SUPersonic Expansion of Nonequilibrium Plasmas

by

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SUPERSONIC EXPANSION ON NON-EQUILIBRIUM PLASMAS

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SUMMARY

In the supersonic expansion of an ionized gas, the dominant factor in describing the atomic processes is the recombination rate constant $K_R$. Several models describing the recombination process have been reviewed in some detail. It has been found that, depending on the adopted definition, different models will yield different values of $K_R$ for the same electron temperature and number density. A comparison of experimentally and theoretically derived values for $K_R$ has to be done with great care, as in the majority of the experiments $K_R$ is determined from the measured rate of disappearance of free electrons. These measurements give the correct "decay coefficient", but only in certain circumstances will it reduce to the correct recombination rate. In the light of the important role that $K_R$ plays in any numerical solution of nonequilibrium expansion flow of plasmas, details of experiments on a 15-degree corner expansion flow of ionized argon are given. In these experiments the plasma flow which was generated by driving strong normal shock waves into quiescent argon, was studied mainly by optical diagnostics. Using a dual-frequency-laser interferometer, the plasma properties around a corner expansion were recorded. The analysis of the interferograms has yielded values for the recombination rate constant as a function of the plasma macroscopic properties. The range of shock Mach-number, electron number density, temperature and initial channel pressure and temperature were as follows:

$$13 < M_s < 19; 10^{16} < n_e < 1.5 \times 10^{17} \text{ cm}^{-3}; 9,000^\circ K < T < 13,000^\circ K; 2.2 < p_i < 10 \text{ torr}; T_1 = 300^\circ K$$

It was found that the theoretically predicted values for the three-body, electron-ion-electron collisional-recombination rate are in good agreement with those measured gasdynamically in a well-defined flow. The measured flow quantities substantiate a previous analysis based on the method of characteristics.
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NOTATION

A  Area, Area ratio, Atom
A_{pq}  Radiation transition rate from level p to level q
a  Speed of sound
B  Magnetic field
c  Thermal velocity
C  The source term in the momentum balance equation (see Eq. 1.1.4), proportionality constant described in Eq. (1.2.27)
D  Constants, defined in Eq. (2.1.11)
d  The distance between particles, fringe spacing
E  Electric field, Energy
E_H  Ionization potential for a hydrogen atom
e  Electron charge
F  Force
f  Velocity distribution function
G  External force acting on the particle, centre of mass velocity
g  Relative velocity between colliding particles, statistical weight
H  Enthalpy
h  Planck's constant, impact parameter
I  Ionization potential
I(\phi_s)  The source term of property \phi_s
i_p  Ion current
K_A  Gladstone-Dale constant for atoms
K_I  Ionization rate constant; Gladstone-Dale constant for ions
K_R  Recombination rate constant
k  Boltzmann constant
K_{pq}  Collision transition rate from level p to level q
K_{pc}  Collision transition rate from level p to continuum, c
K(T)  Equilibrium constant based on concentration
LTE  Local thermodynamic equilibrium
M_s  Principal shock Mach number
m  Mass
N  Number of collisions per unit time
N_A  Avogadro number
n  Number density, refractive index
P  Pressure tensor
p  Pressure
P_1  Pre-shock pressure in a shock tube
Q  Energy source term, appearing in the energy balance Eq. (1.1.6)
Q_{rad}  Radiation loss
q  Heat transferred per unit area per unit time
R  Gas constant per unit mass
r  Thompson distance
S_{ij}  Fringe shift (from zone i to zone j)
s  Distance measured along a streamline
T  Temperature
t  Time
t_s  The time elapsed from the moment the shock front passed the expansion corner until the time the picture was taken
u  Average velocity, velocity in x direction
V  Velocity
v  Velocity in y direction
W  Electron diffusion velocity
x  Relative population
Z  Number of electrons removed from the atom
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>Degree of ionization</td>
</tr>
<tr>
<td>( \beta_p )</td>
<td>Radiative ionization rate from level ( p )</td>
</tr>
<tr>
<td>( \beta_c )</td>
<td>Radiative recombination rate</td>
</tr>
<tr>
<td>( \epsilon )</td>
<td>Internal energy</td>
</tr>
<tr>
<td>( \epsilon_p )</td>
<td>Energy of excited atom in level ( p )</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>Velocity vector direction</td>
</tr>
<tr>
<td>( \Theta_i )</td>
<td>Ionization potential expressed in degree ( K )</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Debye length, wave length</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Collisions frequency; frequency</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
</tr>
<tr>
<td>( \rho_i )</td>
<td>Characteristic ionization density</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Collision cross-section, electrical conductivity</td>
</tr>
<tr>
<td>( \phi_s )</td>
<td>Property of species ( s )</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>Basic distribution function</td>
</tr>
<tr>
<td>( \psi_s )</td>
<td>Total energy of a particle of species ( s )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Frequency</td>
</tr>
<tr>
<td>( \omega_s )</td>
<td>Rate of creation (or disappearance) of particles of species ( s )</td>
</tr>
<tr>
<td>( \Delta \tau )</td>
<td>Volume element</td>
</tr>
</tbody>
</table>

**Subscripts**

- \( a \): atoms
- \( c \): continuum
- \( e \): electrons
- \( E \): equilibrium conditions
- \( i \): ions
- \( k \): particle of species \( K \)
- \( n \): neutrals
- \( o \): stagnation conditions
- \( p, q \): principal quantum number of atomic states (levels)
s species
x,y directions in Cartesian coordinates
gs ground state
exc excited state
ext external

**SUPERSCRIP**
ts i,j directions
c collisional process
r radiative process

**SPECIAL NOTATION**
\[ \frac{dn_e}{dt} \] the rate of creation of free electrons per unit volume
\[ K_{R}^{s,c} \] steady, collisional-radiative recombination rate
\[ K_{I}^{s,c} \] steady, collisional-radiative ionization rate
\[ K_{R}^{s,c} \] steady radiative recombination rate
\[ < \phi_s > = \int_{-\infty}^{\infty} f(V) \phi_s dV \]

LTE local thermal equilibrium
MZI Mach-Zehnder Interferometer
SHG second harmonic generator

**NOTE:** In the literature, several forms of the recombination rate constant have been used. The relations between the different forms are as follows:

\[ K_R \left[ \frac{cm^6}{sec} \right] \]
\[ K'_R = K_R \times n_e \left[ \frac{cm^3}{sec} \right] \]
\[ K'_R = K_R \times N_A^2 \left[ \frac{\text{cm}^6}{\text{mole}^2 \text{sec}} \right] \]

where \( N_A \) is Avogadro number, \( N_A = 6.023 \times 10^{23} \) per mole, and \( n_e \) is the electron number density.

To avoid confusion, the units of \( K_R \) are always noted in the text.
INTRODUCTION

Successful reentry into the earth's atmosphere at hypervelocities by unmanned and manned spacecraft, future sustained terrestrial hypersonic flight and the possible entry into other planetary atmospheres also at hypervelocities, have generated a need for understanding plasma flows at high temperatures. In such flows, aerodynamic, thermochemical and electromagnetic phenomena take place simultaneously, resulting in very complex flow patterns. Thus, in the mathematical formulation there is strong cross-coupling representing the mutual interaction between these effects. Therefore, the solution of even simple cases is rather difficult. There is also a lack of experimental evidence concerning the recombination-rate constant and other effects lying at the interface between classical aerodynamics and particle physics. In fact, a lack of progress in this field can be attributed to a rather biased view of researchers who are well versed in either particle physics or aerodynamics, but rarely in both. It is the object of this work to throw some light on topics relevant to both disciplines. This will hopefully be achieved by first re-deriving the mathematics of this topic in a more illuminating fashion. This is followed by experimental results from which the recombination rate constant was evaluated.

In Chapt. 1, the general form of the equations of motion are derived from the fundamental conservation theorems. The second subsection of this chapter deals with the collisional and radiative processes that can take place in a plasma flow, leading to ionization and recombination. As information about ionization processes is more readily available, the emphasis in the present paper is on the collisional radiative processes leading to recombination. Recombination will be the dominant process in any supersonic expansion of plasma flows. A significant part of Chapt. 1 is dedicated to a detailed description of the various models that have been proposed by different authors for evaluating the recombination rate constant. Preceding the detailed description of these models, the equations of motion are rewritten with the real gas terms being expressed as functions of the plasma gross properties. As can be expected, the equations of motion take on a very complicated form and are almost unsolvable for the general case. Therefore, special cases for which the equations of motion are reduced into manageable form are introduced in Chapt. 2. The first special case to be analyzed is a numerical solution of a steady, quasi-one-dimensional, nonequilibrium expansion flow of ionized argon. The second is a numerical solution of the steady, two-dimensional, nonequilibrium, supersonic corner-expansion flow of ionized argon, using the method of characteristics. However, as these solutions represent only special and limited cases and since a general solution for supersonic plasma flow is not available at present, great importance lies in the experimental results. Chapter 3 reviews various experimental facilities that are suitable for studies of supersonic plasma expansion flows. Special attention is given to experiments leading to the evaluation of the appropriate recombination rate constant. In particular, the experiments conducted recently in the UTIAS hypervelocity shock tube are presented in detail, as they provide the most reliable available data. In this investigation a corner-expansion flow of ionized argon was generated and studied in order to understand reacting flows. In particular, the following two items were considered as the main topics of investigation:

(1) To present reliable experimental values of the recombination rate constant for an argon plasma.
(2) To substantiate experimentally the numerical solution for the two-dimensional, nonequilibrium, supersonic, corner-expansion flow of ionized argon as
The importance of the first objective is better understood if one is aware of the inaccuracies involved in a numerical evaluation of the recombination rate constant, and the large scatter in the available but limited experimentally-deduced values of the recombination-rate constant.

The discussions following the experimental results clearly demonstrate that the above objectives were achieved. That is, new reliable results from a well-defined gasdynamic flow were obtained for the recombination rate constant of ionized argon. Consequently, the present method of investigation may be used for other gases with confidence.

CHAPTER 1 EQUATIONS OF MOTION FOR PLASMA FLOW

1.1 The General Equations of Motion of an Ionized Gas

An ionized gas, or plasma, can be considered as a mixture of several gas species: atoms, ions and electrons. For each of the plasma constituents, a macroscopic balance equation for any property \( \phi \) can be written as follows:

\[
\frac{\partial}{\partial t} (n_s < \phi_s > ) + \frac{\partial}{\partial x^j} (n_s < \phi_s v^j_s > ) = I(\phi_s)
\]  

(1.1.1)

where \( < \phi_s > \) is the average of the property \( \phi_s \), \( n_s \) is the number density of the species \( s \), and \( I(\phi_s) \) denotes the source term of the property \( \phi_s \). The source term expresses the changes in \( < \phi_s > \) as a result of external influences, like electric, magnetic and gravitational fields, and internal influences which are not connected with convective terms, such as the chemical reactions. If we put \( \phi_s = m_s \), the mass of a particle of species \( s \), then Eq. (1.1.1) will give the usual continuity equation,

\[
\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x^j} (\rho_s u^j_s) = \dot{\omega}_s
\]  

(1.1.2)

In this case, the source term, \( I(\phi_s) = \dot{\omega}_s \), is the rate of creation (or disappearance) of particles of species \( s \) per unit volume per unit time, where, \( \rho_s = m_s n_s \) is the density of species \( s \) and \( u^j_s \) is the average velocity of the particles of species \( s \).

Similarly, if we identify the property \( \phi_s \) with the momentum of the particles of species \( s \), i.e., \( < \phi_s > = < m_s V^i_s > \), Eq. (1.1.1) will give the momentum balance for species \( s \):

\[
\frac{\partial}{\partial t} (\rho_s u^j_s) + \frac{\partial}{\partial x^j} (\rho_s u^i_s u^j_s) + \frac{\partial p^{ij}}{\partial x^j} = I(m_s v^i_s)
\]  

(1.1.3)

where \( V_s = \ddot{u}_s + c_s \) is the total velocity of a particle of species \( s \). \( \ddot{u} \) is the average velocity and \( c \) the thermal velocity. From kinetic theory \( < c > = 0 \), and \( \rho_s < c^i_s c^j_s > = p^{ij}_s \), where \( p^{ij}_s \) is the pressure tensor (Ref. 79, Ch. 9). The source term in Eq. (1.1.3), \( I(m_s v^i_s) \) indicates the rate of change per unit volume of the \( i \)-th component of the momentum due to collisions between particles and to externally applied forces. We can express this algebraically as follows:
\[ I(m_s v_i^i) = \frac{1}{\Delta t} \sum_{q} \sum_{k} F_{qsk}^i + \frac{1}{\Delta t} \sum_{q} q_s^i + C_s^i \]  \hspace{1cm} (1.1.4)

where \( F_{qsk}^i \) is the \( i \)-component of the time averaged force exerted by the entire species \( k \), during elastic collisions, on the \( q \)-th particle of species \( s \), contained within the small volume element \( \Delta t \). \( q_s^i \) is the \( i \)-component of the external force acting on the particle \( q \) and \( C_s^i \) is the rate at which momentum is created (or lost) as a result of inelastic collisions, per unit volume.

If we identify the property \( \phi \) with the total energy of the particle \( q \) of species \( s \), i.e. \( \phi_s = \psi_s + \frac{1}{2} m_s v_s^i v_s^i \) where \( \psi_s \) is the internal energy of the particle \( q \), then the energy balance equation of species \( s \) is obtained as

\[ \frac{\partial}{\partial t} \left[ \varepsilon_s + \frac{1}{2} \rho_s u_s^i u_s^i \right] + \frac{\partial}{\partial x^i} \left[ \left( \varepsilon_s + \frac{1}{2} \rho_s u_s^i u_s^i \right) u_s^j + \varepsilon_s^j + q_s^j \right] = I(\psi_s + \frac{1}{2} m_s v_s^i v_s^i) \]  \hspace{1cm} (1.1.5)

where

\[ \varepsilon_s = n_s < \psi_s > + \frac{1}{2} \rho_s < c_s^i c_s^i >, \quad \varepsilon_s^j = \frac{1}{2} \rho_s < c_s^i c_s^j > \]

\( \varepsilon_s \) is the total internal energy of the species \( s \) per unit volume and \( \partial \psi_s / \partial x^j \) is the thermal conduction within the species \( s \). The right-hand side of Eq. (1.1.5) represents the work done by external forces and elastic collisions, and also the rate at which energy is supplied to (or removed from) constituent \( s \), during inelastic collisions. With Eq. (1.1.4), we can express the right hand side of Eq. (1.1.5) as follows:

\[ I(\psi_s + \frac{1}{2} m_s v_s^i v_s^i) = \frac{1}{\Delta t} \sum_{q} \sum_{k} F_{qsk}^i v_s^i + \frac{1}{\Delta t} \sum_{q} q_s^i v_s^i + Q_s \]  \hspace{1cm} (1.1.6)

In the above equation, \( Q_s \) represents the amount of energy supplied to constituent \( s \) during inelastic collisions. From Eqs. (1.1.5) and (1.1.6), after eliminating the kinetic energy term, \( \frac{1}{2} \rho_s u_s^i u_s^i \) with the help of Eqs. (1.1.3) and (1.1.4), we have the final form of the energy balance equation as

\[ \frac{\partial \varepsilon_s}{\partial t} + \frac{\partial}{\partial x^i} \left[ \varepsilon_s u_s^j + p_s^i u_s^i u_s^j \right] = u_s^j \frac{\partial p_s^i}{\partial x^j} - \frac{\partial q_s^i}{\partial x^i} + Q_s + \frac{1}{\Delta t} \sum_{q} \sum_{k} F_{qsk}^i c_s^i \]

\[ + \frac{1}{2} u_s^i u_s^i c_s^i - u_s^i c_s^i \]  \hspace{1cm} (1.1.7)

As can be seen, the left-hand sides (LHS) of Eqs. (1.1.2), (1.1.3) and (1.1.7) contain the usual gasdynamic terms. On the right hand side of these equations, we find terms which take into account the atomic processes that occur in the plasma, namely, the different collisional and radiative processes, and the effect of the external and internal electric and magnetic fields on the charged particles of the plasma. For most of the work done on supersonic flowing...
plasmas, cases were selected in which the atomic processes were either neglected or, at most, given a very small role. In some cases unrealistic oversimplifications were made. On the other hand, the influence of flow phenomena was generally neglected in the work performed on decaying plasmas.

In the following chapters we will try to establish the atomic processes taking part in a decaying plasma and with the models which will be suggested, we will return to the basic conservation equations, Eqs. (1.1.2), (1.1.3) and (1.1.7), and attempt to solve them for certain flows.

1.2 The Atomic Processes in a Plasma

1.2.1 Elastic Collisions

In this section we evaluate the terms which appear in the right hand sides (RHS) of Eqs. (1.1.2), (1.1.3) and (1.1.7); i.e., the terms $\Phi_s$, $F_{sk}$, $G_{sk}$, $C_{sk}$ and $Q_{sk}$. The above terms represent the effects of collisions, radiation, and the external and internal force fields on the particles which constitute the plasma. Generally, the collisions are elastic and inelastic. As a first step we deal only with elastic collisions. To simplify the analysis it is assumed that the plasma is composed of only three species, viz., atoms, ions and free electrons. The electrons have a negative electric charge $e$ and the ions have a positive charge $Ze$, where $Z$ indicates the number of electrons that were removed from the atom. (Subsequently we deal only with a singly ionized species, i.e., $Z = 1$). The collisions between charged particles, in contrast to those between neutrals, can take place even when the distance between the particles is relatively large, due to the long range nature of the Coulomb potential associated with charged particles.

For a description of the elastic collisions, we adopt the binary collision model, since the experimental work shows that the results for the average properties of the plasma calculated from the binary model agree well with the experimental data. In the following we will describe briefly two ways of calculating the forces on particles. It is well known that a charged particle will be essentially shielded from the electric field of its neighbour located at a distance greater than the Debye length. However, the effect of the sum of all the individual fields of the charged particles, over those farther than a Debye length away, is not negligible. Let $E_i$ denote the $i$-th component of the induced electric field in the plasma, which is the sum of all the individual fields of the charged particles. This electric field, $E$, depends on the space distribution of the charged particles in the plasma. When we move charged particles in the induced electric field, $E$, we will have an induced magnetic field $B$. This induced magnetic field will depend on the mean path of the charged particles in the plasma. The average force acting on a charged particle due to collisions with all the other charged particles located outside the Debye sphere is given by

$$
\sum_{(d>\lambda)^k} F_{qsk}^i = e_q s \left[ \hat{E}_i + (\nabla q_s x B)^i \right] \tag{1.2.1}
$$
where the sum is taken over all particles $k$, which are at distance $d > \lambda$, the Debye length for the particle $q$. The fields $\mathbf{E}$ and $\mathbf{B}$ can be reinforced if external electromagnetic fields are present. In such a case the forces acting on all the particles of species $s$ within the volume $\Delta \tau$ are given by

$$
\sum_{q} \sum_{k} F_{qsk}^i + \sum_{q} G_{qs}^i = n_s e_s \left[ \mathbf{E}^i_s + \mathbf{E}_{ext}^i + \left\{ \mathbf{u}_s \times (\mathbf{B} + \mathbf{B}_{ext}) \right\}_s \right] \Delta \tau
$$

(1.2.2)

The rate at which energy is transferred to the charged particles due to the long range collisions can be found by multiplying Eq. (1.2.2) by the particle speed $V_{qs}$, which will yield:

$$
\sum_{q} \sum_{k} F_{qsk}^i V_{qs}^i + \sum_{q} G_{qs}^i V_{qs}^i = n_s e_s \left( \mathbf{E}^i_s + \mathbf{E}_{ext}^i \right) u_s^i \Delta \tau
$$

(1.2.3)

To complete the formulation it is necessary to evaluate $\mathbf{E}$ and $\mathbf{B}$ from the space distribution and mean free path of the charged particles. Some details can be found in Ref. 3.

Another way to tackle the binary collision problem is to use the distribution function and the Boltzmann equation (this is the classical approach used in kinetic theory). We will not develop this technique in any detail, but just quote the final results.

The rate at which particles of species $s$, contained in volume $\Delta \tau$, lose (or gain) momentum, as a result of collisions with particles of species $k$, is given by

$$
- \sum_{q} \mathbf{F}_{qsk} = \frac{m_s m_k}{m_s + m_k} \sum_{q} n_s n_k \int \mathbf{g} \sigma_{sks}(g) f_s f_k dV_s dV_k \Delta \tau
$$

(1.2.4)

and the rate at which the particles of species $s$, lose (or gain) energy due to collisions with particles of species $k$, is given by

$$
- \sum_{q} \mathbf{F}_{qsk} \cdot V_{qs} = \frac{m_s m_k}{m_s + m_k} \sum_{q} n_s n_k \int (\mathbf{g} \cdot \mathbf{G}) \sigma_{sks}(g) f_s f_k dV_s dV_k \Delta \tau
$$

(1.2.5)

where $\mathbf{g}$ is the relative velocity vector before the collision, $\mathbf{G}$ is the velocity vector of the centre of mass, $\sigma_{sk}(g)$ is the collision cross-section, and $h$ is the upper limit of the impact parameter.

Equations (1.2.4) and (1.2.5) can be solved only if the distribution functions $f_s$, $f_k$, and the collision cross section $\sigma_{sk}(g)$ are known. One of the cases for which the equations are solvable is when the particles have a Maxwellian velocity distribution. We show briefly how the integration of Eqs. (1.2.4) and (1.2.5) is carried out in this case.
The assumption of a Maxwellian velocity distribution can be justified when all the gradients in the macroscopic properties of the plasma are small, and no external forces act on the plasma. In such a case the plasma flow is an isentropic flow, and it can be proven that the velocity distribution is Maxwellian. Kantrowitz and Petschek showed that for a simple plasma, as long as the Larmor radius is much greater than the mean free path, the velocity distribution for the electrons and ions is near to a Maxwellian distribution for a wide range of temperatures and densities.

Any plasma is composed of heavy particles (atoms and ions) and very light particles (free electrons). Due to the large difference in mass, the energy transfer during collisions between the heavy particles and the electrons is less efficient than the energy transfer in collisions between the heavy particles themselves. Therefore, generally speaking one can expect two different temperatures in the plasma. One is the temperature of the heavy particles, while the other is the temperature of the free electrons. Only in the case of complete or local thermal equilibrium will the plasma have one temperature.

In the following we assume that the plasma particles have a Maxwellian velocity distribution, though each species will have a distribution with its own characteristic temperature, namely,

$$f_s = \left( \frac{m_s}{2\pi k T_s} \right)^{3/2} \exp \left( - \frac{m_s c_s^2}{2 k T_s} \right),$$

where $T_s = \frac{m_s < c_s^2 >}{3k}$ is the species temperature. To simplify the integration of Eqs. (1.2.4) and (1.2.5) the following assumptions are made:

1. The thermal energy of the heavy particles is smaller or at most of the same order as that of the electrons, i.e., $c_i = 0 \left[ c_e \sqrt{m_e/m_i} \right]$ (in a decaying plasma, the case we are interested in, it is well known that $T_e > T_i \approx T_a$).

2. The atom and ion temperatures are equal. Therefore $u_i^i = u_a^i = u^i$ (This assumption can be justified since the mass of the ions is almost equal to that of the atoms, and therefore only few collisions are necessary to reach a common temperature).

3. The electron diffusion velocity $W_e$, (defined by $W_e^i = u_e^i - u^i$) obeys the condition

$$\frac{W_e}{\sqrt{< c_e^2 >}} = 0 \left[ \sqrt{\frac{m_e}{m_a}} \right]$$

Equations (1.2.4) and (1.2.5) reduce to:

$$\mathbf{F}_{qia} = \mathbf{F}_{qai} = 0 \quad (1.2.6)$$
\[ \sum_{q_k} \sum_{q_e} \overrightarrow{F}_{qek} = -n_e m_e \sum_{q_k} v_{ek} \overrightarrow{v}_e \Delta \tau \]  
(1.2.7)

and

\[ \sum_{q_k} \sum_{q_e} \overrightarrow{F}_{qek} \cdot \overrightarrow{v}_e = 2n_e m_e \sum_{q_k} \frac{v_{ek}}{m_k} \left[ \frac{3}{2} k(T_k - T_e) + \frac{1}{2} m_k \frac{\overrightarrow{v}_e \cdot \overrightarrow{u}}{\overrightarrow{v}_e} \right] \Delta \tau \]  
(1.2.8)

where \( v_{ek} \) is the effective collision frequency of electrons with species \( k \).

The effective collision frequency can be calculated from the distribution function and collision cross-section as follows:\(^1\)

\[ v_{ek} = \frac{4 \pi n_e m_e}{3 kT_e} \int f_e \sigma_{ek} (c_e) \frac{d c_e}{d \epsilon_e}. \]  
(1.2.9)

The energy due to the internal field is given by\(^1\)

\[ \frac{1}{\Delta \tau} \sum_{q_k} \sum_{q_e} F_{qek}^i \overrightarrow{v}_e = 2 n_e m_e \sum_{q_k} \left[ \frac{3}{2} k(T_k - T_e) + \frac{1}{2} m_k \frac{(\overrightarrow{v}_e)^2}{\overrightarrow{v}_e} \right] \frac{v_{ek}}{m_k}. \]  
(1.2.10)

For the case of Coulomb collisions between electrons and ions, the collision cross-section is\(^1\)

\[ \sigma_{ei} = 2 \pi \frac{e^4}{m_i m_e} \ln \left[ 1 + \frac{2 \frac{h^2 e^4}{m_i m_e}}{kT_e} \right] \]  
(1.2.11)

where \( h = \lambda \), \( \lambda \) is the Debye length \( = \left[ \frac{kT_e}{4 \pi n_e e^2} \right] \) c.g.s. units.

The collision frequency between electrons and ions is:

\[ \nu_{ei} = \frac{8}{3} \sqrt{\frac{\pi}{m_e}} n_i e^4 \left( \frac{1}{2kT_e} \right)^{3/2} \ln \left[ \left( \frac{KT_e}{m_i e^6} \right)^3 \right]. \]  
(1.2.12)

Equations (1.2.11) and (1.2.12) agree very well with the results of Petschek and Bryon\(^5\) and Goldsworthy\(^6\) although they neglect the effect of electron diffusion.

The collision frequency between the electrons and atoms is given by

\[ \nu_{ea} = n_a \sigma_{ea} \left( \frac{8 kT_e}{\pi m_e} \right)^{1/2} \]  
(1.2.13)
Values for the collision cross-section $\sigma_{ea}$ can be found from Massey and Burhop, and Morse.  

So far we have accounted only for the contribution of the elastic collisions to the atomic processes appearing in the equations of motion, Eqs. (1.1.2), (1.1.3) and (1.1.7). We evaluated $F^{qek}$ in terms of atomic constants and the plasma gross properties ($n_e, n_i, T_e, T_i, \hat{u}, \hat{u}_e$). To complete the conservation equations, we have to express the rest of the atomic processes, $Q_s, C_s$ and $\omega_s$ appearing in the RHS of Eqs. (1.1.2), (1.1.3) and (1.1.7), in terms of the plasma macroscopic properties. To do so it is necessary to know the exact manner in which the atomic processes take place. For example, $\omega_e$ indicates the rate at which free electrons are created (or captured by the ions) per unit volume. An electron can be removed from a neutral atom directly from the ground state by an inelastic collision (if the energy transferred in the collision is sufficient), or by cascading through successive discrete energy levels of the atom due to several collisions, until it reaches the continuum. It is apparent that the rate of creation of free electrons $\omega_e$, will be different in the two different processes described. In the next section we will deal in some detail with the different ways in which electrons can be removed.

1.2.2 Inelastic Collisions, Excitation and Ionization

We will continue to deal with a three-component elemental plasma composed of neutral atoms, single ions and electrons. Our main interest is in the processes occurring during the expansion of a supersonic flow of an ionized gas. The following reactions can take place simultaneously during an expansion (see Refs. 8, 10, 13, 24, 66)

$$A_p + e \xrightarrow{K_{pq}} A^+ + e + e$$  (1.2.14)

$$A_p + e \xrightarrow{K_{pq}} A_q + e, \ (p < q)$$  (1.2.15)

$$A_p \xrightarrow{A_{pq}} A_q + \nu \ (p > q)$$  (1.2.16)

and

$$A^+ + e \xrightarrow{\beta_{pc}} A_p + \nu$$  (1.2.17)

where $A$ refers to neutral atoms, $p$ and $q$ refer to two discrete energy levels of the atom, $\nu$ is the radiative transition frequency and $K, A$ and $\beta$ indicate the appropriate transition rates. If we can describe the state of the plasma more accurately, i.e., if we know the electron number density and temperature, we can give appropriate weight to the different processes described by Eqs. (1.2.14) to (1.2.17) and accordingly neglect some of them relative to others.
If the plasma density and degree of ionization are high (for example $n_a > 10^{18}$ cm$^{-3}$, $T_e = 1$ eV, $\alpha > 5\%$) the radiation processes can be neglected compared to the collision processes, i.e., we can ignore Eqs. (1.2.16) and (1.2.17). Furthermore, if we look for recombination to excited states and not to the ground state (we will show later that the probability of an electron being captured into a highly excited state is much greater than the probability of falling through many energy levels down to the ground state), then we can ignore Eq. (1.2.15) and the only process we have to deal with is described by Eq. (1.2.14).

A further simplification, which we adopt from now on, is that the plasma is singly ionized. (For an argon plasma it will be valid for $T_e < 1.5$ eV and $u_e = 10^{17}$ cm$^{-3}$.)

In such a simple model (using Eq. (1.2.14) only), the rate of producing free electrons can be expressed as

$$\dot{\omega}_{em} = \frac{dn_e}{dt} = K_I n_e n_p - K_R n_e^3,$$

(1.2.18)

where $dn_e/dt$ is the rate of production of free electrons per unit volume, $K_I$ is the ionization rate constant, cm$^3$ sec$^{-1}$, and $K_R$ is the recombination rate constant, cm$^6$ sec$^{-1}$.

If the rate constants $K_I$ and $K_R$ (which turn out to be highly temperature dependent) are known, then we can express $\dot{\omega}_{em}$ in terms of the plasma macroscopic properties $T_e$, $n_e$ and $n_a$.

