SUPersonic Expansion Flow of an Ionized Gas

by

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Summary

In a supersonic expansion of an ionized gas, the dominant factor in describing the atomic processes is generally 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 between experimental and theoretical values of $K_R$ becomes even more complex since 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 value of $K_R$.

For electron temperatures and number densities in the ranges $10,000 < T_e < 20,000^\circ K$ and $10^{15} < n_e < 10^{18} \text{ cm}^{-3}$, the "collisional-radiative" model, suggested by Bates et al, appears to be the most promising model. It has been used by many authors in their attempt to solve the equations of motion for a supersonically expanding plasma.

In general, for steady, quasi-one-dimension plasma flows, fair agreement exists between theoretical predictions (numerical solutions of the equations of motion) and the experimental results.
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K(T)  Equilibrium constant based on concentration
M_s  Principal shock Mach number
m  Mass
N  Number of collisions per unit time
n  Number density, refractive index
P  Pressure tensor
p  Pressure
P_l  Pre-shock pressure in a shock tube
Q  Energy source term, appearing in the energy balance Eq. (1.6)
Q_rad  Radiation loss
q  Heat transferred per unit area per unit time
r  Thompson distance
S_{ij}  Fringe shift (from zone i to zone j)
s  Distance
T  Temperature
t  Time
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
\alpha  Degree of ionization
\epsilon  Internal energy
\epsilon_p  Energy of excited atom in level p
\theta  Velocity vector direction
\lambda  Debye length, wave length
\( \nu \) Collisions frequency; frequency
\( \rho \) Density
\( \sigma \) Collision cross-section, electrical conductivity
\( \phi_s \) Property of species \( s \)
\( \varphi \) Basic distribution function
\( \psi_s \) Total energy of a particle of species \( s \)
\( \omega \) Frequency
\( \dot{\omega}_s \) Rate of creation (or disappearance) of particles of species \( s \)
\( \Delta r \) Volume element

**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
- \( g s \) ground state
- \( e x c \) excited state
- \( e x t \) external

**SUPERSCRIPTS**

- \( i, j \) directions
- \( c \) collisional process
- \( r \) radiative process
SPECIAL NOTATION

\[ \frac{dn_e}{dt} \] the rate of creation of free electrons per unit volume

\[ K_{c}^{s,c} \] 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

NOTE: In the literature, several forms of the recombination rate constant have been used. The relation between the different forms is;

\[ K_{R}' = K_{R} \times n_e \left[ \frac{cm^3}{sec} \right] \]

\[ K_{R}'' = K_{R} \times N_A^2 \left[ \frac{cm^6}{mole^2 sec} \right] \]

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

This review is a result of a literature survey done as a first step in preparation for an experimental investigation of a corner expansion flow of ionized argon.

The main difficulty one faces when working with supersonic flows of ionized gases stems from the coupling between the flow properties and the atomic processes taking place in the flow. The papers reviewed for this literature survey can be divided into two categories. One category contains the work performed on quiescent plasmas in which emphasis is placed on the atomic processes expressed in terms of ionization and recombination rate constants, and transition probabilities. In this case, gasdynamic effects are either neglected or over-simplified. The reverse is true for the second category generally involving moving plasmas where the gasdynamics is emphasized and the atomic processes are over-simplified. An effort will be made to introduce a model which places emphasis on both. The paper by Appleton and Bray\(^1\) is adopted to describe the general formulation of the flow equations of motion. For the 'collisional-radiative' model describing a decaying plasma, our description follows the work of Bates et al\(^8\) and Byron et al\(^2\), whereas, for steady, quasi-one-dimensional, ionized flow, the paper of Talbot et al\(^28\), is adopted.

The review is designed to supply a background for the experimental program where the electron number densities are in the range of \(10^{16}\) to \(10^{17}\) cm\(^{-3}\), and the temperatures are around 12,000\(^\circ\)K (1 eV). In this region the collisional-radiative recombination model looks most promising.

In the first chapter of this review, the general formulation of the plasma equations of motion is described. These equations contain the effects of gasdynamic and atomic processes on the flow. In Chapter 2, different ways of accounting for the contribution of the atomic processes to the equations of motion will be discussed. In Chapter 3, an application of the suggested collisional-radiative recombination model will be made for solving the simple case of a steady, quasi-one-dimensional, ionized flow. Since the key factor for a proper description of the decaying process in plasmas is the recombination rate constant, some techniques for evaluating this constant experimentally will be given in Chapter 4. The last chapter, Chapter 5, will contain a brief discussion of a steady two-dimensional nonequilibrium ionized flow. In this chapter some of the preliminary results obtained in our research on ionized-argon, corner-expansion flows will be presented.

The principle aim of this review is to present a method for expressing the recombination and ionization rate constants in terms of the plasma properties, such as the electron temperature and number density.

Some misunderstanding appears to exist as to the meaning of the recombination rate constant, \(K_R\). Therefore, various definitions and theoretical models for evaluating the recombination rate constant are reviewed in some detail in chapter 2. As explained in this chapter, most of the theoretical models will lead to values of \(K_R\) different from that obtained experimentally. This arises from the use of different definitions for \(K_R\). In the experimental work the recombination process will be considered as complete when a free electron is captured by an ion to create an atom, independent of the electronic state to which the electron recombined. In most of the theoretical models a recombination event is considered complete only when the free electron is captured.
into low lying states, mainly the ground state, since the probability of re-
ionization is much higher for an excited atom than for a ground-state atom.

For experimental set-ups in which the electron temperature falls very
rapidly, the re-ionization is negligible, and the theoretical predictions are
in fair agreement with the experimental results.

CHAPTER 1. THE GENERAL EQUATIONS OF MOTION OF AN IONIZED GAS

Following the work of Appleton and Bray, we will begin with the general
case of a plasma consisting of several different species. For such a plasma a
general macroscopic balance equation for any property \( \phi_s \) of the species \( s \), can be expressed as:

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

(1.1)

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) will give the usual
continuity equation,

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

(1.2)

In this case, the source term \( I(\phi_s) = \dot{\omega}_s \) is the rate of creation (or disappear-
ance) of particles of the species \( s \) per unit volume per unit time, where,
\( \rho_s = m_s n_s \) is the density of the 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
species \( s \) particles, i.e., \( \phi_s = < \frac{1}{2} m_s v_s^2 > \), Eq. (1.1) will give the momentum
balance for species \( s \):

\[
\frac{\partial}{\partial t} (\rho_s u^i_s) + \frac{\partial}{\partial x^j} (\rho_s u^i_s u^j_s) + \frac{\partial P^{ij}_s}{\partial x^j} = I(\frac{1}{2} m_s v^2_s)
\]  

(1.3)

where \( P^{ij}_s = \rho_s < c^{i}_s c^{j}_s > \) is the pressure tensor and \( c^{i}_s \) is the thermal velocity
for individual particles of the species \( s \), defined by the relation:
\( c^{i}_q = v^{i}_q - u^{i}_q \) for the \( q \)-th particle of the species \( s \). The source term in Eq. (1.3),
\( I(\frac{1}{2} m_s v^2_s) \) 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:

\[
I(\frac{1}{2} m_s v^2_s) = \frac{1}{\Delta t} \sum q \sum k F^{i}_{qs k} + \frac{1}{\Delta t} \sum q C^{i}_{qs} + c^{i}_s
\]  

(1.4)
where $F_{\text{Sk}}^i$ 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 $\Delta V$. $G_{qs}^i$ is the $i$-component of the external force acting on the particle $q$ and $C_{qs}^i$ 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 particle $q$ of the species $s$, i.e. $\phi_{qs} = \psi_{qs} + \frac{1}{2} m_s v_{qs}^i v_{qs}^i$ where $\psi_s$ is the internal energy energy of the particle $q$, then the energy balance equation is obtained as

$$\frac{\partial}{\partial t} \left[ \varepsilon_s + \frac{1}{2} \rho_s u_s^i u_s^i \right] + \frac{\partial}{\partial x_j} \left[ (\varepsilon_s + \frac{1}{2} \rho_s u_s^i u_s^i) u_s^j + p_{ij} u_s^i + q_s^j \right] = I(\psi_s + \frac{1}{2} m_s v_{qs}^i v_{qs}^i) \quad (1.5)$$

where

$$\varepsilon_s = n_s \langle \psi_s \rangle + \frac{1}{2} \rho_s \langle c_i^i \rangle$$

$\varepsilon_s$ is the total internal energy of the species $s$ per unit volume and $\partial \phi_{qs}^i / \partial x_j^j$ is the thermal conduction within the species $s$. The right-hand side of Eq. (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. (1.4), we can express the right hand side of Eq. (1.5) as follows:

$$I(\psi_s + \frac{1}{2} m_s v_{qs}^i v_{qs}^i) = \frac{1}{\Delta V} \sum_q \sum_k F_{qs}^i + \frac{1}{\Delta V} \sum_q G_{qs}^i v_{qs}^i + Q_s \quad (1.6)$$

In the above equation, $Q_s$ represents the amount of energy supplied to constituent $s$ during inelastic collisions. From Eqs. (1.5) and (1.6), after eliminating the kinetic energy term, $\frac{1}{2} \rho_s u_s^i u_s^i$, with the help of Eqs. (1.3) and (1.4), we have the final form of the energy balance equation as,

$$\frac{\partial \varepsilon_s}{\partial t} + \frac{\partial}{\partial x_j} \left[ \varepsilon_s u_s^j + p_{ij} u_s^i \right] = u_s^i \frac{\partial p_{ij}}{\partial x_j} - \frac{\partial q_s^j}{\partial x_j} + \frac{1}{\Delta V} \sum_q \sum_k F_{qs}^i c_{qs}^i$$

$$+ \frac{1}{2} u_s^i u_s^i \omega_s - u_s^i C_s^i \quad (1.7)$$

As can be seen, the left-hand sides (LHS) of Eqs. (1.2), (1.3) and (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 collision processes, and the effect of the external and internal electric and magnetic fields on the charged particles of the plasma. As previously noted, for most of the work done on supersonic flowing plasma, cases were selected in which the atomic processes were either neglected or, at most, given a very small role. In some cases unrealistic over-simplifications were made. On the other hand in the work performed on decaying
plasmas, the influence of the flow phenomena was generally neglected.

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. (1.2), (1.3) and (1.7) and attempt to solve them for certain flows.

CHAPTER 2. THE ATOMIC PROCESSES IN A PLASMA

2.1 Elastic Collisions

In this chapter we will calculate some of the terms which appear in the right hand side (RHS) of Eqs. (1.2), (1.3) and (1.7); i.e., the terms $\omega^s$, $F^s$, $G^s$, $C^s$ and $Q^s$. The above terms represent the effects of the collision processes 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 will deal only with elastic collisions. To simplify the analysis we will assume henceforth 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 $Z e$, where $Z$ indicates the number of electrons that were removed from the atom. (Subsequently we will 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 will adopt the binary collision model, since the experimental work shows that the results for the average properties of the plasma calculated with the binary model, agree well with the experimental results. In the following we will describe briefly two ways for 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. $E^i$ denotes 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. Since we have moving 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:

$$
\sum_{(d > \lambda^s)} F^i_{qs} = e_s \left[ E^i - \left( \nabla^i_{qs} \times B \right) \right]
$$

(2.1)

where the sum is taken over all particles $K$, which are at distance $d > \lambda^s$, the Debye length for the particle $q$. The fields $E$ and $B$ can be reinforced if external fields are present. In such a case the forces acting on all the particles of the species $s$, within the volume $\Delta r$ are given by.
The rate at which energy is transferred to the charged particles due to the long range collisions can be found by multiplication of Eq.(2.2) with the particle speed $V_{qs}$, which will yield:

$$\sum_{q} \sum_{k} f_{qsk} i + \sum_{q} G_{qs} = n e_{s} \left[ E^{i} + E_{ext}^{i} + \left( \hat{u}_{s} \times (\hat{B} + \hat{E}_{ext}) \right)^{i} \right] \Delta \tau$$  \hspace{1cm} (d > \lambda) \hspace{1cm} (2.2)

To complete the formulation it is necessary to evaluate $\mathbf{E}$ and $\mathbf{B}$ from the space distribution and mean 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 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:

$$\sum_{q} \sum_{k} F_{qsk} \cdot v_{qsk} = \frac{m_{s} m_{k}}{m_{s} + m_{k}} n_{s} n_{k} \int (\mathbf{g} \cdot \mathbf{G}) \sigma_{sk}(\mathbf{g}) f_{s} f_{k} \, d\mathbf{\hat{v}}_{k} \, d\mathbf{\hat{v}}_{s} \, \Delta \tau$$  \hspace{1cm} (2.3)

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:

$$\sum_{q} \sum_{k} F_{qsk} \cdot v_{qsk} = \frac{m_{s} m_{k}}{m_{s} + m_{k}} \int (\mathbf{g} \cdot \mathbf{G}) \sigma_{sk}(\mathbf{g}) f_{s} f_{k} n_{s} n_{k} \, d\mathbf{\hat{v}}_{k} \, d\mathbf{\hat{v}}_{s} \, \Delta \tau$$  \hspace{1cm} (2.4)

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

Equations (2.4) and (2.5) can be solved only if the distribution functions $f_{s}, f_{k}$ and the collision cross section $\sigma_{sk}(\mathbf{g})$ are known. One of the cases for which the equations are solvable is when the particles have a
Maxwellian velocity distribution. We will show briefly how the integration of Eqs. (2.4) and (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 for isentropic flow it can be proven that the velocity distribution is Maxwellian. Kantrowitz and Petschek\(^4\) 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\(^6\).

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

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

where \(T_s = \frac{m_s <c_s^2>}{3k}\) is the species temperature. To simplify the integration of Eqs. (2.4) and (2.5) the following assumptions are made\(^1\):

1. The thermal energy of the heavy particles is smaller or at most of the same order as that of the electrons, i.e., \(c_i = 0\) \([c_e \sqrt{m_e/m_i}]\) (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 \(u_{i}^a = u_{i}^i \equiv u^i\) (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 \(W_{e}^i\) (defined by \(W_{e}^i = u_{e}^i - u^i\)) obeys the condition

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

The above assumptions will simplify the integration process in Eqs. (2.4) and (2.5), and after some algebra one obtains\(^1\)
and
\[ \sum \sum \tilde{F}_{qek} \Delta \tau = -n \sum \nu_{ek} \tilde{w}_{e} \Delta \tau \tag{2.7} \]
\[(d<\lambda)\]

where \( \nu_{ek} \) 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:
\[ \nu_{ek} = \frac{4\pi m_{k} m_{e}}{3kT_{e}} \int f_{e} \sigma_{ek}(c_{e}) c_{s}^{5} dc_{e}. \tag{2.9} \]

The energy due to the internal field is given by
\[ \frac{1}{\Delta \tau} \sum \sum \tilde{F}_{qek} \tilde{q}_{e} = 2n \sum \nu_{ek} \frac{m_{k}}{m_{e}} \frac{3}{2} \frac{k(T_{e} - T_{i})}{m_{e}} \frac{(\tilde{w}_{e})^{2}}{m_{k}} \Delta \tau \tag{2.10} \]

For the case of Coulomb collisions between electrons and ions, the collision cross-section is
\[ \sigma_{ei} = 2\pi \frac{4}{m_{e}^{2} m_{i}^{2}} \ln \left[ 1 + \frac{2}{m_{e}^{2} m_{i}^{2}} \right] \tag{2.11} \]

where \( h \approx \lambda, \lambda \) is the Debye length \( = \frac{kT_{e}}{e} \frac{1}{4\pi n_{e} m_{e}} \) c.g.s.

The collision frequency between the electrons and ions is:
\[ \nu_{ei} = \frac{8}{3} \sqrt{\frac{\pi}{m_{e}}} n_{e} \frac{1}{(2kT_{e})^{3/2}} \ln \left[ \frac{(kT_{e})^{3}}{m_{e} n_{e}^{6}} \right] \tag{2.12} \]

Equations (2.11) and (2.12) agree very well with the results of Petschek and Bryon and Goldsworthy although they neglect the effect of electron diffusion.

The collision frequency between the electrons and atoms is:
Values for the collision cross-section \( \sigma_{ea} \) can be found from Massey and Burhop\(^7\) and Morse\(^{27}\).

Until now we have accounted only for the contribution of the elastic collisions to the atomic processes appearing in the equations of motion, Eqs. (1.2), (1.3) and (1.7). We evaluated \( F \) with atomic constants and the gross properties of the plasma \((n_a, n_e, T, T_e, u, u_e)\). To complete the conservation equations, we have to express the rest of the atomic processes, \( Q, C \) and \( \omega \) appearing in the RHS of Eqs. (1.2), (1.3) and (1.7), in terms of the plasma macroscopic properties. To do so we need to know the exact manner in which the atomic processes take place. For example, \( \omega \) 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 \( \omega \), 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.

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 will be in the processes occurring during the expansion of a supersonic flow of an ionized gas. The following processes can take part simultaneously during an expansion (see Refs. 8, 13, 24, 66)

\[
A_p + e \xrightarrow{K_{pc}} A^+ + e + e
\]  
\[
A_p + e \xrightarrow{K_{pq}} A_q + e , \ (p < q)
\]  
\[
A_p \xrightarrow{A_{pq}} A_q + h\nu \ (p > q)
\]

and

\[
A^+ + e \xrightarrow{\beta_p}{\beta_c} A_p + h\nu
\]

where \( A \) refers to neutral atoms, \( p \) and \( q \) refer to two discrete energy levels of the atom, \( \nu \) is the transition radiation 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. (2.14) to (2.17) and accordingly neglect some of them relative to others. If the plasma density and degree of ionization are high (for example \( n_a > 10^{18} \ \text{cm}^{-3}, \ T_e = 1 \ \text{eV}, \ \alpha > 5\% \)) the radiation processes can be neglected compared to the collision processes, i.e., we can ignore Eqs. (2.16) and (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 greater than the probability of falling through many energy levels to the ground state), then we can ignore Eq. (2.15) and the only process we have to deal with is described in (2.14).

