results are shown in Fig. 7 along with the purely radiative recombination rate from Massey\(^{19}\) and purely three body recombination rate from a curve fit of Johnson and Hinnow\(^{20}\) measurements\(^{21}\) for relatively high electron density. The path of molecular ion radiative recombination (45) is not included in the model because of lack of rate information. This path may be improbable compared with dissociative recombination.

The molecular and atomic hydrogen ions may undergo an exchange reaction
\[
H^+_2 + H \rightarrow H_2 + H^+ \quad (46)
\]

where the reaction rate for production of \(H^+\) is given by Karpas, et al.\textsuperscript{22} in Table 3.

The rate of recombination of \(H^+_2\) with electrons to form a neutral molecule is not known (i.e., has not been found in the literature) which probably means that the encounter of electrons with \(H^+_2\) results in dissociative recombination, reaction (44) instead of direct recombination. The rate for this reaction is from Nakashima, et al.\textsuperscript{23}

Two reactions that should be included that involve the ions \(H^-\) and \(H^+_2\) are

\[
e + H_2 \rightarrow H^- + H(1s) \quad k\text{da} \quad (47)
\]

\[
H^+_2 + H_2 \rightarrow H^+_3 + H \quad k\text{e23} \quad (48)
\]

The first, (47) is dissociative attachment and it is significant in hydrogen plasmas. The other is the production of the \(H^+_3\) ion (48). The rates for these reactions derived from data in Janev, et al.\textsuperscript{15} are given in Table 3.

**Neutral Gas Chemistry**

The only reactions in a low gas temperature pure hydrogen plasma that belong to the category of neutral gas chemistry are the recombination and dissociation reactions given by the equations

\[
2H + M \rightarrow H_2 + M \quad k_b \quad (49)
\]

\[
H_2 + H_2 \rightarrow H + H + H_2 \quad k_d \quad (50)
\]

\[
H_2 + H \rightarrow H + H + H \quad k_d \quad (51)
\]

The rates for this three body recombination are found in Cohen and Westburg's\textsuperscript{24} data sheets, and the rate of the recombination reaction is evaluated at the gas temperature \(T\). The rates of the dissociation reaction involve vibrational excitation and therefore depend on the vibrational temperature in a way not yet determined.

The model proposed for computation of the hydrogen/electron chemistry and energy exchange in the microwave plasma is summarized in Table 1. Expressions for collision frequencies and relaxation times to be used in energy exchange calculations are given in Table 2. Rate coefficients for the chemical reactions are given in Table 3.

**Gas/Surface Reactions**

The reactions that occur on surfaces in a hydrogen plasma depend to some extent on the surface materials. It has usually been accepted that almost 100\% of incident ions recombine catalytically on surfaces. We will assume that is true in the present model. The neutral hydrogen atoms may react catalytically on many surfaces to form the hydrogen molecule. There is evidence that the molecules that are formed on metals are in excited states. These states are probably not in thermal equilibrium with the gas or the surface and it may not be possible to ascribe a temperature to these states. It
remains an area of research to determine what effects these excited nonequilibrium species have on the flow and its chemistry.

Another category of reactions that may occur on materials is chemical reaction with the surface atoms and molecules. These reactions may etch away material such as hydrogen or oxygen etching of graphite by forming chemical bonds and volatile products. They also may be involved in the formation of phases such as diamond when carbon is in the mixture. For the present pure hydrogen case we will assume that no chemical reactions involving hydrogen take place.

The reactions assumed in the model are the following catalytic reactions involving ions and atoms. Excited state production and quenching shall be indicated in the reaction equations, but the reactions rates for them shall remain unknown for the present.

\[
\begin{align*}
H^+ + S & \rightarrow H + S \quad (52) \\
\text{or possibly} \quad H^+ + H-S & \rightarrow H_2(\ast,v) + S \quad (53) \\
H_2^+ + S & \rightarrow H_2 + S \quad (54) \\
H + H-S & \rightarrow H_2(\ast,v) + S \quad (55) \\
H_2(v) + S & \rightarrow H_2(w) + S \quad (56) \\
H_2(v) + S & \rightarrow H_2(0) \quad (57)
\end{align*}
\]

The surface materials in the present experiments to be modeled are silicon, graphite, diamond, and adsorbed hydrogen.