In the more general case, the collisional transition rates $K_{pq}$, $K_{qp}$, $K_{p'}$ and $K_{q'}$, appearing in Eqs. (1.2.14) and (1.2.15) can be evaluated for a plasma whose electrons have a Maxwellian velocity distribution, provided the appropriate collision cross-sections are known (e.g. $K_{pq} = \langle \sigma_{pq} V_e \rangle$). The information about the various collision cross-sections is taken either from experimental work, or from theoretical models. An excellent review of the atom-electron inelastic collision cross-sections was done by Rudge. 70

The most widely quoted electron-atom inelastic collision cross-section is the one suggested by Gryzinski 15, 16. He treated the electron-atom collisions as an encounter between a free electron having an energy $E_2$ and a bound electron having an energy $E_1$. In this model he assumed that the only force which contributes to the scattering is the Coulomb interaction between the bound and the incident electrons. Before the collision the bound electron had a velocity $\mathbf{V}_1$, the free electron had a velocity $\mathbf{V}_2$, and $\theta$ is the angle between the velocity vectors $\mathbf{V}_1$ and $\mathbf{V}_2$. If due to the collision the free electron undergoes a change in energy $\Delta E$, the cross-section is given by. 65
\[
\sigma(\Delta E) = \frac{2\pi}{\Delta E^2} \int_{\theta_{\min}}^{\theta_{\max}} f(\theta) \left( \frac{v_1^2 + v_2^2 - 2v_1 v_2 \cos \theta}{V^4} \right) \frac{\sin^2 \theta}{2\Delta E} - E_2 + E_1 \, d\theta ,
\]
(1.2.19)

where \( V = (v_1^2 + v_2^2 - 2v_1 v_2 \cos \theta)^{1/2} \) is the initial relative velocity of the two electrons and \( f(\theta) = \frac{V}{V_2} \sin \theta \) is the relative angular distribution function between the vectors \( \vec{v}_1 \) and \( \vec{v}_2 \). If the free electron (electron 2) moves through a collection of bound electrons (electron 1) which have an isotropic distribution of velocities, then\(^6\)

\[
\cos^2 \theta_{\max,\min} = \begin{cases} 
+ X & \text{if } |X| \leq 1 \\
+ 1 & \text{if } |X| > 1
\end{cases}
\]
(1.2.20)

where

\[
X = \left[ \left( 1 - \frac{\Delta E}{E_1} \right) \left( 1 + \frac{\Delta E}{E_2} \right) \right]^{1/2}
\]

The cross-section for a collision in which the free electron loses energy greater than \( I \) is,\(^6\)

\[
Q(I) = \int_{E_2}^{E_2} \sigma(\Delta E) \, d(\Delta E) .
\]
(1.2.21)

Denoting the velocity distribution of the electrons in the \( j \)-th electronic shell of an atom by \( N_j(v_1) \) and the ionization potential from this shell by \( I_j \), we find that the ionization cross-section for the atom via electron impact is

\[
Q_{\text{ion}} = \sum_j \int_{0}^{\infty} N_j(\vec{v}_1) \, Q_{j} \, d\vec{v}_1 .
\]
(1.2.22)

Gryzinski has shown that the calculation can be greatly simplified if we replace the relative velocity \( V \) by \( (v_1^2 + v_2^2)^{1/2} \), and also replace the exact electron velocity distribution \( N_j(v_1) \) by \( N_j \delta[v_1 - (2I_j)^{1/2}] \), where \( N_j \) is the number of electrons in the \( j \)-th electronic shell and \( \delta \) is the Kronecker delta function. Using these two approximations, one can show that the cross-section for electron ionization from the \( j \)-th shell of the atom is given by\(^6\)

\[
Q_{\text{ion}} = \begin{cases} 
\frac{N_j}{I_j E_2} \left( \frac{E_2}{E_2 + I_j} \right)^{3/2} \left( \frac{5}{3} - \frac{2I_j}{E_2} \right) & \text{if } 2I_j < E_2 \\
\frac{N_j}{I_j E_2} \frac{4\sqrt{2}}{3} \left( \frac{E_2 - I_j}{E_2 + I_j} \right)^{3/2} & \text{if } 2I_j \geq E_2
\end{cases}
\]
(1.2.23)
where $E_2$ is the energy of the incident electron. Similarly, for collisions resulting in excitation of an atom, the inelastic cross-section will be given by \(15,16\):

$$
\sigma_{\text{exc}} = \begin{cases} 
\frac{\sigma_o}{\Delta E^2} \left( \frac{E_2}{E_1 + E_2} \right)^{3/2} \left\{ \frac{2}{3} \left[ \frac{E_1}{E_2} + \frac{\Delta E}{E_2} \left( 1 - \frac{E_1}{E_2} \right) - \left( \frac{\Delta E}{E_2} \right)^2 \right] \right\} & \text{for } \Delta E + E_1 \leq E_2 \\
\frac{\sigma_o}{\Delta E^2} \left( \frac{E_2}{E_1 + E_2} \right)^{3/2} \left\{ \frac{2}{3} \left[ \frac{E_1}{E_2} + \frac{\Delta E}{E_2} \left( - \frac{E_1}{E_2} \right) - \left( \frac{\Delta E}{E_2} \right)^2 \right] \right\} & \text{for } \Delta E + E_1 \geq E_2 
\end{cases}
$$

(1.2.24)

where $\sigma_o = \pi \frac{1}{4} = 6.53 \times 10^{-14}$ cm$^2$ eV$^2$.

In order to determine the range of validity of Gryzinski's semi-classical theory for inelastic electron-atom collisions, Kingston compared Gryzinski's results with the exact classical cross-section for atomic hydrogen, as well as with the Born approximation, and the available experimental results. His conclusions were:

(a) For ionization from the ground state of atomic hydrogen, Gryzinski's classical cross-section reproduces the experimental results to within 25% in an energy range from 0.06 atomic units to about 10 atomic units above the threshold, and to within a factor of two from 0.02 atomic units above the threshold, and to within a factor of two from 0.02 atomic units above the threshold to about 400 atomic units. Although no experimental results are available for ionization of atomic hydrogen from the excited states, Kingston argues that the comparison between the classical and the Born cross-sections for ionization from the $p = 2$ state of hydrogen, suggests that for high energies the classical cross-section under consideration will not be greatly in error.

(b) For excitation from ground state of atomic hydrogen to the first excited state, the classical cross-section reproduces the experimental results to better than a factor of two, from the threshold to about 20 atomic units above it.

(c) For wide range of energy the classical and the Born expressions for the cross-sections agree quite well. Only at very high energies is there serious disagreement between the two approximations. This arises because the classical cross-section falls off as $1/E_2$ compared with log $-1/E_2$ fall-off of the Born cross-section. The experimental results suggest that $\sigma_{e-a} \sim E_2$ at the threshold.$^{10}$

**Evaluation of the Ionization Rate Constant $K_I$**

From statistical mechanics, the number of collisions between atoms and electrons per unit time per unit volume, which will result in ionization of an atom from its ground state is$^{10}$

$$
N = n_a n_e \int_{V_1}^{\infty} \sigma_e(V_e) f_e(V_e) V_e dV_e,
$$

(1.2.25)
where

\[ f_e(V_e) \] is the velocity distribution function of the electrons,

\[ \sigma_e(V_e) \] is the collision cross section between an atom and an electron,

\[ V_i = \left( \frac{2I}{m_e} \right)^{1/2} \] and \( I \) is the ionization potential.

Therefore, the ionization rate constant is given by,

\[ K_I = \frac{N}{n_a n_e} \int V \sigma_e(V_e)f_e(V_e) dV \] (1.2.26)

Assuming that the distribution function \( f_e \) is Maxwellian, then the integral on the R.H.S. of Eq. (1.2.26) can be evaluated, provided it is possible to express \( \sigma_e(V_e) \) explicitly as a function of the velocity. For many gases at temperatures of about 1 eV, most of the electrons that are capable of ionizing the atoms will have an energy near the threshold energy, i.e., \( \epsilon_e = I + kT_e \) (\( I \) is the threshold energy; for an argon atom, \( I = 15.6 \) eV.) In this range of energies, it is well known that the dependence of the collision cross-section on the colliding electron energy can be expressed as

\[ \sigma_e = C(\epsilon_e - I) \] (1.2.27)

where \( C \) is a proportionality constant.

Substituting Eq. (1.2.27) into Eq. (1.2.26) and carrying out the integration, one obtains,

\[ K_I = \bar{\sigma} \bar{V} \left( \frac{I}{kT_e} + 2 \right) \exp \left( -\frac{I}{kT_e} \right), \] (1.2.28)

where

\[ \bar{V} = \sqrt{\frac{3kT_e}{m_e}} = 6.21 \times 10^5 T_e^{1/2} \text{ cm/sec}. \]

and \( \bar{\sigma} \) is the average value of the collision cross-section. This value corresponds precisely to the electron energy, \( \epsilon_e = I + kT_e \) thus \( \bar{\sigma} = C kT_e \).

Therefore, to calculate \( K_I \) (Eq. (1.2.28)), one needs to know the electron temperature and the proportionality gas constant \( C \). The accuracy in evaluating \( K_I \) depends on the accuracy to which the value of \( C \) is known. The only assumption made during the evaluation of \( K_I \), which could be questioned, is whether the electrons have a Maxwellian velocity distribution. Consequently, Eq. (1.2.27) is well justified from experimental and theoretical evidence in the range of temperature that we are concerned with. For electrons whose thermal energy is much smaller than the ionization potential i.e., \( 3/2 kT_e < I \), the probability of ionizing an atom directly from the ground state is very low. For example, for argon gas having electron temperature of 1 eV collisions involving excitation are more probable by a factor of \( e^{-50} \) than those involving
In such circumstances the ionization will take place in steps. The first step will most probably be excitation to the first energy level above the ground state due to collisions with free energetic electrons in the tail end of the velocity distribution. The rate of excitation from ground state may be calculable similar to the evaluation of the ionization rate for unexcited atoms viz:

\[
K_{\text{exc}} = \int_{E_{\text{exc}}}^{\infty} \sigma_{\text{exc}}(V_e) f_e(V_e) V_e dV_e = \bar{\sigma}_{\text{exc}} V_{\text{exc}} (\frac{E_{\text{exc}}}{kT_e} + 2) e^{-\frac{E_{\text{exc}}}{kT_e}}, \tag{1.2.29}
\]

where

\[
V_{\text{exc}} = \left( \frac{2E_{\text{exc}}}{m_e} \right)^{1/2},
\]

is the energy associated with the excited state under consideration, and \( \bar{\sigma}_{\text{exc}} = C_{\text{exc}} (e_e - E_{\text{exc}}) \). In atoms by far the largest energy gap is the one between the ground state and the first excited state, and therefore the rate of population of the first excited state will act as a bottleneck for ionization. The real ionization rate will be somewhere between the values given by Eqs. (1.2.26) and (1.2.29). Wong and Bershader\textsuperscript{73} have studied the ionization processes behind strong normal shock waves in an argon gas. For the flow region controlled by electron-impact ionization they have suggested the following expression for \( K_I \),

\[
K_I = \frac{2 \times 10^{-6} kT_e}{(\pi m_e)^{1/2}} \left[ 4 \times 4 \left( \frac{\beta}{T_e} + 2 \right) e^{-\frac{\beta}{T_e}} + 9.5 \left( \frac{\theta_I}{T_e} + 2 \right) e^{-\frac{\theta_I}{T_e}} \right]
+ \frac{4 \times 4 \beta}{T_e} \left( 1 + \frac{\theta_I}{T_e} \right) \left( \frac{\theta_I}{\beta} - 1 \right) e^{-\frac{\theta_I}{T_e}} + \frac{\theta_I}{T_e}, \tag{1.2.30}
\]

where \( \theta_I = 182,850^\circ K \) and \( \beta = 134,000^\circ K \), are the energies (expressed in degrees) associated with direct ionization and excitation to the first excited state, respectively, for an argon atom. Equation (1.2.30) correlates very well with Wong and Bershader's experimental results. In Fig. 1 Eqs. (1.2.28) and (1.2.30) are shown graphically for an argon plasma at a temperature range, 7000\(^\circ K \) < T < 13,000\(^\circ K \). As expected the ionization rate, directly from the ground state, is smaller than the one predicted from Eq. (1.2.30) for the same temperature.

We have considered ionization via electron impact only, since once sufficient free electrons are present in the plasma, the ionization via atom-atom collisions, which is very inefficient compared with electron impact,\textsuperscript{5,10,73} can be neglected. The atom-atom ionizing collisions will certainly be important in the early stages of ionization such as that occurring just behind a strong shock wave.\textsuperscript{5,73}

Inelastic Collisions, De-Excitation and Recombination

In contrast to the relatively straightforward way in which \( K_I \) was calculated, the evaluation of \( K_R \) is not so simple. In the following we present a few different models to describe \( K_R \). We start with the crudest one, and progress to the most detailed available. The first and simplest case is to find \( K_R \) for a plasma in equilibrium. Strictly speaking, this case is of no interest since we are concerned with the nonequilibrium flow associated with decaying plasmas. However, it will be very instructive to calculate \( K_R \) for equilibrium and then to compare this value with the values of \( K_R \) from other
models for the same electron temperature. The equilibrium constant \( K(T) \) can be calculated with the aid of Saha's equation to obtain\(^\text{10}\)

\[
K(T) = \frac{n_e n_i}{n_a} = \frac{g_1 g_e (2m_e kT)^{3/2}}{g_a h^3} \exp \left( -\frac{I}{kT} \right) \tag{1.2.31}
\]

where \( g_1, g_a, \) and \( g_e \) is the partition functions for the ions, atoms and electrons respectively. \( g_e = 2 \), and \( I \) is the ionization potential. From the principle of detailed balancing,\(^\text{10}\)

\[
K(T) = \frac{K_I}{K_R},
\]

so that

\[
K_I = \frac{g_a}{g_i} \left( \frac{I}{kT} + 2 \right) \frac{h^3 \bar{r}_e}{2 \pi m_e kT_e} = 1.11 \times 10^{-14} C \frac{g_a}{g_i} \left( \frac{I}{kT} + 2 \right) \text{cm}^6 \text{sec}^{-1}, \tag{1.2.32}
\]

where \( C \) is in \( \text{cm}^2 \text{(eV)}^{-1} \).

Equation (1.2.32) gives the recombination rate constant for plasmas in equilibrium, where the electron is captured back into the atom ground state. (As will be shown later, according to Zgrozelski\(^\text{13}\) and Park\(^\text{62}\) as long as the recombination process is purely collisional, the ratio \( K_I \) to \( K_R \) is equal to the equilibrium constant \( K(T) \) although we are dealing with a nonequilibrium process in the plasma.)

Another approach to calculate the recombination rate constant is to follow the definition: recombination occurs when a free electron is captured into one of the ion's energy levels\(^\text{10}\) (the Thompson model). The electron will be caught by the ion if it passes closer to the ion than a distance \( r < r_0 \), the radius at which the potential energy of Coulomb attraction to the ion is equal to the kinetic energy of the electron, viz:

\[
\frac{Ze^2}{r_0} = \frac{3}{2} kT_e \quad \text{or} \quad r_0 = \frac{Ze^2}{3/2 kT_e},
\]

where for the case of single ionization, \( Z = 1 \). When the distance \( r \), between the free electron and the ion is smaller than \( r_0 \) we will say that a collision between them has occurred. The probability of such a collision, per unit volume, is\(^\text{10}\)

\[
n_e \bar{v}_e Z^2 r_0^2 \bar{v}_e n_i.
\]

Since, for a nonradiative recombination, the presence of a third body that will absorb the ionization potential energy released during the process is necessary, we have to calculate the probability of finding two electrons in the volume \( \pi r_o^3 \). This probability is \( Z n_e \bar{v}_e \text{.} \)\(^\text{10}\) The number of these recombination processes per unit time is therefore

\[
N_{\text{rec}} = n_e \bar{v}_e \pi r_0^2 Z^2 n_i Z \pi r_0^3 n_e = K_R n_e n_i \tag{1.2.33}
\]
K = \frac{\frac{2}{m} \frac{e^{10} Z^3}{m_e^{1/2}(kT_e)^{9/2}}}{3^5}

or,

K = \frac{8.75 \times 10^{-27} Z^3}{T_{1000 \text{ deg}}} = \frac{5.2 \times 10^{-23} Z^3}{T_{1000 \text{ deg}}} \text{ cm}^6 \text{ sec}

that is, \( T_e \) is given in eV or in units of 1,000 degrees, as noted.

Using the same concept, but a more detailed analysis of the capturing mechanism, Pitaevskii obtained,

K = \frac{\frac{4\pi \sqrt{2\pi}}{9}}{\frac{1}{m_e} \left(\frac{e^{10} Z^3}{(kT_e)^{9/2}}\right) \ln \Lambda}

where \( \ln \Lambda \) is a Coulomb logarithm and is approximately equal to unity. The difference between (1.2.34a) and (1.2.35) is in the constant \( 27/16 \Lambda \) which is of the order of unity.

Makin and Keck have calculated the three-body, electron-electron-ion collisional recombination rate constant using a classical phase-space concept. A point in phase space is used to represent the impact point of the three colliding particles. The distribution of these points is assumed to correspond to a gas in thermodynamic equilibrium. Makin and Keck used a "trial" surface to separate the free and bound states of the electron-ion pair (similar to \( r_0 \) in the simple treatment) at a selected energy which is less than the ionization limit. By minimizing the rate at which representative points cross the "trial" surface, a least upper bound to the recombination rate constant was calculated. The final result is:

K = 2.3 \times 10^{-8} T_{e}^{-9/2} \text{ cm}^6 \text{ sec}

Equation (1.2.36) is limited to the case of a dense plasma (in which radiative processes can be neglected and the recombination is due purely to three-body, electron-electron-ion collisions) and to temperatures below 1 eV. These limitations are a result of the assumptions involved in their analysis, which are:

1. the reactions can be described by using classical mechanics,
2. the interactions between particles can be described by a potential which is a unique function of the relative position coordinates,
3. the reacting systems are independent of each other, so that ensemble averages may be taken.
Furthermore, in the derivation of Eq. (1.2.36) a recombination event was considered as complete when the free electron was captured into one of the excited states, not necessarily the ground state. Since highly excited states for most atoms can be considered like hydrogenic energy levels, Eq. (1.2.36) does not consider the relevant atomic structure of the species under consideration. Bierberman et al have taken into account the radiation effects as well as the relevant atomic structure of the considered element. Using a similar approach (the Thompson model) they arrived at the following expression,

\[ K_R = \frac{4.3 \times 10^{-32} (E_H/T_e)^{9/2}}{[1 + \frac{g_i}{g_1} (\frac{E_2 - E_1}{T_e})^{1+b} (E_H/T_e)^{3/2} \exp(-E_1/T_e)/13.3 a_j]^2} \text{ cm}^6 \text{ sec}^{-1} \]  

where \( E_H \) is the ionization potential of hydrogen atom, \( g_i \) and \( g_1 \) are the ion and the atom ground state degeneracies respectively, \( E_1 \) is the energy associated with the \( i \)th excited state, \( a \) and \( b \) are constants having the values: \( a = 3.2 \times 10^{-2} \) and \( b = 4/9 \) for \( T_e \leq 0.07 \) (\( E_2 = E_1 \)); \( a = 0.25 \) and \( b = 5/6 \) for \( T_e > 0.07 \) (\( E_2 - E_1 \)).

Equations (1.2.36) and (1.2.37) are shown graphically in Fig. 2.
As can be seen from Fig. 2 and from Table 1, Makin and Keck's predictions are higher than the predictions of the more detailed models, Veselavskii, using a more rigorous analysis suggested that the constant appearing in Eq. (1.2.36) should be \( 0.62 \times 10^{-6} \) rather than \( 2.3 \times 10^{-8} \) as suggested by Makin and Keck.

A more detailed model for \( K_R \) was suggested by Bierberman, Yakubov and Vorobev; this model will be reviewed in the following. The recombination rate constants calculated using the Thompson model, Eq. (1.2.34), and the Makin and Keck's model, Eq. (1.2.36), differ from the recombination rate constant calculated under equilibrium conditions, Eq. (1.2.32) for the same temperature (1 eV) by nearly four orders of magnitude. There are two reasons for this large discrepancy (see Table 1):

(a) In the classical model, most of the recombinations are into highly excited states. It is well known that the rate of de-excitation to the ground state is smaller than the rate of capture by electrons into highly excited states. For Eq. (1.2.32), the recombination is considered completed when the electron has reached the ground state, and has not merely been captured to some bound state. This recombination rate will therefore be dictated by the slowest rate in the de-excitation process.

(b) Equation (1.2.32) assumes equilibrium conditions while the classical model on which Eqs. (1.2.34), (1.2.36) and (1.2.37) are based does not.

The previous discussion will enable us, at least to a first approximation, to express \( \omega_e \) in terms of the plasma gross properties, \( n_e \) and \( T_e \). (This can be done by using Eqs. (1.2.28) or Eq. (1.2.29) or (1.2.30) and (1.2.32), or (1.2.34) or (1.2.36) or (1.2.37) for \( K_I \) and \( K_R \), respectively.)

In the following we will describe in some detail for the model of a "collisional-radiative plasma", developed first by Bates et al. This model will include the four processes described by Eqs. (1.2.14) to (1.2.17). The collisional-radiative model will help us also to account for the radiation terms appearing in the conservation equations. For an optically thin plasma, considering the processes described by Eqs. (1.2.14) to (1.2.17), the rate of change of the population in any level \( p \), can be expressed by the following rate equation,
\[
\frac{dn_p}{dt} = -n_p \left[ n_e (K_{pc} + \sum_{q \neq p} K_{pq}) + \sum_{q < p} A_{pq} \right] + n_e \sum_{q \neq p} n_q K_{pq} \\
+ \sum_{q > p} n_q A_{qp} + n_e (K_{cp} + \beta_p)
\]  
(1.2.38)

where \(K_{ij}\) is the rate coefficient for collisional transition from state \(i\) to state \(j\). \(A_{ij}\) is the radiative transition rate between states \(i\) and \(j\), and \(\beta\) is the rate coefficient for radiative recombination into level \(p\). Index \(c\) indicates continuum, and \(K_{cp}\) is such that \(n_e^2 K_{cp}\) gives the number of appropriate collisions per cm\(^3\) per second. From the principle of detailed balancing

\[
n_e K_{cp} = n_p K_{pc} \quad \text{and} \quad n_e K_{cp} = n_p K_{pc},
\]

where index \(E\) represents equilibrium conditions. Expressing Eq. (1.2.38) with the relative population \(X_p = n_p/n_{pE}\) and making use of the principle of detailed balancing one obtains,

\[
\frac{dn_p}{dt} = -X_p \left[ n_e (K_{pc} + \sum_{q \neq p} K_{pq}) + \sum_{q < p} A_{pq} \right] + \sum_{q \neq p} X_q n_q K_{pq} \\
+ \sum_{q > p} X_q \frac{n_{qE}}{n_{pE}} A_{qp} + n_e K_{pc} + \frac{n_e}{n_{pE}} \beta_p.
\]  
(1.2.39)

The infinite set of coupled differential equations, typified by Eq. (1.2.39), describes the course of the recombination. For equilibrium conditions, one can verify from the Saha equation that the inequality \(n_p < n_e\) for \(p > 1\) will hold. Bates et al.\(^8\) showed further that for a wide range of electron densities and temperatures, this will be valid for nonequilibrium situations.

If, in addition to the above inequality, we assume that the average thermal energy of the plasma is much smaller than the excitation energy of the first excited state of the atom, then we have, \(n_p < n_1\), \(p > 1\) when a steady state is reached.

In a plasma obeying the above inequalities, a quasi-equilibrium number density of the excited states is established almost instantaneously without the number densities of the free electrons and ions being appreciably altered. Thereafter, the rates at which the excited states are populated and de-populated, the RHS of Eq. (1.2.39), are much greater than the net rate of creation or disappearance of a given state, the LHS of Eq. (1.2.39). Another way of describing the situation is to say that the relaxation time of the excited states are much shorter than either the relaxation time of the ground state or that of the free electrons. For a plasma in a quasi-equilibrium (in the sense defined above), the LHS of Eq. (1.2.39) will be zero for all \(p > 1\).
In this case, Eq. (1.2.39) will reduce to a series of simultaneous algebraic equations, which upon solution will give \( X_p \) as a function of \( n_e, n_1, T_e \) and the atomic constants. Equation (1.2.39) for \( p = 1 \), will determine \( \frac{dn_1}{dt} \), which is the rate of disappearance of free charges, and for a singly ionized plasma,

\[
\frac{dn_1}{dt} = -\frac{dn_{1\text{on}}}{dt} = -\frac{dn_e}{dt} = \gamma n_e^2
\]

where \( \gamma \) is an effective two-body rate coefficient referred to as, the "collisional-radiative decay coefficient". This coefficient, which depends on \( T_e, n_e \) and \( n_1 \), describes the net rate of disappearance of free electrons in a decaying plasma. The emphasis on the word, decay coefficient is important since during the processes described by Eqs. (1.2.14) to (1.2.17), both ionization and recombination will occur. In theoretical discussions, it is more convenient to use the ionization and recombination rate constants, and we will later show their relationship to \( \gamma \). In most experimental studies, the only measurable parameter is \( \gamma \). In equilibrium the opposing processes are balanced and \( \gamma \) vanishes.

The number of equations typified by Eq. (1.2.39) which are necessary in order to solve for \( X_p, p > 1 \), can be reduced significantly by realizing that for highly excited states, \( p > 1 \), the collision processes will dominate, and hence these highly excited states will be in equilibrium with the electron gas. For such states the populations can be evaluated by the Saha equation. For practical purposes it is convenient to group together all the excited states for which \( p \) is greater than a given value \( s \), in which case, \( X_1 = 1 \). The sums appearing in Eq. (1.2.39) will be truncated at \( p = s \). This set of simultaneous equations can be solved if a value for \( X_1 \) is assumed, and if the various transition rates are known. In this case the solution can be formally represented as,

\[
X_p = r_0(p) + r_1(p) \ X_1
\]

where \( r_0(p) \) and \( r_1(p) \) are functions of \( T_e \) and \( n_e \). To ensure that a sufficiently large value of \( s \) has been chosen, Eq. (1.2.39) must be solved for different values of \( s \), and the resulting values of \( X_p \) plotted versus \( p \). We know that for the highly excited states \( X = 1 \), they are in equilibrium with the free electrons. Therefore, for the proper choice of \( s \), the curve of \( X_p \) vs. \( p \) should be tangent to the line \( X_p = 1 \) at the point \( p = s \). If this is not the case, \( s \) should be increased until this condition is met.

From Eq. (1.2.39), and the definition of \( \gamma \) (Eq. (1.2.40)), Bates et al. showed that for \( p = 1 \):

\[
\gamma = \frac{\frac{dn_1}{dt}}{n_e^2} = \frac{n_F}{n_e} \left[ \sum_{q > 1} X_q K_{1q} + K_{1q} + K_{1c} \right] + \left[ \sum_{q \neq p} X_q \frac{n_{qE}}{n_{pE}} A_{ql} \right] + \left[ \sum_{q \neq s} \frac{n_{qE}}{n_e} A_{ql} + B_1 \right] - \frac{n_{lE}}{n_e} X_1 \left( K_{1c} + \sum_{q \neq 1} K_{1q} \right) \]

\[
\text{Eq. (1.2.40)}
\]
where the index \( \sigma \) identifies the group of excited states for which \( X_\sigma = 1 \).

The first term on the RHS of Eq. (1.2.41) represents the population of the ground state due to collisional de-excitation and three-body recombination. The second term represents the population of the ground state due to cascading and radiative recombination, and the third term represents the evacuation of the ground state by collisional excitation and ionization. As mentioned previously, the relative population of any excited state can be represented formally as \( X_p = r_0(p) + r_1(p) X_1 \) and hence Eq. (1.2.41) may be rewritten as,

\[
\gamma = K_R - K_I \frac{n_1}{n_e}
\]  

(1.2.42)

In Eq. (1.2.42) \( K_R \) and \( K_I \) are always positive, and depend only on \( n_e, T_e \) and atomic constants. Bates et al. named these terms, the 'collisional radiative' recombination and ionization rate constants, respectively.

In a tenuous plasma, the radiative processes dominate, or \( K_R n_e \gg \gamma n_e \); while in a dense plasma, the collision processes dominate, or \( K_R n_e \approx \gamma n_e \). In both cases, at least at the early stage of the decay from a state in which \( n_1 \) is very low, \( \gamma \) can be put equal to \( K_R \), and the term \( K_I \) may be neglected. In most of the experimental work on decaying plasmas (e.g. Chen, Park, Igra) it is assumed that \( \gamma = K_R \) since \( \gamma \) is the value directly measured.

Bates et al. solved the rate equation, Eq. (1.2.39) for \( X_p \), they solved Eq. (1.2.41) for \( \gamma \), and Eq. (1.2.42) for \( K_R \) and \( K_I \). The solution was carried out for hydrogen using Gryzinski's semi-classical expression for the inelastic collision cross-section (from which \( K_p e \) and \( K_p c \) were deduced). For the radiative processes the tables of Baker, Menzel and Green, Rush and Chandler (for the spontaneous transition probabilities) and the tables of Seaton (for the radiative recombination coefficients \( B_p \)) were used (for details see Ref. 8). The results were presented in tabular form, from which Fig. 3 was obtained. The accuracy of the results for \( K_R \) and \( K_p \), is highly dependent on the degree of accuracy to which the various transition coefficients were obtained. At extreme values of \( n_e \) and \( T_e \) (for example \( n_e = 10^{18} \text{ cm}^{-3}, T_e = 64,000 \text{K} \) the results become meaningless as in this range, the basic assumption of quasi-equilibrium populations of the excited states is no longer valid.

In their second paper Bates et al. modified the model to account for an optically thick plasma as well. The following cases were treated:

(i) The plasma is optically thick towards lines of the Lyman series.

(ii) The plasma is optically thick towards lines of all series.

(iii) The plasma is as in case (i), but also optically thick towards the Lyman continuum.

(iv) As in (ii) but also thick towards Lyman continuum.

For case (i), the Lyman lines are completely absorbed so that the downward radiative transition from any level \( p \), to level 1 are balanced by the reverse upward transitions. It is therefore necessary to remove all the \( A_{pl} \)'s from.
the set of linear equations governing the quasi-equilibrium. In addition, the second state \( p = 2 \), will be effectively stable with respect to radiative transitions, and may not be grouped with the other excited states as was done previously. Hence we can assume that \( n_P \ll n_1 + n_2 \) and \( n_P \ll n_e \) for all except \( p = 1, 2 \). The set of linear equations (like Eq. (1.2.39)) was solved for \( n_P \), with \( p > 2 \). To obtain a solution, it was necessary to assume values for both \( n_1 \) and \( n_2 \). The rate of disappearance of charged particles will be,

\[
\frac{dn_{\text{ion}}}{dt} = \frac{dn_e}{dt} = -\left( \frac{dn_1}{dt} + \frac{dn_2}{dt} \right).
\]

The collisional radiative decay coefficient \( \gamma \), will be,

\[
\gamma = \gamma_1 + \gamma_2 \quad \text{where,}
\]

\[
\frac{dn_1}{dt} = \gamma_1 n_e^2 \quad \text{and} \quad \frac{dn_2}{dt} = \gamma_2 n_e^2.
\]

Bates et al showed that for hydrogen, the relaxation time of the second excited state (\( p = 2 \)) is much shorter than the relaxation time of both the ground state and the free electrons. This fact enabled them to derive a relation between \( \gamma \) and the ionization and recombination rate constants similar to the expressions developed for the optically thin plasma. They presented the results of the calculations for \( K_R \) in tabular form from which Fig. 4 was obtained. The recombination rate constant for case (iii), \( K_R(iii) \), may be readily obtained from \( K_R(i) \) as follows,

\[
K_R(iii) = K_R(i) - \beta_1
\]

where \( \beta_1 \) is the radiative recombination rate into the ground state.

For case (ii), all the line radiation is absorbed, therefore the rate equation, Eq. (1.2.38) is reduced to

\[
n_P \sum_{q \neq P} K_{pq} - n \sum_{q \neq P} K_{pq} \frac{n_q}{n_e} = n_e (K_{op} + \beta_p) \quad (1.2.43)
\]

The solution of Eq. (1.2.43) has the formal form,

\[
n_p = n_t(p) + n_r(p)
\]

where \( n_t(p) \), which is proportional to \( n_e^2 \), arises from the \( K_{op} \) term and \( n_r(p) \), which is proportional to \( n_e \), arises from the radiative recombination. Once the solution for \( n_p \) is known, \( K_R(ii) \) can be evaluated by solving the rate equation Eq. (1.2.39) for \( p = 1 \). The results for this case were presented in tabular form for hydrogen plasma.

The recombination rate constant for case (iv) can be easily obtained from \( K_R(ii) \) as follows,

\[
K_R(iv) = K_R(ii) - \beta_1.
\]
From the figures and tables presented by Bates et al, it is clear that self absorption tends to reduce the 'collisional-radiative' recombination rate. This is expected, since self absorption will promote excitation and ionization. Furthermore, it can also be seen that for the range of $n_e$ and $T_e$ investigated, $K_R^{(i)} > K_R^{(ii)} > \beta_1$. For very high temperature ($T_e > 64,000^\circ K$) the various recombination rate constants, $(K_R^{(i)}, K_R^{(ii)})$ approach $\beta_1$, which mean that for very high temperature, the radiative recombination into ground state is the dominant process.

A slight modification of Bates' theory was made by Zgrozelski. He also assumed that the only processes taking part in the plasma are those described by Eqs. (1.2.14) to (1.2.17), and that the plasma is singly ionized. Like Bates et al, he divided his work into two parts, the first dealing with collision processes only, while the second allows for some radiation trapping.