A further simplification, which we will adopt from now on, is that the plasma is singly ionized (since we are interested in argon plasmas at temperatures around 1 eV and electron densities of approximately \( 10^{17} \ \text{cm}^{-3} \), this assumption is quite justified).

In such a simple model (using Eq. (2.14) only), the rate of producing free electrons can be expressed as

\[
\frac{dn_e}{dt} = K_i n_e n_p - K_R n_e^3,
\]

where \( \frac{dn_e}{dt} \) is the rate of production of free electrons per unit volume,

\( K_i \) is the ionization rate constant, \( \text{cm}^3\text{sec}^{-1} \),

and

\( K_R \) is the recombination rate constant, \( \text{cm}^6\text{sec}^{-1} \).

If the rate constants \( K_i \) and \( K_R \) (which turn out to be highly temperature dependent) are known, then we can express \( \frac{dn_e}{dt} \) in terms of the plasma macroscopic properties \( T_e, n_e \) and \( n_a \).

In the more general case, the collisional transition rates \( K_{pc}, K_{cp}, K_{pq}, \) and \( K_{qp} \), appearing in Eqs. (2.14) and (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. \( K_{pq} = \langle \sigma v \rangle \)). 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.

The most widely quoted electron-atom inelastic cross-section is the one suggested by Gryzinski, which we will now look at in some detail. Gryzinski treats 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 Gryzinski 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 \( \vec{V}_1 \), the free electron a velocity \( \vec{V}_2 \), and \( \theta \) is the angle between the velocity vectors \( \vec{V}_1 \) and \( \vec{V}_2 \). If due to the collision electron 2 undergoes a change in energy \( \Delta E \), the cross-section is given by
\[
\sigma(\Delta E) = \frac{2\pi}{\Delta E^2} \int_{\theta_{\min}}^{\theta_{\max}} \frac{f(\theta)}{\mathbf{V}} \left( \frac{\mathbf{V}_1^2}{2} \mathbf{V}_2^2 \frac{\sin^2 \theta}{2\Delta E} - \mathbf{E}_2^2 + \mathbf{E}_1^2 \right) \, d\theta,
\] (2.19)

where \( V = (\mathbf{V}_1^2 + \mathbf{V}_2^2 - 2\mathbf{V}_1 \mathbf{V}_2 \cos \theta)^{1/2} \) is the initial relative velocity of the two electrons and \( f(\theta) = \frac{V}{V_2^2} \sin \theta \) is the relative angular distribution function between the vectors \( \mathbf{V}_1 \) and \( \mathbf{V}_2 \). If the free electrons (electron2) moves through a collection of bound electrons (electron1) which have an isotropic distribution of velocities, then \( \cos \theta_{\max,\min} = \begin{cases} \pm X & \text{if } |X| \leq 1 \\ \pm 1 & \text{if } |X| > 1 \end{cases} \) (2.20)

where

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

The cross-section for a collision in which electron 2 loses energy greater than \( I \) is \( Q(I) \) (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 \( \sigma \) (2.22)

Gryzinski has shown that the calculation can be greatly simplified if we replace the relative velocity \( V \) by \( (\mathbf{V}_1^2 + \mathbf{V}_2^2)^{1/2} \), 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 \( Q \) (2.23)
where $E_0$ 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

$$
\sigma_{\text{exc}} = \left\{ \begin{array}{ll}
\frac{\sigma_0}{\Delta E^2} \left( \frac{E_2}{E_1+E_2} \right)^{3/2} \left\{ \frac{2}{3} \left[ \frac{E_1}{E_2} + \frac{\Delta E}{E_2} \left( 1 - \frac{E_1}{E_2} \right) - \left( \frac{\Delta E}{E_2} \right)^2 \right] \right\} & \text{for } \Delta E + E_1 \leq E_2 \\
\frac{\sigma_0}{\Delta E^2} \left( \frac{E_2}{E_1+E_2} \right)^{3/2} \left\{ \frac{2}{3} \left[ \frac{E_1}{E_2} + \frac{\Delta E}{E_2} \left( 1 - \frac{E_1}{E_2} \right) - \left( \frac{\Delta E}{E_2} \right)^2 \right] \right\} \times \\
\left[ \left( \frac{1 + \Delta E}{E_1} \right) \left( 1 - \frac{\Delta E}{E_2} \right) \right]^{1/2} & \text{for } \Delta E + E_1 \geq E_2
\end{array} \right. \quad (2.24)
$$

where for both expressions $\sigma_0 = \pi e^4 = 6.53 \times 10^{-14} \text{ cm}^2 \text{ ev}^2$.

In order to determine the range of validity of Gryzinski's semi-classical theory for inelastic electron-atom collisions, Kingston5 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 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 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 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 $E_0/E_2$ fall-off of the Born cross-section. The experimental results suggest that $\sigma_{e-a} \sim E_2$ at the threshold 10.

We will now review several ways of evaluating the rate constants $K_I$ and $K_R$. 

11
Evaluation of the Ionization Rate Constant $K_I$

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

$$N = n_a n_e \int_{V_i}^{\infty} \sigma_{e} (V_e) f_e (V_e) V e dV,$$

where

$$\sigma_{e} (V_e)$$ 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,

$$K_i = \frac{N}{n_a n_e} = \int_{V_i}^{\infty} \sigma_{e} (V_e) f_e (V_e) V e dV.$$

Assuming that the distribution function, $f_e$ is Maxwellian, then the integral on the R.H.S. of Eq. (2.26) can be evaluated, provided it is possible to express $\sigma_{e} (V_e)$ explicitly as a function of the velocity. Since we are dealing with argon plasmas 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., $e_\epsilon \approx I + kT$, ($I = 15.6$ eV for argon). 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

$$\sigma_{e} = C (e_\epsilon - I)$$

where $C$ is a proportionality constant. In Fig. 1 the results of some experimental work on argon total collision cross-sections are presented. As can be seen from this experimental evidence, the proportionality constant $C$ is $C = 1.5 \times 10^{-17} + 12\% cm^2 (eV)^{-1}$ in the small energy range near the threshold energy. Substituting Eq. (2.27) into Eq. (2.26) and carrying out the integration, one obtains,

$$K_i = \bar{\sigma}_e \bar{v}_e \left( \frac{I}{kT_e} + 2 \right) \exp \left( - \frac{I}{kT_e} \right),$$

where

$$\bar{v}_e = \sqrt{\frac{8 kT_e}{\pi m_e}} = 6.21 \times 10^5 T_e^{1/2} \text{ cm/sec}$$

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

Therefore, to calculate \( K_I \) (Eq. 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, and the validity of the assumption that \( f_e \) is a Maxwellian distribution. As can be seen from the experimental work presented in Fig. 1, \( C \) is known to an accuracy of at least \( \pm 12\% \). In Ref. 9, a value of \( C = 2.0 \times 10^{-17} \) is suggested. However, Petschek and Byron\(^5\) give different relations for \( \sigma_e \) vs. \( \varepsilon_e \). They suggest that \( \sigma_e(V_e) = C (\varepsilon_e - I) \)

where \( I \) is the energy at the first excited state (for argon \( I = 11.6 \text{ eV} \)) and \( C = 0.7 \times 10^{17} \text{ cm}^2 (\text{eV})^{-1} \). This can be justified in many cases, since the probability of ionizing an excited atom is very much larger than the probability of ionizing an atom directly from its ground state. Therefore, an excited atom eventually will be ionized, and the ionization rate will be dictated by the rate of excitation to the first excited state. In light of the experimental work summarized in Fig. 1 it seems that the average value of \( C = 1.5 \times 10^{-17} \) obtained from this figure, gives a good description of the proportionality constant \( C \) for ionization from ground state atoms. 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. (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 an electron temperature of 1 \text{eV} collisions involving excitation are more probable by a factor of \( e^{1/2} \sim 50 \) than those involving direct ionization\(^5,7\). 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:

\[
K_{\text{exc}} = \int_{V_{\text{exc}}}^{\infty} \frac{\sigma}{e(V_e)} f_e(V_e) \cdot V_e dV_e = \sigma_{\text{exc}} \left( \frac{E_{\text{exc}}}{kT_e} + 2 \right) e^{-\frac{E_{\text{exc}}}{kT_e}}, \quad (2.29)
\]

where \( V_{\text{exc}} = \left( \frac{2E_{\text{exc}}}{m_e} \right)^{1/2} \), \( E_{\text{exc}} \) is the energy associated with the excited state under consideration, and \( \sigma_{\text{exc}} = C (\varepsilon_e - E_{\text{exc}}) \). 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. A more detailed and rigorous treatment of the ionization of excited atoms can be found in Refs. 5 and 10.

We have considered ionization via electron impact only, since once a sufficient number of free electrons is present in the plasma, the ionization via atom-atom collisions, which is very inefficient compared with electron impact\(^5,10\), can be neglected. The atom-atom ionizing collisions will certainly be important in the early stages of the ionization such as that occurring just behind a strong shock wave\(^5\).
2.3 Inelastic Collisions, De-excitation and Recombination

In contrast to the relatively straightforward way in which $K_r$ was calculated, the evaluation of $K_0$ is not so simple. In the following we will present a few different models to describe $K_R$. We will start with the crudest one, and progress to the most detailed available. The simplest case in which to estimate the recombination rate constant, is 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 $K_R$ that we will obtain from other models at the same electron temperature. In equilibrium, the equilibrium constant $K(T)$ can be calculated with the aid of Saha's equation to obtain

$$K(T) = \frac{n_i n_e}{n_a} = \frac{g_i g_e}{g_a} \frac{(2\pi m_e kT)^{3/2}}{\hbar^3} \exp\left(-\frac{I}{kT}\right)$$

(2.30)

where $g_i$, $g_a$ 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, we have

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

so that, (from $E_q (2.20)$ and $E_q (2.23)$),

$$K_R = \frac{g_a}{g_i} \left(\frac{I}{kT_e} + 2\right) \frac{\hbar^3 e}{2\pi^2 m_e^2 kT_e} = 1.11 \times 10^{-14} C \frac{g_a}{g_i} \left(\frac{I}{kT_e} + 2\right) \text{ cm}^6 \text{ sec}^{-1},$$

(2.31)

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

It is worth mentioning again that Eq. (2.31) gives the recombination rate constant for plasmas in equilibrium, where the electron is captured into the ground state of the atom. (As will be shown later, according to Zgrozelski and Park 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 plasma).

For argon plasmas, at temperature of 1 eV, Eq. (2.31) yields

$$K_R = 4.9 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}.$$

Another approach to calculate the recombination rate is obtained by following the definition that recombination occurs when a free electron is captured into one of the energy levels of the ion. The electron will be caught by the ion if it passes closer to the ion than a distance $r < r_i$, the radius at which the potential energy of Coulomb attraction to the ion is equal to the kinetic energy of the electron, viz:
\[
\frac{Z e^2}{r_o} = \frac{3}{2} kT_e \quad \text{or} \quad r_o = \frac{Z e^2}{\frac{3}{2} kT_e},
\]

where for the case of single ionization, \( Z = 1 \). When the distance \( r \), between the free electron and the ion is smaller than \( r_o \) we will say that a collision between them has occurred. The probability of such a collision, per unit volume is \( 10^{n Z^2 r_e^2 r_o^2} \).

Since, for non-radiative 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 \( \pi r^3 \). This probability is \( 10 Z \pi r^3 n_e \). The number of these recombination processes per unit time is therefore \( 10^{Z n_e} \).

\[
N_{rec} = n_e \pi r^2 \pi Z n_i Z \pi r^3 n_e = K_R n_e^2 n_i \quad (2.32)
\]

from which we have

\[
K_R = \frac{\pi Z^3 r^5}{n_e} = \frac{2^{6/2}}{3^2} \frac{e^{10 Z^3}}{m_e^{1/2} (kT)_9/2}
\]

and

\[
K_R = \frac{8.75 \times 10^{-27} Z^3}{T_e V} = \frac{5.2 \times 10^{-23} Z^3}{T_1000 \text{ deg}} \quad \text{cm}^6 \text{ sec}^{-1} \quad (2.33)
\]

Equation \( (2.33) \) yields for \( T_e = 1 \) eV,

\[
K_R = 8.75 \times 10^{-27} \text{ cm}^6 \text{ sec}^{-1}
\]

Using the same concept, but a more detailed analysis of the capturing mechanism, Pitaevskii \( (2.34) \) obtained

\[
K_R = \frac{4\pi \sqrt{2\pi}}{9} \frac{e^{10 Z^3}}{\sqrt{m_e} (kT)_9/2} \ln \Lambda \quad (2.34)
\]

where \( \ln \Lambda \) is a Coulomb logarithm and is approximately equal to unity. The difference between \( (2.33) \) and \( (2.34) \) is in the constant \( 27/16 \ln \Lambda \) which is of the order of unity.

Makin and Keck \( (2.34) \) have calculated the three-body, electron-electron-ion 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 \( (2.34) \) used a "trial" surface to separate the free and bound states of the electron-ion pair (similar to \( r_o \) 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 was calculated. The final result is:

\[ K_R = 2.3 \times 10^{-8} T_e^{-9/2} \text{ cm}^6 \text{ sec}^{-1} \]

where \( T_e = 1 \text{ eV} \), we have \( K_R = 1.77 \times 10^{-26} \text{ cm}^6 \text{ sec}^{-1} \).

Equation (2.35) 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.

In Fig. 2 some experimental recombination rate constants for different gases are shown, as well as Makin and Keck's theoretical curve. Aleksandrove et al. performed experiments with argon plasmas created by an electrical energy discharge, at 9000 K and \( n_e = 2 \times 10^{16} \text{ cm}^{-3} \), resulting in \( K_R = 2 \times 10^{-27} \text{ cm}^6 \text{ sec}^{-1} \).

For the same temperature, Eq. (2.35) will give \( K_R = 3.7 \times 10^{-26} \text{ cm}^6 \text{ sec}^{-1} \). This agrees with the evidence in Fig. 2 indicating that Eq. (2.35) will nearly always lead to a higher \( K_R \) than the experimental results.

The recombination rate constants calculated using the Thompson model Eq. (2.33) and the Makin and Keck model, Eq. (2.35) differ from the recombination rate constant calculated under equilibrium conditions, Eq. (2.31) for the same temperature (1 eV) by nearly four orders of magnitude. There are two reasons for this large discrepancy.

(a) In the classical model, most of the recombinations are into highly excited states and it is well known that the rate of de-excitation to the ground state is smaller than the rate of capture of electrons to highly excited states. For Eq. (2.31), 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 (2.31) assumes equilibrium conditions while the classical model on which Eq. (2.33) and (2.35) are based does not.

The previous discussion will enable us, at least to a first approximation, to express \( \dot{\omega} \) in terms of the plasma gross properties, \( n_e \) and \( T_e \). (This can be done by using Eqs. (2.28) or Eq. (2.29) and (2.31), or (2.33) or (2.35) for \( \dot{\omega}_I \) and \( \dot{\omega}_R \) respectively).

In the following we will describe in some detail the model of a
"collisional-radiative plasma", developed first by Bates et al. This model will include the four processes described by Eqs. (2.14) to (2.17). The collisional-radiative model will help us also to calculate the radiation terms appearing in the conservation equations. For an optically thin plasma, considering the processes described by Eqs. (2.14) to (2.17), the rate of change of the population in any level \( p \), can be expressed by the following rate equation,

\[
\frac{dn_p}{dt} = -n_p \left[ n_e (K_{pc} + \sum_{q \neq p} K_{pq}) + \sum_{q < p} A_{pq} \right] + n_e \sum_{q \neq p} n_q K_{qp}
\]

\[+ \sum_{q > p} n_q A_{qp} + n_e (K_{cp} + \beta_p), \tag{2.36}\]

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 \( \beta_p \) is the rate coefficient for radiative recombination into level \( p \). Index \( c_p \) indicates continuum, and \( K_{cp} \) is such that \( n_e^2 K_{cp} \) is the number of collisions concerned which occur per cm\(^3\) per second. From the principle of detailed balancing

\[
n_{qE} K_{qp} = n_{pE} K_{pq} \quad \text{and} \quad n_e K_{cp} = n_{pE} K_{pc},
\]

where index \( E \) represents equilibrium conditions. Expressing Eq. (2.36) with the relative population \( X_p = n_p / n_{pE} \) and making use of the principle of detailed balancing one obtains,

\[
\frac{dn_p}{dt} = -X_p \left[ n_e (K_{pc} + \sum_{q \neq p} K_{pq}) + \sum_{q < p} A_{pq} \right] + \sum_{q \neq p} X_q n_e K_{pq}
\]

\[+ \sum_{q > p} X_q n_{qE} A_{qp} + n_e K_{pc} + \frac{n_e^2}{n_{pE}} \beta_p. \tag{2.37}\]

The infinite set of coupled differential equations, typified by Eq. (2.37), 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. 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. (2.37), are much greater than the net rate of creation or disappearance of a given state, the LHS of Eq. (2.37). 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. (2.37) will be zero for all \( p > 1 \). In this case, Eq. (2.37) will reduce to a series of simultaneous algebraic equations, which upon solution will give \( X_p \) as a function of \( n_e \), \( X_1 \), \( T_e \) and the atomic constants. Equation (2.37) for \( p \leq 1 \), will determine \( \frac{dn}{dt} \), which is the rate of disappearance of free charges, and for a singly ionized plasma,

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

(2.38)

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 \( n_i \), 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. (2.14) to (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. (2.37) 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, \( X_s \simeq 1 \). The sums appearing in Eq. (2.37) 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. (2.37) must be solved for different values of \( s \), and the resulting values of \( X_s \), plotted versus \( p \). We know that for the highly excited states \( X_p \simeq 1 \), they are in equilibrium with the free electrons. Therefore, for the proper choice of \( s \), the curve of \( X_s \) vs. \( p \) should be tangent to the line \( X_s = 1 \) at the point \( p = s \). If this is not the case, \( s \) should be increased until this condition is met.