Wall Boundary Conditions for the Species Equations

The wall boundary conditions for a low density partially ionized air were developed by Gupta, Scott, and Moss. The boundary conditions for the ions and atoms in an eleven species air model were subsequently simplified by Scott for a nonslip model. These models are phenomenological in that they do not address chemical mechanisms of the reactions nor the physical processes taking place. One must know from some source the overall reaction probability as a function of wall temperature or other parameters. The probability of recombination \( \gamma \) is simply defined as the fraction of the incident atoms that recombine on the surface. This means that the reaction rate can be written as

\[
k_w = \gamma \sqrt{\frac{kT}{2\pi m}} \quad (58)
\]

and the net normal flux of atoms due to recombination is

\[
M_a = \rho C_a \gamma \sqrt{\frac{kT}{2\pi m}} \quad (59)
\]

for a first order reaction. The net flux of species \( i \) is written in terms of the diffusion of species as
\[ M_i = \rho V_i = \rho \sum_{j \neq i}^{n_s} D_{ij} \frac{\partial C_i}{\partial y} + C_j \frac{\partial n_j}{\partial y} \]  

(60)

where \( D_{ij} \) is the multicomponent binary diffusion coefficient, \( C_i \) is the species mass fraction, and \( \rho \) is the total mass density. By equating (59) and (60) we get a mixed boundary condition for species \( i \) and the other species \( j \). The boundary condition is mixed in the sense that it contains both \( C_i \) and derivatives of \( C_i \). If more than one surface reaction can produce or consume species \( i \), then equation (59) will have additional terms that include these reactions. For example, the consumption/production of H atoms on a surface may involve the recombination of the H atoms and the recombination of the H\(^+ \) ion, viz.

\[ M_H = -C_H \gamma_H \sqrt{\frac{kT_w}{2\pi m_H}} + C_{H^+} \gamma_{H^+} \sqrt{\frac{kT_w}{2\pi m_{H^+}}} \]  

(61)

where we have set the ion recombination coefficient equal to unity. The first term on the right corresponds to consumption of hydrogen atoms by recombination, reaction (55), and the second corresponds to production of hydrogen atoms by hydrogen atomic ion recombination, reaction (52). If atomic hydrogen ions recombine via reaction (53) then equation (61) would have only the first term and the corresponding to equation for H\(_2\) would include the atomic ion recombination term in addition to terms for atom recombination and molecular ion recombination, viz.

\[ M_{H_2} = C_H \gamma_H \sqrt{\frac{kT_w}{2\pi m_H}} + C_{H^+} \gamma_{H^+} \sqrt{\frac{kT_w}{2\pi m_{H^+}}} + C_{H_2} \gamma_{H_2} \sqrt{\frac{kT_w}{2\pi m_{H_2}}} \]  

(62)

Note that (61) and (62) are not consistent with each other since they assume different paths for recombination of H\(^+ \). They are given her as examples of possible species equation boundary conditions.

CONCLUSIONS

A model of a hydrogen plasma at moderate pressures has been proposed for use in calculating the properties of a microwave discharge used for developing diamond film deposition techniques. The model assumes thermal nonequilibrium between the rotational/translational, vibrational, and electron degrees of freedom, but assumes that each degree of freedom can be described by a Boltzmann distribution at a given temperature. Chemical nonequilibrium, including ions, is incorporated in the model. Simple catalytic gas/surface interactions are included. The model is fashioned after that of Lee for air at hypersonic flight conditions and includes specific hydrogen reaction and excitation rates. The model can be included in a flow simulation calculation such as a finite difference solution of the Navier-Stokes equations. Validation of the model must be based on its ability to predict measurements in the hydrogen microwave plasma. The source term for input of energy from the microwave source must be obtained either from a solution to Maxwell's equations for the same geometrical set up as the fluid dynamics equations, or must be obtained from measurements of the electron density and temperature. As confidence is gained for the model and the computational method for pure hydrogen, additional species will be added to permit one to account for deposition of carbon in the forms of graphite and diamond on substrates.
ACKNOWLEDGEMENTS

The author is indebted to Dr. Jong.-H. Lee for his comments in the development of this paper. He pointed out the effect that excited states on the vibrational relaxation time and a method for accounting for the diffusional nature of vibrational relaxation at high temperatures. Discussions with Professor Mario Capitelli and his pointing out and furnishing significant references have been invaluable. Professor Alix Gicquel is greatly thanked for suggesting the modeling problem, providing much support, and providing guidance concerning the conditions that may exist in the plasma reactor.