As in the previous work the basic assumption here is that the relaxation time of excited atomic states is much shorter than the relaxation time for the ground state and the electron gas and therefore, a 'steady state' condition can be assumed, i.e., $d n_p / dt = 0$ for all $p > 1$. To limit the number of algebraic equations (typified by Eq. (1.2.38) without the radiative terms) that have to be solved for $x_p$, Zgrozelski arbitrarily assumed that all the excited states which lie within the range $k T_e$ from the continuum are in equilibrium with the electron gas. The population of these states is related to the electron number density via the Saha equation evaluated at the electron temperature. Once the population of the excited state $p$, $n_p$ is known for all $p > 1$, solving Eq. (1.2.38) for $p = 1$ yields $d n_1 / dt$, and for the 'steady-state' model this is equal to $(- d n_e / dt)$. Zgrozelski argues that since most of the neutrals are in the ground state (at least at lower temperatures, $T_e < 1 eV$), one can approximate the ground state population as follows,

$$x_1 = \frac{n_a}{n_{1E}} \approx \frac{n_a}{n_{aE}}$$

where $n_a$ is the number density of neutrals in the plasma.

This approximation introduced a parameter $r K$, $r K = (n_e^2 / n_a) / (n_e^2 / n_{aE})$, which represents the extent of the departure from equilibrium.

The net rate of electron production can be calculated in the following manner,

$$\frac{d n_a}{d t} = \sum_{p=1}^{m-1} n_{pE} \frac{d X_p}{d t},$$

$$K_R^s = \frac{1}{n_{eE}} \sum_{p=1}^{m=1} K_{pc} n_{pE} X_p$$

the collisional recombination rate constant,

$$K_I^s = \frac{1}{n_{aE}} \sum_{p=1}^{m=1} K_{pc} n_{pE} X_p$$

the collisional ionization rate constant,
where $\varphi_p$ is the "basic distribution function", defined by the relation,

$$X_p = X_1 \varphi_p + \left( \frac{n_e}{n_e E} \right)^2 (1-\varphi_p)$$

$\varphi_p$ depends only on the principal quantum number $p$, and for the 'steady state' model,

$$\frac{dn_a}{dt} = -\frac{dn_i}{dt} = -\frac{dn_e}{dt} = k_s n^3_e - k_i n_e n_a$$ (1.2.44)

It is worth mentioning here that the collisional 'steady-state' rate constants, $K_{RE}^s$ and $K_{IE}^s$ are not equal to the equilibrium rate constants, which are:

$$K_{RE}^s = \frac{1}{n^2_e E} \sum_{p=1}^{m-1} K_{pc} n_p E$$ and $K_{IE}^s = \frac{1}{n^2_{aE}} \sum_{p=1}^{m-1} K_{pc} n_p E,$

although the ratios of these rate constants are the same in the 'steady state' and the equilibrium cases. This ratio is equal to the equilibrium constant $K(T)$,

$$\frac{K_{IE}^s}{K_{RE}^s} = \frac{k_i^s}{k_i^s} = \frac{n^2_{eE}}{n^2_{aE}} \equiv K(T)$$ (1.2.45)

In the second part of Zgrozelski's paper absorption of radiation from free-bound and bound-bound transitions is accounted for. This will modify Eq. (1.2.38) to account for the radiative absorption under consideration. Again the first step is to solve the rate equation for $X_p$ assuming a steady population of the excited states, i.e., $dn_p/dt = 0$ for all $p's > 1$.

For this case the basic distribution function $\varphi_p$, will be a function of $n_e$ and $p$, and not only of $p$ as in the purely collisional model. Once $X_p$ is known, the collisional-radiative recombination and ionization rate constants can be evaluated as follows, 13

$$K_{RE}^{s,c} = \frac{1}{n^2_e E} \sum_{p=1}^{m-1} K_{pc} n_p E \varphi_p$$ and $K_{IE}^{s,c} = \frac{1}{n^2_{aE}} \sum_{p=1}^{m-1} K_{pc} n_p E \varphi_p$

Similar to Bates et al 8,8a Zgrozelski, also used Gryzinski expression for the collision cross-sections in evaluating $K_{pc}$. The radiative recombination rate constant is given by, 13

$$K_{RE}^{s,r} = \sum_{p=1}^{m-1} \beta_p$$

where the radiative transition rates were taken from the works of Bates and Dalgarno 19 and Green et al. 18 The rate of creation of free electrons is given by,
\[
\frac{dn_a}{dt} = - \frac{dn_e}{dt} = K_{s,c} n_e^3 - K_{s,c} n_e n_a + K_{s,r} n_e^2
\]  \hspace{1cm} (1.2.46)

In the 'collisional-radiative' model, \( K_T \) depends on \( n_e \) as well as on \( p \); therefore \( K_{s,c}T \) and \( K_{s,c}r \) are functions of \( n_e \) and the extent of departure from equilibrium \( r_k \). For the present case,

\[
K_{s,c}T \neq K_{s,c}r
\]

Zgrozelski carried out the calculation on the recombination rate constant for hydrogen at \( T = 1000^\circ \text{K} \). The results agree fairly well with those of Bates et al. The main difference between Zgrozelski's and Bates' analyses is that while both assumed the 'steady-state' model, Zgrozelski used this assumption only for the evaluation of the basic distribution function \( \varphi_p \). Once this distribution is known, the rate of change of the population in any given energy level, due to recombination, is not zero but given by \( \frac{dn_p}{dt} = K_{pc} n_p \varphi_p \). The recombination rate constant will result from summing up all the transitions from the continuum to all the different discrete energy levels. In the work of Bates et al actual values of the rate of production of excited atoms are set to be zero, and only the rate of production of ground state atoms is accounted for.

Park used Bates et al, 'collisional-radiative' model for evaluating the population of the excited states of monatomic nitrogen. The knowledge of the populations of the excited states under nonequilibrium conditions is important if one wants to use spectroscopic methods for determining the electron temperature, namely line intensity ratios. Using Bates' model, the excited state populations \( n_p \), can be evaluated as functions of \( n_e \), \( T_e \) and \( n_1 \). Modifying Bates' model for monatomic nitrogen, Park further assumes, that for the rate equation, Eq. (1.2.38), the LHS is zero for all \( p \)'s \( > 4 \). For the low lying states \( p < 3 \), the LHS of Eq. (1.2.38) is not negligibly small compared with each of the terms on the RHS. However, Park assumed that among these states, the collisional processes dominate to the extent that the low levels are essentially in equilibrium among themselves, that is, their populations can be closely related by the Boltzmann factor, i.e.,

\[
\frac{n_p}{n_q} = \frac{n_{pE}}{n_{qE}} = \frac{g_p}{g_q} \exp \left[ \frac{E_p - E_q}{kT} \right]; \quad p; q \leq 3
\]  \hspace{1cm} (1.2.47)

Using the above assumption, and accounting for only 41 energy levels in the atomic structure of monatomic nitrogen (the levels were tabulated by Park), the rate equation for \( p \geq 4 \) becomes,

\[
X_p \left[ K_{pc} + \sum_{q=1}^{41} K_{pq} + \frac{1}{n_e} \sum_{q=1}^{41} A_{pq} \right] - \sum_{q=4}^{41} X_q \left[ K_{pq} + \frac{1}{n_e} \frac{n_{qE}}{n_{pE}} A_{qp} \right]
\]

\[
= X_1 \sum_{q=1}^{3} \left[ K_{pq} + \frac{1}{n_e} \frac{n_{qE}}{n_{pE}} A_{qp} \right] + K_{pc} + \frac{n_e}{n_{pE}} \beta_p
\]  \hspace{1cm} (1.2.48)
As in the work of Bates et al., Park used Gryzinski's expressions for the collisional cross-section to evaluate $K_{pq}$ and $K_{pc}$. The rate coefficient for the radiative transition can be calculated from Refs. 18 to 23 quoted in Park's paper.61

Because of the large departure from a hydrogenic structure of the low lying levels in nitrogen atoms, Park had to modify Bates et al expressions for $K_{pq}$ and $K_{pc}$ for all $p, q < 3$. Using the appropriate modifications it is possible to solve Eq. (1.2.48) for $X_p$ provided the following four parameters are known: $T_e$, $n_1$, $n_e$ and the plasma dimension which enters implicitly in calculating the absorption.61 In a collision dominated plasma, the solution is independent of the last two parameters. From Eq. (1.2.48), one sees that a collision dominates condition exists in any of the three following cases,

(1) Optically thick plasma. For such a case almost all the radiation is absorbed by the plasma, therefore the radiative transitions have the least net effect on the state populations.

(2) Optically thin plasma of sufficiently high electron density. In the optically thin case, the effect of radiative transitions on the state populations is a maximum. However, for this case the plasma still will be collision dominated when,

$$K_{pq} \gg \frac{A_{pq}}{n_e} \quad \text{for } p > q \quad (1.2.49)$$

and

$$K_{pc} \gg \frac{n_e^p}{n_{pE}} \quad (1.2.50)$$

as can be shown from Eq. (1.2.48).

The RHS of inequality (1.2.49) is inversely proportional to the electron density. The same is true for Eq. (1.2.50), as can be seen from the Saha equation, i.e.,

$$n_{pE} = n_e^2 \frac{g_p}{2Z^+} \left( \frac{kT_e}{2\pi m_e kT_e} \right)^{3/2} \exp \left( \frac{I-E_p}{kT_e} \right)$$

where $Z^+$ is the partition function of the ions based on $T_e$, therefore, $n_e/n_{pE} = 1/n_e$. For nitrogen when $n_e > 10^{18}$ cm$^{-3}$ expressions (1.2.49) and (1.2.50) are satisfied for all possible emissive transitions.61

(3) Partially optically thick plasma under certain limitations. When the plasma is partially optically thick, it becomes collision dominated at an electron density between the above two limits. That is, depending on the magnitude of the optical depth, the plasma can be collision dominated at different electron densities; for nitrogen it will be below $10^{18}$ cm$^{-3}$ (Ref. 61).

The relative population of the ground state $X_1$, indicates the degree of nonequilibrium. For a low temperature plasma not far from equilibrium $X_1 = 1$, in this case, most of the atoms are in the ground state and
When the plasma is suddenly heated as behind a shock wave or suddenly cooled as in a supersonic expansion, the electron density change lags behind the change in the electron temperature, because a longer time is required for the electrons to be removed from an atom or to recombine than to equilibrate their temperature. For such events, $X_1$ will deviate significantly from unity.

For example, if a plasma initially at 10,000°K and $n_e = 10^{15}$ cm$^{-3}$ is rapidly expanded so that $T_e$ is reduced very quickly to $T_e = 8,000°K$ while $n_0/n_e^2$ is unchanged, $X_1 = 0.012$ (Ref. 61). Using a computer, Park$^{61}$ solved Eq. (1.2.48) for $X_1$ assuming a collision dominated plasma. The computations were carried out for a few different values of $X_1$ and $4,000°K < T_e < 20,000°K$. The results were presented graphically as $X_1$ vs. energy level index $p$. As can be seen from these figures (Ref. 61) the population of the highly excited states approaches the equilibrium values, i.e., $X_1 = 1$ for large $p$'s.

Once the nonequilibrium populations of the various excited states are known, the ionization and recombination rate constants can be evaluated. In Ref. 62, Park used his computation of $X_1$ for atomic nitrogen$^{61}$ to evaluate $K_I$ and $K_R$. The rate of creation of free electrons in a collision dominated simple plasma consisting of electrons, singly ionized atoms and neutrals can be expressed as;\footnote{62}

$$\frac{dn_e}{dt} = \sum_{p=1}^{s} K_{pc} n_p n_e - \sum_{p=1}^{s} K_{cp} n_e^2$$

(1.2.51)

where both rates, $K_{cp}$ and $K_{pc}$ are expressed in cm$^{-3}$ sec$^{-1}$. The upper limit of the summation $s$, must extend to an energy level close enough to the ionization limit, so that all energy levels below the effective ionization potential will be included in the sum. From the principle of detailed balancing

$$K_{cp} = \frac{n_{pe}^{2}}{n_e} K_{pc}$$

(1.2.52)

and from the Saha equation,

$$n_{pe} = n_e^{2} \frac{g_p}{2Z^+} \left( \frac{\hbar^2}{2 \mu m k T_e} \right)^{3/2} \exp \left( \frac{I-\mu}{k T_e} \right) = n_e^{2} F(T_e,p)$$

(1.2.53)

As was shown before, the populations of the excited states of nitrogen can be evaluated upon solving Eqs. (1.2.48). For a collision dominated plasma this equation will reduce to,

$$-\frac{X_1}{p} \left[ K_{pc} + \sum_{q=1}^{s} K_{pq} \right] + \sum_{q=1}^{s} K_{pq} = -X_1 \sum_{q=1}^{3} K_{pq} - K_{pc}$$

(1.2.54)
The transition rates \( K_{pq} \) and \( K_{pc} \) are functions of \( T_e \) alone and are based on Gryzinski's semi-classical cross-sections. Once the population of the excited states is known, the neutral number density can be evaluated from

\[
n_a = \sum_{p=1}^{s} n_p = \sum_{p=1}^{s} X_p n_p e^{\frac{E_p}{kT_e}}
\]  

(1.2.55)

From Eqs. (1.2.52) and (1.2.53) \( K_{cp} \) can be expressed as:

\[
K_{cp} = n_e F(T_e, p) K_p = n_e f(T_e, p)
\]  

(1.2.56)

where \( f(T_e, p) \) is a function of the electron temperature and the state index, \( p \). Making use of the Saha equation, Eq. (1.2.53), and Eq. (1.2.55), \( X_1 \) can be expressed as,

\[
X_1 = \frac{n_a}{n_{1e}} = \frac{n_a - \sum_{q=2}^{s} X_{q} n_e^{q}}{n_e^{2} F(T_e, 1)} = \frac{n_a - \sum_{q=2}^{s} X_{q} n_e^{q} F(T_e, q)}{n_e^{2} F(T_e, 1)}
\]

or

\[
X_1 = \frac{n_a}{n_e^{2}} f(T_e) - \sum_{q=2}^{s} X_{q} f(T_e, q)
\]  

(1.2.57)

Using the last expression for \( X_1 \) in the rate equation, Eq. (1.2.54), we have

\[
n_p = n_a f_3(T_e, p) + n_e^{2} f_4(T_e, p)
\]  

(1.2.58)

If we will use Eq. (1.2.56) for \( K_{cp} \) and Eq. (1.2.58) for \( n_p \) in the equation describing the rate of creation of free electrons, Eq. (1.2.51) becomes

\[
\frac{dn_e}{dt} = \sum_{p=1}^{s} K_{pc} n_p e^{-\frac{E_p}{kT_e}} - \sum_{p=1}^{s} K_{cp} n_e^{2} = n_a \sum_{p=1}^{s} K_{pc} f_3(T_e, p) + n_e^{3} \sum_{p=1}^{s} K_{pc} f_4(T_e, p)
\]

\[
- \sum_{p=1}^{s} f(T_e, p)
\]

Since the \( K_{pc} \)'s are functions of \( T_e \) alone, we have

\[
\frac{dn_e}{dt} = n_a n_e \sum_{p=1}^{s} F_1(T_e, p) + n_e^{3} \left[ \sum_{p=1}^{s} F_2(T_e, p) - \sum_{p=1}^{s} F_3(T_e, p) \right],
\]

26
\[
\frac{dn_e}{dt} = n_a n_e k_f(T_e) - n_e^3 k_r(T_e) \tag{1.2.59}
\]

where \(k_f\) and \(k_r\) are functions of \(T_e\) alone. The function \(k_f(T_e)\) and \(k_r(T_e)\) can be defined as the effective forward (ionization) and reverse (recombination) rate coefficients in the collision dominated plasma.

Equation (1.2.59) is slightly different from Eq. (1.2.42) suggested by Bates et al to describe the rate of creation of free electrons. While in Eq. (1.2.59), the ionization rate is proportional to \(n_a\), in Bates' model it is proportional to \(n_1\). Equation (1.2.59) is of the same form as the equation suggested by Zgrozelski, Eq. (1.2.44).

Park \(^6\) calculated the values of \(k_f\) and \(k_r\) for atomic nitrogen in the following way. For given values of \(T_e\), \(n_a\) and \(X_1\) all the \(X_p\)'s were evaluated using Eq. (1.2.54). Once the \(X_p\)'s are known, \(n_a\) was calculated using Eqs. (1.2.53) and (1.2.55). From the known values of the \(n_p\)'s and the transition rates, \(dn_e/dt\) was evaluated using Eq. (1.2.51). The known values of \(dn_e/dt\), \(n_e\) and \(n_a\) now can be substituted into Eq. (1.2.59) to evaluate \(k_f\) and \(k_r\). Since we have two unknowns \(k_f\) and \(k_r\) in Eq. (1.2.59) Park \(^6\) repeated the calculation for the same values of \(T_e\) and \(n_a\), but different \(X_1\). Now we have two simultaneous equations for \(k_f\) and \(k_r\) for the same \(T_e\) and \(n_a\). Park carried out his calculations for \(4,000^\circ K \leq T_e \leq 20,000^\circ K\). The simplest best fit curve for the computed results is \(\) \(^6\)

\[
k_r = 1.15 \times 10^{-26} \left[ \frac{T_e}{10,000} \right]^{-5.27} \text{cm}^6 \text{sec}^{-1}\tag{1.2.60}
\]

At equilibrium conditions \(dn_e/dt = 0\) and we showed before that \(k_f\) and \(k_r\) are functions of \(T_e\) alone, therefore, at equilibrium

\[
\frac{k_f}{k_r} = \frac{n_e^2}{n_a^2} = \frac{2Z_a}{Z_+} \left( \frac{2\pi m kT_e}{\hbar^2} \right)^{3/2} e^{-\frac{1}{kT_e}} \tag{1.2.61}
\]

where \(Z_a\) is the partition function for atoms.

The same result was obtained by Zgrozelski \(^13\) in the collision dominated plasma.(see Eq. (1.2.45)). It is important to note that the effective forward and reverse rates (\(k_f\) and \(k_r\)) as defined by Eq. (1.2.59) are not equal to the sum of all upward and downward transitions leading to ionization and recombination, respectively. If one defines these rates as the sum of all upward and downward transitions, Eq. (1.2.51) can be written as,

\[
\frac{dn_e}{dt} = K'_F n_a n_e - K'_R n_e^3
\]

where

\[
K'_F(T_e,n_a,n_1,n_2,\ldots,n_p,\ldots) = \sum_{p=1}^{s} K_p c \frac{n_p}{n_a}
\]
and

$$K'_R(T_e) = \sum_{p=1}^{s} \frac{K_{cp}}{n_e}.$$ 

In practice, as an approximation $K'_F$ and $K'_R$ are evaluated for Boltzmann distributions among the electronic states of the atom. In this case $K'_F$ and $K'_R$ are functions of $T_e$ alone. Although these coefficients are strictly applicable to equilibrium, many authors used them to describe nonequilibrium situations, because of the lack of knowledge of the nonequilibrium distribution among the electronic states. Designating the equilibrium coefficient $K_{FE}$ and $K_{RE}$, it is apparent from the preceding derivation that $K_{FE}$ and $K_{RE}$ are numerically different from $K_F$ and $K_R$, even under equilibrium conditions. In the calculations for nitrogen, Park found at least an order of magnitude difference between the following three sets of coefficients: $K_F$ and $K_R$, $K'_F$ and $K'_R$, and $K_{FE}$ and $K_{RE}$. Park argues that traditionally there has been a misunderstanding on the correct meaning of the reaction rate coefficients. Usually, in analyses $K'_F$ and $K'_R$ or rather $K_{FE}$ and $K_{RE}$ are adopted as the rate coefficients. However they are not useful for the following reasons:

1. $K'_F$ and $K'_R$ are strongly dependent on the population distribution among the different atomic states. Therefore, in nonequilibrium situations the assumptions that $K'_F = K_{FE}$ and $K'_R = K_{RE}$ are very poor.

2. The values of both $K'_F$, $K'_R$ and $K_{FE}$ and $K_{RE}$ are not unique even if the population $n_p$ of any state $p$ is specified, because by making the cutoff level $s$ arbitrarily large, these coefficients can also be made arbitrarily large (see the definition of $K'_F$ and $K'_R$).

3. It is almost impossible to measure these coefficients separately by a macroscopic experiment because the two terms in the RHS of Eq. (1.2.51) are very close to each other in magnitude even under strong nonequilibrium conditions.

On the other hand, it has been verified experimentally that the measured forward rate $k_F$ and the reverse rate $k_R$, are related by the equilibrium constant to a much closer degree than is expected from the definition of $K'_F$ and $K'_R$. This is because $k_F$ and $k_R$, not $K'_F$ and $K'_R$, are being measured experimentally. Furthermore, the two terms on the RHS of Eq. (1.2.59), are significantly different even when the plasma is only slightly out of equilibrium. Therefore, the coefficients $k_F$ and $k_R$ can be distinguished and measured quite readily. This argument reminds us of the note made while describing the Bates et al. 'collisional-radiative' model, that what one really measures in a decaying plasma is the decay coefficient $\gamma$, rather than the recombination rate constant $K_R$.

Before discussing other models for the evaluation of the recombination rate constant, we summarize the main structure of the 'collisional-radiative' model of Bates, Kingston and McWhirter and briefly mention the limitations of this model. Here the population-rate equation for each atomic state is constructed by knowing the following relevant rate constants:

(a) spontaneous transition probabilities,
(b) radiative recombination coefficients,
(c) rate coefficients for the electron collisional excitation,
de-excitation and ionization.

The resultant infinite set of simultaneous equations are reduced to a manageable number and simplified by imposing the assumption that the equilibrium relaxation times for the excited states are much shorter than those for the ground state and/or the electron gas. Then the rate of change of population of the ground state atoms, which is defined as the recombination rate for the 'collisional-radiative' model, can be obtained.

In principle, this scheme is a complete and exact method of studying the 'collisional-radiative' recombination process. However, the applicability of this scheme and the accuracy of the calculations depend very much upon the availability and accuracy of the rate constants mentioned.

A different approach to the evaluation of the recombination rate constant, is the model first presented by Byron et al. They described the recombination as a series of processes, starting with three-body (electron-ion-electron) collisions, in which an electron is captured by the ion creating an excited atom. The captured electron, which is normally in a highly excited state, will start cascading down the energy ladder via many two body (electron-atom) collisions. Under equilibrium conditions there exists a pronounced minimum in the total rate of de-excitation of excited atoms as a function of the principal quantum number \( p \), of the excited state. This minimum serves to limit the net rate of three body recombination to the rate of de-excitation of the level \( p^* \), at which the minimum occurs. The minimum in the equilibrium de-excitation rate occurs because the collisional de-excitation probability increases rapidly with increasing principal quantum number, whereas the radiative de-excitation probability, and also the equilibrium population of the excited states decrease with increasing quantum number. For nonequilibrium situations, Byron et al argue that the rate of crossing the level \( p^* \), has the same influence on the total rate of approach to equilibrium, as the slowest rate in a series of chain reactions has in determining the net reaction rate. For highly excited states the collisional processes dominates, and therefore they maintain an equilibrium relation with the electron gas. Following this argument, Byron et al assumed that the population of all states having principal quantum numbers larger than \( p^* \) is given by the Saha equation Eq. (1.2.53), and for hydrogenic atoms we have,

\[
\frac{n_p n_e}{n_e} = p^{2.2} \left( \frac{h^2}{2m_e kT_e} \right)^{3/2} \exp \left( \frac{E_p}{kT_e} \right), \quad p > p^* \quad (1.2.62)
\]

In this model, the recombination rate is equal to the de-excitation rate through level \( p^* \) by electron collisions and radiative transitions. Using Gryzinski's expressions for the inelastic collision cross-sections, the collisional de-excitation probabilities were deduced. The total radiative transition probability from a state having principal quantum number \( p \), to all states below level \( p^* \) is,\(^{24}\)

\[
A_{p^*} = \sum_{q=1}^{p^*-1} A_{pq} \approx \frac{p^*}{p} A_{p^*} , \quad (1.2.63)
\]
where \( A_p \) is the reciprocal mean radiative lifetime, and for hydrogen atoms

\[
A_p = \frac{166 \times 10^8}{p^{4.5}} \text{ sec}^{-1}
\]  

(1.2.64)

From the above discussion, the three body recombination rate constant \( K_R \) where \( K_R \) is defined as \( K_R = \frac{1}{n_e^2} \frac{dn_e}{dt} \), (similar to the collisional-radiative decay coefficient of Bates et al \(^8\)) is given by, \(^{24}\)

\[
K_R = \left[ A_{p^*} + n_e C(p^*,p^*-1) + \frac{1}{n_{p^*E}} \sum_{q=p^*+1}^{\infty} A_{p^*} \frac{n_q}{n_{p^*E}} \right] \frac{n_{p^*E}}{n_e^2}
\]

(1.2.65)

where, \( C(p,q) \) is the probability of a collisional transition \( p \rightarrow q \). Only \( C(p^*, p^*-1) \) is retained in the collisional de-excitation term, since the probability of de-excitation to an adjacent level is an order of magnitude larger than that to any other level. The energy level, at which the minimum occur may be obtained by solving \( dK_R(p)/dp = 0 \) for \( p \), where \( K_R(p) \) is given by Eq. (1.2.65). Byron et al used Eq. (1.2.65) for evaluating \( K_R \) for atomic hydrogen. The results were compared with those of Bates et al \(^8\) and for a very wide range of electron number densities \((10^9 \text{ cm}^{-3} < n_e < 10^{18} \text{ cm}^{-3})\) they agree very well. (The comparison was made at \( T_e = 16,000 \text{°K} \)). The theory of Byron et al \(^{24}\) can be extended to any gas, provided the atomic structure and the various transition probabilities are known for this gas. Dugan \(^63\) used the Byron model to calculate the three-body (electron-ion-electron) recombination rate for argon seeded with cesium. He accounted for the first 70 energy levels of cesium. Levels which were separated by less than 30 wave numbers were grouped into one degenerate state, therefore, the total number of levels reduced to 47. The 'bottleneck' in the de-excitation exists between levels \( K^* \) and \( L^* \), i.e., the slowest de-excitation is the \( K^* \rightarrow L^* \) transition. All the levels above \( K^* \) were designated levels \( K, (K^* + 1, K^* + 2, \ldots, K^* + n^*) \), and all the levels below \( L^* \) were designated \( L, (L^* - 1, L^* - 2, \ldots, L^* - n^*) \) and of course \( K^* = L^* + 1 \). The rate of crossing the gap \( K^* + L^* \) is \( \Gamma_{\text{dex}} \). Since the Byron model assumes that all the energy levels \( K \) are in equilibrium with the electron gas, and that the excitation through the bottleneck is negligible compared to the de-excitation, Dugan introduced a factor \( \delta \) to relate \( \Gamma_{\text{dex}} \) to \( K_R \). The factor \( \delta \), which depends on \( T_e \), must account for the fraction of the de-excitation rate that is balanced by excitation, as the system approaches equilibrium, as well as for the deviation from equilibrium population of the \( K \) energy levels. In an hypothetical nonequilibrium case, where there is no excitation and all the \( K \) states have equilibrium populations, \( \delta = 1 \) and \( K_R = \Gamma_{\text{dex}} \). On the other hand, for equilibrium conditions, the excitation rate is equal to the de-excitation rate for every state, therefore, the net recombination is zero, and for such a case \( \delta = 0 \). The evaluation of \( K_R \) is done in two steps. First the two levels between which the minimum de-excitation rate exists have to be found, and then \( \Gamma_{\text{dex}} \) can be calculated. Dugan showed that for a plasma in which the free electrons have a Maxwellian velocity distribution, from the principle of detailed balancing, the de-excitation rate from state \( p \) to state \( q \) is given by, \(^{63}\)

\[
r_{\text{dex}} = n_p n_e \frac{\sigma_{pq}}{g_p g_q} \exp \left( \frac{\Delta E}{k T_e} \right) < \sigma \frac{\text{d}v}{\text{d}v} > ,
\]

(1.2.66)
where $\sigma_{pq}$ is the inelastic collision cross-section for transition from level $q$ to level $p$, $(p > q)$ and $\Delta E_{pq}$ is the energy gap between the two levels. The rate of de-excitation across the 'bottle neck' $K^* \rightarrow L^*$, $R_{\text{dex}}$, is the sum of the rates at which an excited atom in state $K^*$ and all states $K$ above $K^*$ can be de-excited by superelastic collisions either past the state $L^*$ to states $L$ below $L^*$, or to the state $L^*$ itself. Therefore, the rate $R_{\text{dex}}$ is given by,

$$R_{\text{dex}} = \sum_{K=K^*}^{K=S} \sum_{L=1}^{L^*} R_{\text{dex}}.$$

The location of the controlling gap $K^* \rightarrow L^*$, depends on $T_e$ and $n_e$. With increasing temperature it will move toward the ground state. The second step is to estimate the factor $\delta$ for the ranges of $n_e$ and $T_e$ under consideration.

Dugan argues that for argon seeded with cesium, for the ranges $10^{13} \text{cm}^{-3} < n_e < 10^{18} \text{cm}^{-3}$, $500^\circ \text{K} < T_e < 11,000^\circ \text{K}$, $\delta = 1/3$ up to $2,000^\circ \text{K}$, $\delta = 1/2$ from $3,000^\circ \text{K}$ to $5,000^\circ \text{K}$ and $\delta = 2/3$ from $5,000^\circ \text{K}$ up to $10,000^\circ \text{K}$. Once $\delta$ is estimated the recombination rate constant is given by,

$$K_R = \delta (R_{\text{dex}}) \min.$$

Dugan presented his results graphically as $K_R$ vs. $T_e$. The temperature dependence of $K_R$ goes from $T_e^{-5}$ in the range $500^\circ \text{K}$ to $3,000^\circ \text{K}$ to $T_e^{-9/2}$ in the range from $4,000^\circ \text{K}$ to $1,000^\circ \text{K}$ (Ref. 63). Included in this paper is a print-out of a computer program for the evaluation of $K_R$ using the above described model. The limitations of this work are:

1. The radiation transitions were completely neglected relative to the collisional transitions. (This neglect allowed the application of the principle of detailed balancing in the derivation of Eq. (1.2.66)).

2. The population of all K states are given by the Saha equation.

3. The collisional transition rates were evaluated using Gryzinski's semi-classical model. This model approximates the inelastic collision cross-sections for the hydrogenic force field only.

An attempt to calculate theoretically and evaluate experimentally the recombination rate constants for the rare gases ($\text{He}, \text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}$) was made by Chen. For his theoretical calculations, Chen adopted Byron et al's method, modifying it to account for radiative transitions as well as collisional transitions. For the inelastic collision cross-section Chen also used Gryzinski's expressions. The radiative transitions were calculated by using the sum rule of line strength for a transition array and the quantum radial integrals which were evaluated by making use of the Coulomb approximation. The experimental work was done in an electric-discharge tube. Great care was taken to ensure high purity of the test gas. The tube diameter was chosen to be relatively large so that diffusion processes could be neglected. Upon release of the electrical energy stored in capacitors, the gas in the tube was ionized. Immediately after the energy discharge was terminated, the plasma started decaying, and during this decay the electron density and temperature were recorded using a triple electrostatic probe and microwave technique. The electron temperature was measured independently by the spectral line intensity ratio method. For an argon plasma the two different
temperature measurements agreed to within 30%.64

In the following, a brief description of Chen's calculations and experimental evaluation of $K_R$ will be given, including his remarks on the validity and accuracy of the calculations. Utilizing Byron's approach to describe the recombination in the 'collisional-radiative' decaying plasmas, the total de-excitation rate can be written in terms of atomic constants and the effective quantum numbers of the various energy levels. Chen showed that the total de-excitation rate can be written as,

$$R_{\text{de}} = \frac{n_e}{p_e} \left[ n_e C(q,p) + A_T \right]$$

where $n_e C(q,p)$ is the probability of collisional transitions from state $q$ to state $p$ and $A_T$ is the total radiative transition probability from the $p$ state to all states $q$ below $p$. The critical effective quantum number $p^*$, at which the minimum de-excitation occurs can be obtained by solving

$$\frac{d}{dp} \left( R_{\text{de}} \right) = 0, \text{ for } p.$$

The recombination rate constant defined as

$$K_R = \frac{1}{2} \frac{d n_e}{d t} \left( \text{cm}^3 \text{sec}^{-1} \right)$$

can be expressed as,

$$K_R = \frac{1}{n_e} \left[ (A_T + n_e C(q,p)) n_{p_e} \right] \text{ at } p = p^*.$$  \hspace{1cm} (1.2.70)

In Eq. (1.2.70) the following two mechanisms of de-excitation to the ground state are not included:

(a) the total transition probability from all states higher than $p^*$ to those lower than $p^*$. (The transitions of this kind can be shown to be negligibly small in the region of $n_e$ and $T_e$ under consideration, namely $10^{10} \leq n_e \leq 10^{16} \text{ cm}^{-3}$ and $1,000 \leq T_e \leq 16,000 \text{ K}$.)