From Eq. (2.37), and the definition of \( \gamma \) (Eq. (2.38)), Bates et al showed that for \( p = 1 \)
\[
\gamma = \frac{dn_1}{d\tau} = \frac{n_{\text{E}}}{n_e^2} \left[ \sum_{q>l} X_q K_{1q} + K_{1c} + K_{1}\right] + \frac{n_{\text{E}}}{n_e^2} \left[ \sum_{q<s} X_q \frac{n_{\text{E}}}{n_p} A_{q1} + \right.
\]
\[
+ \sum_{q>s} \frac{n_{\text{E}}}{n_e^2} A_{q1} + \beta_1 \right] - \left[ \frac{n_{\text{E}}}{n_e} X_1 \left( K_{1c} + \sum_{q \neq 1} K_{1q} \right) \right]
\]

(2.39)

where the index \( \sigma \) identifies the group of excited states for which \( X_\sigma = 1 \).

The first term on the RHS of Eq. (2.39) 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 \( X_p = r_o(p) + r_1(p) X_1 \) and hence Eq. (2.39) may be rewritten as,

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

(2.40)

In Eq. (2.40) \( K_R \) 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, where the radiative processes dominate, \( K_R n_e \gg K_I n_{\text{E}} \), while in a dense plasma the collision processes dominate and \( K_R n_e \sim K_I n_{\text{E}} \). 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 64, and Park 62) it is assumed that \( \gamma \sim K_R \), since \( \gamma \) is the value directly measured. It is worth mentioning that \( K_I \) and \( K_R \) do not correspond to the coefficients giving the rate at which electrons enter and leave the ground state. In fact \( K_I \) and \( K_R \) are smaller than the rate of population and depopulation of the ground state which can be reached from many levels.

Bates et al solved the rate equation, Eq. (2.37) for \( X_1 \), they solved Eq. (2.39) for \( \gamma \), and Eq. (2.40) 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 \( K_R \) and \( K_I \) were deduced), the tables of Baker and Menzel and Green, Rush and Chandler, for the spontaneous transition probabilities, and the tables of Seaton for the radiative recombination coefficients \( \beta_p \). The results were presented in tabular form, from which Fig. 3 was obtained. The accuracy of the results for \( K_R \) and \( K_I \) 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 \( A_{p1} \)'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 Bates et al. Hence we can assume that \( n_p \ll n_1 + n_2 \) and \( n_p \ll n_e \) for all \( p \)'s except \( p = 1,2 \).

The set of linear equations (like Eq. (2.37)) 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, Bates et al.

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

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

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

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 \( K_R(i) \) 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. (2.36) is reduced to

\[
n_p \sum_{q \neq p} K_{pq} n_q E \sum_{q \neq p} n_q K_{pq} = n_e (K_{cp} + \beta_p)
\]

(2.41)
The solution of Eq. (2.41) 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 $K_{cp}$ term and $n_r(p)$ which is proportional to $n_e$ arises from the radiative recombination. Once the solution for $n_p$ is known, $K_{R}^p$ can be evaluated by solving the rate equation Eq. (2.36) 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, from the figures Bates et al. presented, it can be seen that for the range of $n_e$ and $T_e$ investigated, $K_R > K_R^{(i)} > K_R^{(ii)} > \beta$. For high temperature ($T_e > 64,000^\circ K$), the various recombination rate constants, $(K_R, K_R^{(i)}, K_R^{(ii)})$ approach $\beta_1$, which mean that for very high temperature, the radiative recombination into ground state is the dominant process.

So far we have described in some detail the 'collisional-radiative' model developed by Bates et al. We will now briefly review some modifications and applications of this model.

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. (2.14) to (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., $dn_p/\,dt = 0$ for all $p > 1$. To limit the number of algebraic equations, (typified by Eq. (2.36) without the radiative terms) that have to be solved for $X_1$, Zgrozelski arbitrarily assumed that all the excited states which lie within the range $kT_e$ from the continuum are in equilibrium with the electron gas. The population of these states are 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. (2.36) for $p=1$ yields $dn_1/\,dt$ and for the 'steady-state' model this is equal to $(-dn_e/\,dt)$. 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,

$$X_1 = \frac{n_1}{n_{1E}} = \frac{n_a}{n_{aE}}$$

where $n_a$ is the number density of neutrals in the plasma.
This approximation introduced a parameter \( r_k \), \( r_k = (n_e^2/n_a)/(n_{eE}/n_{aE}) \) which represents the extent of the departure from equilibrium, in the rate equation (Eq. (2.37) taken without the radiative terms).

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

\[
\frac{dn_a}{dt} = \sum_{p=1}^{m-1} n_p E \frac{dx}{dt},
\]

\[
K^R = \frac{1}{n_{eE}} \sum_{p=1}^{m-1} K_{pc} n_p E \varphi_p, \text{ the collisional recombination rate constant},
\]

\[
K^I = \frac{1}{n_{aE}} \sum_{p=1}^{m-1} K_{pc} n_p E \varphi_p, \text{ the collisional ionization rate constant},
\]

where \( \varphi_p \) is the "basic distribution function", defined by the relation

\[
X_p = X_1 \varphi_p + \left( \frac{n_e}{n_{eE}} \right)^2 (1-\varphi_p)
\]

\( \varphi \) depends only on the principal quantum number \( p \), and for the 'steady state' model,

\[
\frac{dn_a}{dt} = - \frac{dn_i}{dt} = - \frac{dn_e}{dt} = K^R n^2 e - K^I n e a \quad (2.42)
\]

It is worth mentioning here that the collisional 'steady-state' rate constants, \( K^R \) and \( K^I \) are not equal to the equilibrium rate constants, which are;

\[
K_{RE} = \frac{1}{n_{eE}} \sum_{p=1}^{m-1} K_{pc} n_p E \quad \text{and} \quad K_{IE} = \frac{1}{n_{aE}} \sum_{p=1}^{m-1} K_{pc} n_p E,
\]

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 \( K(T) \),

\[
\frac{K_{IE}}{K_{RE}} = \frac{K^I}{K^R} = \frac{n_{eE}^2}{n_{aE}} = K(T) \quad (2.43)
\]
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. (2.36) 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., $\frac{dn_p}{dt} = 0$ 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$^{13}$,

$$K_{R,c}^{s,c} = \frac{1}{n_e} \sum_{p=1}^{m-1} K_{pc} n_{pE} \varphi_p$$
$$K_{I,c}^{s,c} = \frac{1}{n_a} \sum_{p=1}^{m-1} K_{pc} n_{pE} \varphi_p$$

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

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

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,

$$\frac{dn_a}{dt} = -\frac{dn_e}{dt} = K_{R,c}^{s,c} n_e^3 - K_{I,c}^{s,c} n_e n_a + K_{R,r}^{s,r} n_e^2$$  \hspace{1cm} (2.44)

In the 'collisional-radiative' model, $\varphi_p$ depends on $n_e$ as well as on $p$, therefore $K_{R,c}^{s,c}$ and $K_{I,c}^{s,c}$ are functions of $n_e$ and the extent of departure from equilibrium $r_k$. For this case

$$\frac{K_{R,c}^{s,c}}{K_{I,c}^{s,c}} \neq K(T)$$

as happened to be in the purely collisional case. Zgrozelski carried out the calculation on the recombination rate constant for hydrogen at $T = 1,000^\circ K$. The results agree fairly well with those of Bates et al$^{8,8a}$.

The main difference between Zgrozelski's$^{13}$ and Bates$^{8,8a}$ 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 $\frac{dn_p}{dt} = K_{pc} n_{pE} \varphi_p$. 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$^{19}$ 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$^6$ used Bates et al$^{8,8a}$, '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 \( n_l \). Modifying Bates’ model for monatomic nitrogen, Park further assumes, that for the rate equation, Eq. (2.36), the LHS is zero for all \( p's > 4 \). For the low lying states \( p \leq 3 \), the LHS of Eq. (2.36) 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., 61.

\[
\frac{n_p}{n_q} = \frac{\frac{n_{pE}}{n_{qE}}}{\frac{g_p}{g_q}} \exp \left[ \frac{E_q - E_p}{kT} \right], \quad p; q \leq 3 .
\]  

(2.45)

Using the above assumption, and accounting for only 1 energy levels in the atomic structure of monatomic nitrogen (the levels were tabulated by Park 61), the rate equation for \( p \geq 4 \) becomes,

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

(2.46)

As in the work of Bates et al 8, Park 61 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 in Park’s paper 61.

Since Bates et al 8,8a, using Gryzinski’s semi-classical theory developed the expressions for \( K_{pq} \) and \( K_{pc} \) strictly for a hydrogenic force field, Park used their coefficients with an effective quantum number in place of the principal quantum number. That is, the ionization energy \( E_{1/n} \) (where \( E_1 \) and \( n \) are the ionization potential and principal quantum number of the hydrogen atom, respectively) is replaced by \( (I - E_p) \) where \( I \) is the ionization potential of the nitrogen atom and \( E_p \) is the energy associated with the \( p \) excited state of a nitrogen atom, both measured from the ground state. Because of the large departure from a hydrogenic structure in nitrogen, for the three low lying states, the collisional rate coefficients for transitions to and from them require special consideration 61. In the derivation of the inelastic collision cross-section by Gryzinski’s semi-classical theory it is necessary to integrate the differential cross-section over the field produced by the bound electron (the target). In the case when an atom is in an excited state, one can assume that the resultant field of the core configuration is a point charge, i.e., one can assume a Coulomb potential. When the atom is in the ground state ("S"), each of the three equivalent electrons (that can be knocked to higher energy levels) exerts an
identical force upon the incident free electron, so that the net cross-section becomes three times that of the individual electron. If there is no interaction among the fields of these three electrons, the overall cross-section for ground state nitrogen atom will be represented by three times Gryzinski's value. For the two other excited states, 2D and 2P, the pertinent multiplicative factor would be less than three, because these states are already partially excited. In view of lack of data for collisional transitions for such cases, an arbitrary multiplicative factor of 3/2 was chosen by Park for the 2D and 2P states.

The solution of Eq. (2.46) can now be carried out for $X_\parallel$ provided the following four parameters are known, $T_e$, $n_i$, $n_e$ and the plasma dimension which enters implicitly in calculating the absorption. In a collision dominated plasma, the solution is independent of the last two parameters. From Eq. (2.46), one sees that a collision dominated 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,

$$K_{pq} \gg \frac{A_{pq}}{n_e}$$

and

$$K_{pc} \gg \frac{n_e^{\beta_p}}{n_{\rho E}}$$

as can be shown from Eq. (2.46).

The RHS of inequality (2.47) is inversely proportional to the electron density. The same is true for Eq. (2.48) because as can be seen from the Saha equation, i.e.,

$$n_{\rho E} = n_e^2 \frac{g_p}{2Z_+} \left( \frac{\hbar^2}{2m_e kT_e} \right)^{3/2} \exp \left( \frac{I-E_p}{kT_e} \right)$$

where $Z_+$ is the partition function of the ions based on $T_e$, therefore, $n_e/n_{\rho E} \sim 1/n_e$. For nitrogen when $n_e \geq 10^{18}$ cm$^{-3}$ expressions (2.47) and (2.48) are satisfied for all possible emissive transitions.

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$^{-3}$.

The relative population of the ground state $X_\parallel$, indicates the degree

25
of nonequilibrium. For a low temperature plasma not far from equilibrium \( X_1 \approx 1 \), in this case, most of the atoms are in the ground state and

\[
X_1 = \frac{n_1}{n_{1E}} \approx \frac{n_a}{n_{aE}}.
\]

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 \( n_e = 10^{15} \text{ cm}^{-3} \), is rapidly expanded so that \( T_e \) is reduced very quickly to 8,000°K while \( n_a/n_e^2 \) is unchanged, \( X_1 \approx 0.012 \).

Using a computer, Park solved Eq. (2.46) 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, the population of the highly excited states approaches the equilibrium values, i.e., \( X_p \approx 1 \) 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\(^6\) to evaluate \( K_1 \) and \( K_0 \). 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\(^6\):

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

where both rates, \( K_{pc} \) and \( K_{cp} \) are expressed in \( \text{cm}^3 \text{ sec}^{-1} \). 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

\[
K_{cp} = \frac{n_{pe}}{n_e} K_{pc}
\]

and from the Saha equation,

\[
n_{pe} = n_e^2 \frac{E_p}{2Z_e} \left( \frac{\hbar^2}{2m_e kT_e} \right)^{3/2} \exp \left( \frac{I-E_p}{kT_e} \right) = n_e^2 F(T_e, p).
\]

As was shown before, the populations of the excited states of nitrogen can be evaluated upon solving Eqs. (2.46). For a collision dominated plasma this equation will reduce to,

\[
-X_p \left[ K_{pc} + \sum_{q=1}^{s_p} K_{pq} \right] + \sum_{q=1}^{s_p} X_q K_{pq} = -X_1 \sum_{q=1}^{3} K_{pq} - K_{pc}.
\]

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,

\[ n_a = \sum_{p=1}^{s} n_p = \sum_{p=1}^{s} X_p n_p E \]  

(2.53)

From Eqs. (2.50) and (2.51) \( K_{cp} \) can be expressed as:

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

(2.54)

where \( f(T_e,p) \) is a function of the electron temperature and the state index, \( p \). Making use of the Saha equation, Eq. (2.51) and Eq. (2.53) \( X_1 \) can be expressed as,

\[ X_1 = \frac{n_a}{n_{1E}} = \frac{n_a - \sum_{q=2}^{s} X_q n_q E}{n_e^2 F(T_e,1)} = \frac{n_a - \sum_{q=2}^{s} X_q n_e^2 f(T_e,q)}{n_e F(T_e,1)} \]

or

\[ X_1 = \frac{n_a^2}{n_e^2} f_1(T_e) - \sum_{q=2}^{s} X_q f_2(T_e,q) \]  

(2.55)

Using the last expression for \( X_1 \) in the rate equation, Eq. (2.52) we have,

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

(2.56)

If we will use Eq. (2.54) for \( K_{cp} \) and Eq. (2.56) for \( n_p \) in the equation describing the rate of creation of free electrons, Eq. (2.49) we will have,

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

\[ - n_e^3 \sum_{p=1}^{s} f(T_e,p) \]

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

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

\[
\frac{dn_e}{dt} = n_n k_f(T_e) - n_n^3 k_r(T_e) \tag{2.57}
\]

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 (2.57) is slightly different from Eq. (2.40) suggested by Bates et al to describe the rate of creation of free electrons. While in Eq. (2.57), the ionization rate is proportional to \(n\), in Bates' model it is proportional to \(n_1\). Equation (2.57) is of the same form as the equation suggested by Zgrozelski, Eq. (2.42).

Park \(^{62}\) calculated the values of \(k_f\) and \(k_r\) for atomic nitrogen in the following way. For given values of \(T_e\), \(n_e\) and \(X_1\), all the \(X_p\)'s were evaluated using Eq. (2.52). Once the \(X_p\)'s are known, \(n_a\) was calculated using Eqs. (2.51) and (2.53). From the known values of the \(n_p\)'s and the transition rates, \(dn_e/dt\) was evaluated using Eq. (2.49). The known values of \(dn_e/dt\), \(n_e\) and \(n_a\) now can be substituted into Eq. (2.57) to evaluate \(k_f\) and \(k_r\). Since we have two unknowns \(k_f\) and \(k_r\) in Eq. (2.57), Park \(^{62}\) repeated the calculation for the same values of \(T_e\) and \(n_e\), but different \(X_1\). Now we have two simultaneous equations for \(k_f\) and \(k_r\) for the same \(T_e\) and \(n_e\). Park carried out his calculations for \(4,000^\circ\text{K} \leq T_e \leq 20,000^\circ\text{K}\). The simplest best fit curve for the computed results is

\[
k_r = 1.15 \times 10^{-26} \left[ \frac{T_e}{10,000} \right]^{-5.27} \text{ cm}^6 \text{ sec}^{-1} \tag{2.58}
\]

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

\[
\frac{k_f}{k_r} = \frac{n_e^2}{n_a^3} = \frac{Z_a}{Z_+} \left( \frac{2\pi m kT_e}{h^2} \right)^{3/2} \text{ e}^{-\frac{I}{kT_e}} \tag{2.59}
\]

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

The same result was obtained by Zgrozelski \(^{13}\) in the collision dominated plasma. (see Eq. (2.43)). It is important to note that the effective forward and reverse rates \((k_f\) and \(k_r\)) as defined by Eq. (2.57) 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. (2.49) can be written as,
where
\[ K'_F (T_e, n_a, n_1, n_2, \ldots, n_p, \ldots) = \sum_{p=1}^{n} K_{pc} \frac{n_p}{n_a} \]
and
\[ K'_R (T_e) = \sum_{p=1}^{n} \frac{K_{cp}}{n_e} \]

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 \( K'_F \sim K'_{FE} \) and \( K'_R \sim K'_{RE} \) 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 cut-off 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. (2.49) 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. (2.57), 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. The 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 will summarize the main structure of the 'collisional-radiative' model of Bates, Kingston and McWhirter and briefly mention the limitations of this model.
In this model\textsuperscript{8,8a} 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 very much shorter than those for the ground state 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\textsuperscript{24}. 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 deexcitation 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 deexcitation of the level \( p^* \), at which the minimum occurs. The minimum in the equilibrium deexcitation rate occurs because the collisional deexcitation probability increases rapidly with increasing principal quantum number, whereas the radiative deexcitation probability, and also the equilibrium population of the excited states decrease with increasing quantum number. For nonequilibrium situations, Byron et al\textsuperscript{24} 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, Bryron et al\textsuperscript{24} assumed that the population of all states having principal quantum numbers larger than \( p^* \) is given by the Saha equation Eq. (2.51), and for hydrogenic atoms we have,

\[
\frac{n_{pE}}{n_e} = \frac{2}{\pi e^2} \left( \frac{\hbar^2}{2m_e K_e} \right)^{3/2} \exp \left( \frac{E_p}{K_e} \right), \quad \text{for } p > p^* \tag{2.60}
\]