REFERENCES

Table 1. Summary of some possible gas phase reactions and energy exchange mechanisms for hydrogen microwave plasma

<table>
<thead>
<tr>
<th>No.</th>
<th>Type</th>
<th>Designation</th>
<th>Reaction Equation</th>
<th>Used in terms</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>electron-translation</td>
<td>e-T</td>
<td>$e + H_2 \rightarrow e + H_2$</td>
<td>$Q_{e-T}, \theta_L$</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>electron-vibration</td>
<td>e-V</td>
<td>$e + H_2(v) \rightarrow e + H_2(w)$</td>
<td>$Q_{e-V}, \theta_L$</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>electron-electronic-vibration</td>
<td>E-V</td>
<td>$e + H_2(v) \rightarrow e + H_2(B^1\Sigma^+ u, C^1\Pi_u) \rightarrow e + H_2(v) + h\nu$</td>
<td>$Q^{1v}<em>{e-V}, Q</em>{rad}$</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>electron-dissociation</td>
<td>e-D</td>
<td>$e + H_2(v) \rightarrow e + H_2^* \rightarrow e + 2H$</td>
<td>$k_f, Q_d^3, k_d, \theta_L$</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>dissociative excit. of atom by electron</td>
<td>e-D</td>
<td>$e + H_2(v) \rightarrow e + H_2^* \rightarrow e + H + H^*$</td>
<td>$k_f, \theta_L, k_d^*$</td>
<td>15, 17</td>
</tr>
<tr>
<td>6</td>
<td>ionization of molecule by electron</td>
<td>e-Im</td>
<td>$e + H_2(v) \rightarrow e + H_2^+ + e$</td>
<td>$k_{im}, \theta_L$</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>ionization of atom by electron</td>
<td>e-ia</td>
<td>$e + H \rightarrow e + H^+ + e$</td>
<td>$k_{ia}, \theta_L$</td>
<td>15</td>
</tr>
<tr>
<td>8</td>
<td>excitation of atom</td>
<td>excitation</td>
<td>$e + H \rightarrow e + H^*(n=3)$</td>
<td>$\theta_L, Q_{rad}$</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>dissociative recombination</td>
<td>drv</td>
<td>$e + H_2^+(v) \rightarrow H + H^*$</td>
<td>$k_{drv}$</td>
<td>23</td>
</tr>
<tr>
<td>10</td>
<td>vibration-translation coupling</td>
<td>V-T</td>
<td>$H_2(v) + H \rightarrow H_2(v-1) + H_2$</td>
<td>$Q_T-v$</td>
<td>11</td>
</tr>
<tr>
<td>11</td>
<td>vib. quenching by atoms</td>
<td>V-T</td>
<td>$H_2(v) + H \rightarrow H_2(w) + H$</td>
<td>$Q_T-v$</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>3 body recomb. of atoms</td>
<td>recomb</td>
<td>$2H + M \rightarrow H_2 + M$</td>
<td>$M=H_2, H, k_b$</td>
<td>24</td>
</tr>
<tr>
<td>13</td>
<td>3 body recomb. of atom ions</td>
<td>deionization</td>
<td>$2e + H^+ \rightarrow e + H$</td>
<td>$k_{rl}$</td>
<td>18, 20</td>
</tr>
<tr>
<td>14</td>
<td>radiative recomb. of atom ions</td>
<td>deionization</td>
<td>$e + H^+ \rightarrow h\nu + H$</td>
<td>$k_{rll}$</td>
<td>18, 20</td>
</tr>
<tr>
<td>15</td>
<td>dissociative attachment</td>
<td>da</td>
<td>$e + H_2 \rightarrow H^+ + H^*$</td>
<td>$k_{da}$</td>
<td>27</td>
</tr>
<tr>
<td>16</td>
<td>charge exchange</td>
<td>cx</td>
<td>$H + H_2^+ \rightarrow H_2 + H^+$</td>
<td>$k_{cx}$</td>
<td>22</td>
</tr>
<tr>
<td>17</td>
<td>exc. prod. $H_3^+$</td>
<td>e23</td>
<td>$H_2^+ + H_2 \rightarrow H_3^+ + H$</td>
<td>$k_{e23}$</td>
<td>22</td>
</tr>
<tr>
<td>18</td>
<td>vib. exc. by $H^+$</td>
<td></td>
<td>$H^+ + H_2(v=0) \rightarrow H^+ + H_2(v&gt;0)$</td>
<td>3.2.2</td>
<td>15</td>
</tr>
</tbody>
</table>
Table 2 - Formulas for relaxation times and collision frequencies for a moderate pressure hydrogen plasma