(b) the purely radiative capture of free electrons into states lower than $p^*$. Because of such omissions, a correction factor $\delta$, should appear in front of the RHS of Eq. (1.4.70). This factor will account also for

(1) the nonequilibrium population of states above the 'bottle neck'.

(2) the finite rate of excitation.

Chen put $\delta = 1$ because the errors caused by inaccuracy in the rate constants involved in the calculation of $K_R$ are comparable in magnitude to the error due to ignoring $\delta$. Chen presented his calculations of $K_R$ for the rare gases in a tabular form, from which Fig. 5 was constructed. As can be seen from this figure, $K_R$ depends on $n_e$ as well as $T_e$. Only for high electron densities can the radiative transitions be neglected relative to the collisional transitions, and then the results for $K_R$ should approach those of Makin and Keck.
Due to possible errors in the various transition rate constants and the errors introduced by the effects neglected in the analysis, which were mentioned before, Chen argues that the accuracy in the calculated results for $K_R$ is probably within a factor of 4 (Ref. 64).

In the empirical part of his work, Chen evaluated the recombination rate constant in the following manner, from measurements of $n_e$ as function of time the value $dn_e/dt$ was obtained by differentiating the data using a computer. Now the values of $n_e$, $T_e$ and $dn_e/dt$ are known at any time, so that $K_R$ can be evaluated for the appropriate temperature. It is worth mentioning here again that we will get the recombination rate constant only if the ionization is very small, i.e., $K_I n_p < K_R n_e^2$ and this would not be the case when the system approaches equilibrium. When $K_R$ is calculated from the definition,

$$K_R = \frac{1}{n_e^3} \frac{dn_e}{dt}$$

the result is generally that of the plasma decay coefficient, which is different from the true $K_R$ of $K_I$. The experimental error in Chen's work is mostly due to the error in obtaining $dn_e/dt$ and was estimated to be within a factor of two.64

Chen’s calculated and experimentally determined values for $K_R$ agree quite well. (The two values are always of the same order of magnitude, for the published values for $H_e$, $N_e$ and $A_p$). Chen also performed the calculations for hydrogen in order to compare the results with those of Bates et al.8 The comparison was made in the ranges $10^{10}$ cm$^{-3}$ < $n_e$ < $10^{16}$ cm$^{-3}$ and $500^\circ$K < $T_e$ < $16,000^\circ$K and the agreement was very good, especially for high temperatures.

We have presented a few different models for the evaluation of the recombination rate constant. The last two models8,24 take into account the detailed structure of the atoms under consideration and are relatively difficult to use for numerical calculations. The accuracy of the results obtained from these models is highly dependent on the accuracy to which the various transition rates are known and the detailed knowledge of the atomic structure of the plasma under consideration. While in principle the model due to Bates et al8 gives the most exact description of the 'collisional-radiative' plasma, it seems that the model of Byron et al24 is somewhat easier to use for numerical applications.

Rather than go through the numerical scheme suggested by Bates et al8,8a, Biberman et al87 offer an alternative simple model described briefly below. Its main advantage is that it yields an analytical expression for $K_R$ which is much easier to use, especially for calculations in which $K_R$ is an intermediate target in the calculations of a more general problem, i.e., plasma flows.

In their model Biberman et al87 essentially combined two approaches, each suitable for a different temperature range. In the high temperature range the real discrete structure of the atomic level diagram is replaced with an equivalent atom having only two or three "effective" levels. In the low temperature range the discrete structure is replaced by quasi-continuum. This approximation is valid particularly for the highly excited states. As a result, the transfer of an electron down the energy levels during the
recombination could be regarded as a diffusion process. The first approach is similar to the "bottle neck" model of Byron et al. Its application is particularly good in the cases in which \( T_e \) is of the order of \( E_1 \) and the electron density is sufficiently high. The diffusion approximation, suitable for low temperatures is based on the fact that the most probable of the collisional transitions are the ones between energetically neighbouring levels. (Based on the diffusion model, Pitaevsky\(^{20}\) reached the expression presented in Eq. (1.2.35).) However, in the simplest two approaches mentioned above, radiative processes and the possible deviation from Maxwellian energy distribution among the electrons was not accounted for. Their contribution provided a general form of expression for \( K_R \) which include these phenomena, the results of their analytical manipulations regarding the recombination rate constant for the entire temperature range reads:\(^{87}\)

\[
K_R = \frac{a_1 \alpha_2}{a_2 + \chi \alpha_1} \tag{1.2.71}
\]

where \( \alpha_1 \) represents the recombination rate constant for the high temperature case and \( \alpha_2 \) for the low temperature case.

\[
a_1 = \frac{\hbar^3 e}{\pi m_e^2 g_1} \frac{I_H}{g_1} \frac{1}{(E_1 - E_2)} \exp \left( \frac{E_2}{T_e} \right) \tag{1.2.72}
\]

\[
a_2 = \frac{\hbar^3 e}{\pi m_e^2} \frac{2}{I_H} \frac{1}{3} \sqrt[3]{n} \left( \frac{I_H}{T_e} \right)^{9/2} \tag{1.2.73}
\]

where \( \hbar \) is the Planck constant, \( e \) is the electron charge, \( m_e \) is the electron mass, \( E_1 \) is the energy of the \( i \)-th level (measured from the continuum), \( I_H \) is the ionization energy (temperature) of the hydrogen atom, \( g_1 \) and \( g_4 \) are the atom and ion ground state statistical weight, \( A_1 \) is a factor which depends solely on \( \frac{K T_e}{(E_1 - E_2)} \) and is given graphically in Ref. 87. For \( 0.01 \leq \frac{K T_e}{(E_1 - E_2)} \leq 0.1 \) \( A_1 \) is in the range of \( 5 \times 10^{-3} < A_1 < 10^{-2} \). \( F_1 \) is a factor that takes account of the non-Maxwellian effect on the inelastic process rate. The number \( \chi \) depends only on the ratio \( E_2/T_e \) and is given graphically in Ref. 87. For \( E_2/T_e \geq 4 \), \( \chi \geq 0.8 \), the whole range of \( \chi \) is \( 0 < \chi < 1 \). For the number \( \Lambda \) Ref. 87 suggests the value 0.2.

The factor \( F_1 \) can be evaluated as follows:\(^{87}\)

\[
F_1 = \frac{1}{C} \left\{ \frac{1 + 4C - 1}{\sqrt{1 + 4C + 1}} \right\} \tag{1.2.74}
\]

\[
C = \frac{n_1}{n_e} \frac{2T_e}{E_1 - E_2} \frac{A_1}{\Lambda}
\]
For typical conditions $\lambda = 10$, $A_1 = 0.01 \sim 0.05$ (see also Fig. 2 in Ref. 87).

From the above discussions it is clear that the Biberman et al model is much easier to use in numerical evaluations of $K_R$ compared with the models of Bates et al. 8, 8a and Byron et al. 24. Biberman et al state that the results obtained for hydrogen using Eq. (1.2.71) are in good agreement with the predictions of Bates et al. 8, 8a. For the elements, good agreement is also obtained between the predictions of Eq. (1.2.71) and experimental results. 87

It is also evident from Table 2 that for argon plasma at temperatures around 1 ev, the low temperature approximation, Eq. (1.2.73), yields better results than from the general case, Eq. (1.2.71).

In Tables 1 and 2 the various experimental results and formulations of $K_R$, mainly for argon, are collected. As can be seen from these tables, for given values of $n_e$ and $T_e$, the scatter in $K_R$ is quite significant.

It is important to note again that when one compares experimental results with the theoretical predictions for $K_R$, great care should be taken in choosing the appropriate model for the recombination rate constant. It was already noted that in most of the experiments the measurable quantity is the plasma decay coefficient [at least if one follows the definition $K_R = 1/n_e^3 (dn_e/dt)cm^6/sec$, and not the recombination rate constant as defined in the work of Bates et al. 8]

At relatively low temperatures, it is possible to have recombination of a monatomic gas through a transient state of an ionized molecule that will quickly dissociate into atoms. For argon at temperatures lying between 1,000°K and 3,000°K, Fox and Hobson 21 suggested that the following processes are dominant:

$$2Ar + e \rightarrow Ar_2^+ + e + e \quad \text{for ionization} \quad (1.2.75)$$

$$Ar_2^+ + e \rightarrow Ar^+ + Ar \quad \text{for recombination} \quad (1.2.76)$$

From their experiments they presented a plot of $K_R$ vs. $T$, and the slope of this curve supports the assumption of dissociative recombination. Unfortunately, in measurements done with a mass-spectrometer, no molecules of $Ar_2$ or $Ar_3$ were detected for this range of temperatures. 67 Bray 22 also pointed out the possibility of such a recombination. For argon gas at temperature of about 1 ev it is very likely that even if argon molecules do exist, they will be completely dissociated and the plasma will consist solely of electrons, atoms and ions. The results reported by Desai and Corcoran 68 seem to contradict the last statement. They carried out a spectroscopic study on an argon plasma jet at atmospheric pressure. For a singly ionized plasma and defined the recombination rate constant as,

$$\frac{dn_e}{dt} = -K_R n_e^2$$

35
where, $K_R$ is expressed in $\text{cm}^3\text{sec}^{-1}$. The experimental work was done in the ranges, \(8,000^\circ\text{K} \leq T_e \leq 11,000^\circ\text{K}\) and \(10^{12} \text{ cm}^{-3} \leq n_e \leq 10^{15} \text{ cm}^{-3}\). The analysis of the results showed that the dissociative molecular-ion recombination could satisfactorily explain the observed recombination rates for the given experimental conditions. An empirical equation relating the observed values of $K_R$ to $T_e$ and $n_e$ was fitted to the data points and found to have the following form (Ref. 68).

\[
K_R = 1.28 \times 10^5 \times T_e^{1.8} \times 10^{-\frac{3410}{T_e}} \times n_e^{-0.64} \quad (\text{cm}^3\text{sec}^{-1})
\]

or

\[
K_R = 1.28 \times 10^5 \times T_e^{1.8} \times 10^{-\frac{3410}{T_e}} \times n_e^{-1.64} \quad (\text{cm}^6\text{sec}^{-1})
\]

Desai and Corcoran argue that the observed values of $K_R$ are consistent with the following dissociative mechanisms involving $\text{Ar}_2^+$ and $\text{Ar}_2$:

a. $\text{Ar}^+ + \text{Ar}(1) + \text{Ar}(1) \rightarrow \text{Ar}_2^+ + \text{Ar}(1)$, Three body process
b. $\text{Ar}_2^+ + e \rightarrow \text{Ar}_2(p)$, $p > 1$, Two body recombination
c. $\text{Ar}_2(p) \rightarrow \text{Ar}(1) + \text{Ar}(p)$, Dissociation of the molecule

In the above processes, 1 stands for ground state and p for an excited state.

In their work the electron number density and temperature were deduced from line intensity measurements. First the population of an excited state, $p$, is evaluated from the absolute line intensity emanating from the $p$-state. Once $n_p$ is known, under the assumption of LTE the electron number density is calculated using the Saha equation. At this point it is important to note, that at the early stages of the recombination, in a rapid cooling plasma, one can expect an overpopulation of the highly excited states due to the fact that free electrons are primarily captured into the highly excited states and only later they cascade down towards the ground state. Therefore, the assumption of an equilibrium population is questionable. Furthermore, under the LTE assumption, $T_e = T$ and while the time to reach $T_e = T$ is almost $10^{-8}$ sec (Ref. 76). Therefore, at least at the beginning of the recombination process the assumption, $T = T_e$ is wrong.

Desai and Corcoran admitted that the accuracy in measuring $n_e$ is \(\pm 30\%\), therefore, their values of $K_R$ will be at most within an order of magnitude of the true decay coefficient. The above arguments lead us to believe that the dissociative recombination of a dense argon plasma at temperatures above $10,000^\circ\text{K}$ is questionable. It seems that the only definite evidence for the existence of such mechanisms will be the detection of a significant amount of $\text{Ar}_2$ and $\text{Ar}_2^+$ molecules in the plasma, using a mass-spectrometer. It should be noted here that Biberman et al in their review paper on the kinetics of collisional-radiative recombination argue that;

(a) In strongly rarefied plasma, like in astro-physical applications ($n_e < 10^8 \text{ cm}^{-3}$), process of dissociative recombination may acquire importance, whereas in laboratory conditions the process does not seem to be significant.
(b) At $T_e < 3000^\circ K$, $K_R$ is proportional to $T_e^{-9/2}$ for all the elements (see Eq. (1.2.73)). This contradicts Fox and Hobson findings.21

A detailed account on dissociative recombination can be found in Ref. 23.

In the previous discussions we presented some models for calculating the ionization and recombination rate constants, from which the rate of creation of free electrons $\dot{\omega}_e$, can be evaluated using the plasma properties like $n_e$ and $T_e$ and the transition probabilities. To complete the description of Eqs. (1.1.2), (1.1.3) and (1.1.7), we have to express $C_s$ and $Q_s$ in terms of the plasma macroscopic properties. Neglecting external fields and allowing only small gradients in the flow, the momentum equation for the electron gas will be (see Eq. (1.1.3)):

$$\frac{\partial}{\partial t} (p e u^i_e) + \frac{\partial}{\partial x^j} \left( p e u^i_e u^j_e \right) + \frac{\partial p e}{\partial x^j} = \frac{1}{\Lambda_T} \sum_q \sum_k F_{qek} + C_e^i$$

(1.2.78)

Since $m_e << m_i = m_i$ and $\partial p_e / \partial x^j$ is of the same order of magnitude as $\partial p / \partial x^j$, it is possible to neglect the inertia terms $\partial / \partial t (p e u^i_e)$ and $\partial / \partial x^j (p e u^i_e u^j_e)$ relative to $\partial p_e / \partial x^j$ which is of the same order as the inertia terms of the heavy particles. Based on the same arguments, we will neglect the electron momentum source term $C_e$. The omission of the electron momentum source term, indicates that the electron pressure gradient is balanced by the forces acting on them due to their elastic collisions with the heavy particles. After neglecting $C_e$, it is logical to assume that the atom and ion momentum source terms are given by:

$$C_{ion}^i = -C_a^i = - \frac{dn_a}{dt} m_a u^i_a,$$

since this obeys the necessary conservation condition for the plasma, i.e.

$$\sum_s C_s^i = 0$$

The last term which remains to be expressed with the plasma macroscopic properties is the energy source terms $Q_s$. The average energy lost by the ion gas per recombination is

$$\frac{3}{2} k T_i + \frac{1}{2} m_i u^2_i,$$

which is equal to the energy gained by the neutral atoms. Therefore, the energy source terms for the ions and atoms are,

$$Q_i = \frac{dn_i}{dt} \left[ \frac{3}{2} k T_i + \frac{1}{2} m_i u^2_i \right]$$

and

$$Q_a = \sum_{p=1}^{\infty} \frac{dn_p}{dt} \left[ \frac{3}{2} k T_a + \frac{1}{2} m_a u^2_a \right]$$

respectively.
Since we have assumed \( T_i = T_a = T \) and also \( m_i = m_a \), we will have

\[
Q_a = \frac{dn_a}{dt} \left[ 3kT + \frac{1}{2}m_i^2 \right].
\]

The net energy which the electron gas will gain during a three body collision resulting in recombination into state \( p \) is \( I_p \). The net energy gained (or lost) by the electron during an inelastic collision resulting in the atom transition from level \( p \) to level \( q \) is \( (I_p - I_q) \). Due to the radiative recombination, the electron loses an average energy of \( 3/2 kT_e \) per event. Hence the electron energy source term can be written as

\[
Q_e = \sum_{p=1}^{\infty} K_{cp} n_i n_e I_p - \sum_{p=1}^{\infty} K_{pc} n_p n_e I_p + \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} K_{pq} n_p n_q (I_p - I_q) - \sum_{p=1}^{\infty} \sum_{q=p}^{\infty} K_{pq} n_p n_q (I_q - I_p) - \sum_{p=1}^{\infty} \beta_p n_e \frac{3}{2} kT_e \quad (1.2.79)
\]

Multiplying Eq. (1.2.38) by \( I_p \) and then summing over all \( p \), an expression is obtained that enables us to replace all the collisional terms in Eq. (1.2.79) by radiation terms and the rate of productions, \( \frac{dn}{dt} \).

For an optically thin plasma, after some algebra, \( Q_e \) becomes

\[
Q_e = \sum_{p=1}^{\infty} \frac{dn_p}{dt} I_p - \sum_{p=1}^{\infty} \sum_{q=1}^{p} A_{pq} n_p (I_p - I_q) - \sum_{p=1}^{\infty} \beta_p n_e^2 (I_p + \frac{3}{2} kT_e) \quad , (1.2.80)
\]

and for the 'steady-state' model \( \frac{dn_p}{dt} = 0 \) for \( p > 1 \), therefore,

\[
Q_e = \frac{dn_1}{dt} I_1 + Q_{rad} \quad (1.2.81)
\]

where

\[
Q_{rad} = - \sum_{p=1}^{\infty} \sum_{q=1}^{p} A_{pq} n_p (I_p - I_q) - \sum_{p=1}^{\infty} \beta_p n_e^2 (I_p + \frac{3}{2} kT_e) \quad . (1.2.82)
\]

Equation (1.2.81) indicates that the rate at which the electron gas gains energy is equal to the difference of the rates at which energy is released during recombination to the ground state and the rate at which energy is radiating out of the plasma. If the plasma is optically thick for a particular radiation, then the appropriate terms in \( Q_{rad} \) can be omitted. The other energy loss which we did not account for is the free-free transition radiation. This radiation is important only at very high temperatures, when the atom is fully ionized.\(^1\),\(^3\),\(^6\),\(^9\) Hence, \( Q_e = 0. \)
Chen has computed the partition of energy among the electron gas and radiation during a three body (electron-ion-electron) 'collisional-radiative' recombination. The energy released in this type of recombination is partly carried away by the colliding electrons and partly transferred into radiation. The partition of the recombination energy among the electrons and radiation is determined by the rates of the two competing processes, namely, the collisional de-excitation and the spontaneous radiation transitions. Chen carried out experimental work on decaying plasmas in the rare gases He, Ne, Ar, Kr, and Xe, produced in a discharge tube. The partition of energy among electrons and radiation, obtained by comparing the probability of electron collisional de-excitation with the spontaneous transition probability of electron collisional de-excitation with the spontaneous transition probability of bound electrons to all lower states. The former was evaluated using Gryzinski's formulation for the inelastic collisions and the latter is evaluated by using the sum rule for line strengths and the central field approximation. Chen defined a variable $\Lambda$ as

$$\Lambda = \frac{\text{Recombination energy carried away the electron gas}}{\text{Ionization potential}} = \frac{E_e}{I}$$

(in the case of pure collisional decay, $\Lambda = 1$). Chen presents his calculations in the form of $\Lambda$ vs. $n_e$ for two cases, (a) when the resonance radiation is trapped and (b) for an optically thin plasma. The experimental work was done at different pressures and the results compared well with the theoretical predictions. From his figures, $\Lambda$ is practically unity for both cases when $n_e > 10^{17}\text{ cm}^{-3}$. This indicates that for $n_e > 10^{17}\text{ cm}^{-3}$, we can ignore the term $Q_{\text{rad}}$ in our energy equations. The curves in Chen's work are for relatively low temperature $300^\circ\text{K} \leq T_e \leq 7,000^\circ\text{K}$, but it seems unlikely that above $7,000^\circ\text{K}$ the curves shape will change significantly. A more detailed description of the radiation mechanisms in hot plasmas can be found in Refs. 10, 33, 69. Of special importance are the expressions developed in Sepucha's work. In this paper the radiation terms were developed for nozzle flow of singly ionized argon. A general criteria for checking whether the radiative processes are significantly important during the recombination process is given in the review paper of Biberman et al. The criteria says that as long as

$$n_e \ll \frac{10^{17}}{\ln n} \left(\frac{T_e}{\theta_{I,H}}\right)^{1/2}, \quad (1.2.83)$$

radiative processes cannot be ignored. The opposite is true when the inequality sign changes. In expression (1.2.83) $n$ is the heavy particle number density and $\theta_{I,H}$ is the characteristic ionization temperature of a hydrogen atom. It is clear from the last expression, (Eq. 1.2.83), that for the conditions discussed in Chapter 3 (i.e. $T_e \approx 1\text{ ev}$ and $n \approx 10^{18}\text{ cm}^{-3}$) radiative processes can be ignored.

All the terms appearing in RHS of Eqs. (1.1.2), (1.1.3) and (1.1.7) now can be expressed with the plasma macroscopic properties. For a Maxwellian velocity distribution (each species has a Maxwellian distribution with the appropriate species temperature) the equations of motion for the electron gas are,
\[ \frac{\partial n_e}{\partial t} + \sum_j \frac{\partial}{\partial x^j} (n_e u_e) = \frac{\dot{\omega}_e}{m_e} \]  \tag{1.2.84} \\
\frac{\partial p_e}{\partial x^j} = -n_e e \left[ E^i + (\vec{u}_e \times \vec{B})^i \right] + n_e m_e (v_{ea} + v_{ei})(u_e^i - u_e^i)  \tag{1.2.85} \\
\frac{\partial \varepsilon}{\partial t} + \sum_j \frac{\partial}{\partial x^j} \left[ (v_e + p_e) u_e^j \right] = u_e^j \frac{\partial p_e}{\partial x^j} + \frac{dn_e}{dt} + Q_{\text{rad}} \\
+ 2n_{em}^e (v_{ea} + v_{ei}) \left[ \frac{3}{2} k(T - T_e) + \frac{1}{2} m_a (u_e^i - u_e^i)^2 \right] \tag{1.2.86} \\

and from the definition of \( \varepsilon \) and \( p \), \( \varepsilon + p = \frac{5}{2} n_e kT_e \). The assumptions made in deriving Eqs. (1.2.84), (1.2.85) and (1.2.86) were:

(1) the electron velocity distribution is Maxwellian. (This assumption eliminates the thermal conductivity term and degenerates the tensor \( p_{ij} \) to the scalar \( p \).)

(2) the electron inertia terms were neglected relative to the heavy particle inertia terms.

(3) the term \( Q_{\text{rad}} \) is given by Eq. (1.2.82).

Assumption (3) is valid only for the case of optically thin plasmas and when the 'steady state' model can be applied.

The equations of motion for the whole plasma are obtained by summing each of the Eqs. (1.1.2), (1.1.3) and (1.1.7) for all the plasma constituents. Thus

\[ \frac{\partial \rho}{\partial t} + \sum_j \frac{\partial}{\partial x^j} (\rho u^j) = 0 \]  \tag{1.2.87} \\
\rho \frac{Du^i}{Dt} = -\frac{\partial p}{\partial x^i} + (n_i - n_e) e \left[ E^i + (\vec{u} \times \vec{B})^i \right] + n_e e \left[ (\vec{u} - \vec{u}_e) \times \vec{B} \right]^i  \tag{1.2.88} \\

and

\[ \rho \frac{DH}{Dt} - \frac{\partial p}{\partial x^j} \left[ (\varepsilon + p_e)(u_e^i - u_e^i) \right] + Q_{\text{rad}} \frac{dn_e}{dt} = 0 \]  \tag{1.2.89}
where

\[ \rho = \sum_s \rho_s, \quad p = \sum_s p_s, \quad \epsilon = \sum_s \epsilon_s, \quad s = e, i, a, \]

\[ H = \frac{\epsilon + p}{\rho}, \quad \epsilon = \frac{3}{2} k \left[ n_e kT_e + \left( n_i + n_a \right) kT \right], \]

\[ p = \left( n_e + n_a \right) k \left( T + \frac{n_e}{n_e + n_a} T_e \right), \quad \rho = m_a \left( n_e + n_a \right) \]

and

\[ H = \frac{5}{2} \frac{k}{m_a} \left( T + \frac{n_e}{n_e + n_a} T_e \right). \]

In Eqs. (1.2.84) to (1.2.89), the following dependent variables appear; viz \( T, T_e, u, u_e, n_a \) and \( n_e \). This set of equations will be solvable if one can express the internal magnetic and electric fields as functions of the above mentioned variables.

To summarize the discussion on the equations of motion we will list below the assumptions made during the analysis and check their validity. The assumptions are:

1. The plasma consists of three species only, i.e., electrons, neutral atoms and single ions.

2. Each of the three species has a Maxwellian velocity distribution, described by the species temperature.

3. The processes that occur in the plasma are those described by Eqs. (1.2.14) to (1.2.17).

4. The relaxation time for reaching a steady population for the excited states is much shorter than the relaxation time for the ground state and the electron gas.

5. The elastic encounter is represented as a binary collision.

6. The only diffusion process existing in the plasma is that of the free electrons diffusing into the heavy particle gas. For this process we assumed

\[ W = 0 \left[ \frac{m_e}{m_a} < c_e^2 > \right]^{1/2} \]

7. The state of each species and the plasma as a whole can be described by the equation of state for an ideal gas (i.e., \( p = \rho RT \)) and by Dalton's law of partial pressures.
Further limiting assumptions were made during the evaluation of $K_I$ and $K_R$ for the different models. The most basic assumption is that each species maintains its own Maxwellian velocity distribution. This assumption eliminates the thermal conduction and viscous dissipation phenomena. However, these processes cannot always be neglected, e.g., at the beginning of an expansion flow\textsuperscript{37} we will have a higher electron temperature than anticipated from theory.\textsuperscript{25} This difference between the experimental temperature and the theoretical one can be explained by heat conduction in the electron gas. Some authors added the heat conduction term to the electron energy balance in an ad hoc manner.\textsuperscript{71} On the average, however, the theoretical prediction (based on the model described herein) agrees well with the experimental results. Only for certain flow conditions do we need to modify the theory to account for these irregularities. In addition it should be remembered that the solution of Eqs. (1.1.2), (1.1.3) and (1.1.7) without assuming a Maxwellian distribution is extremely difficult.

CHAPTER 2 NUMERICAL SOLUTIONS FOR STEADY SUPERSONIC EXPANSION OF PLASMA FLOWS

In the present chapter the equations of motion Eqs. (1.2.79) to (1.2.80) will be solved numerically for two special cases. In the first section the steady quasi-one-dimensional expansion flow will be discussed. Many authors have dealt with this type of plasma flow. Our description will follow closely the paper of Talbot et al.\textsuperscript{28} as it is most representative. Following the numerical solution, some experimental results on quasi-one-dimensional flow are noted and explained in the light of the theoretical analysis. The second part of the chapter is devoted to the numerical solution of the steady, two-dimensional, supersonic expansion flow of ionized argon. For this purpose the work of Glass and Takano,\textsuperscript{37} is adopted and explained in detail. Some additional modifications are also made to support the basic assumptions made in the original paper.

2.1 Steady One-Dimensional Flow of Ionized Argon

For a steady, one-dimensional flow of singly ionized plasma, Eqs. (1.2.84) to (1.2.89) reduce to:

\[
\frac{\partial}{\partial x} \left( n_e u_e \right) = \frac{\partial n_e}{\partial t}, \tag{2.1.1}
\]

\[
\frac{d}{dx} \left[ \frac{5}{2} n_e k T_e u_e \right] = u_e \frac{d}{dx} \frac{e}{e} + 2n_e \frac{m_e}{m_a} (v_e + v_i)(u - u_e), \tag{2.1.2}
\]

\[
\frac{d}{dx} \left[ \frac{1}{2} m_a (u - u_e)^2 \right] - \frac{dn_e}{dt} \frac{T_e}{1 + Q_{rad}} \tag{2.1.3}
\]
\[ \frac{d}{dx} (\rho u) = 0, \quad \text{(2.1.4)} \]

\[ \rho u \frac{du}{dx} = - \frac{dp}{dx}, \quad \text{(2.1.5)} \]

\[ \rho u \frac{dH}{dx} - u \frac{dp}{dx} = - n_e \epsilon \left[ (\mathbf{u} - \mathbf{E}) \times \mathbf{B} \right] \cdot \mathbf{u} + n_e \epsilon E (u - u_e) + \]

\[ \frac{d}{dx} \left[ \frac{5}{2} \frac{n_e k T_e}{\rho} (u - u_e) \right] + Q_{\text{rad}} - \frac{dn_e}{dt} \quad \text{(2.1.6)} \]

where, as before,

\[ \epsilon = \frac{3}{2} \left[ n_e k T_e + (n_a + n_e) k T \right], \quad H = \frac{e + p}{\rho}, \quad p = \frac{\rho}{m_a} k(T + \alpha T_e), \]

\[ \rho \approx m_a (n_a + n_e) \quad \text{and} \quad \alpha = \frac{n_e}{n_e + n_a}. \]

Eqs. (2.1.1) to (2.1.6) contain six dependent variables: \( n_e(x), n_a(x), T(x), T_e(x), u(x) \) and \( u_e(x) \). Therefore if the internal fields \( E \) and \( B \) can be expressed in terms of the above variables, Eqs. (2.1.1) to (2.1.6) can be solved. Since the numerical solution of these equations depends on the model one adopts to describe \( \frac{dn_e}{dt} \) and \( Q_{\text{rad}} \), it clearly has to be checked against some experimental results before one can claim that the analysis is appropriate.

A few numerical solutions have been reported for steady quasi-one-dimensional flows of singly-ionized argon plasmas.\(^{22,28,32,66}\) Independently of these theoretical analyses, some experiments on one-dimensional plasma flows have also been performed.\(^{21,29,30,31,33,36,72}\) In the following Talbot et al solution will be discussed in some detail. The geometry of the quasi-one-dimensional flow solved by Talbot et al is shown in Fig. 6. For a given inlet condition (pre-throat) the post-throat flow field was numerically evaluated. As discussed in Chapter 1, in order to solve the equations of motion one has to express the atomic processes taking part in the expanding plasma in terms of the plasma parameters. Talbot et al have used the collisional-radiative model of Bates et al for this purpose.\(^{23}\)

Along with the practical case when only the resonance radiation is absorbed, Talbot et al calculated the decaying plasma properties for the limiting cases of optically-thin and thick plasmas. The validity of the collisional-radiative recombination model of Bates et al\(^8\) was checked experimentally for stationary plasmas (it was one of Talbot's aims to check this model for supersonic plasmas). Another important feature is the way the difference, \( (T_e - T) \), changes along the flow downstream of the expansion nozzle. The calculations were carried out for hydrogen and argon plasmas so as to get some knowledge of the effects of atomic weight on the expansion processes. The basic assumptions made in Talbot's work are:

1. Steady, quasi-one-dimensional flow.
2. Species have a Maxwellian velocity distribution at the corresponding temperature.
3. Diffusion, viscosity and heat conduction are neglected.

4. The ion and atom temperatures are equal.

5. The mean free path is much smaller than a typical flow length and the continuum approach to the flow is valid.

6. All types of wall recombination are neglected.

7. Magnetic or electric fields are assumed to be absent.

8. The individual plasma species and the plasma as a whole can be described by the equation of state of an ideal gas and Alton's law of partial pressures is assumed to be applicable.

The equations of motion presented by Talbot et al. are identical with Eqs. (2.1.1) to (2.1.6), after the diffusion and the electromagnetic field terms are omitted. These are:

\[
\frac{d}{dx} (\rho u A) = 0, \tag{2.1.7}
\]

\[
\rho u \frac{du}{dx} = - \frac{dp}{dx} \tag{2.1.8}
\]

\[
u \frac{d}{dx} \left( H + \frac{1}{2} u^2 \right) = - \frac{Q_{\text{rad}}}{\rho} \tag{2.1.9}
\]

\[
\frac{d\alpha}{dx} = - \left[ (K_R + K_I) \alpha - K_I \right] \frac{n_e}{u} \tag{2.1.10}
\]

\[
\frac{dT_e}{dx} = \frac{2}{3} \frac{T_e}{\rho} \frac{dp}{dx} - \frac{T_e + 2/3 I_1/k}{\alpha} \frac{d\alpha}{dx} \frac{2m_a Q_{\text{rad}}}{3\alpha u k} - \frac{\rho}{u} \left[ D_1 \alpha T_e^{-3/2} \ln \left( \frac{D_2 T_e^3}{\rho \alpha} \right) + (1-\alpha) D_3 \right] (T_e - T), \tag{2.1.11}
\]

\[
p = \frac{\rho k}{m_a} (T + \alpha T_e), \quad H = \frac{5}{2} \frac{k}{m_a} (T + \alpha T_e) + \frac{\alpha}{m_a} I_1
\]

and \( \rho = (n_a + n_e) m_a \) \( \tag{2.1.12} \)

where \( A \) is the expansion nozzle cross-section, \( \alpha \) is the degree of ionization and the constants \( D_1, D_2, D_3 \) are given by:

\[
D_1 = \frac{2 e^4}{3 m_a^2 k} \left( \frac{8 \pi m_e^2}{k} \right)^{1/2}, \quad D_2 = \frac{9 k m_a}{8 \pi e^6} \text{ and } D_3 = \frac{5 \pi (m_B)^{1/2}}{3 m_a^2}
\]
B is the intermolecular force constant (appearing in the expression for the electron-atom collision frequency). The values for B are taken from experimental data (for details see Appendix II in Ref. 28).