In this model, the recombination rate is equal to the deexcitation rate through level \( p^* \) by electron collisions and radiative transitions. Using Gryzinski's\textsuperscript{15, 16} expressions for the inelastic collision cross-sections, the collisional deexcitation probabilities were deduced\textsuperscript{24}. The total radiative transition probability from a state having principal quantum number \( p \), to all states below level \( p^* \) is\textsuperscript{24},
\[ A_p^{p^*} = \sum_{q=1}^{p^*-1} A_{pq} = \frac{p^*}{p} A_p, \quad (2.61) \]

where \( A_p \) is the reciprocal mean radiative lifetime, and for hydrogen atoms\(^{24}\)
\[ A_p \approx \frac{166 \times 10^8}{p^{4.5}} \text{ sec}^{-1}. \quad (2.62) \]

From the above discussion, the three body recombination rate constant \( K_R \), where \( K_R \)
defined as \( K_R = \frac{1}{n_e^2} \frac{\partial n_e}{\partial t} \), (similar to the collisional-radiative decay coefficient
of Bates et al\(^{8}\)) is given by\(^{24}\),
\[ K_R = \left[ A_{p^*} + n_e C(p^*, p^*-1) + \frac{1}{n_e^2} \sum_{q=p^*+1}^{\infty} A_{pq} n_q n_E \right] \frac{n_{p^*} n_E}{n_e^2} \quad (2.63) \]

Where \( C(p,q) \) is the probability of a collisional transition \( p \rightarrow q \). Only
\( C(p^*, p^*-1) \) is retained in the collisional deexcitation term, since the probability
of deexcitation to an adjacent level is an order of magnitude larger than that
to any other level\(^{24}\). The energy level, at which the minimum occur may be ob­
tained by solving \( \frac{\partial K_R(p)}{\partial p} = 0 \) for \( p \), where \( K_R(p) \) is given by Eq. (2.63). Bryon
et al\(^{24}\) used Eq. (2.63) 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
done at \( T_e = 16,000^0 \text{K} \)). The theory of Bryon 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-
on-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 'bottle neck' in the deexcitation exists
between levels \( K^* \) and \( L^* \), i.e., the slowest deexcitation is the \( K^* \rightarrow L^* \) tran­
sition. All the levels above \( K^* \) were designated levels \( K, (K^* + 1, K^* + 2, \ldots, 47) \),
and all the levels below \( L^* \) were designated \( L, (L^* - 1, L^* - 2, \ldots, 1) \) and of
course \( K^* = L^* + 1 \). The rate of crossing the gap \( K^* \rightarrow L^* \) is \( R_{\text{dex}} \). Since the
Byron model assumes that all the energy levels \( K \) are in equilibrium with the elec­
tron gas, and that the excitation through the bottle neck is negligible compared
to the deexcitation, Dugan\(^{63}\) introduced a factor \( \delta \) to relate \( R_{\text{dex}} \) to \( K_R \). The
factor \( \delta \), which depends on \( T_e \), must account for the fraction of the deexcitation
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 \( K_R = R_{\text{dex}} \). On the other hand,
for equilibrium conditions, the excitation rate is equal to the deexcitation
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 deexcitation rate exists have to be found, and then
\( R_{\text{dex}} \) can be calculated. Dugan showed that for a plasma in which the free
electrons have a Maxwellian velocity distribution, then from the principle
of detailed balancing, the deexcitation rate from state \( p \) to state \( q \) is given by
\[ 63 \]
\[ r_{\text{dex}} = n_{n} n_{p} \frac{g_{q}}{g_{p}} \exp \left( \frac{\Delta E_{pq}}{kT_{e}} \right) \sigma_{q p v e} \]  

(2.64)

Where \( \sigma_{q p} \) is the inelastic collision cross-section resulting in a transition from level \( q \) to level \( p \), \( (p > q) \) and \( \Delta E_{pq} \) is the energy gap between the two levels.

The rate of deexcitation 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 deexcited by superelastic collisions either past the state \( L^{*} \) to states \( L \) below \( L^{*} \), or to the state \( L^{*} \) itself\(^{63}\). Therefore, the rate \( R_{\text{dex}} \) is given by,

\[ R_{\text{dex}} = \sum_{K=K^{*}}^{K=S} \sum_{L=1}^{L^{*}} r_{\text{dex}}. \]  

(2.65)

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\(^{63}\). 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 \( 10^{13} \text{ cm}^{-3} < n_{e} < 10^{18} \text{ cm}^{-3} \), \( 500 \text{ K} < T_{e} < 10,000 \text{ K} \), \( \delta = 1/3 \) up to \( 2,000 \text{ K} \), \( \delta = 1/2 \) from \( 3,000 \text{ K} \) to \( 5,000 \text{ K} \) and \( \delta = 2/3 \) from \( 5,000 \text{ K} \) up to \( 10,000 \text{ K} \)\(^{63}\). Once \( \delta \) is estimated the recombination rate constant is given by,

\[ K_{R} = \delta (R_{\text{dex}})_{\text{min}}. \]  

(2.66)

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 \( 500 \text{ K} \) to \( 3,000 \text{ K} \) to \( T_{e}^{-9/2} \) in the range from \( 4,000 \text{ K} \) to \( 10,000 \text{ K} \). 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. (2.64)\(^{63}\)).

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

3. The collisional transition rates were evaluated using Gryzinski's semiclassical 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 \( (H_{e}, N_{e}, A_{r}, K_{r}, X_{e}) \) was made by Chen\(^{64}\). For his theoretical calculations, Chen adopted Byron et al's method\(^{24}\), 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%.

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:

$$R_{\text{dex}} = n_p E \left[ n_e C(q,p) + A_T \right]$$

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 $p$ 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

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

The recombination rate constant defined as

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

can be expressed as

$$K_R = \frac{1}{n_e^2} \left[ (A_T + n_e C(q,p)) n_p E \right] \text{ at } p = p^*.$$  

In Eq. (2.68) the following two mechanisms of deexcitation 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 negligible small in the region of $n_e$ and $T_e$ under consideration, namely $10^{10} \text{ cm}^{-3} < n_e < 10^{16} \text{ cm}^{-3}$ and $1,000^\circ K < T_e < 16,000^\circ K$)

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. (2.68). 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 $T$. 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. As can be seen for electron density of $n_e = 10^{16}$ cm$^{-3}$ and $T_e = 14,000$°K in an argon plasma Chen got $K_R = 1.2 \times 10^{-27}$ cm$^6$ sec$^{-1}$ while Makin and Keck obtained $K_R = 5 \times 10^{-27}$ cm$^6$ sec$^{-1}$, and for the same conditions, Chen obtained for helium (which is the most hydrogenic atom considered)

$$K_R = 4.1 \times 10^{-28} \text{ cm}^6 \text{ sec}^{-1}.$$  

These results are in line with a previous statement saying that most of the available results (see Fig. 2) indicate that Makin and Keck's equation, Eq. (2.35) overestimates the recombination rate constant especially for temperature above 1 eV, when radiation becomes important. 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.

$K_R$ was deduced from the experimental data in the following manner; from $n_e$ 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., $K_p n_p \ll K_R n_e$ 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 $K_R$ or $K_e$. 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.

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 $H$, $N$, and $A$). Chen also performed the calculations for hydrogen in order to compare the results with those of Bates et al. The comparison was made in the ranges $10^{10}$ cm$^{-3} \leq n_e \leq 10^{16}$ cm$^{-3}$ and $500$°K $< T_e < 16,000$°K, and the agreement was very good, especially for high temperatures. So far we have presented a few different models for the evaluation of the recombination rate constant. The last two models 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 the model due to Bates et al gives the most exact description of the 'collisional-radiative' plasma, it seems that the model of Byron et al is somewhat easier to use for numerical applications.
In Table 1 the various experimental results and formulations of $K_R$, mainly for argon, are collected. As can be seen from this table, 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 an experimental result with a theoretical predictions of $K_R$, great care should be taken in choosing the appropriate model for the recombination rate constant. As we pointed out before, in most of the experiments the measurable quantity is the plasma decay coefficient (at least if one follows the definition $K_R = 1/n_e^3 \cdot \frac{dn_e}{dt} \text{cm}^3/\text{sec}$) and not the recombination rate constant as defined in the work of Bates et al.

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 $1,000^\circ \text{K}$ and $3,000^\circ \text{K}$, Fox and Hobson suggested that the following processes are dominant

$$2\text{Ar} + e \rightarrow \text{Ar}^+ + e + e \quad \text{for ionization} \quad (2.69)$$

and

$$\text{Ar}^+ + e \rightarrow \text{Ar} + \text{Ar} \quad \text{for recombination} \quad (2.70)$$

From their experiments (which will be described in the next chapter) 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 $\text{Ar}_2$ or $\text{Ar}_2^+$ were detected for this range of temperatures. Bray also pointed out the possibility of such a recombination. Since we are concerned with argon at temperature of about $1 \text{ eV}$ 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 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, they defined the recombination rate constant as,

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

$K_R$ is expressed in $\text{cm}^3 \text{sec}^{-1}$. The experimental work was done in the ranges, $3,000^\circ \text{K} \leq T_e \leq 11,000^\circ \text{K}$ and $10^{-12} \text{ cm}^3 < n_e < 10^{15} \text{ cm}^3$. 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,

$$K_R = 1.28 \times 10^5 \times T^{1.8} \times 10^{-0.64} \times n_e^{-0.64} \text{ (cm}^3 \text{sec}^{-1})$$

or

$$K_R = 1.28 \times 10^5 \times T^{1.8} \times 10^{-1.64} \times n_e^{6} \text{ (cm}^3 \text{sec}^{-1})$$

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

a. \( \text{Ar}_2^+ + \text{Ar}(1) + \text{Ar}(1) \rightarrow \text{Ar}_2^+ + \text{Ar}(1) \), Three body process

b. \( \text{Ar}_2^- + \text{e} \rightleftharpoons \text{Ar}_2^- (p) \), \( p > 1 \), 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 \( n \) 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 for temperatures of 1 eV, the time to reach a unique value of \( T_e \) is \( 10^{-13} \) sec while the time to reach \( T_e = T \) is \( 10^{-8} \) sec, (see the appropriate equations in the appendix), so that at least at the beginning of the recombination process the assumption, \( T = T_e \) is wrong.

Desai and Corcoron admitted that the accuracy in measuring \( n \) 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 argon at temperatures above 10,000 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. 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. (1.2), (1.3) and (1.7), we have to express \( C \) and \( Q \) in terms of the plasma macroscopic properties. Neglecting external fields and allowing only small gradients in the flow, the momentum equation for the electrons will be (see Eq. (1.3)):

\[
\frac{\partial}{\partial t} \left( \rho_e u_e \right) + \frac{\partial}{\partial x^j} \left( \rho_e u_e u_e \right) + \frac{\partial p_e}{\partial x^j} = \frac{1}{\Delta t} \sum_q \sum_k F_q^i q_{ek} + C_e^i \tag{2.72}
\]

Since \( m_e \ll m_a \sim m_i \) and

\[
\frac{\partial p_e}{\partial x^j} = 0 \left[ \frac{\partial p}{\partial x^j} \right]
\]
then it is possible to neglect the inertia terms \( \partial / \partial t (\rho \frac{u^i}{e}) \) and \( \partial / \partial x^j (\rho \frac{u^i u^j}{e}) \) 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 \( C^i \). 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 1:

\[
C^i_{\text{ion}} = -C^i_{a} = -\frac{\text{dn}}{\text{dt}} \frac{m_u^i}{m_a},
\]

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

\[
\sum_s C^i_s = 0.
\]

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

\[
\frac{3}{2} k T_i + \frac{1}{2} m_i u_i^2,
\]

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

\[
Q_i = \frac{\text{dn}_i}{\text{dt}} \left[ \frac{3}{2} k T_i + \frac{1}{2} m_i u_i^2 \right]
\]

and

\[
Q_a = \sum_{p=1}^{\infty} \frac{\text{dn}_p}{\text{dt}} \left[ \frac{3}{2} k T_a + \frac{1}{2} m_a u_a^2 \right] \text{ respectively.}
\]

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

\[
Q_a = \frac{\text{dn}_a}{\text{dt}} \left[ \frac{3}{2} kT + \frac{1}{2} m u^2 \right].
\]

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 \((I_q - I_p)\). Due to the radiative recombination, the electron loses an average energy \( \frac{3}{2} kT_e \) per event. Hence, the electron energy source term can be written as

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

\[ - \sum_{p=1}^{\infty} \sum_{q=p}^{\infty} K_{pq} n_p n_q (I_q - I_p) - \sum_{p=1}^{\infty} \beta_p n_p n_e \frac{3}{2} k T_e \]  

Equation (2.73)

Multiplying Eq. (2.36) by \( I \) and then summing over all \( p \), an expression is obtained that enables us to replace all the collisional terms in Eqs. (2.73) by radiation terms and the rate of productions, \( \frac{dn}{dt} \).

For an optically thin plasma, (see Appendix A) after some algebra:

\[ Q_e = \sum_{p=1}^{\infty} \frac{dn}{dt} I_p - \sum_{p=1}^{\infty} \sum_{q=1}^{P} A_{pq} n_p (I_p - I_q) - \sum_{p=1}^{\infty} \beta_p n_p n_e^2 (I_p + \frac{3}{2} k T_e) \]  

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

\[ Q_e = \frac{dn}{dt} I_1 + Q_{rad} \]  

where

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

Equation (2.75) indicates that the rate at which the electron gas gains energy is equal to the difference of the rate 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 \( Q_{rad} \) have to 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. 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 die-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 bound electrons to all lower states. The former was evaluated using Gryzinski's formulation for
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

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

Ionization potential

(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 $n_e \geq 10^{17}$ cm$^{-3}$. This indicates that for $n_e \geq 10^{17}$ 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 $300^\circ K \leq T_e \leq 7,000^\circ K$, but it seems unlikely that above $7,000^\circ K$ 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. All the terms appearing in RHS of Eqs. (1.2), (1.3) and (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,

$$\frac{\partial n_e}{\partial t} + \frac{\partial}{\partial x_j} (n_e u_j) = \frac{\omega_e}{m_e}$$

(2.77)

$$\frac{\partial p_e}{\partial x_j} = - n_e [B_x^i + (\bar{u}_e \times B)^i] + n_m (\nu_{ea} + \nu_{ei})(u_i^j - u_e^j)$$

(2.78)

$$\frac{\partial e_e}{\partial t} + \frac{\partial}{\partial x_j} [(\epsilon_e + p_e)u_e^j] = u_e^j \frac{\partial p_e}{\partial x_j} + \frac{\partial n_e}{\partial t} I_1 + Q_{\text{rad}}$$

$$+ 2n_e \frac{m_e}{m_a} (\nu_{ea} + \nu_{ei}) \left[ \frac{3}{2} k(T_e - T_a) + \frac{1}{2} m_a (u_i^j - u_e^j)^2 \right]$$

(2.79)

and from the definition of $\epsilon$ and $p$, $\epsilon + p = \frac{5}{2} n_e k T_e$. The assumptions made during evaluation of Eqs. (2.77), (2.78) and (2.79) were:

1) the electrons 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. (2.76).
This describes the radiation loss only in the case of optically thin plasmas for the 'steady state' model.

The equations of motion for the whole plasma are obtained by summing each of the Eqs. (1.2), (1.3) and (1.7) for all the plasma constituents. Thus

\[
\frac{\partial p}{\partial t} + \frac{\partial}{\partial x} \left( \rho u^j \right) = 0, \tag{2.80}
\]

\[
\rho \frac{Du_i}{Dt} = -\frac{\partial p}{\partial x_i} + (n_i - n_e) e \left[ E^i + (\vec{u} \times \vec{B})^i \right] + n_e e [(\vec{u} - \vec{u}_e) \times \vec{B}]^i, \tag{2.81}
\]

and

\[
\rho \frac{DH}{Dt} - \frac{DP}{Dt} = -n_e e \left[ (\vec{u} - \vec{u}_e) \times \vec{B} \right]^i u^i + n_e e E^i (u^i - u^i_{e}) + \frac{\partial}{\partial x^j} \left[ (e_e + p_e) (u^i - u^i_{e}) \right] + Q_{rad} - \frac{dn_e}{dt} I_1, \tag{2.82}
\]

where

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

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

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

and

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

In Eqs. (2.77) to (2.82), the following dependent variables appear; viz \( T, T_e, u, u_e, n_e, n_i, \) and \( n_a \). This set of equations will therefore 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) The three species have a Maxwellian velocity distribution, described by the species temperature.
3) The processes that occur in the plasma are those described by Eqs. (2.14) to (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

\[ W = 0 \left( \frac{m_e}{m_a} < \frac{c^2}{e} > \right)^{1/2} \]

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 \( K_e \) and \( K_R \) for the different models. The most basic assumption is that each species maintains its own Maxwellian velocity distribution. However, these processes cannot always be neglected, e.g., at the beginning of an expansion flow we will have a higher electron temperature than anticipated from theory. 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. On the average, however, the theoretical prediction (based on the model described herein) agrees well with the experimental results. Only for certain flow conditions will we need to modify the theory to account for these irregularities. In addition it should be remembered that the solution of Eqs. (1.2), (1.3) and (1.7) without assuming a Maxwellian distribution is extremely difficult.