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Constants, $a_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>$a_0$</td>
</tr>
<tr>
<td>electron-translation (momentum exchange)</td>
<td>$\frac{\tau_T}{n} = \sum_{i=0}^{5} a_i T_e^i$</td>
</tr>
<tr>
<td>$\sigma^*$</td>
<td>7.3739e-9</td>
</tr>
<tr>
<td>electron-translation (momentum exchange)</td>
<td>$\frac{\tau_T}{n} = \sum_{i=0}^{5} a_i T_e^i$</td>
</tr>
<tr>
<td>$\sigma^{**}$</td>
<td>4.3970e-9</td>
</tr>
<tr>
<td>electron-vibration</td>
<td>$\log\left(\frac{1}{n_e \tau_{ev}}\right) = \sum_{i=0}^{3} a_i \log(T_e)^i$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.41620</td>
</tr>
<tr>
<td>vibration-translation (H+H₂ → H+H₂) quenching</td>
<td>$4.707e-16$</td>
</tr>
<tr>
<td>vibration-translation (H₂) coupling</td>
<td>$P_{T_{H_2H_2}} = 3.9\times10^{-10}\exp(-100/T^{1/3})$</td>
</tr>
</tbody>
</table>

†Except as noted calculated from cross sections in Buckman and Phelps
§Gorse, et al.
Table 3 - Reaction rates for a moderate pressure hydrogen plasma

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Constants</th>
<th>Temp. Range</th>
<th>Gov. Temp</th>
<th>Source of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + H₂(v) → e + H₂⁺ + e</td>
<td>$k_{im}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e + H → e + H⁺ + e</td>
<td>$k_{ia}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e + H₂(v) → e + H₂⁺ → e + 2H</td>
<td>$k_d$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e + H₃⁺ → 3H</td>
<td>$k_{im}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ H₂⁺(v&gt;5) + H⁺(n=2)</td>
<td>8.0×10¹⁷</td>
<td>-0.404</td>
<td>0</td>
<td>0.1-1 eV</td>
</tr>
<tr>
<td></td>
<td>3.2×10¹⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5:1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e + H₃⁺ → e + H⁺ + 2H</td>
<td></td>
<td>1.22×10¹⁷</td>
<td>-1.45</td>
<td>9592</td>
</tr>
<tr>
<td>e + H₂(v) → H + H⁻</td>
<td>$k_{da}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v≥4</td>
<td>2.24×10²²</td>
<td>-1.45</td>
<td>9592</td>
<td>5000-50000 K</td>
</tr>
<tr>
<td>e + H₂⁺ → e + H⁺ + H(n=2)</td>
<td></td>
<td>1.43×10¹⁶</td>
<td>0</td>
<td>195820</td>
</tr>
<tr>
<td>e + H₂⁺ → H + H(n)</td>
<td></td>
<td>9.44×10¹⁸</td>
<td>-0.604</td>
<td>0</td>
</tr>
<tr>
<td>e + H₂⁺ → e + H⁺ + H</td>
<td></td>
<td>1.46×10¹⁷</td>
<td>0</td>
<td>37460</td>
</tr>
<tr>
<td>e + H₂⁺(v) → H(1s) + H(nl)</td>
<td>$k_{dprv}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v=0</td>
<td>8.78×10⁻⁶</td>
<td>-0.29</td>
<td>0</td>
<td>0.02-1.0 eV</td>
</tr>
<tr>
<td>v=1</td>
<td>1.81×10⁻⁶</td>
<td>-0.50</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>v=2</td>
<td>2.80×10⁻⁷</td>
<td>-0.66</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>v=3</td>
<td>8.64×10⁻⁸</td>
<td>-0.32</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>v=4</td>
<td>1.13×10⁻⁶</td>
<td>-0.77</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2e + H⁺ → e + H</td>
<td>$k_{r1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.63×10⁰⁷</td>
<td>-4.0</td>
<td>0</td>
<td>300-5500 K</td>
</tr>
<tr>
<td>e + H⁻ → 2e + H</td>
<td></td>
<td>1.34×10¹³</td>
<td>0.9</td>
<td>22700</td>
</tr>
<tr>
<td>e + H⁺ → hv + H</td>
<td>$k_{r1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.46×10¹⁴</td>
<td>-0.699</td>
<td>0</td>
<td>250-64000 K</td>
</tr>
<tr>
<td>2H + H₂ → H₂ + H₂</td>
<td>$k_{b2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0×10¹⁷</td>
<td>0.6</td>
<td>0</td>
<td>50-5000 K</td>
</tr>
<tr>
<td>2H + H → H₂ + H</td>
<td>$k_{b1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.2×10¹⁵</td>
<td>0</td>
<td>0</td>
<td>50-5000 K</td>
</tr>
<tr>
<td>H₂⁺ + H → H⁺ + H₂</td>
<td>$k_{cx}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.85×10¹⁴</td>
<td>0</td>
<td>0</td>
<td>not given</td>
</tr>
<tr>
<td>H₂⁺ + H₂ → H₃⁺ + H</td>
<td></td>
<td>1.27×10¹⁵</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H₂ + H₂ → H + H + H₂</td>
<td></td>
<td>8.61×10¹⁷</td>
<td>-0.7</td>
<td>52530</td>
</tr>
<tr>
<td>H₂ + H → H + H + H</td>
<td></td>
<td>2.7×10¹⁶</td>
<td>-0.1</td>
<td>52530</td>
</tr>
<tr>
<td>H + H⁻ → e + 2H</td>
<td></td>
<td>4.5×10⁸</td>
<td>1.5</td>
<td>698</td>
</tr>
<tr>
<td>H + H⁻ → e + H₂(v)</td>
<td></td>
<td>1.43×10¹⁵</td>
<td>-0.146</td>
<td>815.</td>
</tr>
<tr>
<td>H⁺ + H₂ → H + H⁺</td>
<td></td>
<td>7.63×10¹³</td>
<td>0.32222</td>
<td>1100-11000 K</td>
</tr>
<tr>
<td>H⁺ + H⁻ → H(n=3) + H(1s)</td>
<td></td>
<td>1.78×10¹⁷</td>
<td>0</td>
<td>1768.</td>
</tr>
</tbody>
</table>