The solution of Eqs. (2.1.7) to (2.1.12) was attempted for three different flow regimes:

(a) **Frozen Flow**: In this case the degree of ionization is constant throughout the expansion flow. As a result Eq. (2.1.10) is redundant and Eqs. (2.1.9) and (2.1.11) can be simplified. The case of a frozen flow is of academic interest only; in practice, such flows do not exist. However, this solution can serve as a limiting case of real flows in which there is no change in composition, although reactions do take place.

(b) **Equilibrium Flow**: For this case the degree of ionization can be expressed as a function of any two thermodynamic parameters, say T and ρ (the Saha equation). Again the equations of motion can be simplified.

(c) In the general case of nonequilibrium flow, Eqs. (2.1.7) to (2.1.12) have to be solved. Talbot et al solved them numerically, using Adams four-point technique. Before the integration can be performed, one needs to express $K_I$, $K_R$ and $Q_{\text{rad}}$ in terms of $N_e$, $T_e$ and $T_a$. Talbot et al fitted polynomials to describe the tabulated values for $K_I$, $K_R$ and $Q_{\text{rad}}$ suggested by Bates et al.

The graphical presentation of the plasma macroscopic properties as a function of the area ratio shows, as expected, that these properties are always between the frozen and equilibrium values, for example see Figs. 7, 8, 9, 10 and 11. It is of special interest to know how the difference $(T_e-T)$ behaves along the nozzle axis. From Eqs. (2.1.7) to (2.1.11), after some algebra, the following equation is obtained:

$$
\frac{d}{dx} (T_e - T) = -\frac{2}{3} \frac{m a Q_{\text{rad}}}{\mu k} - \frac{1}{\alpha} (T_e + \frac{2}{3} \frac{T_e}{k}) \frac{d\alpha}{dx} + \frac{2}{3} \frac{d(\epsilon_{\text{mp}})}{dx} (T_e - T)
$$

$$-\rho \frac{1 + \alpha}{u} \left[ D_1 \alpha T_e^{-3/2} \ln(D_2 \frac{T_e}{\rho \alpha}) + (1-\alpha) D_3 \right] (T_e - T) \tag{2.1.13}$$

In the absence of recombination (frozen flow), $d\alpha/dx = 0$ and $Q_{\text{rad}} = 0$, therefore, Eq. (2.1.13) reduces to a first order differential equation which has the formal solution

$$T_e - T = C \exp \left[ \int D \, dx \right], \tag{2.1.14}$$

where C is the integration constant and D is given by

$$D = \frac{2}{3} \frac{d(\epsilon_{\text{mp}})}{dx} - \rho \frac{1 + \alpha}{u} \left[ D_1 \alpha T_e^{-3/2} \ln(D_2 \frac{T_e}{\rho \alpha}) + (1-\alpha) D_3 \right]$$
This solution shows that if at the starting point $T_e = T$, then $C = 0$ and $T_e$ will remain constant and equal to $T$ during the expansion. In the actual case, i.e., $Q_{\text{rad}}$ and $da/dx$ are not zero, the electron gas will gain energy and therefore $T_e \neq T$. The first two terms in the RHS of Eq. (2.1.13) describe the net rate of energy gained by the electron gas. The third term (the negative pressure gradient in the expansion) will tend to reduce the temperature difference ($T_e - T$). The thermalizing collisions (the fourth term in the RHS of Eq. (2.1.13)) will also tend to reduce the temperature difference ($T_e - T$). Therefore, the final value of this difference ($T_e - T$), represents the net effect of the energy gained and lost by the electron gas during recombination. This result will enable us to compare the effectiveness of the various competing processes. The rate of energy transfer in a collision between the electrons and the heavy particles (given by the fourth term in the RHS of Eq. (2.1.13)) is directly proportional to $\rho D_1$ and $\rho D_3$. According to the definition of the constants $D_1$ and $D_3$, the energy transfer rate during such collision is inversely proportional to the atom mass, $m_a$. Therefore for heavy atoms, the energy transfer rate during collisions with electrons is less effective, and we can expect to get a larger temperature difference ($T_e - T$) in the expansion of a heavy-atom plasma. In the calculations of Talbot et al, it was shown that $(T_e - T)$ for an expanding argon plasma is larger than $(T_e - T)$ for a hydrogen plasma for the same conditions (see Fig. 10b).

The tendency of the negative pressure gradient in the diffuser to reduce the temperature difference ($T_e - T$) can generally be ignored due to its logarithmic dependence (see Eq. (2.1.13)). In the case of a very rapid expansion, the difference ($T_e - T$) will be very large, as for such cases the term representing the thermalizing collisions ($4^{th}$ in the RHS of Eq. (2.1.13)) become ineffective due to the very low value of the factor $\rho/u$. Lordi and Dunn checked the relative weight of each term appearing in the electron energy balance for one-dimensional ionized nitrogen flow. For electron temperatures around $4,000{\text{K}}$ and $10^{10} < n_e < 10^{12}\text{cm}^{-3}$ they found that the largest terms are the inelastic and thermalizing collision terms. The heat conduction, ohmic heating and the radiation terms are a few orders of magnitude smaller, and therefore they can be neglected by comparison with the inelastic and thermalizing collision terms. This reduces the complexity of the energy balance equation, and one can use the equation to check the validity of the experimental results for $T_e$. Although the works of Bray and Talbot et al are essentially the same, it is impossible to compare their final results. That is, the plasma gross properties vs. area ratio, since the inlet conditions used for the numerical solution are different. All one can say is that the curves describing the plasma properties are of the same shape. It seems that Talbot's work is more detailed, since the recombination model is more realistic and the electron energy balance equation is of general validity. From Talbot's results (some of which are presented in Figs. 7, 8, 9 and 11) we can draw the following conclusions:

1. Upon comparing the optically thin and thick plasmas at the same station in the expansion nozzle, one finds that the radiation loss has the effect of further cooling the gas, and increasing the temperature difference, ($T_e - T$).

2. Due to the larger atomic mass of argon relative to hydrogen, the energy exchange between electrons and heavy particles during the collision is less effective in the former, hence resulting in a larger temperature difference ($T_e - T$) in argon.
(3) For low degrees of ionization ($\alpha = 0.01$), apart from affecting $n_e$ and $T_e$, the recombination processes will have no effect on the flow gross properties ($\rho, p, T$). This is not the case at high degrees of ionization ($\alpha = 0.62$).

A very detailed theoretical work on the one-dimensional expansion of ionized gas was done by Sepucha. The gas used in his model was singly ionized argon. Neglecting diffusion, all wall effects and heat conduction, Sepucha developed the equations of motion for the general quasi one-dimensional flow. The radiative processes were described in detail and therefore, the equations of motion became a set of integro-differential equations, which is almost unsolvable. This complexity encourages the use of approximations such as the grey-gas model, local thermal equilibrium, and the extreme cases of optically-thin and thick plasmas. Due to the extreme mathematical complexity of the set of equations describing the plasma flow, no solution was attempted. However, this paper is very useful for understanding the basic physics of one-dimensional plasma flow.

Theoretical and experimental work was done by Park on the behaviour of fully-dissociated and partially-ionized nitrogen expanding supersonically through a nozzle. The flow equations of motion which were solved numerically, are similar to Eqs. (2.1.7) to (2.1.11). During the experimental work, the electron gas density and the population of excited states were obtained from spectroscopic measurements of light emission at different positions along the nozzle.

The main purpose of the work in Ref. 29 was to find the nonequilibrium population of the excited states in expanding flows of ionized nitrogen. The results show that the population distribution of excited electronic states deviates severely from an equilibrium distribution. Under these nonequilibrium conditions the lower energy levels are underpopulated compared to their equilibrium population for the same temperature.

In Ref. 30, an attempt was made to measure the rate of three-body recombination in a dense nitrogen plasma. The electron temperature and density were measured spectroscopically. If one neglects the ionization process during expansion, then from electron-number-density measurements along the nozzle, the recombination-rate constant can be evaluated. By neglecting the ionization process, the rate of creation of free electrons is given by (see Eq. (1.2.18)).

$$\frac{dn_e}{dt} = K_R n_e^3$$

which upon integration becomes,

$$K_R = \frac{1}{2\Delta t} \left[ \left( \frac{1}{n_e^2} \right)_{x = x_o + \Delta x} - \left( \frac{1}{n_e^2} \right)_{x = x_o} \right]$$

where $\Delta t$ is the time required for the plasma to move from $x = x_o$ to $x = x_o + \Delta x$. Some of the experimental results of this study are presented in Fig. 12.
Before one tries to draw any conclusions from Park's work,\textsuperscript{30} it is important to emphasize again that the accuracy of the spectroscopic measurements of electron temperature and number density are usually no better than ±15%. (For more details see Ref. \textsuperscript{43}, pp. 267-312.) The basic assumption, under which KR was evaluated will be justified only when one can show that \(K_R n_e^3 \gg K_T n_e n_a\) everywhere in the field under investigation. However, this requires a knowledge of \(K_R\), the quantity to be calculated. When this is not the case, the calculation of \(K_R\) from the known \(n_e\) is not as simple as indicated by Eq. (2.1.16) and what one really measures is the decay coefficient.

Very interesting experimental results on the properties of an expanding plasma are presented in the paper of Goldfarb et al.\textsuperscript{31} They generated plasma jets by exhausting gases (Ar, H, He) from a high pressure vessel into a vacuum chamber through a supersonic conical nozzle. The pressure vessel was operated at pressures between 300 to 500 mmHg, and the vacuum chamber pressures between 0.02 to 1 mmHg. The gas parameters were found from dynamic pressure measurements. The electronic plasma parameters (\(T_e\) and \(n_e\)) were measured spectroscopically (absolute and relative line intensities) and with Langmuir probes. The results for \(n_e\) and \(T_e\) vs. distance from the nozzle throat are presented in Figs. 13 and 14. While the Langmuir probe measurements show the same trends as those calculated by Bray\textsuperscript{22} and Talbot et al.\textsuperscript{26} the spectroscopic measurements show a local maximum in \(T_e\) and \(n_e\), just after the nozzle throat. One explanation for these peculiar maxima is as follows. Due to the fast cooling of the plasma jet exhausting into a vacuum, rapid collisional-radiative recombination takes place. This nonequilibrium recombination results in an overpopulation of highly excited electronic states relative to lower-lying states, as compared with the Boltzmann population ratio, \(n_m/n_n = \text{constant} \times \exp \left( (\epsilon_m-\epsilon_n)/kT \right)\). Measurement of such a population ratio via a radiation intensity technique would therefore lead to an incorrect (too high) value of \(T_e\). As mentioned before, Park\textsuperscript{29} reported a severe departure from equilibrium population in expanding nitrogen plasma.

Fox and Hobson\textsuperscript{21} have performed an experimental study of the recombination rate for one-dimensional, argon-plasma flows. A shock tube was used to provide the high temperature gas environment. The shocked gas temperature was always lower than the minimum temperature necessary for detectable ionization. By discharging RF pulses into a certain slab of the shocked gas, the gas contained within this slab was ionized. The ionized gas will start decaying immediately after the discharge. The change in the ion number density during the decay was obtained by measuring the current between two platinum electrodes, located at known distances downstream of the discharge port. This measure current can be related to the ion density, by the following expression\textsuperscript{21}

\[
i_p = CA_p \frac{1}{4} n_i \left( \frac{8kT_i}{m_i} \right)^{1/2},
\]

where, \(i_p\) is the measured current, \(A_p\) is the probe surface area and \(C\), a proportionality constant. From the ion number density (and for singly ionized gas \(n_i = n_e\)), the recombination rate constant can be calculated (see Eq. (2.1.15)). The results are shown in Fig. 15. Unfortunately these experiments were carried out at relatively low temperatures (\(1000^\circ \text{K} \leq T_e \leq 4000^\circ \text{K}\)), and as mentioned before, for this temperature range, Fox and Hobson\textsuperscript{21} suggested that the recombination is of the dissociative type described by Eqs. (1.2.71) and (1.2.73). Due to the low temperature in their experiments it is possible
to have both neutral and ionic molecular argon but no direct evidence of their presence was presented. 67

To conclude the discussion, we summarize the main points:

(1) Although Bray22 solved the same flow field as Talbot's et al.,28 it is not possible to compare their numerical results as each author adopted different starting conditions. A comparison might be very fruitful since one model was more detailed than the other, and if a direct comparison was possible it might give an idea about the relative importance of the details omitted in Bray's simple model.

(2) It is impossible to compare the available numerical solutions with the experimental results. Here, not only are the nozzle inlet conditions different for each experiment, but the geometry and the diagnostic techniques as well. The numerical solutions indicate that the flow properties will lie between the frozen and equilibrium values, generally nearer to the frozen flow values.

(3) For the decay process \((T_e - T) > 0\), this difference will increase with increasing atomic mass. For a very rapid expansion, the factor \(\rho/u\) is a very small number, and since this factor appears in front of the thermalizing collision term, this term can be neglected (Eq. (2.1.13)) resulting in an increase in the temperature difference \((T_e - T)\). In addition, the radiation loss will cool the plasma, which will increase the recombination rate.

(4) Generally speaking, the shape of the profiles of \(T_e\) vs. \(x\) and \(n_e\) vs. \(x\) where \(x\) is the axial distance measured from the nozzle throat, is similar for both experimental and theoretical results.

(5) When full account is taken of the radiation processes, the equations of motion become practically insoluble.

2.2 Steady, Two-Dimensional Flow of Ionized Argon

For a steady force-free, two-dimensional flow expressed in Cartesian coordinates, Eqs. (1.2.84) to (1.2.89) reduce to:

\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = \frac{u}{n_a + n_e} \left( \frac{\partial T}{\partial x} + \frac{T}{(n_a + n_e)} \frac{\partial n_a}{\partial x} + \frac{n_e}{(n_a + n_e)} \frac{\partial T}{\partial x} \right) + \frac{T + T_e}{(n_a + n_e)} \frac{\partial n_e}{\partial x} + \frac{n_e}{(n_a + n_e) m_a} (v - v_e) B_z ,
\]

\[
\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} = \frac{u}{n_a + n_e} \left( \frac{\partial T}{\partial y} + \frac{T}{(n_a + n_e)} \frac{\partial n_a}{\partial y} + \frac{n_e}{(n_a + n_e)} \frac{\partial T}{\partial y} \right) + \frac{T + T_e}{(n_a + n_e)} \frac{\partial n_e}{\partial y} - \frac{n_e}{(n_a + n_e) m_a} (u - u_e) B_z ,
\]
\[
\frac{3}{2} k (n_a + n_e) \left( u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2} k n_e \left( u \frac{\partial T_e}{\partial x} + v \frac{\partial T_e}{\partial y} \right) + k \left( \frac{3n_a - 2n_e}{2(n_a + n_e)} T_e \right) \\
- T \left( u \frac{\partial n_e}{\partial x} + v \frac{\partial n_e}{\partial y} \right) - k \left( \frac{n_T e}{n_e + n_a} + T \right) \left( u \frac{\partial n_a}{\partial x} + v \frac{\partial n_a}{\partial y} \right) \\
= - n_e \left( (v - v_e) B_z u - (u - u_e) B_z v \right) + n_e \left( E_x (u - u_e) + E_y (v - v_e) \right) \\
+ \frac{\partial}{\partial x} \left( \frac{5}{2} n_k T e (u - u_e) \right) + \frac{\partial}{\partial y} \left( \frac{5}{2} n_k T e (v - v_e) \right) - \frac{\partial n_e}{\partial t} I + Q_{\text{rad}},
\]

(2.2.4)

\[
\frac{\partial}{\partial x} (n_e u_e) + \frac{\partial}{\partial y} (n_e v_e) = \frac{\partial n_e}{\partial t},
\]

(2.2.5)

\[
k \left( n_e \frac{\partial T_e}{\partial x} + T_e \frac{\partial n_e}{\partial x} \right) = - n_e \left( E + u e z \right) + n m_e (v_e + v_{ei}) (u - u_e),
\]

(2.2.6)

\[
k \left( n_e \frac{\partial T_e}{\partial y} + T_e \frac{\partial n_e}{\partial y} \right) = - n_e \left( E - v e z \right) + n m_e (v_{ea} + v_{ei}) (v - v_e),
\]

(2.2.7)

\[
\frac{5}{2} k \frac{\partial}{\partial x} \left( n_e T e e e \right) + \frac{5}{2} k \frac{\partial}{\partial y} \left( n_e T e e e \right) = k u_e \left( n_e \frac{\partial T_e}{\partial x} + T_e \frac{\partial n_e}{\partial x} \right) \\
+ k v_e \left( n_e \frac{\partial T_e}{\partial y} + T_e \frac{\partial n_e}{\partial y} \right) - \frac{\partial n_e}{\partial t} I + Q_{\text{rad}} + 2n_e \frac{m_e}{m_a} (v_{ea} + v_{ei}) \left( \frac{3}{2} k (T - T_e) \right) \\
+ \frac{1}{2} m_a \left\{ (u - u_e)^2 + (v - v_e)^2 \right\}
\]

(2.2.8)
To solve Eqs. (2.2.1) to (2.2.8) the internal electromagnetic fields $\mathbf{E}$ and $\mathbf{B}$ must be expressed as functions of the macroscopic plasma properties. This can be done with the aid of Maxwell's equations. For the two-dimensional steady case,

$$\mu e n_e (u-u_e) = \frac{\partial B_z}{\partial y} - \frac{\partial B_y}{\partial z}, \quad (2.2.9)$$

$$\mu e n_e (v-v_e) = \frac{\partial B_x}{\partial z} - \frac{\partial B_z}{\partial x}, \quad (2.2.10)$$

$$\frac{\partial B_x}{\partial y} - \frac{\partial B_y}{\partial x} = 0, \quad (2.2.11)$$

$$\frac{n_e}{\sigma} (u-u_e) = E_x + (v-v_e) B_z, \quad (2.2.12)$$

$$\frac{n_e}{\sigma} (v-v_e) = E_y + (u-u_e) B_z, \quad (2.2.13)$$

$$E_z + (u-u_e) B_y = (v-v_e) B_x, \quad (2.2.14)$$

where, $\mu$ is the plasma permeability and $\sigma$ is the electrical conductivity.

We now have 14 equations (Eqs. (2.2.1) to (2.2.14)) to solve for 14 independent variables: $n_e$, $n_a$, $T_e$, $T$, $u$, $v$, $u_e$, $v_e$, $E_x$, $E_y$, $E_z$, $B_x$, $B_y$ and $E_y$. In principle this set of equations is solvable. However, to the author's knowledge, no numerical solution has been carried out because of the great complexity. Furthermore, any numerical solution will depend on the model adopted to describe the atomic processes (at least for plasmas with a significant degree of ionization), in particular the terms $dn_e/dt$ and $Q_{rad}$. Consequently, a comparison between experimental results and the numerical solution will be crucial in assessing the validity of the model.

It is usually helpful to express the equations of motion in nondimensional form. In the nondimensionalizing procedure the following factors were used:

$$x' = \frac{1}{L} x; \quad y' = \frac{1}{L} y; \quad z' = \frac{1}{L} z$$

$$n'_a = \frac{1}{n_o} n_a; \quad n'_e = \frac{1}{n_o} n_e$$

$$u' = \frac{1}{u_o} u; \quad v' = \frac{1}{v_o} v$$

$$T' = \frac{T_o}{T_o}; \quad m'_a = \frac{m_a}{m_e}; \quad m'_e = \frac{m_e}{m_o}$$

$$k' = \frac{u_o^2}{m_o} k; \quad E' = \frac{Le}{m_o u_o^2} E; \quad B' = \frac{Le}{m_o u_o} B$$
where subscript "o" indicates some known reference values (for example in a corner-expansion flow, the available precorner parameters) and primes stand for nondimensional quantities. \( L \) is a typical flow length.

After some algebra one arrives at the following set of nondimensional equations that govern the plasma motion. (For convenience, primes have been omitted.)

\[
\frac{\partial}{\partial x} \left[ (n_a + n_e) u \right] + \frac{\partial}{\partial y} \left[ (n_a + n_e) v \right] = 0 \tag{2.2.15}
\]

\[
u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{k}{m} \left[ \frac{\partial T}{\partial x} + \frac{T}{n_a + n_e} \frac{\partial n_a}{\partial x} + \frac{n_e}{n_a + n_e} \frac{\partial T_e}{\partial x} + \frac{T + T_e}{n_a + n_e} \frac{\partial n_e}{\partial x} \right]
+ \frac{1}{m} B_z \frac{n_e}{n_a + n_e} (v - v_e) \tag{2.2.16}
\]

\[
u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{k}{m} \left[ \frac{\partial T}{\partial y} + \frac{T}{n_a + n_e} \frac{\partial n_a}{\partial y} + \frac{n_e}{n_a + n_e} \frac{\partial T_e}{\partial y} + \frac{T + T_e}{n_a + n_e} \frac{\partial n_e}{\partial y} \right]
- \frac{1}{m} B_z \frac{n_e}{n_a + n_e} (u - u_e) \tag{2.2.17}
\]

\[
\frac{3}{2} (n_a + n_e) \left( u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) + \frac{3}{2} n_e \left( u \frac{\partial T_e}{\partial x} + v \frac{\partial T_e}{\partial y} \right) + \left[ \frac{3n_a - 2n_e}{2(n_a + n_e)} T_e - T \right]
\left( u \frac{\partial n_a}{\partial x} + v \frac{\partial n_a}{\partial y} \right)

= \frac{R_1}{k} n_e \left[ \frac{(u - u_e)^2 + (v - v_e)^2}{2} \right] - \frac{1}{k} B_z \left[ (v - v_e) u - (u - u_e) v \right] + \frac{5}{2} \frac{\partial}{\partial x} \left[ n_e T_e (u - u_e) \right] + \frac{5}{2} \frac{\partial}{\partial y} \left[ n_e T_e (v - v_e) \right] - R_2 \theta_I \frac{k^{3/2}}{\sqrt{m_e}} n_e n_a T_e^{3/2} \theta_I \tag{2.2.18}
\]

\[
\frac{\partial}{\partial x} \left( n_e u_e \right) + \frac{\partial}{\partial y} \left( n_e v_e \right) = R_2 \frac{k^{3/2}}{\sqrt{m_e}} n_e n_a T_e^{3/2} - R_3 \left( \frac{n_e}{T_e} \right)^3 \tag{2.2.19}
\]

\[
\frac{\partial T_e}{\partial x} + T_e \frac{\partial n_e}{\partial x} = -\frac{n_e}{k} (E + u B) + \frac{R_4}{R_5} \frac{\sqrt{m_e}}{k^{5/2}} \frac{n_e (u - u_e)}{T_e^{3/2}}
\]

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\[
\left\{ \frac{4}{3} \sqrt{\pi} \frac{1}{2} n_e \ln \left[ R_5 \frac{k^3}{\pi} \frac{T_e^3}{n_e} \right] + C_3 n_a \right\} (2.2.20)
\]
\[
n_e \frac{\partial T_e}{\partial y} + T_e \frac{\partial n_e}{\partial y} = - \frac{n_e}{k} (E - v_e B) + \frac{R_4}{R_5} \frac{\sqrt{m_e}}{k^{5/2}} \frac{n_e (v-v_e)}{T_e^{3/2}}
\]
\[
\times \left\{ \frac{4}{3} \sqrt{\pi} \frac{1}{2} n_e \ln \left[ R_5 \frac{k^3}{\pi} \frac{T_e^3}{n_e} \right] + C_3 n_a \right\} (2.2.21)
\]
\[
\frac{5}{2} \frac{\partial}{\partial x} \left( n_e T e u_e \right) + \frac{5}{2} \frac{\partial}{\partial y} \left( n_e T e v_e \right) = u_e \left( n_e \frac{\partial T_e}{\partial x} + T_e \frac{\partial n_e}{\partial x} \right) +
\]
\[
v_e \left( n_e \frac{\partial T_e}{\partial y} + T_e \frac{\partial n_e}{\partial y} \right) + 2 \frac{R_4}{R_5} \frac{\sqrt{m_e}}{m k^{5/2}} \frac{n_e}{T_e^{5/2}} \left\{ \frac{4}{3} \sqrt{\pi} \frac{1}{2} n_e \ln \left[ R_5 \frac{k^3}{\pi} \frac{T_e^3}{n_e} \right] + C_3 n_a \right\} \left\{ \frac{3}{2} k (T-T_e) + \frac{1}{2} m \left[ (u-u_e)^2 + (v-v_e)^2 \right] \right\} -
\]
\[
R_2 \theta_1 \frac{k^{3/2}}{\sqrt{T_e}} n_e a e^{3/2} e^{\theta I/T_e} + R_3 \theta_1 \left( \frac{n_e}{T_e^{3/2}} \right)^3 (2.2.22)
\]
\[
n_e (u-u_e) = P_1 \left( \frac{\partial B_z}{\partial y} - \frac{\partial B_y}{\partial z} \right) (2.2.23)
\]
\[
n_e (v-v_e) = P_1 \left( \frac{\partial B_x}{\partial z} - \frac{\partial B_z}{\partial x} \right) (2.2.24)
\]
\[
0 = \frac{\partial B_x}{\partial y} - \frac{\partial B_y}{\partial x} (2.2.25)
\]
\[
n_e (u-u_e) = \frac{1}{R_1} \left[ E_x + (v-v_e) B_z \right] (2.2.26)
\]
\[
n_e (v-v_e) = \frac{1}{R_1} \left[ E_y - (u-u_e) B_z \right] (2.2.27)
\]
\[
B_x (v-v_e) = E_z + (u-u_e) B_y (2.2.28)
\]
\[
where:\quad R_1 = \frac{n_e^2 L}{m o u_o \sigma} ; \quad R_2 = \sqrt{\frac{8}{\pi}} C_1 n_o m_o u_o L
\]
\[
R_3 = \frac{C_2 n_o^2 L}{T_o^{9/2} u_o} ; \quad R_4 = \frac{m L u_o^2}{e^2} ; \quad R_5 = \frac{m^3 u_o^6}{n_o e^6}
\]

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\[ P_1 = \frac{m_e}{n_0 e^{1/2}} \quad ; \quad C_1 = C, \text{ the proportionality constant appearing in Eq. (1.2.27).} \]

For argon plasma at temperature around the threshold (T \( \approx \) 1 ev), \( C_1 = 2 \times 10^{-17} \text{ cm}^2/\text{ev} \), \( C_2 = 2.3 \times 10^{-6} \text{ cm}^6(\text{OK})^{9/2} \text{ sec}^{-1} \), this factor is obtained when the Makin and Keck model for the three-body (electron-ion-electron) collisional recombination is used (see Eq. (1.2.36)).

\[ \theta_I = \frac{\text{Ionization Temperature}}{T_0} \quad \text{(for argon plasma)} \]

In obtaining Eqs. (2.2.15) to (2.2.28), it was assumed that the recombination rate constant can be described by Eq. (1.2.36), and the ionization rate constant by Eq. (1.2.28). For simplicity, the radiation losses have been omitted. The collision frequencies \( v_{ea} \) and \( v_{ei} \) were described with the use of Eqs. (1.2.12) and (1.2.13).

Usually one can hope that an order of magnitude analysis will lead to a simplified set of equations relative to the full set (Eqs. (2.2.15) to (2.2.28)). However, in the present case the magnitude of the nondimensional factors, namely \( K_k, R_1, R_2, R_3, R_4, R_5, P_1, C_1 \) and \( C_2 \) strongly depend on the given reference values (\( N_0, U_0, T_0 \)), the type of gas under consideration (\( N_0, e, \mu, C_1, C_2 \)) and the flow geometry (L). As a result, no general simplified form, different to Eqs. (2.2.15) to (2.2.28), is possible, and the dimensional analysis was not profitable. For special cases, as we shall see later on, it is possible to use the order of magnitude analysis, and to omit some 'difficult' terms.

A few simplified cases have been treated in order to gain some insight into the changes of the plasma properties during supersonic expansion. Understandably these solutions can only describe the plasma under certain limited conditions.

An interesting approximate solution is available in Glass and Takano's work\(^{37}\) based on the method of the characteristics. In the following a brief description is given of their solution, along with a critical discussion of its validity.

A steady, inviscid, two-dimensional flow is considered. In writing the basic equations of motion, the natural coordinates system (along a streamline (s) and normal to it (n)) is used (see Fig. 16). In this coordinate system the velocity vector is expressed by its magnitude \( u \) and direction \( \theta \).

The equations of overall mass conservation, momenta and energy balance can be written as follows:

**Continuity:** \[ u \frac{\partial p}{\partial s} + \rho \frac{\partial u}{\partial s} + \rho u \frac{\partial \theta}{\partial n} = 0 \quad (2.2.29) \]

**Momentum s-direction:** \[ u \frac{\partial u}{\partial s} + \frac{1}{\rho} \frac{\partial p}{\partial s} = 0 \quad (2.2.30) \]

**Momentum n-direction:** \[ u^2 \frac{\partial \theta}{\partial s} + \frac{1}{\rho} \frac{\partial p}{\partial n} = 0 \quad (2.2.31) \]

**Energy:** \[ \frac{5}{2} R(1+\alpha) \frac{\partial T}{\partial s} + \left( \frac{5}{2} + \frac{\theta_I}{T} \right) \frac{RT}{T} \frac{\partial \theta}{\partial s} - \frac{1}{\rho} \frac{\partial p}{\partial s} = 0 \quad (2.2.32) \]

**Equation of state:** \[ p = \rho RT (1 + \alpha) \quad (2.2.33) \]
In order to specify completely the problem of nonequilibrium flow, it is necessary to have the continuity equation for each species, namely, the mass production rate equation. For the singly ionized flow, the rate production of free electrons is given by

\[ u \frac{\partial \alpha}{\partial s} = K_R \frac{\rho^2 \alpha}{m_a} \left[ \frac{\alpha^2}{1 - \alpha} \frac{e^2}{1 - \alpha} \right] \]  

(2.2.34)

where \( \alpha_e \) is a reference degree of ionization based on equilibrium at the local temperature and pressure (\( \alpha_e \) if found from the Saha equation), \( \theta_I \) is the characteristic ionization temperature in °K.

Equations (2.2.29) to (2.2.34) were derived from the basic equations of motion, Eqs. (1.2.84) to (1.2.89), after employing the following assumptions (in addition to those already made in Chap. 1):

1. There are no external or internal electromagnetic fields in the plasma flow.

2. Diffusion processes can be neglected.

3. Radiation losses can be neglected.

4. The only reaction taking place in the plasma is \( A + e \rightarrow A^{+} + e + e \) (no electronic excitation).

5. The plasma is in thermal equilibrium, i.e. \( T_e = T_i = T_a = T \).

While assumptions 1 to 4 can be justified for a wide range of nonequilibrium flows, assumption 5 will be valid only for dense plasmas at a moderate temperature. The range for which assumption 5 is valid was not clearly specified in Ref. 37. However, as we will compare the experimental results for the quasi-steady two dimensional corner-expansion flow with the predictions of the Glass and Takano (see Chap. 3), it is important to discuss this assumption in more detail.