CHAPTER 3: STEADY ONE-DIMENSIONAL FLOW OF IONIZED ARGON

For a steady, one-dimensional flow of singly ionized plasma Eqs. (2.77) to (2.82) reduce to:

\[ \frac{d}{dx} \left( n_e u_e \right) = \frac{dn_e}{dt}, \quad (3.1) \]

\[ \frac{dp_e}{dx} = - n_e e \left( E^x + (\vec{u} \times \vec{B})^x \right) + n_m \left( \nu_{ea} + \nu_{ei} \right) (u-u_e), \quad (3.2) \]

\[ \frac{d}{dx} \left[ \frac{2}{3} n_e k T u_e \right] = u_e \frac{dp_e}{dx} + 2n_e \frac{m_e}{m_a} \left( \nu_{ea} + \nu_{ei} \right) \left[ \frac{3}{2} k(T-T_e) + \frac{1}{2} m_a (u-u_e)^2 \right] - \frac{dn_e}{dt} I_1 + Q_{rad}, \quad (3.3) \]
\[
\frac{d}{dx} (p u) = 0 ,
\]
(3.4)

\[
p u \frac{du}{dx} = - \frac{dp}{dx} ,
\]
(3.5)

and

\[
p u \frac{dH}{dx} - u \frac{dp}{dx} = - n_e e \left[ (\vec{u} - \vec{u}_e) \times \vec{B} \right] \cdot \vec{u} + n_e e E (u - u_e) +
\]
\[
\frac{d}{dx} \left[ \frac{5}{2} n_e k T_e (u - u_e) \right] + Q_{rad} - \frac{dn_e}{dt} I_1 ,
\]
(3.6)

where, as before,

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

Eqs. (3.1) to (3.6) 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. (3.1) to (3.6) can be solved. Since the numerical solution of these equations depends on the model one adopts to describe \( dn_e/\rho \) and \( Q_{rad} \), it clearly has to be checked against some experimental results before one can claim that the analysis is appropriate.

Few theoretical results have been reported for a steady quasi-one dimensional flow of singly ionized argon plasmas i.e., numerical solutions of Eqs. (3.1) to (3.6) were obtained, after applying certain simplifications. Independently of these theoretical analyses, some experiments on one-dimensional plasma flows have been performed. In the following we will give a brief discussion of some of these papers.

Bray solved numerically the flow through a supersonic nozzle of singly ionized argon plasma. For the range of temperature and pressure in the nozzle, \( (T \approx 10,000^\circ K, P \approx 0.5 \text{ atm}) \) Bray assumed that the three-body recombination is the dominant process. This process can be described in two steps,

Recombination to an excited state \( Ar^+ + e + e \rightarrow Ar_p^+ + e \)
(3.7)

and

De-excitation to the ground state \( Ar_p^+ + e \rightarrow Ar_{gs}^+ + e \)
(3.8)

Since the process given by Eq. (3.8) is slower than that of Eq. (3.7), the recombination rate will be dictated by the slowest process in Eqs. (3.8). The limiting assumptions in Bray's work are:

1. The flow is quasi-one dimensional, steady, adiabatic and inviscid.
2. The fluid is a monatomic ideal gas.
3. The plasma is optically thin and the only reactions considered are those of Eqs. (3.7) and (3.8).

4. The expansion commences from an equilibrium state far upstream of the nozzle throat.

5. Conduction, all types of diffusion, wall recombination and magnetogas-dynamics effects are neglected.

Since normally $T_{e} \neq T_{i}$ in a decaying plasma, one needs an extra equation for $T_{e}$, apart from those of continuity, momentum, energy and state. For this reason Bray presents two alternative energy balance equations for the electron gas. At sufficiently low density and for sufficiently small scale expansion nozzle the energy balance equation will be dominated by the terms of conduction, work done and internal energy so that one can neglect the contribution of heat supplied to the electrons due to both recombination and elastic thermalizing collisions\textsuperscript{22}. At a sufficiently high density and large expansion nozzle the opposite is true. Bray solved the flow for the two categories for all points through the supersonic nozzle. The solution was expressed in terms of the independent variable, $A$, which represents the area ratio at a distance $x$ from the nozzle throat. Due to the expansion, the temperature, density and the degree of ionization decrease whereas the velocity and the flow Mach number increase. All the flow properties during the expansion are located between the appropriate frozen and equilibrium values\textsuperscript{22}. The limitation of Bray's work lies in the limited model used to describe the recombination (no radiative processes are accounted for), and the restricted application of the electron energy balance. On the other hand Eq. (3.6) is independent of the plasma density and the geometry of the expansion nozzle provided we have quasi one-dimensional flow. Talbot et al\textsuperscript{28} solved numerically the very same problem. They described the recombination processes by using Bates et al's\textsuperscript{8} collisional-radiative model which is more general than Eqs. (3.7) and (3.8), as explained in Chapter 2.

Along with the practical case when only the resonance radiation is absorbed, Talbot et al\textsuperscript{28} 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\textsuperscript{8} was checked experimentally for stationary plasmas, it was one of Talbot's aims to check this model for supersonic moving plasmas\textsuperscript{28}. 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 so that $u_{i} = u_{a} = u$.

5. The mean free path is much smaller than a typical flow length and the continuum approach to the flow is valid.
6. All kind of wall recombination is 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 Dalton's law of partial pressures is assumed to be applicable.

The equations of motion presented by Talbot et al.\textsuperscript{28} are identical with Eqs. (3.1) to (3.6), after the diffusion and the electromagnetic field terms are omitted. These are:

\[
\frac{d}{dx} \left( \rho u A \right) = 0 , \tag{3.9}
\]

\[
\rho u \frac{du}{dx} = - \frac{dp}{dx} \tag{3.10}
\]

\[
u \frac{d}{dx} \left( H + \frac{1}{2} u^2 \right) = - \frac{Q_{\text{rad}}}{\rho} , \tag{3.11}
\]

\[
\frac{d\rho}{dx} = - \left[ (K_R + K_I) \alpha - K_I \right] \frac{n_e}{u} \tag{3.12}
\]

\[
\frac{dT_e}{dx} = \frac{2}{3} \frac{T_e}{\rho} \frac{dp}{dx} - \frac{T_e + \frac{2}{3} \frac{I_1}{k}}{\alpha} \frac{dx}{dx} - \frac{2m_e Q_{\text{rad}}}{3\rho u k} - \frac{p}{u} \left[ D_1 \alpha^{-3/2} \ln \left( \frac{D_2 T_e^3}{\rho \alpha} \right) + (1-\alpha) D_3 \right] (T_e - T) , \tag{3.13}
\]

\[
p = \frac{9k}{m_a} (T + \alpha T_e) , \quad H = \frac{5}{2} \frac{k}{m_a} (T + \alpha T_e) + \frac{\alpha}{m_a} I_1
\]

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:

\[
D_1 = \frac{2}{3} \frac{e^4}{m_a^2 k} \left( \frac{8\pi m_e}{k^2} \right)^{1/2} , \quad D_2 = \frac{9k^3}{8\pi e^6} \text{ and } D_3 = \frac{5\pi (m_B)^{1/2}}{3m_a} \tag{3.14}
\]

\( B \) 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.\textsuperscript{28}).

Equations (3.9) to (3.14) were solved numerically, using Adams four point integration technique\textsuperscript{28}. 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 \( T \). Talbot et al.\textsuperscript{28} fit polynomials to describe the tabulated values for \( K_I, K_R \) and \( Q_{\text{rad}} \) suggested by Bates et al.\textsuperscript{28}. These polynomials are functions of \( n_e, T_e, T \) and are limited to hydrogenic plasma at the temperature and density ranges investigated by Bates et al.\textsuperscript{28}. 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. 6, 7, 8, 9 and 10. The values are always nearer to the frozen ones. It is of special interest to know how the difference \((T_e - T)\) behaves along the nozzle axis. From Eqs. (3.9) to (3.13) after some algebra, the following equations are obtained:

\[
\frac{d}{dx} (T_e - T) = -\frac{2}{3} \frac{m_e \rho_{\text{rad}}}{\rho u x k} - \frac{1}{\alpha} \left( T_e + \frac{2}{3} \frac{T}{k} \right) \frac{d\alpha}{dx} + \frac{2}{3} \frac{d(lnp)}{dx} (T_e - T)
\]

\[
- \rho \frac{1/k}{u} \left[ D_1 \frac{a^n_{\text{eff}}}{T_e^{3/2}} \ln(D_2 \frac{T_e}{\rho_{\alpha x}}) \right] + \left( 1 - \alpha \right) D_3 (T_e - T) \quad (3.15)
\]

In the absence of recombination (frozen flow), \(d\alpha/dx = 0\) and \(\rho_{\text{rad}} = 0\), therefore, Eq. (3.15) reduces to a first order differential equation which has the formal solution:

\[
T_e - T = C \exp \left[ \int D \, dx \right], \quad (3.16)
\]

where \(C\) is the integration constant and \(D\) is given by

\[
D = \frac{2}{3} \frac{d(lnp)}{dx} - \rho \frac{1/k}{u} \left[ D_1 \frac{a^n_{\text{eff}}}{T_e^{3/2}} \ln(D_2 \frac{T_e}{\rho_{\alpha x}}) \right] + \left( 1 - \alpha \right) D_3 \;
\]

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 \(d\alpha/dx\) are not zero, the electron gas will gain energy and therefore \(T_e \neq T\). The first two terms in the RHS of Eq. (3.15) 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. (3.15)) 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. (3.15)) 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, \(m\). 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.\(^{28}\) it was shown that \((T_e - T)\) for anion expanding plasma is larger than \((T_e - T)\) for hydrogen plasma for the same conditions; (see Fig. 9b).

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 dependance (see Eq. (3.15)). 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 (4th in the RHS of Eq. (3.15)) become ineffective due to the very low value of the factor \(\rho/u\). Lordi and Dunn\(^{71}\) checked the relative weight of each term appearing in the electron energy balance for one-dimensional ionized nitrogen flow. For electron temperature around \(4,000^\circ\)K and
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 this equation to check the validity of the experimental results for $T_e$. Although the works of Bray$^{22}$ and Talbot et al$^{28}$ are essentially the same, it is impossible to compare their final results, viz. 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$^{28}$ is more detailed, since the recombination model is more realistic and the electron energy balance equation is of general validity. From Talbot's$^{28}$ results (some of which are presented in Figs. 6,7,8,9 and 10) 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$^{66}$. 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.

Hoffert and Lien$^{32}$ also obtained a numerical solution to one-dimensional, steady argon flow. Their equations of motion are essentially the same as Eqs. (3.9) to (3.13), after neglecting the radiation loss. Similar to Bray$^{22}$, they considered only two processes in the plasma, viz

$$A_q + M \Rightarrow A_p + M \quad \text{where} \quad p > q$$

and

$$A_p + M \Rightarrow A^+ + e + M,$$

where $M$ represents either argon atoms or free electrons. The value for the ionization rate constant is based on the collision cross-section suggested by Petschek and Byron$^5$. A questionable assumption in this work, is their evaluation of $K_e$ for nonequilibrium flow, with the aid of the equilibrium constant $K(T)$. (The same procedure as described by Eqs. (2.30) and (2.31)). The
Numerical solution was carried out only for the relaxation zone immediately behind the primary shock wave in a shock tube. In this zone, the flow cross-section is constant and the dominant process is ionization. (Because ionization is the dominant process, the unrealistic method used by Hoffert and Lien to calculate $K_R$ will not affect the final results too much).

Similar work, taking into account the radiation process as well as collisions (Eqs. (2.14) to (2.17)), and adopting the Bates et al. model for calculating the recombination and ionization rates, was done by Oettinger. In this work, experiments were also performed to measure the gas and free electron densities. The measurements were done interferometrically. Since these papers were not primarily concerned with the decay processes during expansion, but rather with the establishment of equilibrium behind a primary shock wave, we will not discuss them any further.

Theoretical and experimental work was done by Park on the behaviour of a fully dissociated and partially ionized nitrogen stream expanding supersonically through a nozzle. The flow equations of motion which were solved numerically, are similar to Eqs. (3.9) to (3.13). 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. 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 non-equilibrium conditions the lower energy levels are underpopulated compared to their equilibrium population for the same temperature.

In Ref. 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. (2.18)).

\[
\frac{d n_e}{d t} = K_R n_e^3
\]

which upon integration becomes,

\[
K_R = \frac{1}{2\Delta t} \left[ \left( \frac{1}{n_e^2} \right) x = x_o + \Delta x - \left( \frac{1}{n_e^2} \right) x = x_0 \right],
\]

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.11.

Before one tries to draw any conclusions from Park's work, it is important to emphasize again that the accuracy of spectroscopic measurements of the electron temperature and number density are usually no better than \pm 15%. (For more details see Ref., pp.267-312). The basic assumption, under which $K_R$ was evaluated will be justified only when one can show that $K_R n_e^3 \gg K_I n_e a$. 

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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. (3.18) 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. 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. 12 and 13. While the Langmuir probe measurements show the same trends as those calculated by Bray and Talbot et al., 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 the vacuum, rapid collisional-radiative recombination will take place. This nonequilibrium recombination will result in overpopulation of highly excited electronic states relative to lower-lying states, as compared with Boltzmann's population ratio, $n_e/n_T = \text{constant} \times \exp(-E_n/E_T)$. Measurement of such a population ratio via the radiation intensity technique would therefore lead to an incorrect (too high) value of $T_e$. As mentioned before, Park reported a severe departure from equilibrium population in expanding nitrogen plasma.

Fox and Hobson have done 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 measured current can be related to the ion density, by the following expression:

$$i_p = CA \frac{1}{Ap} \frac{1}{n_i} n_i e \left( \frac{8kT}{m_i \mu} \right)^{1/2},$$

where, $i_p$ is the measured current, $Ap$ 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. (3.17). The results are shown in Fig. 14. Unfortunately these experiments were carried out at relatively low temperatures ($10^4^0$K < T < $4000^0$K), and as mentioned before, for this temperature range, Fox and Hobson suggested that the recombination is of the dissociative type described by Eqs. (2.69) and (2.70). 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.

Enough experimental work has been done on stationary plasmas (generally created by discharging a capacitor) to confirm the applicability of the 'collisional-radiative' model for the description of the recombination processes at the densities and temperature we are concerned with. ($10^{15}$ ≤ $n_e$ ≤ $10^{18}$ cm$^{-3}$
$8,000^\circ K \leq T_e \leq 15,000^\circ K)$. However, a question arises as for the validity of this model in a supersonically moving plasma were the changes in $T_e$ and $n$ are moderate, in comparison with the discharge type facilities. Therefore, one of the most important steps before presenting a model to describe a supersonic decaying plasma is to compare the experimental data on the plasma properties with those obtained analytically using the proposed model. Since for low degrees of ionization, the gross flow properties, i.e., $p$, $ho$, $T$ would not be affected by the atomic processes, namely recombination, therefore, one should concentrate on measuring the electronic plasma properties $T_e$ and $n$. Due to the interest in experimental evaluation of $K_R$ for a supersonically moving plasmas, a number of different ways in which such an experimental investigation can be performed have been suggested by several authors. In the following chapter we will review some of these techniques. To conclude the discussion, we will summarize the main points mentioned in this chapter.

1. It is not possible to compare the numerical solutions for the quasi-one-dimensional, supersonically-expanding plasma described in this chapter 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 the 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 so are the geometry and the diagnostic techniques. The numerical solutions indicate that the flow properties will lie between the frozen and equilibrium cases, 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 thermalizing collision term, this term can be neglected (Eq. (3.15)) 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 $n$ 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 of the radiation processes is taken, the equations of motion become practically insoluble.

CHAPTER 4: EXPERIMENTAL TECHNIQUES FOR EVALUATING RECOMBINATION RATE CONSTANTS

As we have seen, in order to be able to solve the equations of motion of a supersonically-expanding plasma, one should know the relation between the recombination rate constant and the plasma macroscopic properties. The most convenient facility to use, for the determination of $K_R$ in a moving plasma, is one which produces one-dimensional flow, since in this case the gasdynamic formulation reduces to the simplest form.

From this point of view, the technique used by Fox and Hobson looks very promising. However, this technique is limited to relatively low temperatures.
since the basic idea is that the temperature behind the primary shock is not high enough to support ionization and therefore the recombination starts immediately after the energy discharge. The way Fox and Hobson\textsuperscript{21} 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.\textsuperscript{2} 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\textsuperscript{21} case, immediately after the extra pulse, the plasma will start recombining. Aleksandrov et al.\textsuperscript{2} 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\textsuperscript{21} cannot be used. To evaluate $K_R$ in this temperature range, an experiment following the flow geometry of Bray\textsuperscript{22} and Talbot\textsuperscript{28} 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\textsuperscript{29} and Dunn\textsuperscript{72} have done their experimental work in such a facility. The main advantage of such a geometry compared to the one-dimensional, shock-tube flow (reported by Fox and Hobson\textsuperscript{21}) 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 is feeding 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.

Duffy\textsuperscript{36} 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\textsuperscript{29} used spectroscopic methods but as already mentioned, the accuracy of these measurements is low and the measurements 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\textsuperscript{29} 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\textsuperscript{48}, 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 the conical nozzle is a difficult requirement to meet, which is a disadvantage in using a shock tunnel facility. We will elaborate on interferometric work in the next chapter.

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. 15. 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 we will have a purely one-dimensional flow of decaying plasma. In such a configuration we will be able to use flat windows in the recombination zone and 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 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, since 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 ($\gamma \sim 1.67$) we can expect a detached shock wave in front of the wedges at relatively low Mach numbers (see Fig. 16). This will limit the temperature range of the experimental work and will introduce a limit to the usable 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 the one-dimensional case. At UTIAS we have started some experimental investigations of the recombining flow of argon plasmas over a corner expansion in a shock tube. Two different models to create the expansion flow were used. One, the wedge model produces a very thin boundary layer, for which only density measurements were made (using the Mach-Zehnder interferometer). The second model, the 'wall model' introduces a thick boundary layer to the corner expansion region. In this model pressure measurements are also possible. The two main disadvantages of this work are:

1. The difficulty in obtaining numerical solutions to the two-dimensional
flow equations, with which the experimental results may be compared,

2. The fact that unlike $T_e$, $n_e$ has only a second order effect on $K_R$.

Another method of measuring the recombination rate constant was suggested by Jacobs et al., also using a shock tube. In this technique the expansion chamber is located a few tube diameters from the shock-tube end 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 will be ruptured by the high pressure behind the reflected shock wave, is surrounded by a vacuum chamber. Upon breaking, the plasma will expand to the vacuum chamber, and a recombination process will take place (see Fig.18). Using this technique, a comparison between experimental results and theory will be extremely difficult if not impossible, due to the three-dimensional nature of the expanding plasma. The numerical solution will be also very difficult, as even in the one-dimensional case a computer solution is very time consuming. In addition, the actual measurements will be difficult to make relative to one- and two-dimensional flows. For the shock tube and Mach-Zehnder interferometer currently being used at UTIAS, it looks most promising to perform the experimental work on a two-dimensional corner expansion using the wedge model shown in Fig. 17c. Some preliminary results will be described in the next chapter.