¹These reactions actually depend on $T_v$ as well as $T$, but I have not found cross section data that depend on vibrational excitation state that are needed to calculate the vibrational temperature dependence.

†Rate must be reduced by Boltzman factor for $v>4$. 
Fig. 1. Hydrogen microwave plasma apparatus for diamond deposition
Fig. 2 Momentum exchange collision frequency based on moment of electron distribution function and on energy moment of electron distribution function.
Fig. 3 Curve fit of peak values of electron-vibration rate coefficients

\[ y = -17.199 - 2.4093x \quad R^2 = 1.000 \]
Figure 4. Curve fit of electron-vibration relaxation time

\[ y = 0.41620 + 0.19289x - 2.3658x^2 + 0.53046x^3 \]

\[ R^2 = 0.999 \]

\[ \log(1/(N_e \cdot \tau)) \text{ cm}^3/\text{s} \]
Fig. 5 Rate coefficient for hydrogen molecule dissociation by electrons

\[ y = 2.1474 \times 10^{-8} \times 10^{(-4.3019x)} \]

\[ R^2 = 1.000 \]
Fig. 6 Hydrogen molecule ionization rate coefficient
Fig. 7 Recombination rates for H^+ + e reactions
**Title:** A Nonequilibrium Model for a Moderate Pressure Hydrogen Microwave Discharge Plasma

**Author:** Carl D. Scott

**Abstract:**
This document describes a simple nonequilibrium energy exchange and chemical reaction model to be used in a computational fluid dynamics calculation for a hydrogen plasma excited by microwaves. The model takes into account the exchange between the electrons and excited states of molecular and atomic hydrogen. Specifically, electron-translation, electron-vibration, translation-vibration, ionization and dissociation are included. The model assumes three temperatures, translational/rotational, vibrational, and electron, each describing a Boltzmann distribution for its respective energy mode. The energy from the microwave source is coupled to the energy equation via a source term that depends on an effective electric field which must be calculated outside the present model. This electric field must be found by coupling the results of the fluid dynamics and kinetics solution with a solution to Maxwell's equations that includes the effects of the plasma permittivity. The solution to Maxwell's equations is not within the scope of this present paper.