It is possible to estimate the ranges of plasma temperature and density for which thermal equilibrium can be assumed during an expansion flow. This could be done by estimating the appropriate collision time between the various species composing the plasma. The species or the plasma temperature is associated with the establishment of a Maxwellian velocity distribution among all the particles. (This distribution will come about as a result of collisions among the particles.) In the following we estimate the required relaxation time to reach a unique temperature for each species of the plasma, and for the plasma as a whole. The general relaxation time for a collision between particles of masses \( m_1 \) and \( m_2 \) is given by

\[ t = \frac{m_1}{m_2} \left( \frac{1}{v_2 \sigma_{1-2} n_2} \right) \text{sec} \]  

(2.2.35)
where $\sigma_{1-2}$ is the elastic collision cross-section between particles 1 and 2.

The required time to reach a unique species temperature and the time needed to equilibrate the atoms, ions and electrons temperatures will be estimated. In particular, these times will be calculated for the following conditions:

$$T = 10,000^\circ K, \ n_e = 0.6 \times 10^{17} \ cm^{-3}, \ \alpha = 0.06$$

which represent average values for the experimental work reported in Chap. 3. We shall show that the Glass and Takano model\textsuperscript{37} is valid for plasmas having temperature and electron number density in the above-mentioned range and therefore, a comparison between the experimental results and their numerical solution is justified.

For collisions among identical particles, Zeldovich and Raizer suggest the following relaxation time:\textsuperscript{10}

$$t = \frac{A^{1/2}}{8.8 \times 10^{-2} \ n_e \ Z^{1/4} \ lnA} \ \ \ \ \text{(2.2.36)}$$

where, $A$ is the atomic weight of the particles and $\ln (\Lambda)$ is a factor having an order of magnitude of 10. Specific values of $\ln A$ can be found in tabular form in Ref. 10. Equation (2.2.36) was derived from Eq. (2.2.35) for a fully ionized plasma. In the derivation, a 'collision' was understood to denote an interaction between particles involving a significant change in velocity and energy, with an appreciable angular deflection. This will occur in the case of charged particles when the particles approach each other within a distance at which the kinetic and potential (coulomb) energies become comparable. For the electron gas Eq. (2.2.36) reduces to,\textsuperscript{10}

$$t_{ee} = \frac{T^{3/2}}{3.8 \ n_e \ lnA} \ \ \ \ \text{sec. (2.2.36a)}$$

For a typical average value of the argon plasma used in the experimental work reported in Chap. 3, $T = 10,000^\circ K$ and $n_e = 0.6 \times 10^{17} \ cm^{-3}$ (such values were used by Glass and Takano\textsuperscript{37} to obtain their numerical solutions), Eq. (2.2.36a) yields $t_{ee} = 7.3 \times 10^{-13} \ sec$. Similarly, from Eq. (2.2.36) for the above-mentioned values of $T$ and $n_e$, $t_{ii} = 2.0 \times 10^{-10} \ sec$. If $T_i$ is smaller than $T(T = 10,000^\circ K)$ then $t_{ii}$ will be even shorter.

The relaxation time required to equilibrate the ion and the electron temperatures was estimated by Zeldovich and Raizer to be,\textsuperscript{10}

$$t_{ie} = \frac{252 \ A_i \ T^{3/2}}{n_i^2 \ Z^{1/2} \ lnA} \ \ \ \ \text{sec. (2.2.37)}$$

where $A_i$ and $n_i$ are the ion-atomic weight and number density, respectively. Equation (2.2.37) is based on the collision cross-section between an electron and an ion when it is assumed that the electron temperature is not much lower than that of the ion. (This assumption is valid for an
expanding plasma where $T_e > T_i$). Hence, the relative velocity for the colliding particles is almost equal to that of the electron. For representing density and temperature values in the experimental work, reported in Chap. 3 ($n_e = 0.6 \times 10^{-17} \text{cm}^{-3}, T = 10,000^\circ \text{K}$), Eq. (2.2.37) yields $t_{ie} = 2.8 \times 10^{-3} \text{sec}$.

For a weakly ionized gas, relaxation time required to equilibrate the neutrals and electrons temperatures can be estimated from Eq. (2.2.35) to be

$$t \sim \frac{m_a}{2m_e n_a v_e \sigma_{ea(\text{elas})}} \text{sec.} \quad (2.2.38)$$

where $V_e$ is the mean thermal speed of the electrons, $V_e = 6.21 \times 10^5 \text{cm/sec}$ and $\sigma_{ea(\text{elas})}$ is the average elastic-collision cross-section between neutrals and electrons. This cross-section is of the order of $10^{-15} \text{cm}^{-2}$ (Ref. 10). The expanding plasma experiments reported in Chap. 3 (Eq. (2.2.35) yields $t_{ea} = 6.3 \times 10^{-10} \text{sec}$.

According to Spitzer\(^3\) the relaxation time required for reaching a unique temperature among identical particles is given by

$$t = 11.4 \frac{A_{1/2} T^{3/2}}{n Z_{\Lambda}^2 \ln \Lambda} \text{sec.} \quad (2.2.39)$$

Like Zeldovich and Raizer\(^10\) Eq. (2.2.39) was derived for a fully ionized gas and a collision was defined as an event in which the test particle is deflected by $90^\circ$ from its pre-collision course. For $T = 10,000^\circ \text{K}$ and $n_e = 0.6 \times 10^{-17} \text{cm}^{-3}$ Eq. (2.2.39) yields $t_{ee} = 7.4 \times 10^{-13} \text{sec}$ and $t_{ij} = 2.0 \times 10^{-10} \text{sec}$.

The relaxation time for unlike particles was estimated by Spitzer to be

$$t_{eq} = \frac{5.87 AA_1}{n Z_{\Lambda}^2 Z_{\Lambda}^2 \ln \Lambda} \left( \frac{T}{A} + \frac{T_i}{A_i} \right)^{3/2} \text{sec.} \quad (2.2.40)$$

Assuming that $T_\text{e}$, $T_i$ and $T_\text{a}$ are approximately the same, the required time to reach a unique equilibrium temperature for average condition in the investigated expansion flow (see Chap. 3) (i.e. $T = 10,000^\circ \text{K}$, $n_e = 0.6 \times 10^{-17} \text{cm}^{-3}$, $\alpha = 0.06$) is $t_{eq} = 2.8 \times 10^{-8} \text{sec}$. When $T_e$ is higher than $T_i$ and/or $T_a$ then $t_{eq}$ will be even shorter.

Grien, when discussing the conditions for local thermal equilibrium in a transient plasma, suggested the following expressions for the required time to equilibrate the electron-atom and the electron-ion temperature:\(^{43}\)

$$t_{e-a} = \frac{n_a/n_e m_a/m_e}{3 \times 10^{-7}(E_H/kT)^{3/2} n_e} \text{sec.} \quad (2.2.41)$$
where \( E_H \) is the ionization potential for the hydrogen atom. Equations (2.2.41) and (2.2.42), like the previous relaxation time expressions, were derived from Eq. (2.2.37) and the appropriate collision cross-sections for the species under consideration. For \( T = 10,000^\circ \text{K} \), \( n_e = 0.6 \times 10^{17} \text{ cm}^{-3} \) and \( \alpha = 0.06 \), Eqs. (2.2.41) and (2.2.42) yield: \( t_{ea} = 0.97 \times 10^{-7} \text{ sec} \) and \( t_{ei} = 6.4 \times 10^{-8} \text{ sec} \).

### Table A

**SUMMARY OF RELAXATION TIMES**

<table>
<thead>
<tr>
<th>Source</th>
<th>( t_{ee} ) (sec)</th>
<th>( t_{ii} ) (sec)</th>
<th>( t_{ei} ) (sec)</th>
<th>( t_{ea} ) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeldovich and Raizer(^\text{10})</td>
<td>( 7.3 \times 10^{-13} )</td>
<td>( 2.0 \times 10^{-10} )</td>
<td>( 2.8 \times 10^{-8} )</td>
<td>( 6.3 \times 10^{-7} )</td>
</tr>
<tr>
<td>Spitzer(^\text{3})</td>
<td>( 7.4 \times 10^{-13} )</td>
<td>( 2.0 \times 10^{-10} )</td>
<td>( 2.8 \times 10^{-8} )</td>
<td>-</td>
</tr>
<tr>
<td>Griem(^\text{43})</td>
<td></td>
<td></td>
<td></td>
<td>( 6.4 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

The results for every individual relaxation time as suggested by Zeldovich and Raizer, Zpiteer and Griem have the same order of magnitude and they clearly indicate that for plasmas at which \( T = 10,000^\circ \text{K} \) and \( n_e = 0(10^{17}) \text{ cm}^{-3} \), a unique species temperature will be achieved almost instantaneously (see Table A). The longest relaxation time is the one required to equilibrate \( T_e \) with \( T_a \) and for the above-mentioned conditions (which are typical for the experiments described in Chap. 3) and is of the order of \( 10^{-7} \text{ sec} \). For the highest shock Mach number experiment covered by the experimental investigations (Chap. 3 and Ref. 76), the flow residence time at the post-corner zone (L ~ 5 in) is at least \( 10^{-5} \text{ sec} \). Normally it is of the order of \( 10^{-4} \text{ sec} \), which is two orders of magnitude longer than \( t_{ea} \). Therefore, we can safely assume that the plasma can be represented by one temperature throughout the investigated expansion flow, and the comparison between the experimental results and the numerical predictions of Glass and Takano is fully justified.

At this point it is is worth commenting on the studies of nonequilibrium plasma expansion flows which have been done in shock tunnels. In such experiments the plasma is generated by the reflected shock wave from the tube end wall. The plasma can expand through a small orifice into a fast-expanding nozzle. In such a facility, owing to the low electron number density, the relaxation times are very long, while the flow speed is very high (short
residence time in the expansion region). Hence, the electron temperature will remain higher than the heavy particles temperature throughout the expansion. To demonstrate this point we have calculated the required time to reach a unique temperature for the whole plasma in Dunn and Lordi's experiments, which were conducted in a shock-tunnel facility. Typical average values for their experiments are, $T_e = 4000^\circ K$, $n_e = 5 \times 10^{10} \text{ cm}^{-3}$ and $\alpha = 1\%$. For these conditions, $t_{ea} = 2 \text{ sec}$.

Returning to the equations of motion in natural coordinates, Eq. (2.2.29) to (2.2.34), it is apparent that this set is solvable, as we have six equations for the six dependent variables $p, \rho, T, \alpha, u$ and $\theta$.

The simplest case to solve is for a frozen flow. For such a case one assumes that the plasma composition is arbitrarily fixed at some initial value. This will be the situation if the reactions could in some way suddenly be inhibited so that, although particle collisions still take place, there is no accompanying change in atomic structure. As a result, such flows can be treated as reaction-free flows. It is worth commenting here that although one might consider the flow at the very corner of an expansion flow to be a frozen flow, this is not the case. However, in all real flows, due to viscosity, a boundary layer will be present on the surface, and as a result, there can be no sharp corner in the flow. Hence, the frozen-flow solutions are of academic interest only. In the following, the solution of Eqs. (2.2.29) to (2.2.34) for frozen, equilibrium and non-equilibrium corner expansion flow will be presented. The presentation follows that of Glass and Takano, work with some modifications.

(a) Frozen Flow

For this case, the degree of ionization changes instantaneously at the very corner to a constant value. Since $\alpha = $ const. downstream of the expansion corner (see Fig. 16), the five Eqs. (2.2.29) to (2.2.34) are sufficient to describe the whole flow field. (The variables now are only $p, \rho, T, u, \theta$.) The energy equation, (Eq. 2.2.37), reduces to

$$\frac{2}{2} R (1 + \alpha) \frac{\partial T}{\partial s} - \frac{1}{\rho} \frac{\partial P}{\partial s} = 0$$

(2.2.32a)

Since $p$ is given by the equation of state and it is a function of $p, T$ and $\alpha$, where $\alpha$ is a constant, the above energy equation can be integrated resulting in the following isentropic relation:

$$\left(\frac{p}{p_r}\right)^{\gamma/\gamma-1} = \left(\frac{T}{T_r}\right)^{\gamma-1}$$

(2.2.43)

where index $r$ indicates a reference value. The power index $\gamma$, should be the frozen isentropic index which for a monatomic gas is equal to the ideal gas specific heat ratio, $\gamma = 5/3$.

Using the equation of state, (Eq. 2.2.33), the last equation can be written as

$$\left(\frac{p}{p_r}\right)^{1/\gamma-1} = \left(\frac{T}{T_r}\right)^{\gamma-1}$$

(2.2.44)
A relation between the flow temperature and the Mach number can be obtained by the integration of the S- momentum equation, (Eq. (2.2.30)), together with the energy equation, (Eq. (2.2.31)). The result is

\[
\frac{T}{T_f} = \frac{1 + \gamma^{-1/2} M_f^2}{1 + \gamma^{-1/2} M^2}
\]  

(2.2.45)

where \( M \) is the frozen Mach number = \( \left( \frac{u}{a} \right)_{\text{frozen}} \).

In Ref. 37, a formal proof of isentropy for a frozen flow and a proof that \( \gamma_{\text{frozen}} = \gamma_{\text{ideal gas}} \) are given. The remaining two equations, (2.2.29) and (2.2.31), can be transformed into characteristic form, from which a relation between \( \theta \) and \( M \) can be obtained, similar to the classic Prandtl-Meyer expression for corner expansion flow.\(^{37}\)

(b) Equilibrium Flow

For an equilibrium flow we assume that all the atomic processes that take place within the plasma does so infinitely rapidly. In other words, the plasma can adjust instantaneously to changes in its environment. For such conditions the degree of ionization can be expressed as functions of any two state variables (like \( a, \rho, p, T \)); for example:\(^{37}\)

\[
\frac{\alpha^2}{1-\alpha} = \frac{\rho I}{\rho} \left( \frac{T}{\theta I} \right)^{3/2} e^{-\theta I/T}
\]

(2.2.46)

\( \rho I \) and \( \theta I \) are the characteristic ionization density and temperature, respectively.

The above equation known as the Saha equation is derived from the principle of detailed balance among collisions and the Boltzmann distribution function. (For details see Ref. 37.)

The equations of motion for equilibrium flow are:\(^{37}\)

\[
u \frac{\partial \rho}{\partial s} + \rho \frac{\partial u}{\partial s} + \rho u \frac{\partial \rho}{\partial u} = 0
\]

(2.2.29)

\[
u \frac{\partial u}{\partial s} + \frac{1}{\rho} \frac{\partial \rho}{\partial s} = 0
\]

(2.2.30)

\[
u^2 \frac{\partial \theta}{\partial s} + \frac{1}{\rho} \frac{\partial \rho}{\partial s} = 0
\]

(2.2.31)

\[rac{5}{2} R(1 + \alpha) \frac{\partial T}{\partial s} + \left( \frac{5}{2} + \frac{\theta I}{T} \right) RT \frac{\partial \alpha}{\partial s} - \frac{1}{\rho} \frac{\partial \rho}{\partial s} = 0
\]

(2.2.32)

\( p = (1 + \alpha) \rho RT \)

(2.2.33)
Although an equilibrium flow is also isentropic, as shown in Ref. 37, it would not be possible now to obtain the isentropic relations as was done for the frozen flow case. The reason is that now $\alpha$ is a function of $T$ and $p$ hence making Eq. (2.2.32) nonlinear. For the present case the equations of motion must be solved numerically. Like the frozen flow, the present case is also of academic interest only, for corner expansion flows. This is because in a real corner expansion the flow properties will change from the precorner equilibrium values, via a nonequilibrium flow towards a postcorner equilibrium condition. The final equilibrium state (postcorner), if reached, is not necessarily equal to the equilibrium solution presented here, as the present case assumes a change from one equilibrium condition (precorner flow field) to another condition (postcorner flow field) via an equilibrium process. This fact is illustrated in Figs. 36 and 37.

(c) Nonequilibrium Flow

For completely specifying the problem of a nonequilibrium flow it is necessary to have the continuity equation for each of the plasmas species, namely the mass production rate equation. As in the present analysis it is assumed that $T = T_e$ and $E = B = 0$, there is no need to have the momentum and energy equations for every species, and only the gross flow-conservation equations should be regarded. In Glass and Takano model, it was assumed that the only chemical reaction which takes place during the expansion flow is

$$A + e \xrightarrow{K_1} A^+ + e + e \quad (2.2.47)$$

where $A$ and $A^+$ are at their ground levels. For the above reaction, one can write the following rate equation.

$$\frac{d[e]}{dt} = K_1 [A] [e] - K_R [e]^2 [A^+] \quad (2.2.48)$$

where $[\cdot]$ indicates concentration (moles per unit volume). For a singly ionized flow

$$\frac{d[e]}{dt} = K_1 [A] [e] - K_R [e]^3 \quad (2.2.48a)$$

Using the Avogadro number $N_A$, the concentrations can be expressed with the previously used flow parameters as follows:

$$[A] = \frac{n_a}{N_A} = \frac{\rho(1-\alpha)}{m N_A}$$

$$[A^+] = [e] = \frac{\rho \alpha}{m N_A}$$
where \( m \) is the atom mass. Using this notion, Eq. (2.2.48a) reduces to

\[
\frac{d(\rho \alpha)}{dt} = K_R \rho \alpha^3 \left[ K_c \frac{m}{\rho} (1-\alpha) - \alpha^2 \right] \tag{2.2.49}
\]

where \( m_a, m_A \) and \( K_c = \frac{K_I}{K_R} \).

When chemical equilibrium prevails due to detailed balancing, \( \frac{d(\rho \alpha)}{dt} = 0 \) or:

\[
K_c \left|_{eq} \right. = \frac{\rho_{eq}}{m_a} \left( \frac{\alpha}{1-\alpha}_{eq} \right) \tag{2.2.49a}
\]

In the equilibrium situations, \( \alpha_{eq} \) could be evaluated using the Saha equation, Eq. (2.2.47) to obtain

\[
\frac{\alpha_{eq}^2}{1-\alpha_{eq}} = \frac{\rho_I}{\rho_{eq}} \left( \frac{T_{eq}}{\theta_I} \right)^{3/2} e^{-\theta_I/T_{eq}} \tag{2.2.47a}
\]

therefore,

\[
K_c \left|_{eq} \right. = \frac{\rho_I}{m_a} \left( \frac{T_{eq}}{\theta_I} \right)^{3/2} e^{-\theta_I/T_{eq}} = f(T) \tag{2.2.49b}
\]

and Eq. (2.2.49) could be rewritten as

\[
\frac{d(\rho \alpha)}{dt} = K_R \rho \alpha^3 \left[ \frac{\alpha_{eq}^2}{1-\alpha_{eq}} (1-\alpha) - \alpha^2 \right] \tag{2.2.50}
\]

Where \( \frac{d}{dt} \) denotes differentiation with respect to time \( t \), in the coordinates following a particle path and \( \alpha_e \) is the local equilibrium value of the degree of ionization at the local temperature and pressure. For a steady flow, expressed in natural coordinates system,

\[
\frac{d(\rho \alpha)}{ds} = u \frac{\partial(\rho \alpha)}{\partial s} \tag{2.2.50a}
\]

and with the aid of the continuity equation, Eq. (2.2.29), one obtains,

\[
u \frac{\partial \alpha}{\partial s} = K_R \rho \alpha^3 \left[ \frac{\alpha_{eq}^2}{1-\alpha_{eq}} (1-\alpha) - \alpha^2 \right] \tag{2.2.50a}
\]

The set of equations describing the nonequilibrium corner expansion flow will therefore be Eqs. (2.2.29) to (2.2.33) plus (2.2.50a). (Note that \( \alpha \) is not the equilibrium value.) Before proceeding with the solution of these equations, using the method of the characteristics, the equations will be non-dimensionalized as follows:

\[
P = P_I P'; \quad T = \theta_I T'; \quad \rho = \rho_I \rho'; \quad h = R \theta_I h'
\]

\[
u = \sqrt{R \theta_I} u'; \quad s = L s'; \quad n = L n'; \quad L = \frac{m_a^2 \sqrt{R \theta_I}}{K' \rho_I^2}
\]
where primed quantities are nondimensional and $P_\prime$, $\theta_\prime$, $\rho_\prime$ are characteristic ionization pressure temperature and density respectively.

For argon flow, Glass and Takano show that:

$P_\prime = 5.6443 \times 10^7$ atm; $\rho_\prime = 150.27$ g/cm$^3$; $\theta_\prime = 182, 850^0K$

$R = \frac{K}{m} = 0.2081 \times 10^7 \frac{\text{erg}}{\text{g} \cdot \text{K}}$; $L = 1.8421 \times 10^{-11}$ cm

Characteristic Method of Solution

The nondimensional set of equations describing the expansion flow field are: (primes have been omitted)

continuity
\[ u \frac{\partial \rho}{\partial s} + \rho u \frac{\partial u}{\partial s} + \rho u \frac{\partial \theta}{\partial n} = 0 \tag{2.2.51} \]

s-momentum
\[ u \frac{\partial u}{\partial s} + \frac{1}{\rho} \frac{\partial \rho}{\partial s} = 0 \tag{2.2.52} \]

n-momentum
\[ u^2 \frac{\partial \theta}{\partial s} + \frac{1}{\rho} \frac{\partial \rho}{\partial n} = 0 \tag{2.2.53} \]

energy
\[ A \frac{\partial T}{\partial s} + B \frac{\partial \alpha}{\partial s} - \frac{1}{\rho} \frac{\partial \rho}{\partial s} = 0 \tag{2.2.54} \]

state
\[ p = (1 + \alpha) \rho T \tag{2.2.55} \]

rate production
\[ u \frac{\partial \alpha}{\partial s} = W \tag{2.2.56} \]

where
\[ A = \frac{5}{2} (1 + \alpha); \quad B = \left( \frac{5}{2} + \frac{1}{T} \right) T \]

\[ W = K_R T^{-9/2} \rho^2 \alpha \left[ \frac{\alpha}{1-\alpha} (1-\alpha) - \alpha^2 \right] \]

The only difference between the above set of equations (Eqs. (2.2.51) to (2.2.56)) and those of Glass and Takano is in the recombination rate constant $K_R$. However, as the difference has significant effect on the computed expansion field properties, we should elaborate more on this point. Glass and Takano used the Bray and Wilson approximation for the recombination rate constant. This rate constant is derived from the assumption that detailed balance exists between collisions leading to ionization, and recombination. In general this would not be the case in a supersonic corner expansion flow, due to nonequilibrium process, like radiation losses and population inversion. Furthermore, Bray and Wilson assumed that a bound electron, after reaching the first excited state, is practically free. Due to these idealizations they arrive at the following term for the recombination rate constant:

\[ K_R = 2.366 \times 10^{15} \left( \frac{T_{\text{exc}}}{T} + 2 \right) e^{\frac{\theta_\prime - T_{\text{exc}}}{T}} \text{cm}^6 \text{mole}^{-2} \text{sec} \]

or
\[ K_R = 0.652 \times 10^{-32} \left( \frac{T_{\text{exc}}}{T} + 2 \right) e^{\frac{\theta_\prime - T_{\text{exc}}}{T}} \text{cm}^6 \text{sec} \]
where, for argon gas, $\theta_I = 182850^0K$ and $T_{\text{exc}} = 134000^0K$. Inspecting Tables 1 and 2 clearly demonstrate that the above $K_R$ is about three orders of magnitude smaller than the expected value for a temperature of the order of 1 ev. Furthermore, the experimental investigation on the supersonic corner expansion flow of an ionized argon have been demonstrated that the simplest analytical expression for $K_R$, that is in good agreement with the experimental results, is the expression suggested by Makin and Keck:

$$K_R = 2.3 \times 10^{-8} \frac{T_{e}^{-9/2}}{\text{sec}}$$

Using this expression in the rate equation (2.2.56), the nondimensional rate equation will read:

$$W = 8.25 \frac{T_{e}^{-9/2}}{\rho^2 \alpha} \left[ \frac{\alpha_e^2}{1-\alpha_e} \right]$$

Equation (2.2.57) replaced the one used by Glass and Takano.  

$$W = K(T) \rho^2 \alpha \left[ \frac{\alpha_e^2}{1-\alpha_e} \right]$$

where

$$K(T) = \left( \frac{T_{\text{exc}}/\theta_I}{T} + 2 \right) \exp \left[ \frac{\theta_I - T_{\text{exc}}}{T \theta_I} \right]$$

(All variables in the last two equations are nondimensionalized.) The numerically computed results for the nonequilibrium expansion flow which are presented in Figs. 36 and 37 were derived from Eqs. (2.2.57) and (2.2.51) to (2.2.56).

For the case of nonequilibrium flow, like the supersonic corner expansion flow of an ionized gas, it is necessary to solve the system of dimensionless equations Eqs. (2.2.51) to (2.2.56). The method of characteristic can be used for this purpose. The detailed derivations of the characteristic equations for an ionized gas flow is given in Refs. 37 and 78.

In the following the results of these papers are summarized:

Inspection of Eqs. (2.2.51) to (2.2.56) shows that four of them are expressed in the characteristic form, i.e., along streamlines and can easily be integrated (Eqs. (2.2.52) and (2.2.54) to (2.2.56)). The remaining two have to be transformed into characteristic form. Designating by $\eta$ and $\xi$ the characteristic directions (see figure below).
where \( \mu = I \frac{1}{\sqrt{M_f^2 - 1}} \); \( M_f = \frac{u}{\sqrt{\gamma R T}} \); \( \gamma = \frac{5}{3} \).

Equations (2.2.51) and (2.2.53) will reduce to,\(^3\)

\[
\begin{align*}
G \frac{\partial p}{\partial x} + \frac{\partial \theta}{\partial x} &= F \\
G \frac{\partial p}{\partial \eta} - \frac{\partial \theta}{\partial \eta} &= F
\end{align*}
\]

(2.2.58)

where \( G = \frac{\sqrt{M_f^2 - 1}}{\rho u^2} = \frac{\sqrt{M_f^2 - 1}}{\gamma P M_f^2} \); \( F = W \left( \frac{1}{1 + \alpha} - \frac{B}{A T} \right) \).

The set composed of Eqs. (2.2.52) and (2.2.54) to (2.2.56) plus Eq. (2.2.58) can be solved numerically for the nonequilibrium expansion flow, using the method of the characteristics. Details of these computations are given in Refs. 37 and 78. Figure 16 (taken from Ref. 37) shows the flow field along with a schematic description of the changes in the flow properties downstream from the expansion corner. In the next chapter, the numerical solutions outlined here (Glass and Takano model) are used for comparison with experimental results of a quasi-steady, two-dimensional corner-expansion flow of ionized argon.

CHAPTER 3 EXPERIMENTAL TECHNIQUES FOR EVALUATING THE RECOMBINATION RATE CONSTANT

As we have shown before, in order to solve the equations of motion of a supersonic expanding plasma, one should know the relation between the recombination rate constant and the plasma macroscopic properties. The most convenient facility to use for this purpose is one which can produce one-dimensional flows, since for such cases the gasdynamic formulation reduces to the simplest possible form. From this point of view, the technique used by Fox and Hobson\(^2\) is valuable (see Chap. 2), but it is limited to relatively low temperatures, as the basic idea hinges on the temperature behind the primary shock not being high enough to support ionization and therefore the recombination starts immediately after the energy discharge. The way Fox and Hobson\(^2\) suggest to measure the ion densities also seems very attractive, since it avoids the difficulties of spectroscopic measurements. A similar idea was suggested by Aleksandrov et al\(^1\) for stationary plasmas. In their facility, an argon plasma was obtained by superimposing a pulsed electric field on a steady arc discharge. Using this extra pulse the number of free electrons was artificially increased above the equilibrium level and as in Fox and Hobson's case, immediately after the extra pulse, the plasma starts recombing. Aleksandrov et al measured the electron number density and temperature as a function of time, using spectroscopic techniques. From the \( n_e \) vs. time curve, a recombination rate constant was evaluated.

When it is necessary to measure \( K_R \) at high temperature, say around 1 eV, the technique of Fox and Hobson\(^2\) cannot be used. To evaluate \( K_R \) in this temperature range, an experiment following the flow geometry of Bray\(^2\) and Talbot et al\(^2\) would seem most useful. A shock tube with a nozzle mounted in the end wall is all that is required to perform the experiment.
Park and Dunn have done their experiments using such a facility. The main advantage of such a geometry compared to the one-dimensional, shock-tube flow (reported by Fox and Hobson21) is the long flow period obtained in the expansion nozzle. The long flow time, which is at least an order of magnitude longer than the flow time in a conventional shock tube, is due to the stagnation region created at the end wall of the shock tube, which feed the small orifice nozzle. The disadvantages of such a facility are mainly due to the difficulties of measuring the plasma properties in the expansion nozzle, where the decaying processes take place, and maintaining the necessary gas purity. The measurement of static and dynamic pressures will be affected by the boundary layer, and possible flow detachment from the diffuser wall.

Duffy36 has shown how some of these difficulties can be overcome when a study of recombination is done in a shock tunnel. His work was done on the recombination of air and oxygen, but the problems of deducing the flow properties from the static and total-pressure measurements will be essentially the same for all gases. A more serious difficulty arises when the measurements of the electronic properties of the plasma such as $T_e$ and $n_e$ is done spectroscopically. Park used spectroscopic methods but as already mentioned, the accuracy of his measurements is low and are generally limited to transitions for which the oscillator strength is known. Further problems are introduced in this case due to the rapid cooling of the flow through the nozzle. In this flow it is possible to obtain a population inversion of the excited atomic states which breaks down the temperature calculation based on line intensity ratio. Park mentioned the existence of this effect in his work on ionized nitrogen flows. The measurement of temperature changes seems most attractive as it undergoes the largest change of all the thermodynamic variables. The pressure changes will be smaller and the smallest change during the expansion process will be exhibited by the density. Due to low accuracy of the spectroscopic measurements and the difficulties in measuring the pressure ('ringing' phenomenon, effect of finite gauge size, gauge calibration, and gauge response time), it looks most promising to concentrate on density-change measurements. With an interferometer, these measurements can be performed to a high degree of accuracy and it gives the local density everywhere in the field of view regardless of the state of equilibrium. The data reduction is relatively simple and is not dependent on spectroscopic data. Also this diagnostic technique does not disturb the flow. It should be mentioned that in order to use an interferometer it is necessary to have high-quality optics, which in the case of a conical nozzle is a difficult requirement to meet, that is an added disadvantage in using a shock tunnel facility.

In light of the difficulties of using a facility similar to the geometry adopted by Bray and Talbot et al in their numerical solutions, other experimental configurations were suggested. An arrangement suggested by Wilson and by Slack et al uses a shock tube for creating the argon plasma. The expansion is generated by two wedges located in an area change section as shown in Fig. 18. These wedges introduce an oblique shock on the outside and an expansion wave on the inside. The flow is then sampled with a rectangular 'cookie cutter' in which it is assumed, the recombination occurs. If this assumption is true, then one obtains a one-dimensional decaying plasma. In such a configuration flat windows can be used to study the recombination zone and to perform interferometric and spectroscopic studies. Pressure gauges can also be installed in the walls of this sector and many different measurements can be made without disturbing the flow. For such a geometry no flow detachment from the sampler walls is possible and one can adjust the configuration to minimize the boundary layer thickness.
The main disadvantages of this technique are:

1. Only for certain conditions of shock Mach number, $M_s$, and initial pressure, $p_1$, is it possible to have a frozen flow through the expansion for a fixed expansion angle. Departure from these "tailored" conditions results in recombination during the expansion itself so that in some cases the test section flow will be in near-equilibrium. In this situation the changes in the plasma properties will be marginal and might be within the range of experimental error.

2. It is important to have an attached oblique shock wave at the compression leading edge of the wedges, and not a detached one. If a detached shock wave is present, the flow in the rectangular flow sampler would not be uniform and one-dimensional, and hence measurements in the recombination zone will indicate the local readings instead of the plasma values as expected. Unfortunately, for a monatomic gas ($\gamma = 1.67$) we can expect a detached shock wave in front of the wedges at relatively low Mach numbers\(^{35}\) (see Fig. 19). This limits the temperature range of the experimental work and the useful range of expansion angles.

Another way to study the recombination processes is by density change measurements during a corner expansion. This flow is two-dimensional and the numerical solution of the flow equations is much more complicated than in the one-dimensional case. At UTIAS,\(^{37,38,48,76}\) such experimental investigations were made of the recombinining flow of argon plasmas over a corner expansion in a shock tube. Two different models were used to create the expansion flow. One, the wedge model\(^{48}\) (see Fig. 29a), produced a very thin boundary layer, for which only density measurements were made (using a Mach-Zehnder interferometer). The second model, the 'wall model',\(^{48}\) (Fig. 20b), introduced a thick boundary layer in the corner expansion region. In this model pressure measurements are also possible.