CHAPTER 5: STEADY TWO-DIMENSIONAL IONIZED FLOW

5.1 Formulation of the Steady, Two-Dimensional Equations of Motion For
an Ionized Gas

Equations (2.77) to (2.82), for a steady, two-dimensional, singly-
ionized gas case (expressed in Cartesian co-ordinate), yields after some
algebra:

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

$$
u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} = -\frac{k}{m} \left[ \frac{\partial T_e}{\partial x} + \frac{T_e}{n_a + n_e} \frac{\partial n_e}{\partial x} + \frac{n_e T_e}{(n_a + n_e)a} \frac{\partial T_e}{\partial x} + \frac{T_e}{n_a + n_e} \frac{\partial n_e}{\partial y} \right] + \frac{n_e \frac{m_e}{a}}{n_a + n_e} (v - v_e) B_z ,
$$

$$
u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} = -\frac{k}{m} \left[ \frac{\partial T_e}{\partial y} + \frac{T_e}{n_a + n_e} \frac{\partial n_a}{\partial y} + \frac{n_e T_e}{(n_a + n_e)a} \frac{\partial T_e}{\partial y} + \frac{T_e}{n_a + n_e} \frac{\partial n_e}{\partial y} \right] - \frac{n_e \frac{m_e}{a}}{n_a + n_e} (u - u_e) B_z ,
$$

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

$$
\left( u \frac{\partial n_e}{\partial x} + v \frac{\partial n_e}{\partial y} \right) - k \left( \frac{5}{2} \frac{n_e T_e}{n_a + n_e} + T \right) \left( u \frac{\partial n_a}{\partial x} + v \frac{\partial n_a}{\partial y} \right) =
$$
where \( k \) is the Boltzmann constant, \( Q_{rad} \) is the radiation loss, which for optically thin plasma is given in Eq. (2.76) (for the general case see Chapters 3 and 5 in Ref. 66), \( \nu \) is the collision frequency (see Eqs. (2.12) and (2.13)), \( E \) is the electric field, \( B \) the magnetic field, \( e \) the electron charge and \( u \) and \( v \) the average velocities in the \( x \) and \( y \) directions, respectively.

To solve Eqs. (5.1) to (5.8), one has to express the internal electromagnetic fields \( E = E(x, y, z) \) and \( B = B(x, y, z) \) as functions of the plasma gross properties. This can be done with the aid of Maxwell's equations. For the two-dimensional, steady case, we obtain

\[
\mu e (u-u_e) = \frac{\partial B_z}{\partial y} - \frac{\partial B_y}{\partial z},
\]

\[
\mu e (v-v_e) = \frac{\partial B_x}{\partial z} - \frac{\partial B_z}{\partial x},
\]

\[
\frac{\partial B_y}{\partial x} - \frac{\partial B_x}{\partial y} = 0,
\]

\[
\frac{\partial e}{\partial t} (u-u_e) = E_x + (v-v_e) B_z,
\]
\[
\frac{n_e e}{\sigma} (v-v_e') = E_y - (u-u_e') B_z,
\]
and
\[
E_z + (u-u_e) B_y = (v-v_e) B_x,
\]
where \(\mu\) is the plasma permeability and \(\sigma\) the electrical conductivity.

We have now 14 equations, (Eqs. (5.1) to (5.14)) to solve for the 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 \(B_z\). In principle, this set of equations is solvable. However, to the author's knowledge no numerical solution of these equations has been performed due to the tremendous complexity, as any numerical solution will depend (at least for high degrees of ionization) on the model adopted to describe the atomic processes, namely the terms \(dn_e/\text{d}t\) and \(Q_{\text{rad}}\), a comparison between experimental results and the calculated values will be crucial in assessing the validity of the model. This emphasizes the necessity for numerical solutions. Owing to the complexity, a few simplified cases were treated in order to gain some insight into the changes of the plasma properties during the decay processes. Understandably, these solutions can only describe the plasma under certain limited conditions. For example, the numerical solution of Glass and Takano\(^{37}\) neglects the following phenomena:

1. External and internal fields \((E = B = 0)\),
2. Diffusion \((u = u_e, v = v_e)\),
3. Radiation loss \((Q_{\text{rad}} = 0)\),

The only reaction assumed to occur in the plasma is \(A_1^+ + e \rightarrow A_1^+ + e + e\) (no electronic excitation). These assumptions can be justified in certain nonequilibrium expansions. However, the assumption that \(T = T_e\)\(^{37}\) is unrealistic for all nonequilibrium expansions of ionized gases, since it is valid only when the plasma reaches equilibrium. A natural flow co-ordinate system \((s, n)\) was used in Ref.\(^{37}\) for expressing the equations of motion.

continuity \(u \frac{\partial \rho}{\partial s} + \frac{\partial u}{\partial s} + \rho u \frac{\partial \theta}{\partial n} = 0\)  

(5.15)

momentum s-direction \(u \frac{\partial u}{\partial s} + \frac{1}{\rho} \frac{\partial \rho}{\partial s} = 0\)  

(5.16)

momentum n-direction \(u^2 \frac{\partial \theta}{\partial s} + \frac{1}{\rho} \frac{\partial \rho}{\partial n} = 0\)  

(5.17)

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

(5.18)

rate of electron production \(u \frac{\partial \alpha}{\partial s} = K \frac{\rho}{m_a} \frac{2 \alpha}{\gamma} \left(\frac{\alpha_e^2}{1-\alpha_e} (1-\alpha) - \alpha^2\right)\)  

(5.19)

for many non-equilibrium expansions of ionized gases, since it is valid only for a very dense plasmas, for which the thermalizing collisions are the dominant process, or when the plasma reaches thermal equilibrium.
state \[ p = (1 + \alpha) \rho RT \] (5.20)

where \( s \) and \( n \) are the distances along and normal to a streamline respectively \( p, \rho \) and \( T \) are the plasma pressure, density and temperature, \( \alpha \) is the degree of ionization and \( \alpha_e \) is a reference degree of ionization based on equilibrium at the local temperature and pressure (this equilibrium value \( \alpha_e \) is found from the Saha equation), \( u \) and \( \theta \) are the magnitude and direction of the velocity vector.

The dependent variables are \( p, \rho, T, u, \theta \) and \( \alpha \). Since we have six equations, the set is solvable. Glass and Takano\(^{37}\) expressed Eqs. (5.15) and (5.17) in characteristic form and then solved the flow field by building a mesh of cells from intersecting characteristics. Even by accepting all the assumptions made, it is extremely difficult to compare experimental measurements from the present expansion model (Fig. 17c) with the numerical solutions. Whereas the numerical solution is done along the streamlines in an inviscid flow, one cannot identify the streamlines on the interferograms from which the density field can be deduced. Furthermore, density evaluation is affected by the boundary layer. The same is true of pressure measurements along the model walls and spectroscopic measurement of temperature and electron density. All these measurements will give us the local plasma properties as functions of \( (x,y) \) instead of \( (s,n) \). The density distribution downstream of the corner, as predicted by Glass and Takano is shown in Fig. 19. As we will see in the next section, this distribution is very similar to the experimental results. In the following section we will describe in some detail how density measurements can be done by using an interferometer.

### 5.2 Experimental Techniques for Measuring Decaying Plasma Properties Employed at UTIAS

The largest change in the plasma properties during the decay processes in the expansion of an ionized gas is the temperature. There is no way to measure the temperature in a supersonic flow directly. The most widely adopted technique for plasma flows is a spectroscopic measurement of the emitted radiation from which the temperature can be deduced. This kind of measurement, apart from being of low accuracy (an accuracy of \( \pm 15\% \) is considered good; see Ref. 43, pages 267 to 295), it is normally limited to transitions for which the oscillators strengths are known. The pressure changes in the decay process, which is smaller than the temperature change is still significant. However, the technique of pressure measurements (mainly by using fast response pressure transducers) suffers from the following disadvantages. The static pressure recorded on the wall does not represent that of the inviscid flow owing to the presence of the boundary layer.\(^{48}\) Due to the rigid connection between the transducer and the model, "ringing" effects complicate the actual pressure readings.\(^{48}\) In addition, because of the transducer's finite surface area, one reads only an average pressure instead of a local one. This means that the pressure measurements will also be inaccurate. Therefore, although the change in density during nonequilibrium expansion is the smallest of all the plasma macroscopic properties,\(^{38}\) its measurement can be made the most accurate by using an interferometer (Mach-Zehnder in our case). This technique does not disturb the flow field. With a "snapshot" one gets the whole density field at a given time. From such a picture the boundary layer growth can also be observed (see Fig. 20). However, the limitation of interferometric studies are:

(a) The flow should ideally be two-dimensional (no change in the refractive index in the direction of the light propagation).
(b) The test section windows must be of high quality optical glass which is quite costly, especially when a large piece is needed to provide a larger view field (e.g., to see the transition from one equilibrium condition to the one following relaxation).

(c) Since a coherent light source is needed, a laser is most desirable.

(d) Corrections must be made due to the presence of boundary layers.

The Institute for Aerospace Studies is equipped with a 4 in. x 7 in. cross-section shock tube, suitable for chemical kinetic work, which is used in conjunction with a 9 inch field of view Mach-Zehnder interferometer. It is therefore possible to obtain detailed measurements of the flow density and the density of the free electrons simultaneously during the nonequilibrium expansion by means of the technique of two-wavelength interferometry.

In the following, we present a brief description of the expansion model used, the density-evaluation technique for the interferograms and the results of some preliminary experiments. An ideal experiment for generating an expansion flow must meet the following requirements: The model geometry and in particular the expansion angle have to be chosen in such a way that the relaxation length is visible over the ranges of $M$ and $p$, for which the experimental work is performed. By this we mean that the nonequilibrium flow must cover most of the viewing area. Some calculations for the optimum model geometry for our shock tube have been performed by Glass and Kawada. Since the numerical solution is valid only for an inviscid flow, a proper choice of model will introduce a minimum boundary layer growth. Originally two models were proposed, the wall model (see Fig. 17b) and the wedge model (see Fig. 17a). The boundary layer on the latter is much thinner and of a different type than on the former. The wall model is also equipped with pressure transducers. As mentioned by Slack et al. there is a maximum in the area reduction one can employ and yet obtain a uniform flow in the test section. Once this is exceeded, a detached shock wave will destroy the flow uniformity and hence the density measurements will be difficult to make. Since argon has a relatively high specific heat ratio ($\gamma \approx 1.67$), a very small area reduction can create such a detached shock wave. Fortunately, the experimental results for the shielded wedge model (Fig. 17c) show that the flow before the expansion is very uniform (Fig. 20) in spite of theoretical predictions to the contrary.

The relation between the fringe shift $S$ and the changes in the refractive index, $n$, is given by

$$S_{ij} = \frac{\Delta_l - \Delta_j}{d} = \frac{L}{\lambda} (n_j - n_i)$$  \hspace{1cm} (5.21)

where

- $L$ is the test section width,
- $\lambda$ is the light source wavelength,
- $n$ is the refractive index,
- $d$ is the fringe spacing (for other details, see Fig. 21)
The relation between the plasma densities and the refractive index is

\[(n-1) = \rho \left[ K_A(1-\alpha) + K_I \alpha \right] - \frac{\omega^2}{2\omega^2} \]

(5.22)

where

- \( \rho \) is the gas density,
- \( \alpha \) is the degree of ionization,
- \( K_A \) is Gladstone-Dale constant for the atoms,
- \( K_I \) is Gladstone-Dale constant for the ions,
- \( \omega_p \) is the plasma frequency \( \left( \frac{4\pi n_e e^2}{m} \right)^{1/2} \),
- \( \omega \) is the angular frequency of the light source.

Since \( n_e = \alpha \rho/m_a \) and for argon \( m_a = 6.632 \times 10^{-23} \text{ g} \) and \( \omega_p^2/2\omega^2 = 4.46 \times 10^{-14} \lambda^2 n_e \), then Eq. (5.22) will yield

\[(n-1) = \rho \left[ K_A(1-\alpha) + K_I \alpha - 0.67 \times 10^{-7} \lambda^2 \alpha \right] \]

(5.23)

where \( \lambda \) is the wavelength in angstroms. Upon substitution of Eq. (5.23) into Eq. (5.21), one has

\[S_{ij} = \frac{L}{\lambda} \left[ K_A(\rho_j - \rho_i) - (\rho_j \alpha_j - \rho_i \alpha_i)(K_A - K_I + 0.67 \times 10^{-7} \lambda^2) \right] \]

(5.24)

Referring to \( i \) as the pre-corner flow and \( j \) as the flow in the expansion, the gas density and the degree of ionization can be evaluated if one has two simultaneous equations for \( S_{ij} \). This is true only when \( K_A K_I \) and the flow properties, \( \rho \) and \( \alpha \) before the expansion are known.

For the flow properties before the expansion, we use a computer program to evaluate the Hugoniot properties behind the primary shock wave. This program takes account of the excited electronic levels and is based on the thermodynamic model used by Cambel et al.\(^{45}\).

The values of \( K_A \) at room temperature are known with great accuracy\(^{39}\), but at elevated temperature this information is unknown. We therefore assume that \( K_A \) will remain constant i.e. the excited states do not contribute to \( K_A \). The situation regarding \( K_I \) is somewhat more uncertain and some authors\(^{38,40}\) adopted the value \( K_I = 0.67 K_A \) based on a Slater screening constant calculation. Work has just been completed by Bristow at this Institute, which verifies the above assumptions\(^{51}\). For one of the runs performed on a nonequilibrium expanding argon flow, different values for \( K_I \) were suggested, and accordingly, \( \rho \) and \( \alpha \) were calculated. As can be seen from Fig. 2\(^{22}\) the effect of changing \( K_I \) from \( K_I = 0.25 K_A \) through to \( K_I = K_A \) on \( \rho \) is very small and is practically zero for \( n_e \). Therefore, the fact that an accurate value for \( K_I \) is not known, would not seem to affect...
the measurements of \( n_e \) and \( \rho \) in any significant way.

From Eq. (5.24) one can see that the fringe shift due to the heavy-particle density change \( \Delta \rho \), is proportional to \( 1/\lambda \), while the fringe shift due to the free electron density change \( \Delta (\rho_e) \), is proportional to \( \lambda \), and in a direction opposite to the fringe shift for the heavy particles. Because of the negative phase refractive index of the free electrons, the maximum sensitivity for the two-wavelength interferometry technique is achieved when the wavelengths of the dual frequency light source occupy the extremes of long and short wavelengths which are sensitive to the electrons and heavy particles, respectively.

In the experimental work done in our facility, a ruby laser with a second harmonic generator was used as a light source. In this arrangement the primary wavelength lies in the red at \( \lambda = 6943 \, \text{Å} \), with the second harmonic at \( 3471 \, \text{Å} \). Figure 20 shows a typical interferogram for this laser in which the boundary layer is clearly seen. From a thickness point of view, the boundary layers for electrons and heavy particles are generally not identical, as expected from diffusion considerations.

Since the electron number density is known over the whole field from the interferograms, we can thus find its value along the 'effective boundary layer' edge which is defined for this purpose, as the location at which the fringe shift is less than 5\% of the fringe shift on the wall (measured relatively to the undisturbed zone). The results of such calculations for the gas density and electron number density along the 'boundary layer edge' are shown in Fig. 22.

From the plot of \( n_e \) vs. distance from the corner (Fig.22) an estimation of \( K_R \) can be made using Eq. (3.18) with a correction accounting for the drop in \( n_e \) due to volume increase. This is a good approximation if \( K_R n_e^2 >> K_I n_e \). In Fig.23 \( K_R \) calculated from Eq. (3.18) is presented. As can be seen, for the temperature in which the experimental work has done \( T_e \approx 12,000^\circ \), \( K_R \) is of the same order of magnitude as the one suggested by the numerical calculations of Chen, using Byron et al approach (see Fig.5).

If the numerical solution of Eqs. (5.1) to (5.14) is known then, by feeding in the experimental values of \( \rho \) and \( n_e \), one can calculate the value of \( K_R \) and assess the dependence of \( K_R \) on \( T_e \). Since the experimental work on the expansion of ionized argon is still in its early stage, no more will be said regarding the analysis of the results. In the future, interferograms will be taken using a neodymium glass laser for which the primary wavelength is 10,600 Å and the second harmonic wavelength is 5,300 Å. The resulting fringe shifts will be much more sensitive to the free-electron contribution and hopefully will give a clearer and more definite idea about the electron diffusion and the electron gas boundary layer.

To summarize this chapter, we can say that an interferometric study of an expanding ionized flow can give accurate results on the changes of \( \rho \) and \( n_e \) in the nonequilibrium flow. From the limited work done so far, the shape of the curves for \( n_e \) and \( \rho \) along the wall (measured outside the 'effective boundary layer') is as expected from the work of Glass and Takano. A numerical solution of the flow equations is essential for establishing the validity of the model describing the atomic processes, unfortunately the solution of the general case is not expected in the near future. Since the exact value of Gladstone-Dale constant for the ions does not play an important role in the
evaluation of \( p \) and \( n_e \), a reasonable value can be assumed. However, additional experimental data is forthcoming from Ref. 51.

CONCLUSIONS

In this review, an attempt was made to describe as fully as possible the equations of motion for supersonically-expanding plasmas. The main difference between the classical gasdynamics and the present study is the appearance of three new terms in the equations of motion, viz. the thermalizing collisions, the chemical reactions and the radiative processes. These terms will have a predominant effect on the macroscopic properties of the plasma, and should therefore be accounted for in any realistic study. While the description of the thermalizing collisions is relatively simple (see Sec. 2.1), the description of the other two terms becomes quite complicated. For argon plasma in the ranges of \( 10,000^\circ K < T_e < 20,000^\circ K \) and \( 10^{15} < n_e < 10^{17} \text{ cm}^{-3} \), only the reactions described by Eqs. (2.14) to (2.17) were considered, viz. collisional and radiative excitation, de-excitation, ionization and recombination. For the special case of a collision-dominated plasma, the description of the chemical reactions, i.e., ionization and recombination, take a relatively simple analytical form, such as Eq. (2.35) of Makin and Keck. Unfortunately, for the above mentioned ranges of \( T_e \) and \( n_e \), the radiative processes cannot be completely neglected, and a more refined model for the chemical reactions is necessary, such as the 'collisional-radiative' model of Bates et al 8 or Byron et al 24.

Once the radiative effects have been accounted for, the governing equations form a very complex system. This is due mainly to the fact that, in general, the radiation contributions appear in an integral form 66, resulting in an integro-differential form of the equations of motion. This makes a numerical solution of the general case very difficult. As a result; it is more encouraging to search for special limiting cases in which the equations of motion reduce to manageable form, as in the case of LTE, or optically thin or thick plasma.

Some numerical solutions for special cases (mainly one-dimensional flows) were reviewed. Even for these limited models the numerical solution, achieved using a computer, was very time consuming 28.

One of the parameters describing the atomic processes is the recombination rate constant. For a supersonically expanding plasma (and/or decaying plasma) this parameter is dominant, and it is therefore of great importance to know its value in the ranges of the study or experiment under consideration, and its dependence on the macroscopic properties of the plasma. As mentioned in the review, there is a misunderstanding (or at least different definitions) regarding the meaning of \( K_R \). In most theoretical studies 8,13,24 \( K_R \) is the rate of capturing free electrons into low lying bound states, mainly the ground state, and these processes take place simultaneously with ionization of neutral atoms. On the other hand, in the experimental evaluation of \( K_R \), the ionization rate is completely ignored, and the recombination rate is based solely on the rate of disappearance of free electrons 12,30,64,68,72. These measurements give the decay coefficient, and only in very special cases will the decay coefficient equal \( K_R \). As the plasma approaches equilibrium, the difference between \( K_R \) and the decay coefficient increases.

In almost all of the numerical solutions of the equations of motion for expanding plasmas, one of the models described in Sec. 2.3 was adopted for
As noted before, different models may yield different values of $K_R$, for the same $T_e$ and $n_e$. For example, Chen's calculations using the approach of Byron et al.\textsuperscript{24} gives $K_R = 4.1 \times 10^{-28}$ cm$^6$ sec$^{-1}$ for a helium plasma at $T_e = 14,000\textdegree$ and $n_e = 10^{16}$ cm$^{-3}$, while the pure collisional model of Makin and Keck\textsuperscript{11} gives $K_R = 5.0 \times 10^{-27}$ cm$^6$ sec$^{-1}$. This difference in $K_R$, when used in the equations of motion, may result in different values for the calculated macroscopic plasma quantities.

Owing to the good agreement between the results of the two 'collisional-radiative' models (Bates et al.\textsuperscript{8} and Byron et al.\textsuperscript{24}) and the fair agreement of these predictions with the available experimental data, it appears that these models rather than the pure collisional description should be adopted to describe the plasma in the ranges of $10^{15} \leq n_e \leq 10^{17}$ cm$^{-3}$ and $1 \text{ eV} \leq T_e \leq 2 \text{ eV}$. It is believed that the experiments described in Sec. 5.2 will support this statement. The preliminary results obtained at UTIAS for the decay coefficient, which reduce to $K_R$ (at least for the early stage of the expansion), agree very well with Chen's\textsuperscript{64} calculations for argon plasma, based on Byron's model\textsuperscript{24}. The plasma density distribution downstream of the expansion corner is very similar to the predictions from the numerical calculations of Glass and Takano\textsuperscript{37} as can be seen from Figs. 19 and 22.
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APPENDIX A:

Some useful relations for plasmas:

Saha equation:
\[ \frac{n_e n_i}{n_a} = A \left( \frac{g_i}{g_a} \right)^{3/2} \exp \left( \frac{I}{kT} \right) \]  \tag{A1}

where, \[ A = 2 \left( \frac{2\pi m e^2}{\hbar^2} \right)^{3/2} = 4.83 \times 10^{15} \text{ cm}^{-3} \text{ deg.} \]  \tag{A2}

Maxwell distribution function normalized to unity,
\[ f(V) \, dV = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left( -\frac{mV^2}{2kT} \right) V^2 \, dV \]  \tag{A3}

or, when expressed in energy terms
\[ f(\epsilon) \, d\epsilon = \frac{2}{\sqrt{\pi}} \frac{\sqrt{\epsilon}}{(kT)^{3/2}} \exp \left( -\frac{\epsilon}{kT} \right) \, d\epsilon \]  \tag{A4}

Plasma transport coefficients. (the following apply to fully ionized plasmas, and kT is expressed as eV)\(^6\)

Electrical conductivity;
\[ \eta = \frac{32(kT_e)^{3/2}}{1/6 \ln \Lambda} \text{ mho cm}^{-1} \]  \tag{A5}

Kinematic viscosity;
\[ v = \frac{\mu_i}{\rho_i} = \frac{3.2 \times 10^{12}(kT_i)^{5/2}}{n_i^{1/6} \ln \Lambda} \text{ cm}^2 \mu\text{sec}^{-1} \]  \tag{A6}

Thermal conductivity;
\[ \kappa = \kappa_e = \frac{3.2 \times 10^{14}(kT_i)^{5/2}}{1/6 \ln \Lambda} \text{ (\mu sec cm)}^{-1} \]  \tag{A7}

where \[ \ln \Lambda = 6 + \frac{1}{2} (3 \ln \frac{kT}{4} - \ln \frac{n}{10^{17}}) \] and is very nearly 6 under most conditions, thus \[ 1/6 \ln \Lambda \approx 1 \] for all practical calculations\(^6\).

Various cross-sections.

The collision cross-section for charged particles having masses of the same order (first approximation using Thompson model)\(^1\),
\[ \sigma \approx \frac{4}{9} \pi \left( \frac{2e^2}{(kT_e)^2} \right)^{4/9} \text{ cm}^2 \]  \tag{A8}
and a more refined model yields, \(10\)

\[
\sigma = \frac{6 \times 10^{-6} Z^4}{T^2} \ln \Lambda \text{ cm}^2 \quad (A9)
\]

\(\ln \Lambda\) is of the order of 10 for \(1,000^\circ \text{K} < T < 10^6\text{K}\) and \(10^{12} < n_e < 10^{21}\).

The total cross-section of an electron for scattering a photon, \(3\)

\[
\sigma_s = \frac{8\pi}{3} \left( \frac{e^2}{m_e c^2} \right)^2 = 6.65 \times 10^{-25} \text{ cm}^2 . \quad (A10)
\]

The cross-section for the radiative capture of free electrons into bound states of a hydrogenic atom, \(3\)

\[
\sigma_{\text{cp}} = \frac{\nu}{\nu_v} \frac{gh\nu_v}{\frac{1}{2} m_e V^2} \quad \text{cm}^2 \quad (A11)
\]

where,

\[
W = \frac{2^4}{3^{3/2}} \frac{\hbar e^2}{m_e c^2} = 2.11 \times 10^{-22} \text{ cm}^2 , (-h\nu_v) \text{ is the energy of the ground state, } (-h\nu) \text{ is the energy of the } p \text{ state into which the free electron is captured and } g \text{ is a correction factor, approximately unity}. \quad (3)\]

One of the commonly used approximations for describing a plasma is the LTE assumption. In the following we will give very briefly the definition of this situation and the condition that must be met before applying this approximation. A plasma in complete equilibrium can be fully described by the following four equations, \(5\)

a) the radiation is described by the Planck equation, viz

\[
E(\lambda,T) = \frac{2h\nu^2}{\lambda^5} \exp \left( \frac{hc}{\lambda kT} \right) \frac{1}{1 - \exp \left( \frac{hc}{\lambda kT} \right)}, \quad (A12)
\]

b) the plasma particles have a Maxwellian velocity distribution,

\[
dn(V) = 4\pi m \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left(-\frac{mV^2}{2kT} \right), \quad (A13)
\]

c) the excited states population is described by the Boltzmann equation, viz

\[
\frac{n_p}{n_q} = \frac{g_p}{g_q} \exp \left( \frac{I_p-I_q}{kT} \right), \quad (A14)
\]
d) the degree of ionization is described by the Saha equation,

\[
\frac{n_{e}n_{i}}{n_{a}} = \frac{g_{i}}{g_{a}} 2 \left( \frac{2\pi m kT}{e h^{2}} \right)^{3/2} e^{-\frac{I}{kT}} \tag{A15}
\]

McWhirter\textsuperscript{55} defined LTE as a case for which, in a sufficiently dense plasma, equations b, c and d can describe the state of the plasma to some degree of approximation. Density-wise the condition, \(n_{e} > 1.6 \times 10^{12} \times T^{1/2} (1 - I)\), where \(T\) is in degrees and \(I\) in eV should be met before the LTE approximation is possible. Besides being dense enough, sufficient time should be given to the plasma to allow the passing of all transient phases. The following equations, quoting from various sources, describe the time necessary to complete some transient phases in a reacting plasma. The collision-relaxation time, required for reaching a unique translational temperature, for identical particles is

\[
t = \frac{A^{1/2} T^{3/2}}{8.8 \times 10^{-2} n Z^{4} \ln \Lambda} \quad \text{sec, from Ref. 10.} \tag{A16}
\]

and

\[
t = \frac{1.14 A^{1/2} T^{3/2}}{n Z^{4} \ln \Lambda} \quad \text{sec, from Ref. 3.} \tag{A17}
\]

where \(A\) is the atomic weight (for electrons \(A = 1/1823\)), \(T\) in degree K and \(\ln \Lambda\) is a function of \(n_{e}\) and \(T\), given in tabular form in Refs. 3 and 10. For \(n_{e}\) between \(10^{10}\) to \(10^{18}\) cm\(^{-3}\) and \(T\) between \(10,000\) K to \(100,000\) K \(\ln \Lambda\) is around 6. The time given in Ref. 10 is one order of magnitude larger than the appropriate time of Ref. 3. For unlike particles, the time needed for equipartition of energy among the two species is given by

\[
t_{\text{equ}} = 5.87 \frac{A A_{1}^{1/2}}{n_{1}^{2} Z_{1}^{2} Z_{1}^{2} \ln \Lambda} \left( \frac{T}{A} + \frac{T_{1}}{A_{1}} \right)^{3/2} \text{sec.} \tag{A18}
\]

Griem suggested the following conditions for LTE, when considering a stationary plasma\textsuperscript{43}

a) To apply LTE equations (Eqs. A13 to A15) to all the neutrals (i.e. including ground state atoms), the electron density should obey the condition

\[
n_{e} \geq 9 \times 10^{17} \left( \frac{E_{2}}{E_{H}} \right)^{3} \left( \frac{kT}{E_{H}} \right)^{1/2} \text{cm}^{-3} \tag{A19}
\]

b) To apply LTE conditions to excited states only, (from energy level \(p\) and above) the electron number density should obey the relation

\[
n_{e} \geq 7 \times 10^{18} \frac{Z^{7}}{p^{17/2}} \left( \frac{kT}{Z E_{H}} \right)^{1/2} \text{cm}^{-3}, \tag{A20}
\]

where \(E_{H}\) is the ionization potential of a hydrogen atom, \(E_{2}\) the energy
associated with the second energy level, \(T\) is in degree K. For a transient plasma, except for the above two conditions, Griem argues that the following times should be much shorter than a typical plasma time \(T_{plasma}\). (A typical plasma time, for a plasma created by an electrical discharge can be the plasma lifetime and for plasma created in a shock tube, the residence time in the investigated geometry, for example the nozzle).

1. The time to reach a unique temperature for atoms and electrons i.e., \(T_a = T_e\), for singly ionized gases.

\[
\text{t}_{eq,a-e} = \frac{n_a}{n_e} \frac{m_a}{m_e} \frac{1}{3 \times 10^{-7} \left( \frac{E_H}{kT} \right)^{3/2} n_e} \quad \text{sec.} \tag{A21}
\]

2. The time to reach a unique temperature to describe both the ion and electron gas, is

\[
\text{t}_{eq,i-e} = \frac{m_i}{m_e} \frac{1}{3 \times 10^{-7} \left( \frac{E_H}{kT} \right)^{3/2} n_e} \quad \text{sec.} \tag{A22}
\]

where \(m_a\), \(m_i\), and \(m_e\) are the masses of the atom ion and electron, respectively, \(n_e\) and \(n_a\) the number density of electrons and neutrals respectively in \(\text{cm}^{-3}\). Zeldovitch and Raizer\(^{10}\) suggested the following for the above mentioned times,

\[
\text{t}_{eq,a-e} = \frac{m_a}{n_a \bar{V}_e \sigma_{e,elas} 2 m_e} \quad \text{sec,} \tag{A23}
\]

and

\[
\text{t}_{eq,i-e} = \frac{252 A_i T^{3/2}}{n_z^2 \ln \Lambda} \quad \text{sec,} \tag{A24}
\]

where, \(A_i\) is the atomic weight of the ions. Other typical times for a reacting flow are; The recombination relaxation time,

\[
\text{t}_{rec} = \frac{1}{K_R n_e^2} \quad \text{(A25)}
\]

where \(K_R\) is expressed in \(\text{cm}^6 \text{sec}^{-1}\).

The relaxation time for energy level \(p\),
for collision processes
\[ t_{\text{relax.}} = \frac{1}{K_{pq} n_p} \text{ sec.} \] (A26)

and for radiative processes
\[ t_{\text{relax.}} = \frac{1}{A_{pq} n_p} \text{ sec.} \] (A27)

The typical flow time,
\[ t_{\text{flow}} = \frac{L}{u} \]

Where \( L \) is a typical flow distance, for many plasma flows the mean free path \( \lambda \) might serve as typical distance, \( u \) is a flow speed.

Radiation:

Equilibrium radiant energy density
\[ E = 7.56 \times 10^{-15} \frac{T_{\text{deg}}^4}{\text{erg/cm}^3} \] (A28)

Spectral equilibrium radiant energy density
\[ E_{\nu \nu'} = \frac{8\pi \nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \text{ d\nu} \frac{\text{erg}}{\text{cm}^3} \] (A29)

where \( c \) is the speed of light. The equation is a maximum for \( h\nu = 2,822 kT \).

Spectral equilibrium radiation intensity.
\[ I_{\nu} = \frac{c E_{\nu \nu'}}{4} = \frac{2\nu^3}{c^2} \frac{\text{d\nu}}{e^{\frac{h\nu}{kT}} - 1} \frac{\text{erg}}{\text{cm}^2 \text{ sterad}} \] sec-1 sterad. (A30)

The frequency-integrated volume emission coefficients for a LTE hydrogen plasma are,69
\[ E_{\text{cc}} = Y n_e \left( \frac{I}{kT} \right)^{-1/2} \tilde{g}_{\text{cc}} \text{ free-free transitions} \] (A31)
\[ E_{\text{cp}} = Y n_e \left( \frac{I}{kT} \right)^{1/2} \frac{2\tilde{g}_{\text{cp}}}{p^3} \text{ free-bound transitions} \] (A32)
\[ E_{\text{pq}} = Y n_e \left( \frac{I}{kT} \right)^{3/2} \exp \left( \frac{I}{p^2 kT} \right) \frac{4\tilde{g}_{\text{pq}}}{p^3} \text{ bound-bound transitions} \] (A33)

where \( Y = \frac{64}{3} \left( \frac{\pi}{3} \right)^{1/2} (\alpha a_o)^3 \frac{I}{n} \approx 3.54 \times 10^{-13} \text{ eV} \times \text{cm}^3 \text{ sec}^{-1} \) and \( \tilde{g} \) is the average Gaunt factor. From Spitzer3 the total amount of energy radiated in free-free transitions, per \text{cm}^{-3}, per sec, for a Maxwellian distribution of electron velocities is,
\[ E_{cc} = 1.42 \times 10^{-27} Z^3 n_i^2 T_e^{1/2} \text{ erg cm}^{-3} \text{ sec}^{-1} \] (A34)

For a singly ionized plasma the equation of Meehan\textsuperscript{69} and Spitzer\textsuperscript{3} agree very well.

Because of the complexity of the radiative terms, it is common practice to solve the equations of motion for reacting plasmas under the assumption of optically thin or thick plasmas. In the following we will briefly review the definition and conditions for such cases.