Another method of measuring the recombination rate constant was suggested by Jacobs et al.,\(^{44}\) also using a shock tube. In this technique the expansion chamber is located a few tube diameters from the shock-tube and plate. A cylindrical diaphragm lying flush with the inside diameter of the shock tube is used to control the time of initiation of an expansion wave. This cylindrical diaphragm which is ruptured by the high pressure behind the reflected shock wave, is surrounded by a vacuum chamber. Upon breaking, the plasma expands into the vacuum chamber, and a recombination process takes place (see Fig. 21). Using this technique, a comparison between experimental results and theory would be extremely difficult if not impossible, due to the three-dimensional nature of the expanding plasma. The numerical solution would also be very difficult. Even in the one-dimensional case\(^{28}\) a computer solution is very time consuming. In addition, assessing the actual measurements relative to one- and two-dimensional flows would raise many problems.\(^{47}\)

3.1 An Experimental Investigation of a Nonequilibrium Corner-Expansion Flow of Ionized Argon

A successful way of producing a clean and uniform plasma flow is to use a shock tube. Provided the primary shock wave is strong enough the gas behind can be readily ionized. Such experiments are conducted at UTIAS are described in the following.
3.2 Shock Tube Facility

The UTIAS 4 in x 7 in hypersonic shock tube was used to produce argon plasmas. Overall views of the facility are shown in Fig. 22. The design, basic instrumentation and general performance have been presented in detail in Ref. 47. Hence, only a brief description of the shock tube and its operation will be given here.

The shock tube consists of five major components: a 6-in-id driver, a transition section changing the cross-section from circular to rectangular, a 4 in x 7 in driven section, a test section and a dump tank. The driven section of the shock tube is approximately 50 ft long and is terminated by the vertical, cylindrical dump tank 6.5 ft high and 3 ft in diameter. The test section is approximately 46 ft downstream of the diaphragm station.

A mixture of stoichiometric hydrogen and oxygen with a 77.5% dilution of other gases (72.5% helium and 5% hydrogen) is used as the driver gas. The mixture proportions were chosen to ensure complete combustion and a relatively fast rise time for the pressure increase just after ignition. Ignition of the gaseous mixture is accomplished by means of an impulsively-heated tungsten wire located along the centre line of the driver section, using a high voltage capacitor. Stainless steel diaphragms were used and these were scribed to ensure rupture at the desired diaphragm pressure ratio.

For the experimental work reported here, an average value for the ultimate vacuum was 10^-5 mm of Hg and the overall leak rate and outgassing was not more than 0.05 microns Hg per minute. The initial pressure of the test gas was in the range of 2.25 to 10 mm of Hg and the maximum time between admission of the test gas to firing was 5 minutes. The test gas used for all runs was 99.998% argon and it was supplied by Union Carbide. Due to the above-mentioned factors, impurity levels between 200 to 50 ppm were experienced during the course of this work.

The initial pressure in the driven section was measured at a position about 8 ft downstream of the diaphragm station, just before admitting the test gas, using a hot-cathode ionization gauge. This gauge is sensitive down to 10^-8 mm Hg. The pressure of the test gas was monitored independently by three manometers,

1. An oil manometer using oil of density 1.069 g/cm^3 at 25°C and a temperature coefficient of expansion of -1 x 10^-3 g/(cm^3 °C),
2. A dial gauge (Wallace and Tiernan model FA160) with a range between 0 to 20 mm of Hg,
3. A McLeod gauge (product of F.J. Stokes Company) ranging from 0 to 5 mm Hg.

The accuracy of the various sensors will be discussed subsequently, where an estimate of the experimental errors is presented.

The primary shock wave was timed using Atlantic Research type LD-25 pressure transducers located at various points along the shock-tube wall. This was done in order to determine the extent of the attenuation
experienced by the primary shock wave. The results show that for all runs the attenuation is not more than 2% (see Fig. 23). Therefore, the shock velocity was based only on readings across the test section. Details of the electronic layout for a typical run is shown in Fig. 24.

Amont other instruments used in the experimental work, there were three Tetronix oscilloscopes, two Racal time-interval counters having a resolution of 1 μsec, a UTIAS counter with a 0.1 μsec resolution and three Hewlett-Packard Counters (Model 3734A) having a resolution of 10 μsec. The resolution of the latter counters was increased to 1 μsec by adding an external crystal. Kistler transducers (type 605 and 601A) and Kistler charge amplifiers were used to monitor the combustion and post-shock pressures. Figure 24 shows a block diagram of the location of above mentioned instrumentation.

The combustion-driver pressure was monitored using a Kistler gauge (type 605). This measurement was not a necessary part of the experiments, but was used to provide a record of the nature and performance of the combustion process. The performance and repeatability of the combustion-driver process was unusually good, thereby providing a close tolerance on the variation of the primary shock-wave Mach number from run to run.

3.3 Test Models

In a previous investigation done at UTIAS on a nonequilibrium corner-expansion flow of dissociated oxygen, two types of expansion models were checked. One was called 'the wall model' and had a length of 19 ft (Fig. 20a), while the second was called 'the wedge model' and had a length of 9 in (Fig. 20b). Both models had a 15-degree corner-expansion. The basic difference between the two models lay in the type of boundary layer produced. Aside from the considerable difference in the boundary layer thickness owing to the different lengths of the two models, the boundary layer on the wall model is unsteady (a typical shock tube boundary layer), while the boundary layer on the wedge is quasi-steady and of the flat-plate type, at least in the pre-corner portion of the wedge model. Consequently, it was recommended in Ref. 48 that the wedge model be used for future studies. Unfortunately, during runs at relatively high Mach number (M > 12) while using the wedge model, the high quality optical windows of the test section suffered severe surface etching. The burns on the windows were produced by the quasi-steady flow field of hot, dense gas behind the oblique shock wave, generated at the leading edge of the upper part (compression side) of the wedge model and the shock emanating from the supporting strut of the model. This surface etching severely limited the number of runs. Therefore, a new shielded-wedge model was designed (Fig. 20c) and was used throughout the experimental work. The model was built from stainless steel and also provided a 15-degree corner-expansion.

3.4 Interferometer

A Mach-Zehnder type interferometer was used as the main diagnostic instrument for the supersonic corner-expansion flow investigations. A complete description of this interferometer is given in Ref. 49.

It will be shown in the next subsection that for interferometric studies of plasmas, two interferograms taken simultaneously with different wavelengths are an essential requirement. To meet this need, a laser equipped
with a second-harmonic generator (SHG) was used as the light source. The laser was capable of operating with either of two rods: a ruby rod having as the primary wavelength \( \lambda_1 = 6.943\text{\AA} \) and due to the SHG, \( \lambda_2 = 3.471.5\text{\AA} \) and a neodymium glass rod for which the basic wavelength was 10,600\text{\AA} and the SHG provided 5,300\text{\AA}. Furthermore, the laser is especially suited for taking interferograms in plasmas due to its high intensity over a very narrow wavelength band. As plasmas radiate over a wide range of wavelengths, the interferometer light source must have the dominant intensity at its own wavelength in order to avoid a 'wash-out' of the fringes by the background radiation of the plasma.

For aligning the laser with respect to the interferometer and the shock-tube test-section, a continuous low-power He-Ne gas laser was used. Figure 25 shows schematically a Mach-Zehnder interferometer and the optical arrangement of the light source. At the camera station a beam splitter and appropriate filters were used for separating the two wavelengths and eliminating the plasma radiation (see Fig. 25). For the visible wavelengths (3.471.5\text{\AA}, 5,300\text{\AA} and 6.943\text{\AA}), Kodak R-S Pan (650 ASA) negatives were used for recording the interferograms. For the infrared (10,600\text{\AA}) Kodak spectroscopic plates (type I - Z), after a hypersensitization treatment with ammonia, were used.

By blocking the compensating chamber beam, it was possible to use the Mach-Zehnder interferometer for taking schlieren and shadowgraph pictures. For schlieren studies a knife edge was placed at the focal point of the second parabolic mirror of the interferometer (see Ref. 49).

For a space resolved interferogram of a very rapid flow (the flow velocity ranged up to 5 x 10^5 cm/sec), the exposure time of the negatives should be as short as possible. The Q-switched laser (Pockel-cell effect) used as a light source in this work, produced a giant pulse (20 megawatts) (power supply, Q-switch, delay unit, Pockel-cell and SHG) were supplied by Hardon/TRG. The laser used is a TRG 104A model.

### 3.5 Analysis of Interferograms

#### 3.5.1 Interferometric Measurements

The interferometer operation is based on the fact that the speed of light depends on the refractive index of the medium through which it passes. Basically, the interferometer is composed of two light beams which emanate from a monochromatic light source and travel through different media. Therefore, they experience different optical paths. When these two beams recombine, owing to the fact that they passed through different optical lengths, an interference between the two beams takes place. When the two beams meet such that their paths differ by an even number of wavelengths, their intensity will be the sum of the individual intensities. However, when this difference corresponds to an odd number of wavelengths, the intensity of the recombined beams is the difference between the individual intensities. As a result, white and black interference lines will appear on a viewing screen. For detailed descriptions of various interferometers and their operation see Refs. 38, 40 and 81 to 83.

For the experimental work reported here, a Mach-Zehnder interferometer (MZI) was used. A schematic outline of this instrument is given in Fig. 25. The MZI can operate in a single (infinite) fringe mode (for which the two beams are adjusted to travel identical optical path) or it is adjusted to provide a uniformly space (finite) fringe pattern. In the second mode, one of
the MZI beam splitters is rotated slightly from its equal path position, causing a linearly increasing difference in the optical path between the two beams. The net result is a set of parallel fringes on the viewing screen. All the quantitative results reported here were obtained from finite fringe interferograms. A typical finite fringe interferogram with and without a disturbance in the test section is shown in Fig. 26.

The basic quantity measured from an interferogram is the nondimensional fringe shift. The fringe shift can be related to a change in the refractive index of the medium in the following way,

$$S_{ij} = \frac{L}{\lambda} \left\{ (n_j - 1) - (n_i - 1) \right\}$$

where $S_{ij}$ is the nondimensional fringe shift measured from region i to region j, $L$ is the test section width (for a beam normal to the test-section windows), $\lambda$ is the light source wavelength and $n$ is the refractive index. When the medium is composed of several species, the relation between the refractive index and the densities of the various species is given by,

$$n - 1 = \sum_s K_s \rho_s,$$

where $\rho_s$ is the density of the s-species and $K_s$ is the corresponding Gladstone-Dale constant. Using Eqs. (3.1) and (3.2) for a singly-ionized plasma,

$$S_{ij} = \frac{L}{\lambda} \left( K_A (\rho_j - \rho_i) - (\rho_j \alpha_j - \rho_i \alpha_i) (K_A - K_I + 0.67 \times 10^9 \lambda^2) \right)$$

where $K_A$ and $K_I$ are the Gladstone-Dale constants for atoms and ions, respectively. All terms in Eq. (3.3.) are expressed in cgs units. As can be seen from Eq. (3.3.), in order to solve for $\rho$ and $\alpha$ (or $n_e$ since $n_e = \rho\alpha/m_e$), one must meet the following requirements,

1. two interferograms taken simultaneously with different wavelengths have to be available;
2. the plasma density and degree of ionization have to be known at some reference zone (zone i) on the interferograms;
3. the Gladstone-Dale constant for atoms and ions have to be known.

The first condition is met by using a laser equipped with a SHG as a light source, thereby providing the two frequencies required. For a reference zone, as required in 2, the pre-corner flow region was used. The plasma properties in this region were obtained by solving the Rankine-Hugoniot relation across the primary shock wave, using the initial test gas pressure and temperature and the measured shock velocity. This solution represents the plasma equilibrium properties, reached at the end of the narrow relaxation zone that follows the primary shock. However, since we are dealing with a plasma which is not perfectly opaque, some radiation losses will take place, and, as a result, the plasma downstream of the end of the relaxation zone will be cooler and have a lower degree of ionization than the predicted equilibrium values. In general, the changes in $T$ and $\rho$ due to radiation
losses are small. However, the drop in $\alpha$ is significant. Horn$^{84}$ and Oettinger$^{33}$ have studied the cooling effects on an argon plasma generated in a shock tube. Figure 27 taken from Horn's work$^{84}$ shows clearly that for a temperature drop of the order of 5%, one can expect a 50% drop in $\alpha$. In the experiments, the reference values were corrected to account for radiation losses, in accordance with the results of Horn,$^{84}$ Oettinger$^{33}$ and the present data shown in Fig. 28. Figure 44 shows the kind of unrealistic results one obtains when radiation losses are not taken into account.

The Gladstone-Dale constant for room-temperature argon gas is accurately known,$^{39}$ but not at elevated temperatures. Therefore, it was assumed that $K_A$ for the excited argon atoms will remain equal to their ground-state value (i.e. all atoms are at their ground-temperature ($T = 1$ e.v.) the number density of the excited atoms is very small in comparison with ground state atoms and/or free electron number densities, the contribution of the excited atoms to the plasma refractive index can be neglected. The experimental results of Bristow$^{51}$ justify the last assumption.

As to the Gladstone-Dale constant of ions, several authors adopted the value $K_I = 0.67K_A^{38,40}$ based on the Slater screening constant calculations$^{40}$. The experimental work of Bristow$^{51}$ verified this value for an argon plasma. For one of the runs, the data reduction was carried out using different values for $K_I$. As can be seen from the results presented in Fig. 29, as $K_I$ changes from $K_I = 0.25 K_A$, there is only a small change in the calculated values of $\rho$. This demonstrates the point that an accurate value for $K_I$ is not of critical importance for the evaluation of $\rho$ and $n_e$ from the interferograms.

### 3.5.2 Data Reduction from Interferograms

To compensate for possible fringe distortion due to optical imperfections in the MZI, a no-flow interferogram was always taken just before the actual run. A typical no-flow picture along with the associate flow interferogram is shown in Fig. 26. If the fringes were all absolutely straight in the regions of uniform flow, the fringe shift measurements could be taken directly from the flow interferogram as shown schematically in Fig. 30. However, this is not the case. Therefore, both the flow and no-flow pictures were plotted together on a large scale and the fringe shifts were measured relative to the nearest no-flow fringe as shown schematically in Fig. 31. As the numerical analysis of the expanding plasma flows was done only for the inviscid flow,$^{28,37}$ in order to compare the experimental results with the theoretical predictions, the fringe shift measurements had to be made outside the boundary layer. From the interferograms it is easy to identify the boundary-layer edge which is marked by a significant shift of the fringes once they penetrate this layer (see Fig. 26). The 'effective boundary-layer edge' was defined as the location where the fringe shift is 2% or less of its value on the wedge wall, measured relative to the inviscid, uniform flow above the boundary layer. Further evidence to substantiate the boundary layer edge can be obtained from a single (infinite) fringe interferogram and interferometric plots of the changes of $\rho$ and $\alpha$ in the boundary layer. The only available numerical solution for a two-dimensional, steady, supersonic corner-expansion flow of ionized argon, is the work of Glass and Takano$^{37}$. In this analysis, the solution was for an inviscid flow using a natural coordinate system. Therefore, in order to compare our experimental results with the numerical predictions of Ref. 37, the fringe shift measurements have to be made along
a streamline. However, a streamline location can be calculated for two special cases of frozen and equilibrium flows. In nonequilibrium flows, the streamline location will probably be somewhere between the frozen and the equilibrium positions. As shown by Glass and Takano for the nonequilibrium flow, all streamlines near the wall will be parallel to the model surface (except for a small region near the expansion corner). Furthermore, our calculations have shown that for a suggested streamline (parallel to the wall and outside the boundary layer) small deviations from this suggested location have little bearing on the calculated results for \( \rho \) and \( \alpha \), provided that the deflections do not 'push' the suggested streamline into the boundary layer. As a result of the above arguments, the fringe shift measurements were done along a line just outside the 'effective boundary-layer edge'.

Once the appropriate reference values, the Gladstone-Dale constants and the measured fringe shifts are known, the evaluation of \( \rho \) and \( \alpha \) and \( n_e \) can be made using Eq. (3.3). However, for two-wavelength interferometry, resulting in a doubling of the fringes, the fringe shift data are not available at the same geometrical location on both interferograms. Therefore, a polynomial curve fit through the measured fringe shift has to be made for each interferogram and the plasma properties (\( \rho \), \( \alpha \) and \( n_e \)) are evaluated from this polynomial equation. For the work reported here, the coefficients of the polynomial equation were evaluated using a computer. (The mathematical background for the curve fits is given in Ref. 76.) A typical curve fit for one of the runs along with the derivatives of the equation are shown in Fig. 39. As can be seen from this figure, the derivatives of the equation are quite 'smooth' even for the high order polynomials. This result will be very useful for estimating the recombination rate constant.

### 3.5.3 Pressure Measurements

In order to check the accuracy of the calculation of the post-shock plasma properties, the post-shock pressure was monitored using a Kistler transducer. Several pressure records are shown in Fig. 33. As can be seen from this figure, the pressure behind the primary shock is fairly constant (no filters were used during most of the measurements) and in good agreement with real-gas theory. As can be seen, there are considerable fluctuations about the average pressure. 'Ringing' comes about from the natural frequencies associated with the transducer diaphragm. Noise is also introduced by shocks travelling through the shock tube walls. These effects are greatly reduced simply by filtering the resulting pressure trace as is evident in the filtered trace shown in Fig. 33.

### CHAPTER 4 RESULTS AND DISCUSSIONS

All interferograms obtained during the course of this work were taken approximately 30 to 50 \( \mu \text{sec} \) after the primary shock wave had passed the expansion corner. This was done in order to avoid the nonsteady wave interaction zone at the start of the flow. Some features of this nonsteady flow shown in the interferogram of Fig. 34 are: the primary shock, the contact surface and the upstream-facing shock, generated to match the pressure between the gas behind the primary shock and the expansion region. The expansion wave and the boundary layer are also clearly shown. Since Fig. 34 was taken for a relatively low shock Mach number, the relaxation zone that follows the primary shock front is not present. In Fig. 35, which was taken
at a much higher shock Mach number ($M_s = 19$), the relaxation zone is clearly visible. From interferograms like the one in Fig. 35, it can be seen that in the range of our experimental work ($2 < p_1 < 10$ torr, $13 < M_s < 20$, $T_1 = 300^\circ$K), the apparent width of the relaxation zone is about 9 mm (corresponding to $\approx 1.5$ usec), which is well within the wave interaction zone shown in Fig. 34. (When the impurity level is higher the extent of the relaxation zone can be doubled.) As explained before, the values of $\rho$, $\alpha$, and $n_e$ were deduced from the interferograms. Typical results for one of the experiments are shown in Figs. 36, 37 and 38. (In Ref. 76, results of more runs are available.) As expected in supersonic expansion flows, the density, degree of ionization and the electron number density decrease downstream of the expansion corner. In Figs. 36 and 37, the predictions of Glass and Takano for the expansion flow based on our pre-corner flow properties are also shown. It should be noted that the scale subdivisions are not conventional as the original figures were drawn by a computer that automatically selected scales according to paper size. In order to compare the experimental results with the predictions of Glass and Takano in proper perspective, the basic concepts of their theoretical model will be briefly restated. As explained in Chapter 2, the equations of motion (Eqs. (2.2.28) to (2.2.33) plus (2.2.50a) were solved by Glass and Takano using the method of characteristics. On performing the numerical calculations, the entire flow field was divided into zones, as shown schematically in Fig. 39. Zone 1 is the uniform precorner flow field; zone 2 is the 'frozen' Prandtl-Meyer expansion flow, limited to the actual sharp corner point only; zone 3 covers the flow field between the expansion wave head and tail; zone 4 contains the flow downstream from the expansion-wave tail. The equations of motion were simplified to describe specifically zones 2, 3 and 4 (see Ref. 37 and 78). As can be seen from Fig. 39, all characteristics in zone 3 emanate from the expansion corner and are based on the initial frozen Prandtl-Meyer expansion flow values at this point. The characteristics in zone 4, in turn, are derived from those in zone 3. Hence, the flow properties on streamlines near the wall will change from the frozen values towards the equilibrium values far behind the corner. However, this is not the case along streamlines far from the wall, since the flow properties on the characteristics intersected by these streamlines will have already relaxed from the frozen values they had at the corner. This is demonstrated in Fig. 17, taken from Ref. 31. In order to compare the experimental results with the predictions of Ref. 37, a streamline close to the 'boundary-layer edge' was chosen. The results shown in Figs. 36 and 37 are based on such streamlines. However, due to the presence of boundary layer in real flows there is no sharp corner, and therefore, the frozen values for a real flow are of academic interest only. Hence a comparison between the experimental results and the predictions of Glass and Takano near the corner are not meaningful. As the frozen value for $\alpha$ is identical to the precorner value $\alpha_2$, the plots of $\alpha$ versus distance were drawn to the corner.

An analytical formulation for describing the three-body, electron-ion-electron collisional recombination rate was given by Glass and Takano, as, (the Bray and Wilson model, for details see Sec. 2.2)

$$K_R = 3.349 \times 10^{16} \left( \frac{a N_A}{\rho_1} \right)^2 \left( \frac{T_{\text{exc}}}{T} + 2 \right)$$

$$\exp \left( \frac{\Theta - T_{\text{exc}}}{T} \right) \text{ cm}^6/\text{sec.}$$

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This rate equation has been modified by replacing it with that suggested by Makin and Keck\(^{11}\) in order to bring out the simple temperature dependence,

\[
K_R = (\text{constant})T^{-9/2}
\]  
\(\text{(4.2)}\)

For small degrees of ionization \((\alpha_2 < 5\%)\), this change has a significant effect on the calculated degree of ionization downstream of the expansion corner, although it has little or no effect on \(p, \rho\) and \(T\). However, the modification is justified since the Bray and Wilson model describes the recombination rate at equilibrium only, while recent studies show that in a dense plasma the recombination rate constant will generally be related to \(T^{-9/2}\) (see Chapt. 1 and Tables 5 and 6). In light of the arguments mentioned above, the agreement between the interferometric results and those predicted by Glass and Takano is very good. This demonstrates that the method of characteristics can be used in the analysis of complex reacting flows.

With regard to Figs. 36, 37, 38 (and those in Ref. 76), the following comments can be made:

1. In most of the experimental results there is a slight increase in \(\alpha\) just downstream of the corner and only further on does it decrease as expected (see also Figs. A3, A10, A17, A24, A31, A38, A45 and A54 in Ref. 76). This initial increase in \(\alpha\) is caused by an inaccurate knowledge of the reference value \(\alpha_2\). As explained before, the plasma properties will change, relative to the Saha equilibrium values, because of radiation losses. The largest change will occur in \(\alpha\). In making the corrections for these losses it was assumed that one value of \(\alpha_2\) can represent the plasma in the entire precorner zone. Strictly speaking this is incorrect, as the part of this reference zone which is nearer to the primary shock will have experienced radiation losses for a shorter period of time. In other words, a 'floating' reference for \(\alpha_2\) should be used. However, as these variations are small, this was not necessary. In any case, this initial rise in \(\alpha\) is within the experimental error bar, and should not be regarded as representing any 'real' phenomena. (The error bars shown will be explained later.)

2. In some cases the plasma density reaches a minimum just behind the corner (see Fig. 36 for example) and then increases. This indicates an over-expansion such as that predicted by Glass and Takano for a streamline near the wall (Fig. 17). However, this measured variation in density is almost always within the experimental error. Hence, no definite conclusion can be formulated regarding this point. It should be noted that, unlike the maximum in the plot of \(\alpha\) versus distance from the expansion corner, the minimum in \(\rho\) remains regardless of changes in the initial reference values of \(\rho_2\) and \(\alpha_2\).

3. For all experiments the electron number density \(n_e\) decreases over the entire expansion region under investigation. This will be true even after a correction for the decrease in \(n_e\) due to volumetric expansion is made, as shown in Fig. 38. This fact was used as an indication that the plasma was decaying and it will facilitate the evaluation of \(K_R\) later on.
The frozen and equilibrium flow properties, as defined in Refs. 37 and 38, are shown in several figures. These values should be regarded as convenient indicators only, since neither one is actually attained in a real flow.

The experimental results, evaluated directly from the measured fringe shifts, having now been discussed, the next step is to estimate the recombination rate constant in the investigated plasma based on these results \((\rho, \alpha, n_e)\). For the flow conditions under consideration (dense plasma), the most probable recombination process is the one starting with a three-body, electron-ion-electron collision. This collision results in an excited atom which will cascade down the energy ladder, towards its ground state via two-body inelastic collisions and/or radiative transitions. For these reactions the recombination rate constant \(K_R\) can be related to the plasma properties as follows (see Chap. 1, Eq. (1.2.18)).

\[
\frac{dn_e}{dt} = \frac{K_R n_e^3}{\rho u} - K_R n_e^3
\]

as long as the plasma is singly ionized.

For a steady parallel flow, the plasma continuity equation will be \(\partial / \partial x (\rho u) = 0\), and for the electron gas, \(\partial / \partial x (n_e u_e) = d n_e / dt\). Here \(x\) is a distance measured along a streamline and \(u\) is an average flow speed in the streamtube. Neglecting diffusion (i.e. \(u - u_e\)) and expressing \(n_e\) in terms of \(\rho\) and \(\alpha\), the electron gas continuity equation will read,

\[
\frac{\partial}{\partial x} \left( \frac{\rho \alpha}{u} \right) = \frac{dn_e}{dt}
\]

Since \(\partial / \partial x (\rho u) = 0\), the last equation can be rewritten as

\[
\frac{\rho u}{m_a} \frac{d\alpha}{dx} = \frac{dn_e}{dt}
\]

Returning to our estimate of \(K_R\) for the expansion region where the plasma temperature is decreasing, after substituting Eq. (1.4.3) into Eq. (4.2) and neglecting the ionization term, one obtains

\[
\frac{\rho u}{m_a} \frac{d\alpha}{dx} = - K_R n_e^3
\]

or

\[
K_R = - \frac{\rho u}{n_e^3 m_a} \frac{d\alpha}{dx}
\]

Equation (4.5) expresses the recombination rate constant in terms of the measured quantities. It can be seen that the temperature dependence of \(K_R\) upon \(T\) appears only implicitly. The values for \(d\alpha / dx\) were obtained from the derivatives \(d S(\lambda_1) / dx\) and \(d S(\lambda_2) / dx\). The results for \(K_R\) based on Eq. (4.5) are shown in Fig. 4.0. (Results from some more runs are available in Ref. 76, Figs. A5, A12, A19, A26, A33, A40, A47 and A54.) With increasing
distance downstream of the expansion corner, the plasma temperature decrease and as a result, \( \text{KR} \) increases. When the calculations for \( \text{KR} \) are performed using Eq. (4.5) the plasma temperature appears implicitly. Since it is well known that \( \text{KR} \) is strongly temperature dependent,\(^3\),\(^{3a}\),\(^{10}\),\(^{11}\),\(^{63}\),\(^{63a}\),\(^{74}\),\(^{75}\) it would be advantageous to estimate the temperature at which \( \text{KR} \) was evaluated. It was shown in Chapter 1 that for a dense plasma, it can be assumed that thermal equilibrium exists throughout the investigated expansion region. The precorner temperature is known from the solution of the shock-wave relations with appropriate corrections for radiation losses. Glass and Takano\(^{37}\) have calculated the temperature change through the nonequilibrium expansion flow, and have shown that for streamlines not too close to the wall, the temperature will drop from its precorner value towards the equilibrium value (see Fig. 17). A typical value for \( T_2 - T_3 \) (2 indicates the precorner while 3 stands for the equilibrium flow past the expansion tail) in the investigated experimental range is 2,000°K for \( T_2 = 12,000°K \) (Ref. 37, for \( M_s = 14, P_l = 10 \text{ torr}, T_l = 300°K \)). This indicates an overall temperature drop of the order of 17%. Keeping in mind that the changes in \( T \) through the expansion are relatively small, the temperature was estimated by using the measured values for \( P \) and \( n_e \) in the Saha equation. Strictly speaking, this is incorrect as we are dealing with a nonequilibrium situation. However, as the change in \( T \) is small, the use of the Saha equation may introduce errors but these will be within the experimental error. An alternate approach is made possible by using the measured values of \( \text{KR} \) in the theoretically derived expression relating \( \text{KR} \) and \( T \) (Eq. (4.2)). As an example, the Makin and Keck\(^{11}\) relation was used and the results agreed fairly well with those derived from the Saha equation (see Fig. 41).

Consequently, we can present \( \text{KR} \) as a function of \( T \). This is shown in Fig. 42 (and Figs. A7, A14, A21, A28, A35, A42, A49 and A56 in Ref. 76). As expected, \( \text{KR} \) increases with decreasing temperature. The results for \( \text{KR} \) at relatively high temperatures (11,000°K and higher) must be corrected, as in this temperature range, neglecting the ionization term is no longer justified. For such cases, \( \text{KR} \) should be evaluated using Eq. (4.3) rather than Eq. (4.4).

4.1 Sources of Errors

In general, three sources contribute to the total errors in the values obtained for \( \rho, \alpha \) and \( \text{KR} \). These are:

1. errors associated with the optical technique used in the experiments,

2. errors involved in the measurements of the initial conditions \( (P_l, T_l \) and \( M_s) \) from which the reference values (the precorner flow) required for the interferometric measurements were deduced,

3. errors resulting from the indirect determination of \( \rho, \alpha \) and \( \text{KR} \).

(These sources of error will be discussed independently.)

When a MZI is used for studies of plasma density and electron number density in a region where large density gradients occur, it is necessary to consider the possibility of an error in the measured fringe shift as a result of the refraction of light rays. In other words, the gradient in density will cause a light ray to bend in the direction of increasing density and follow a curved path through the test section rather than the straight one, as assumed in the derivation of Eq. (3.3) (the simple interferometry theory). This phenomenon results in two main effects:
1. each ray will travel over a longer optical path and along this path the refractive index will be constantly changing (hence, so will \( \rho \) and \( \alpha \)),

2. the location of the fringe with respect to the wall is shifted since the ray does not actually pass through the point from which it appears to originate.

Thus, the interferograms evaluated on the basis of Eq. (3.3) (unrefracted light rays) will, in general, be in error. Bunting and Devoto,\(^50\) in their study of thermal boundary layers in argon flows, have analyzed the refractive error involved in interferometric studies. Figure 43, taken from their report shows schematically the geometry of the investigated end wall thermal boundary layer, along with the refracted and unrefracted rays of light. It was found that even in the severe case of a thermal boundary layer, where large density gradients exist near the end wall, the total refractive error will be much smaller than the fringe shift reading error.\(^50\) In the cases investigated by Bunting and Devoto, the fringe shift reading error was ±0.025 fringes, while the maximum total refractive error was of the order of 10^{-3} fringes.\(^50\) Since the present work is limited to the inviscid part of the flow, the density gradient is much smaller than that in the thermal boundary layer. Furthermore, the total refraction of a light ray is less in the case of a plasma flow than in the case of a gas flow having the same density gradient. This comes about since the electron gas refracts a light ray in a direction opposite to the heavy particle gas (see Eq. (3.3)).

Another source of error in \( \rho \) and \( \alpha \) arises from using Eq. (3.3) which does not consider the presence of the viscous boundary layer on the test section windows (see Fig. 43). The light rays will be deflected when passing through these layers. Bunting and Devoto have shown that the errors introduced by this source are also much smaller than the fringe shift reading error (around 5 x 10^{-4} as compared with ±0.025 reading error, for details see Ref. 50). From the above evidence, it is seen that refractive errors are negligible in the present case and have therefore been neglected in the data reduction.

The errors of the second category will have a significant effect on the experimental results. It was shown in Chapter 3 that when the reference value for the degree of ionization is not known accurately, a physically meaningless result may be obtained (see Fig. 44). For the interferometric results reported here, the precorner flow properties were used as a reference. The flow values in this region were obtained by solving the shock-wave relations for the initial (unshocked) conditions in the shock tube. In solving these equations, the partition function along with a proper cut-off scheme was used in the energy equation. The equations of motion through the normal shock wave were solved by using an iterative technique on a computer (for details see Ref. 51). In order to evaluate the effect of the errors in measurement of the preshock conditions and shock velocity on the computed postshock parameters, the computation was initially run using the nominal values of the measured quantities. The program was then rerun using the maximum and minimum limits of each measured value in turn. Thus the separate effect of each error was determined as follows:

1. Errors in the measurement of shock velocity.

The shock velocity was recorded using Atlantic Research LD-25 pressure transducers and a microsecond timer. The width of each transducer face
is about 8 mm compared with the between-centers-separation of the two shock detectors of 609.6 mm (2ft). Hence the distance travelled by the shock in the measured time interval is $609.6 \pm 8$ mm. The transducer rise time is less than 1 $\mu$sec and the timer resolution is $\pm 0.05$ $\mu$sec. Hence, the error in the measured time interval is $\pm 1$ $\mu$sec. As a result of the above arguments the following values may be obtained for shock velocity,

$$v_s\text{ nominal} = \frac{x_n}{t_n}, \quad v_s\text{ min} = \frac{x_n - \Delta x}{t_n + \Delta t}, \quad \text{and}$$

$$v_s\text{ max} = \frac{x_n + \Delta x}{t_n - \Delta t}, \quad (4.6)$$

where $x_n = 609.6$ mm, $t_n$ is the counter reading, $\Delta x = 8$ mm and $\Delta t = 1$ $\mu$sec. Performing the computations corresponding to the above three shock velocities, it is apparent that $\alpha$ is the parameter most affected by these errors (see Table 3 which represents the worst case observed). In the extreme case shown in the table, an error in $\alpha$ of almost 9% of the nominal value is possible.

2. Errors in the measurement of the initial pressure.

For the range of $1 < p_1 < 5$ torr, the McLeod gauge was the most reliable instrument. For the lower pressure range ($1 < p_1 < 2.5$ torr), the accuracy was within $\pm 0.05$ torr and improves with increasing $p_1$. Computations were made for both $p_1$ and $p_1 \pm \Delta p_1$ and in the extreme case of error, all postshock properties were within 5% of the nominal values.

3. Errors in the measurement of the initial temperature.

The initial temperature can be read to $\pm 0.5^\circ$C and this error has practically no effect on the calculated postshock properties, as can be seen in Table 3.

The findings reported here, based on the shock-wave solutions, were backed by experimental measurements. Bristow\textsuperscript{51} has deduced from his interferometric studies on normal shock waves in argon, that the electron number density at the end of the relaxation zone which follows the primary shock front, agrees to within 2% with the Saha prediction computed from the measured initial conditions. Furthermore, during this work the postshock static pressures were also recorded. The results presented in Fig. 33 indicate that the change in the static pressure due to radiation losses are small, as expected from the results of Horn\textsuperscript{84} and Oettinger.\textsuperscript{33} The agreement between the calculated pressures and the 'average' pressures measured by the Kistler transducers is very good. To summarize, it can be said that the reference value of $\rho$ and $\alpha$ are known to within 5% for most of the experiments performed during the course of this work. These values will be used in evaluating the errors associated with category '3'.

The errors resulting from the indirect measurement of $\rho$ and $\alpha$ can be estimated by using the following procedure. Let $A = f(a_1, a_2, a_3, \ldots)$, where $a_1, a_2, a_3, \ldots$ are quantities measured directly and $A$ is a deduced
quantity. Let \( q_1, q_2, q_3, \ldots \) represent the errors in \( a_1, a_2, a_3, \ldots \). Then \( Q \), the error in \( A \), is given by the relation:

\[
Q = (\frac{\partial f}{\partial a_1})^2 q_1^2 + (\frac{\partial f}{\partial a_2})^2 q_2^2 + (\frac{\partial f}{\partial a_3})^2 q_3^2 + \ldots
\]  

(4.7)

From the interferometric equation, Eq. (3.3), after some algebra, one obtains,

\[
\rho = \rho_2 - \frac{\lambda_1 S_1}{a L} C + \frac{\lambda_2 S_2}{a L} B,
\]

(4.8)

\[
\alpha = \frac{1}{\rho} \left( \rho_2 \alpha_2 - \frac{\lambda_1 S_1 K_1}{a L} + \frac{\lambda_2 S_2 K_2}{a L} \right),
\]

(4.9)

where the subscript 2 denotes the reference quantities (precorder), \( S_1 \) is the measured fringe shift at wavelength \( \lambda_1 \), \( S_2 \) is the measured fringe shift at wavelength \( \lambda_2 \) (both fringe shifts are measured at the same geometrical location), and \( K_1 \) and \( K_2 \) are the Gladstone-Dale constants for wavelengths \( \lambda_1 \) and \( \lambda_2 \), respectively. In these equations:

\[
B = 0.33 K_1 + 0.67 \times 10^9 \lambda_1^2,
\]

\[
C = 0.33 K_2 + 0.67 \times 10^9 \lambda_2^2,
\]

\[
a = K_2 B - K_1 C.
\]

For the interferograms taken with the ruby rod, the above quantities have the following values:

\[
\lambda_1 = 0.6943 \times 10^{-4} \text{ cm}, \quad \lambda_2 = 0.34715 \times 10^{-4} \text{ cm},
\]

\[
K_1 = 0.15726 \text{ cm}^3/\text{g}, \quad K_2 = 0.16273 \text{ cm}^3/\text{g},
\]

\[
B = 3.2816 \text{ cm}^3/\text{g}, \quad C = 0.8611 \text{ cm}^3/\text{g}, \text{ and}
\]

\[
a = 0.3986 \text{ cm}^6/\text{g}^2.
\]

For the interferograms taken with the neodymium-glass rod:

\[
\lambda_1 = 1.0600 \times 10^{-4} \text{ cm}, \quad \lambda_2 = 0.5300 \times 10^{-4} \text{ cm},
\]

\[
K_1 = 0.15627 \text{ cm}^3/\text{g}, \quad K_2 = 0.15852 \text{ cm}^3/\text{g},
\]

\[
B = 7.5797 \text{ cm}^3/\text{g}, \quad C = 1.9343 \text{ cm}^3/\text{g}, \text{ and}
\]

\[
a = 0.8993 \text{ cm}^6/\text{g}^2.
\]
For both cases, $K_1 = 0.67 K_A$ and $L = 10.16$ cm was used.

Using Eq. (4.7), the errors associated with the indirect measurements of $\rho$ and $\alpha$ can be expressed as,

$$
(\Delta \rho)^2 = (\Delta \rho_2)^2 + \left( \frac{1}{a L} \right)^2 (\Delta S_1)^2 + \left( \frac{1}{a L} \right)^2 (\Delta S_2)^2 \quad \text{and} \\
(\Delta \alpha)^2 = \left( \frac{\rho_2 a L}{\rho} - \frac{\lambda K_1}{a L} + \frac{\lambda^2 S_2 K_2}{a L} \right)^2 (\Delta \rho)^2 + \left( \frac{\lambda K_1}{a L} \right)^2 (\Delta S_1)^2 + \left( \frac{\lambda^2 S_2 K_2}{a L} \right)^2 (\Delta S_2)^2
$$

(4.10)

$$
(\Delta \alpha_2)^2 + \left( \frac{\rho_2 a L}{\rho} \right)^2 (\Delta \alpha_2)^2 + \left( \frac{\rho_2 a L}{\rho} \right)^2 (\Delta \alpha_2)^2 + \left( \frac{\rho_2 a L}{\rho} \right)^2 (\Delta \alpha_2)^2
$$

(4.11)

where $\Delta S$ is the fringe shift reading error.

For a given $\Delta S$, Eq. (4.10) yields a constant error in the interometrically deduced values for $\rho$ throughout the investigated expansion flow. This is not the case for the error in the calculated degree of ionization where $\Delta \alpha$ depends on the local value of $\rho$. Because of this, only the one constant error bar was shown in the plots of $\rho$ versus $x$ (see Figs. 36, 37). The calculation of these error bars was done by the computer after evaluating $\rho$ and $\alpha$ from the fitted curves through the measured fringe shifts. During the course of these computations, the reading errors were set equal to $\Delta S_1 = \Delta S_2 = 0.05$ fringes. This value is very conservative since for many of the experiments performed, a reading error of 0.02 fringes was obtained. The errors in the reference properties ($\Delta \rho_2$ and $\Delta \alpha_2$) were set to 5% of the initial values for the majority of the runs, and this is also a conservative estimate. Therefore, the error bars shown in Figs. 36 and 37 can be regarded as giving upper limits on the experimental errors.

An estimation of the errors involved in the evaluation of $K_R$ may be carried out in a similar manner. From Eq. (4.5), after applying the procedure described in Eq. (4.7),

$$
(\Delta K_R)^2 = \left( \frac{\rho u}{m a \frac{3}{n_e}} \right)^2 \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2 + \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2 + \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2
$$

$$
+ \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2 + \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2 + \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2
$$

(4.12)

Since $n_e = \rho \alpha m_a$, the above equation can be rewritten as,

$$
(\Delta K_R)^2 = K_R \left( 10 \left( \frac{\Delta \rho}{\rho} \right)^2 + \left( \frac{\Delta u}{u} \right)^2 + \left( \frac{\alpha}{dx} \right)^2 (\Delta \rho)^2 \right) + 9 \left( \frac{\alpha}{\alpha} \right)^2
$$

(4.12)
As shown previously, the error bars on $\rho$ and $\alpha$ will be of the order of $|\Delta \rho/\rho| \approx 0.15$ and $|\Delta \alpha/\alpha| \approx 0.4$. The limiting values of $\Delta u$ may be taken as the frozen and the equilibrium values, and from Ref. 37 and 38 $|\Delta u/u|$ will be about 0.2 for the extreme cases of this work. Using various curves to fit the experimental fringe shifts, it was found that,

$$\frac{\Delta (\alpha dx)}{\alpha dx} < 1.$$ 

With the above mentioned values, the order of the error in $K_R$ will be,

$$\frac{\Delta K_R}{K_R} = 1.644.$$ 

This type of evaluation was carried out for each experiment. In total, it was found that the values of $K_R$ are accurate to within a factor of two. It is important to note that this will be the case for all evaluations of $K_R$ done at temperatures lower than about 10,800$^o$K. For these temperatures, the term, $K_I n_a$, is less than 10% of $K_R n_e$ (as calculated from Eq. 4.5) and can therefore be neglected. However, for higher temperatures $K_R$ should be calculated from Eq. (4.3). (The value of $K_I$ was obtained using the expression, Eq. (1.2.30) given by Wong.)

The details of the recombination phenomenon are extremely complex and therefore the process is difficult to model. As a result, all the models which have been proposed should be regarded as approximations and no accurate error estimation for $K_R$ based on these models is possible. Generally speaking, for some of the more detailed models the collision cross-section for transitions between various energy levels must be known. Frequently, the Gryzinski expressions for the collision cross-section are used. As this model was developed for hydrogen atoms only, the accuracy of the results decreases when using the expressions for other atoms, especially for low energy levels. Chen performed detailed calculations for $K_R$ in the rare gases using Byron et al.'s approach and the Gryzinski expressions for the collision cross-sections. He claimed a probable accuracy to within a factor of four. It would seem appropriate to use this value (factor of four) as a general upper limit (best accuracy) on the error from theoretical predictions, as the model due to Byron is among the more detailed descriptions of the recombination phenomena. This low accuracy for the theoretical predictions lends further importance to the present experimental work, as our results are to within a factor of two.

With regard to other experimental work in the field, the picture is even poorer. The majority of experimental work in evaluating the plasma recombination rate constant has been carried out in discharge tubes. In this type of facility, the plasma is ionized by discharging a high energy capacitor bank through electrodes located inside the discharge tube. With this method, some of the electrode particles are released and this results in an impure and nonuniform plasma. Furthermore, in most of these experiments, spectroscopic techniques were used. Such diagnostics are limited to specified equilibrium states which do not necessarily exist in a plasma, thereby rendering the results questionable.
value (see for example Fig. 13). On the other hand, in the experimental work reported here, a relatively pure and uniform plasma was produced by driving a strong shock front into quiescent argon. In addition, the diagnostic technique used (two-wavelength interferometry) does not depend on the thermodynamic states of the investigated media and it does not disturb the plasma flow. Consequently, the present data may be used with considerable confidence.

A summary of several experimental results along with Makin and Keck's prediction is given in Fig. 45. Except for the results of Fox and Hobson,21 the data from the present investigation are the only ones obtained from shock tube experiments. As can be seen from Fig. 45, their data was obtained for temperatures below 4,000K and they suggested a higher recombination rate than that of Makin and Keck11 as well as the other experimental values of $K_R$. Furthermore, the slope for $K_R$ versus $T$ from the data of Fox and Hobson is $-3/2$ and not $-9/2$ as suggested by other results. This discrepancy was explained by Fox and Hobson (and later substantiated in Refs. 85 and 86) as a result of dissociative recombination, via $A_0^+$ and $A_0^-$ metastable molecules, rather than a three-body collisional recombination.21,85,86 However, for the elevated temperatures associated with the present work, the existence of such molecules is questionable. As can be seen from Fig. 45, the Makin and Keck11 model gives a good description of the three-body, electron-ion-electron recombination rate constant for various atoms, provided an accuracy of about a factor of 4 is considered acceptable. This is not surprising as energy levels near the continuum (highly excited states) can be treated as hydrogenic levels. Only in the case of low energy levels will the specific structure of the atoms under consideration play an important role and only for these levels will the radiative transitions become significant. As the model of Makin and Keck11 neglects all radiative transitions, the low energy levels do not play any role. This explains the difference between the results of Biberman et al74 and those of Makin and Keck,11 as shown in Fig. 2. Since the present experimental work was performed for a very limited temperature range, it is impossible to verify the $(-9/2)$-power dependence of $K_R$ upon $T$. Even if one accepts the $(-9/2)$-power law as the appropriate relationship between $K_R$ and $T$, it is not possible to pin-point the value of the constant appearing in the Makin and Keck formulation because of the low accuracy to which $K_R$ is known (within a factor of 2). ($K_R = 2.3 \times 10^{-6} T^{-9/2} cm^6/sec$, Ref. 11).

However, the results shown in Fig. 45 and those presented in Table 2 substantiate the theoretical predictions for the three-body collisional recombination rate. The more detailed results from several theoretical models presented in Table 2 are seen to agree with the present data to within a factor of 4. (This accuracy can be considered as an optimum for a numerical evaluation of $K_R$.) An exception appears in the present results. The experimental value for a temperature of 11,000K (in Table 2) is much smaller than the values suggested by the theoretical models. This is explained by the fact that, at high temperature, the ionization term appearing in the rate equation (4.3) cannot be neglected as was done in the course of this work.

The reader may wonder about the narrow temperature range of the present experimental work. It can be explained by the following comments. A lower temperature limit is imposed by the minimum shock Mach number that will produce enough free electrons; in this case $T_{min} \approx 9,000K$. On the other hand, the maximum temperature of the plasma is also limited owing to the following reasons:
1. There is a structural limitation on the maximum driver pressure ($P_{\text{max}} \leq 10,000$ psi), which in turn introduces an upper limit on the primary shock Mach number. This maximum Mach number will dictate the maximum temperature behind the primary shock front.

2. As the primary shock Mach number increases, the post-shock temperature also increases. When the temperature behind the shock is sufficiently high, the inert degrees of freedom will be activated, which results in a decrease in temperature (due to the equipartition of energy). Therefore, as the primary shock Mach number is increasing, the degree of ionization will increase and little or no temperature increase will occur.\(^\text{80}\)

3. As the post-shock temperature increases, the radiation losses become more pronounced and this results in a decrease in temperature.

As a result of the above arguments, for primary shock Mach numbers $M_s > 18$ ($P_1 < 5$ torr), the post-shock temperature will remain approximately $13,000^\circ$K.

From the interferograms, such as those shown in Fig. 26 and Figs. A1, A8, A15, A22, A29, A36, A43 and A50 in Ref. 76) the angle of the expansion wave head can be measured. This was done using an enlarged format of these interferograms and the results are shown in Table 4. As can be seen, the best agreement is obtained between the experimental measurements and those based on the frozen flow Mach number after the appropriate correction for radiation losses have been made. Although the difference between the radiation-corrected and uncorrected wave angles for the frozen case is small (the effects of the radiation losses on the plasma temperature is moderate, see Fig. 27), the difference between the appropriate equilibrium and frozen wave-head angles is significant. This substantiates that the frozen Mach angles will describe the slope of characteristics in a reacting flow, as noted by Glass and Takano.\(^\text{37}\) The measurements of the expansion wave-head and tail angles can also be made using schlieren techniques. Results from a few schlieren pictures also appear in Table 3. As in the case of angles deduced from the interferograms, the schlieren results also agree very well with the frozen wave angles.

CHAPTER 5 CONCLUSIONS

In the review portion of the present work, an attempt was made to describe as fully as possible the equations of motion for supersonic expanding plasmas. It is apparent from this literature survey that a numerical evaluation of the recombination rate constant, $K_R$, imposes a significant difficulty. By adopting appropriate models, one can obtain values of $K_R$ that differ by up to four orders of magnitude for the same electron temperature and number density (see Table 1). This stems from the fact that, in general nonequilibrium, collisional and radiative processes have to be considered simultaneously, resulting in a very complex form of the governing rate equations. Naturally, various authors give different weight to the competing processes, in order to simplify the solution of the rate equations, and as a result there is great scatter in $K_R$ for given conditions.
In turn, the recombination process plays an important role in the supersonic expansion flow of plasmas. Therefore, the solution of a given expansion flow field will be highly dependent on the model adopted for $K_R$. This is especially the case for highly ionized gases.

Motivated by these arguments, experiments were performed in order to obtain some reliable data for $K_R$. The experimental findings, reported in Chapter 3, demonstrated that a Mach-Zehnder interferometer, equipped with a laser as a light source, can provide accurate results for plasma properties. The sensitivity of this diagnostic technique can also be adjusted to favour certain species of the plasma (electrons or heavy particles) by choosing the proper wavelengths of the light source. (As can be seen from Eq. (3.3) the fringe shift due to density changes in the electron gas is proportional to $\lambda$ while in the heavy particle gas it is proportional to $1/\lambda$).

Very good agreement was obtained between the experimental values for $\rho$ and $\alpha$ and those predicted by Glass and Takano. These results substantiate that the method of characteristics can be applied successfully even to complex supersonic flows. Measurements of the expansion-wave head show that the 'frozen' Mach angle describes the characteristic slope in a reacting flow in agreement with theory.

Measurements of the small attenuation of the primary shock wave ruled out the possibility that the viscous boundary layer growth will contribute to the changes in the plasma properties downstream of the shock front. This leaves the radiation loss as the main loss mechanism (heat transfer into the viscous layer is also a factor. It was found that it will have a significant effect on the post-shock degree of ionization and only a moderate influence on the other parameters.

The values obtained for the plasma recombination-rate constant in argon substantiate the theoretical predictions for three-body, electron-ion-electron collisional recombination. The values obtained are more accurate than other experimental values, as the present facility creates a relatively clean and well-defined (uniform) plasma. The interferometric diagnostics used are not limited to certain thermodynamic equilibrium states. The data for $K_R$ are the first gasdynamically obtained values reported for temperature higher than 5,000$^\circ$K. The accuracy of these values is to within a factor of two. However, due to limitations inherent in the investigated system, the temperature range of this experimental work is rather narrow by current high-temperature studies ($9,000 < T < 13,000^\circ$K). Consequently, no definite conclusion about the power law dependency of $K_R$ upon $T$ can be drawn. In any case, the numerical results based on the (-9/2) power law dependency are in good agreement with those obtained in the present study. This law can be used as a reliable guide in extrapolating the expected value of $K_R$ to very high temperatures.
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CURVE A, \[ K_1 = 10^{-6} \frac{2KT}{(\pi m_0)^{1/2}} \left\{ 4.4 \left( \frac{\beta}{T} + 2 \right) e^\frac{\Theta}{T} + 9.5 \left( \frac{\Theta}{T} + 2 \right) e^\frac{\Theta}{T} + 4.4 \frac{\beta}{T} \left( 1 + \frac{\Theta}{T} \right) \frac{T}{T^2} \right\} \]

\[ \Theta = 182,850^\circ K \]
\[ \beta = 134,000^\circ K \]

CURVE B, \[ K_2 = 1.5 \times 10^{-12} T_{ev} \times 6.21 \times T^{1/2} \left( \frac{\Theta}{T} + 2 \right) e^\frac{\Theta}{T} \]

FIG. 1 VARIATION OF IONIZATION RATE CONSTANT, \( K_1 \), WITH ELECTRON TEMPERATURE, \( T_e \), FOR ARGON PLASMA
**FIG. 2** VARIATION OF RECOMBINATION RATE CONSTANT, $K_R$, WITH ELECTRON TEMPERATURE, $T_e$, FOR ARGON PLASMA

\[ K_R = 2.3 \times 10^{-8} \frac{T_e^{-9/2}}{T} \]  

(Ref. II)

\[ K_R = \frac{4.3 \times 10^{-32} \frac{E_H}{T}^{9/2}} {\left( 1 + \frac{g_i}{g_f} \left( \frac{E_i}{T_e} \right) + b \frac{E_H}{T_e} e^{\frac{-E_2}{T_e}} (13.3 a)^{-1} \right)^2} \]
FIG. 3 VARIATION OF THREE-BODY (ELECTRON-ION-ELECTRON) RECOMBINATION RATE CONSTANT, $K_R$, WITH ELECTRON TEMPERATURE, $T_e$, FOR OPTICALLY THIN HYDROGEN PLASMA (REF. 8)
FIG. 4 VARIATION OF THREE-BODY (ELECTRON-ION-ELECTRON) RECOMBINATION RATE CONSTANT, $K_R$, WITH ELECTRON TEMPERATURE, $T_e$, FOR OPTICALLY THICK (TOWARDS THE LYMAN SERIES) HYDROGEN PLASMA (REF. 8)
FIG. 5 VARIATION OF THREE-BODY (ELECTRON-ION-ELECTRON) RECOMBINATION RATE CONSTANT, $K_R$, WITH ELECTRON TEMPERATURE, $T_e$, FOR ARGON PLASMA (REF. 64)
FIG. 6

GEOMETRY OF QUASI-ONE-DIMENSIONAL FLOW OF A NOZZLE CONTOUR WITH $\theta = 15$
HYDROGEN 
$\sigma(\lambda)=0$, THE PLASMA IS OPTICALLY THIN
$\sigma(\lambda)=\infty$, THE PLASMA IS OPTICALLY THICK

FIG. 7

HYDROGEN 
$\sigma(\lambda)=0$
$\theta = 15^\circ$
$\sigma(\lambda)=\infty$

FIG. 8A

FIG. 8B

FIG. 9A

FIG. 9B
FIG. 9B
ELECTRON NUMBER DENSITY VS NOZZLE AREA RATIO (REF. 2D).

FIG. 10A
HEAVY-PARTICLE AND ELECTRON TEMPERATURE VS NOZZLE AREA RATIO (REF. 2D).

FIG. 10B
HEAVY-PARTICLE AND ELECTRON TEMPERATURE VS NOZZLE AREA RATIO (REF. 2D).

FIG. 11
MASS NUMBER VS NOZZLE AREA RATIO (REF. 2D).
FIG. 12A MEASURED VALUES OF THE MEAN ELECTRON DENSITY AT MEASURED POINTS ALONG THE NOZZLE (REF. 30).

FIG. 12B MEASURED RATE COEFFICIENT AS FUNCTION OF ELECTRON DENSITY AT UPSTREAM STATION (FIRST WINDOW) (REF. 30).
FIG. 13 VARIATION OF ELECTRON TEMPERATURE, $T_e$, WITH DISTANCE MEASURED ALONG THE NOZZLE AXIS FOR ARGON PLASMA (REF. 31)

FIG. 14 VARIATION OF ELECTRON NUMBER DENSITY, $N_e$, WITH DISTANCE MEASURED ALONG THE NOZZLE AXIS FOR ARGON PLASMA (REF. 31)
FIG. 15 VARIATION OF RECOMBINATION RATE CONSTANT WITH ELECTRON TEMPERATURE FOR ARGON PLASMA (REF. 21)
FIG. 16

PHYSICAL COORDINATE SYSTEM OF A STEADY, INVISCID, TWO DIMENSIONAL FLOW (REF. 37)
FIG. 17  NONEQUILIBRIUM FLOW OF IONIZING ARGON AROUND A CORNER (REF. 37)
FIG. 18 X-T WAVE DIAGRAM FOR SUGGESTED EXPERIMENTAL SET-UP TO MEASURE THE RECOMBINATION RATE CONSTANT (REF. 35)
FIG. 19  MAXIMUM FLOW MACH NUMBER ($M_2$) FOR A GIVEN GEOMETRY WHERE AN ATTACHED SHOCK IS STILL POSSIBLE (REF. 35)²
FIG. 20B  WALL MODEL (REF. 48) USED IN CORNER-EXPANSION STUDIES OF IONIZED GASES

FIG. 20A  WEDGE MODEL (REF. 48) USED IN CORNER-EXPANSION STUDIES OF IONIZED GASES
FIG. 20C MODIFIED WEDGE MODEL WITH WINDOW-SHIELD USED IN CORNER-EXPANSION STUDIES OF IONIZED GASES
FIG. 21  SUGGESTED FACILITY FOR RECOMBINATION STUDIES IN EXPANDING PLASMA FLOW
(REF. 44)
(a) Driver Section

(b) Driven Section

FIG. 22 VIEWS OF SHOCK TUBE FACILITY
FIG. 23 PRIMARY SHOCK WAVE ATTENUATION MEASUREMENTS

A, B, C, D, E, H, I, J = ATLANTIC RESEARCH LD-25 PRESSURE TRANSDUCERS
F, G = KISTLER TRANSDUCERS

(PRIMARY SHOCK WAVE ATTENUATION MEASUREMENTS

(RUN 36, \( P_i = 4.25 \) TORR, \( T_i = 299.8^\circ K, M_s = 16.8 \))

X (FT)
FIG. 24 ELECTRONIC BLOCK DIAGRAM

1. HEWLETT-PACKARD 465A AMPLIFIER
2. U.T.I.A.S. COUNTER, RESOLUTION 0.1 µSec.
3, 4, 5. HEWLETT-PACKARD 3734A ELECTRONIC COUNTER
   (RESOLUTION 10 µSec., 1 µSec. WITH EXTERNAL CRYSTAL)
6, 17. RACAL DIGITAL MICROSECOND CHRONOMETER TYPE SA.45
   (RESOLUTION 1 µSec.)
7. TEKTRONIX SCOPE 555
8. J2, J1, B. IMPEDANCE MATCHING UNIT
10. HEWLETT-PACKARD UNIVERSAL COUNTER 5325 A
    (RESOLUTION 0.1 µSec.)
11. POCKEL-CELL POWER SOURCE & DELAY UNIT
12. TRG-104A LASER POWER SOURCE
13. TRG-104A PULSED-LASER (EQUIPPED WITH Q-SWITCH &
    SECOND HARMONIC GENERATOR)
FIG. 25: SCHEMATIC MACH-ZEHNDER INTERFEROMETER
FIG. 26  FINITE-FRINGE INTERFEROGRAM OF CORNER-EXPANSION FLOW OF AN ARGON PLASMA
FOR A SHOCK MACH NUMBER $M_s = 13.5$, INITIAL PRESSURE $p_1 = 9.06$ TORR,
INITIAL TEMPERATURE $T_1 = 295.4^\circ$K AND $t_s = 52.5$ nSEC
FIG. 27 EFFECTS OF RADIATION LOSSES BEHIND A NORMAL SHOCK WAVE IN ARGON (REF. 84) WITH $M_s = 16.3$ AND $T_\perp = 296 \text{ K}$
FIG. 28A VARIATION OF TOTAL PLASMA DENSITY, $n_e$, VERSUS DISTANCE $x$. INITIAL CONDITIONS ARE AT $M_s = 19.05$, $P_1 = 1.83$ TORR AND $T_l = 296.1$ K.

FIG. 28B VARIATION OF DEGREE OF IONIZATION, $\alpha$, WITH DISTANCE $x$. INITIAL CONDITIONS ARE GIVEN IN FIG. 28A.
FIG. 28C

$\alpha$ VERSUS $X$

$P_r=278$ Torr, $T_i=29746^\circ K, M_a=165$

FIG. 28D

$n_e$ VERSUS $X$

$P_r=278$ Torr, $T_i=29746^\circ K, M_a=165$
FIG. 29 VARIATION OF TOTAL PLASMA DENSITY, $\rho$, VERSUS DISTANCE X.
INITIAL CONDITIONS ARE $M_s = 13.5$, $p_i = 9.06$ TORR AND $T_1 = 295.4$ K.
INTERFEROMGRAM (RUN 10) WAS TAKEN 52.4 $\mu$SEC AFTER THE PRIMARY SHOCK WAVE PASSED THE CORNER.
FIG. 30 SCHEMATIC FRINGE PATTERN FOR EXPANDING PLASMA
FIG. 31 SCHEMATIC SUPERPOSITION OF FLOW AND NO-FLOW INTERFEROGAMS
FIG. 33 STATIC PRESSURE BEHIND PRIMARY SHOCK FRONT
FIG. 34  INITIAL FLOW STRUCTURE DOWNSTREAM OF EXPANSION CORNER. THE INITIAL CONDITIONS ARE \( M_s = 6.68 \), \( p_1 = 9.80 \) TORR AND \( T_1 = 296.8 \) K
FIG. 35 RELAXATION ZONE BEHIND STRONG SHOCK WAVES. INITIAL CONDITIONS ARE $M_s = 19.05$, $p_1 = 1.83$ TORR AND $T_1 = 296.1$ K (~2000 P.P.M. HYDROGEN IN ARGON)
FROZEN WAVE HEAD

FREE STREAM

ZONE 1

FROZEN P-M EXPANSION FLOW AT THE CORNER

ZONE 2

ZONE 3

EXPANSION WAVE TAIL

ZONE 4

FIG. 39 SCHEMATIC DIAGRAM OF CHARACTERISTIC NET FOR A CORNER-FLOW EXPANSION

$P_i, T_i, \rho_i, \alpha_i, M_i, \theta_i = 0^\circ$
FIG. 40  $K_R$ VERSUS $X$, Run 10

$p_i = 9.06$ torr, $T_i = 295.4 \degree K$, $M_s = 13.5$, $t_s = 52.5 \mu s$
FIG. 41

FIG. 42

FIG. 43

ILLUSTRATION OF DIFFRACTION OF LIGHT RAYS DUE TO DENSITY GRADIENT (Ref. 27)
Fig. 44 Variation of degree of ionization, $\alpha$, with distance from corner $X$. Initial conditions are $M = 15.64$, $P_1 = 2.25 \text{ mmHg}$ and $T_1 = 298.9 \text{ K}$ (Run 1).
FIG. 45  VARIATION OF RECOMBINATION RATE CONSTANT WITH ELECTRON TEMPERATURE, T. 
PRESENT EXPERIMENTAL RESULTS ARE COMPARED WITH OTHER THEORETICAL 
AND EXPERIMENTAL RESULTS
In the supersonic expansion of an ionized gas, the dominant factor in describing the atomic processes is the recombination rate constant $K_r$. Several models describing the recombination process have been reviewed in some detail. A comparison of experimentally and theoretically derived values for $K_r$ has to be done with great care, as in the majority of the experiments $K_r$ is determined from the measured rate of disappearance of free electrons. In the light of the important role that $K_r$ plays in any numerical solution of non-equilibrium expansion flow of plasmas, details of experiments on a 15-degree corner expansion flow of ionized argon are given. Using a dual-frequency-laser interferometer, the plasma properties around a corner expansion were recorded. The analysis of the interferograms has yielded values for the recombination rate constant as a function of the plasma macroscopic properties. The range of shock Mach-number, electron number density, temperature and initial channel pressure and temperature were as follows:

$$13 < M_s < 19; \quad 10^{16} < n_e < 1.5 \times 10^{17} \text{cm}^{-3}; \quad 9,000 \text{K} < \tau < 13,000 \text{K}$$

$$2.2 < p_i < 10 \text{ torr}; \quad T_1 = 300 \text{K}$$

It was found that the theoretically predicted values for the three-body, electron-ion-electron collisional-recombination rate are in good agreement with those measured gasdynamically in a well-defined flow. The measured flow quantities substantiate a previous analysis based on the method of characteristics.

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