Optically thin plasma: for this case the photon mean free path \( 1/\rho \kappa_\nu \), greatly exceeds the characteristic length in the problem, i.e., \( 1/\rho \kappa_\nu \gg L \), \( \kappa_\nu \) is the mass absorption coefficient at frequency \( \nu \). In this case radiation absorption can be neglected. Optically thick plasma: the photon mean free path is much shorter than the characteristic length in the problem, i.e., \( 1/\rho \kappa_\nu \ll L \). In this case all radiation is trapped in the plasma. To decide whether the plasma is optically thin or thick, the photon mean free path must be determined for each of the components constituting the radiation field. For bound-free transitions, Ref.\textsuperscript{10} suggests that,

\[ \rho \kappa_{pc} = 9.6 \times 10^{-8} \frac{n_T Z^2}{T^2} \frac{\exp \left( \frac{h \nu - I}{k T_e} \right)}{\left( \frac{h \nu}{k T_e} \right)^3} \text{ cm}^{-1} , \] (A35)

and for transitions involving the ground state,

\[ \rho \kappa_{lc} = 9.6 \times 10^{-8} \frac{n_T Z^2}{T^2} \frac{2 I}{k T_e} \frac{1}{\left( \frac{h \nu}{k T_e} \right)^3} \text{ cm}^{-1} , \] (A36)

where \( n_T \) is the number density of the heavy particles, \( I \) the ionization potential of the gas under consideration, \( \kappa_{pc} \) is the mass absorption coefficient for bound-free radiative transitions involving excited atoms, and \( \kappa_{lc} \) is the mass absorption coefficient for bound-free radiative transitions involving ground state atoms. For an electron temperature in the range of 1 eV to 2 eV for singly ionized argon plasmas, the last two equations reduce to

\[ \rho \kappa_{pc} \approx n_T x 10^{-19} \text{ cm}^{-1} , \] (A37)

and

\[ \rho \kappa_{lc} \approx 5 n_T x 10^{-18} \text{ cm}^{-1} , \] (A38)

If the division between optically thin and thick plasmas is taken to be when \( L = 1 \text{ cm} \), then the radiation from bound-free transitions involving excited states only, will be optically thin for \( n_T < 10^{19} \text{ cm}^{-3} \). Similarly the
radiation from bound-free transitions involving ground state atoms is optically thin if $n_m < 2 \times 10^{17} \text{ cm}^{-3}$. In many experimental situations, the plasma behaves optically thin toward radiation involving excited states, but is optically thick for the resonance transitions.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Formulation</th>
<th>Remarks</th>
<th>Validity Range</th>
<th>Value at $T_e=10,000^0K$, $n_e=10^{16}$ cm$^{-3}$</th>
<th>Evaluated for</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$K_R = 5.2 \times 10^{-23} \frac{Z^3}{(T_e/1000)^{9/2}}$ cm$^3$/sec</td>
<td>Three-body, e-e-i recombination pure collision model</td>
<td>very dense plasma</td>
<td>$1.6 \times 10^{-27}$ cm$^3$/sec</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$K_R = 1.11 \times 10^{-14} \frac{g_a}{g_i} \left( \frac{T_e}{KT_e} + 2 \right)$ cm$^3$/sec</td>
<td>Three body e-e-i recombination pure collisions, recombination to ground state, equilibrium conditions. For symbols see Eq(2.31) in Sec.2.3</td>
<td>dense plasma equilibrium</td>
<td>$5.6 \times 10^{-31}$ cm$^3$/sec</td>
<td>Ar</td>
</tr>
<tr>
<td>11</td>
<td>$K_R = 2.3 \times 10^{-8}T_e^{-9/2}$ cm$^3$/sec</td>
<td>collisions only</td>
<td>very dense plasma $T_e &lt; 1$ e.v.</td>
<td>$2.3 \times 10^{-26}$ cm$^3$/sec</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$K_R = \gamma + K_I \frac{n_{\perp}}{n_e}$ cm$^3$/sec</td>
<td>collisional-radiative model. For details see Sec.2.3, and results, Fig. 3 and 4.</td>
<td>$10^8 \leq n_e \leq 10^{18}$ cm$^{-3}$, $500^0 \leq T_e &lt; 25,000^0$ for optically thin plasma and $9.4 \times 10^{-28}$ cm$^3$/sec for optically thick towards Lyman lines</td>
<td>$4 \times 10^{-27}$ cm$^3$/sec</td>
<td>H</td>
</tr>
<tr>
<td>Ref.</td>
<td>Formulation</td>
<td>Remarks</td>
<td>Validity Range</td>
<td>Value at</td>
<td>evaluated for</td>
</tr>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$T_e=10,000^\circ K$</td>
<td>$n_e=10^{16}, \text{cm}^{-3}$</td>
</tr>
<tr>
<td>24, 64</td>
<td>$K_R = \frac{1}{n_e} \left{ \frac{[A_T + n C q_p]}{n_p} \right}$</td>
<td>Collisional-radiative model. For details see Sec. 2.3 Eqs. (2.67) and (2.68)</td>
<td>$10^9 \leq n_e \leq 10^{17}$</td>
<td>$2.3 \times 10^{-26}$</td>
<td>Ar</td>
</tr>
<tr>
<td>63</td>
<td>at $p = p^*$</td>
<td></td>
<td>$500 \leq T_e \leq 25,000$</td>
<td>$6 \times 10^{-26}$</td>
<td>Ar seeded with cesium</td>
</tr>
<tr>
<td>62</td>
<td>$K_R = 1.15 \times 10^{-26} (T/10,000)^{-5.27}$</td>
<td>Results from the model of Ref. 8 when only collisions processes are accounted for. Developed for nitrogen. The equation presented is a curve fit to the calculated values.</td>
<td>very dense plasma</td>
<td>$4,000 \leq T_e \leq 20,000$</td>
<td>N</td>
</tr>
<tr>
<td>68</td>
<td>$K_R = 1.28 \times 10^5 x T^{-1.8} \left{ 10^{-\frac{3410}{T} n_e^{1.64}} \right}$</td>
<td>Curve fitting to experimental data on argon plasma jet. In the data reduction, LTE condition was assumed. It was suggested that dissociative recombination is the main mechanism.</td>
<td>$10^{12} \leq n_e \leq 10^{15}$</td>
<td>$2.1 \times 10^{-27}$</td>
<td>Ar</td>
</tr>
<tr>
<td>22</td>
<td>$K_R = 0.652 \times 10^{-32} \left( \frac{T_{exc}}{T} + 2 \right)$</td>
<td>Collisional plasma, LTE condition.</td>
<td>dense plasma</td>
<td>$1.3 \times 10^{-29}$</td>
<td>Ar</td>
</tr>
</tbody>
</table>

$\exp \left( \frac{\theta - T}{T_{exc}} \right)$

for argon $\theta = 182,850^\circ K$,

$T_{exc} = 134,000^\circ K$
FIG. 1: IONIZATION OF ARGON ATOM BY ELECTRON IMPACT,
TOTAL IONIZATION CROSS-SECTION VS. ELECTRON ENERGY

\[ \sigma = C(E_e - I) \]

- \( C_{\text{min.}} = 1.286 \times 10^{-17} \text{cm}^2/\text{eV} \)
- \( C_{\text{max.}} = 1.720 \times 10^{-17} \text{cm}^2/\text{eV} \)
- \( C = 1.5 \times 10^{-17} \text{cm}^2/\text{eV} \)
FIG. 2 RECOMBINATION RATE CONSTANT VS ELECTRON TEMPERATURE (REF. 41)

\[
3 \text{-body recombination rate constant } K_R (\text{cm}^6/\text{mole}^2\text{sec}) = 8.34 \times 10^{39} T^{-4.5} \text{ cm}^6/\text{mole}^2\text{sec.}
\]
FIG. 3  THE THREE-BODY (ELECTRON-ION-ELECTRON) RECOMBINATION RATE CONSTANT FOR OPTICALLY THIN HYDROGEN PLASMA (Ref. 8)
FIG. 4  THE THREE-BODY (ELECTRON-ION-ELECTRON) RECOMBINATION RATE CONSTANT FOR OPTICALLY THICK (TOWARDS THE LYMAN SERIES) HYDROGEN PLASMA (Ref. 8a)
FIG. 5 THE THREE-BODY (ELECTRON-ION-ELECTRON) RECOMBINATION RATE CONSTANT FOR ARGON PLASMA (Ref. 64)
FIG. 6a. PLASMA DENSITY VS NOZZLE AREA RATIO (REF. 20).

FIG. 6b. PRESSURE VS NOZZLE AREA RATIO (REF. 20).

FIG. 6c. ELECTRON NUMBER DENSITY VS NOZZLE AREA RATIO (REF. 20).

FIG. 7. PRESSURE VS NOZZLE AREA RATIO (REF. 20).
FIG. 9a. ELECTRON NUMBER DENSITY VS NOZZLE AREA RATIO (REF. 28).

FIG. 9b. HEAVY-PARTICLE AND ELECTRON TEMPERATURE VS NOZZLE AREA RATIO (REF. 28).

FIG. 9c. HEAVY-PARTICLE AND ELECTRON TEMPERATURE VS NOZZLE AREA RATIO (REF. 28).

FIG. 9d. MACH NUMBER VS NOZZLE AREA RATIO (REF. 28).
NITROGEN

MEAN ELECTRON DENSITY, \( N_e \times 10^{-15} \text{ cm}^{-3} \)

DISTANCE FROM THROAT

(1 cm. NOZZEL PROFILE (TO SCALE))

FIG. 11a. MEASURED VALUES OF THE MEAN ELECTRON DENSITY AT MEASURED POINTS ALONG THE NOZZLE (REF. 30).

RECOMBINATION RATE COEFFICIENT, \( k, \text{ cm}^3/\text{sec} \)

ELECTRON DENSITY AT MEASURED UPSTREAM POINT

FIG. 11b. MEASURED RATE COEFFICIENT AS FUNCTION OF ELECTRON DENSITY AT UPSTREAM STATION (FIRST WINDOW) (REF. 30).
FIG. 12. ELECTRON TEMPERATURE VS DISTANCE MEASURED ALONG THE NOZZLE AXIS (REF. 3).

FIG. 13. ELECTRON NUMBER DENSITY VS DISTANCE MEASURED ALONG THE NOZZLE AXIS (REF. 3).
FIG. 14. RECOMBINATION RATE CONSTANT VS TEMPERATURE (REF. 21).
FIG. 15. X-T WAVE DIAGRAM FOR SUGGESTED EXPERIMENTAL SET-UP TO MEASURE THE RECOMBINATION RATE CONSTANT (REF. 35).
FIG. 16  MAXIMUM FLOW MACH NUMBER ($M_2$) FOR A GIVEN GEOMETRY WHERE AN ATTACHED SHOCK IS STILL POSSIBLE (REF. 35).
FIG. 17A, THE WEDGE MODEL (REF. 48).

CORNER EXPANSION MODELS
FIG. 17C. MODIFIED WEDGE MODEL WITH WINDOW-SHIELD USED IN THE CORNER-EXPANSION STUDIES OF IONIZED GASES.
FIG. 18. SUGGESTED FACILITY FOR RECOMBINATION STUDIES IN EXPANDING PLASMA FLOWS (REF. 44).
FIG. 19  DENSITY VERSUS DISTANCE ALONG THE WEDGE WALL MEASURED FROM THE EXPANSION CORNER (Ref. 37)
FIG. 20a. INTERFEROGRAM ($\lambda = 6993 \text{"A}^\circ$) OF SUPERSOINIC EXPANDING IONIZED ARGON FLOW. $P_1 = 9.06 \text{ mm Hg}$. $T_1 = 297 \text{ K}$. $M_2 = 13.5$.

FIG. 20b. INTERFEROGRAM ($\lambda = 3472 \text{"A}^\circ$) OF SUPERSOINIC EXPANDING IONIZED ARGON FLOW. $P_1 = 9.06 \text{ mm Hg}$. $T_1 = 297 \text{ K}$. $M_2 = 13.5$.
FIG. 21. SCHEMATIC FRINGE PATTERN FOR EXPANDING PLASMA.
FIG. 22. PLASMA PROPERTIES FOR AN IONIZED ARGON PLASMA MEASURED ALONG THE 'EFFECTIVE BOUNDARY LAYER' EDGE FOR DIFFERENT VALUES OF $K_I$. 

$\rho$ v.s. $S$(cm) 

- $K_I = K_A$
- $K_I = 0.75 K_A$
- $K_I = 0.67 K_A$
- $K_I = 0.50 K_A$
- $K_I = 0.25 K_A$

$N_e$ v.s. $S$(cm) $\Delta$ FOR ALL $K_I$'s

$M_3 = 13.5$, $P_i = 9.06\text{ mm Hg}$, $T_i = 297^\circ\text{K.}$
FIG. 23 THE RECOMBINATION RATE CONSTANT (BASED ON MEASURED VALUES OF Ne ALONG THE 'EFFECTIVE BOUNDARY LAYER' EDGE) VS. DISTANCE FROM THE EXPANSION CORNER.
SUPERSOONIC EXPANSION FLOW OF AN IONIZED GAS

Scientific Interim

O. Igra

March, 1970.

AF-AFOSR-1368-68

 UTIAS Review No. 30

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

AFOSR 70-0765 TR

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In a supersonic expansion of an ionized gas, the dominant factor in describing the atomic processes is generally 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 between experimental and theoretical values of $K_R$ becomes even more complex since 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 value of $K_R$. For electron temperatures and number densities in the ranges of $10,000 < T_e < 20,000$ K and $10^{15} < n_e < 10^{18}$ cm$^{-3}$, the "collisional-radiative" model, suggested by Bates et al, appears to be the most promising model. It has been used by many authors in their attempt to solve the equations of motion for a supersonically expanding plasma. In general, for steady, quasi-one-dimension plasma flows, fair agreement exists between theoretical predictions (numerical solutions of the equations of motion) and the experimental results.
1. Ionized Argon Flows
2. Recombination Rate Constants
3. Corner Expansion Flows
4. Nozzle Flows

<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th>LINK B</th>
<th>LINK C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROLE</td>
<td>WT</td>
<td>ROLE</td>
<td>WT</td>
</tr>
</tbody>
</table>

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In a supersonic expansion of an ionized gas, the dominant factor in describing the atomic processes generally is the recombination rate constant $K_\text{r}$. 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 $K_\text{r}$ for the same electron temperature and number density. A comparison between experimental and theoretical values of $K_\text{r}$ becomes even more complex since in the majority of the experiments $K_\text{r}$ 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 value of $K_\text{r}$. For electron temperatures and number densities in the ranges $10,000 < T_e < 20,000$ K and $10^{15} < n_e < 10^{18}$ cm$^{-3}$, the "collisional-radiative" model, suggested by Bates et al., appears to be the most promising model. It has been used by many authors in their attempt to solve the equations of motion for a supersonically expanding plasma. In general, for steady, quasi-one-dimension plasma flows, fair agreement exists between theoretical predictions (numerical solutions of the equations of motion) and the experimental results.

A comparison between experimental and theoretical values of $K_\text{r}$ becomes even more complex since in the majority of the experiments $K_\text{r}$ 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 value of $K_\text{r}$. For electron temperatures and number densities in the ranges $10,000 < T_e < 20,000$ K and $10^{15} < n_e < 10^{18}$ cm$^{-3}$, the "collisional-radiative" model, suggested by Bates et al., appears to be the most promising model. It has been used by many authors in their attempt to solve the equations of motion for a supersonically expanding plasma. In general, for steady, quasi-one-dimension plasma flows, fair agreement exists between theoretical predictions (numerical solutions of the equations of motion) and the experimental results.
ERRATA

Please note the following corrections:

PAGE 3:  
The 7th line should read, "...where \( \Psi_s \) is the internal energy of the..."

PAGE 9:  
The 3rd line before the end should read, "...\( \theta \) is the angle between the velocity vector \( \vec{V}_1 \) and...."

PAGE 11:  
The last paragraph should read; We will now review several ways......

PAGE 12:  
Equation (2.25) should read, \[ \int_{V_1}^{\infty} \sigma_e(V_e) \rho_e(V_e) V_e dV \]

PAGE 13:  
The first line after Eq(2.29) should read, \[ v_e^{\text{exc}} = \left( \frac{2E_{\text{exc}}}{m_e} \right)^{1/2} \]

PAGE 14:  
The line before Eq(2.31) should read,...so that,(from Eq(2.30) and Eq(2.28)),

PAGE 31:  
In the second line from the end of the page, the word 'then' should be omitted

PAGE 32:  
The first line after Eq(2.64) should read, where \( \sigma_{qp} \) is.....

PAGE 32:  
In the 5th line after Eq(2.65) the temperature range should be 500°K < T < 1,000°K

PAGE 34:  
The sixth line in the third paragraph should read, "\( K_{n_p} \ll K_{n_e} \) and this would not be the case when"......

PAGE 42:  
Equation (3.8) should read \[ A_{p} + e = A_{gs} + e \]

PAGE 52:  
Equations (5.2) and (5.3) should read,

\[
\begin{align*}
    u \frac{\partial u}{\partial x} + V \frac{\partial u}{\partial y} &= -\frac{k}{m_a} \left[ \frac{\partial T}{\partial x} + \frac{T}{n_{a+e}} \frac{\partial n_a}{\partial x} + \frac{n_e}{n_{a+e}} \frac{\partial T_e}{\partial x} + \frac{T + T_e}{n_{a+e}} \frac{\partial n_e}{\partial x} \right] \\
    &\quad + \frac{n_e}{(n_{a+e})m_a} (V - V_e) B_z 
\end{align*}
\]  
(5.2)
\[
\frac{n_e}{(n_a+n_e)m_a} (u-u_e) B_z,
\]

(5.3)

PAGE 53:
The L.H.S. of Eq(5.7) insert right parenthesis before equal sign.

PAGE 54:
At the beginning of line #22 the number 4 should be deleted.

PAGE 54:
From the beginning of line #25 until the sentence which starts with "A natural flow co-ordinate......"it should read as follows: for many non-equilibrium expansions of ionized gases, since it is valid only for a very dense plasmas, for which the thermalizing collisions are the dominant process, or when the plasma reaches thermal equilibrium.

PAGE 55:
In the 5th line of the second paragraph the word 'extremely' should be deleted.

PAGE 57:
The last word in the 9th line should be 'source'.

PAGE 63:

PAGE A3: (Appendix A)
The sentence: "The time given in Ref.10 is one order of magnitude larger than the appropriate time in Ref.3", which starts in the 4th line after Eq.(A17) should be omitted.

FIGURE 6A
Please add the following scale units for \( \rho(g/cm^3) \) \(10^{-11}, 10^{-10}, 10^{-9}, 10^{-8}\).

FIGURE 11B
The units of the recombination rate constant should be \(cm^6/sec^{-1}\).