A STUDY OF MINORITY ATOMIC ION RECOMBINATION
IN THE HELIUM AFTERGLOW

APPROVED:

Graduate Committee:

R. E. J. Sears
Major Professor

Carl B. Collins
Research Professor

James A. Roberts
Minor Professor

WD Deering
Committee Member

A. L. H. Thomas
Committee Member

Director of the Department of Physics

Dean of the Graduate School

Electron-ion recombination has been under study for many years, but comparisons between theory and experiment have been very difficult, especially for conditions where the ion under evaluation was a minority in concentration. This study describes a direct measurement of the recombination-rate coefficient for the recombination of minority as well as majority ions in the afterglow.

For this evaluation, statistical determination of the photon emission from the afterglow which corresponded to each recombination event indicated the total number of recombination events per unit time. This measurement alone required approximately one billion individual measurements of the radiation from the afterglow, which were accumulated and processed with the aid of a computer. This measurement gave the three-fold product of the recombination-rate coefficient and the densities of the recombining ion and electron. To determine the recombination-rate coefficient, an evaluation of the product of the ion and electron densities was made by the measurement of the population of an excited state in the region known as the Saha region. In this region the excited states are in a thermal equilibrium with the corresponding ion
and electron densities, and the knowledge of the population of one of these states is paramount to the knowledge of the density product of the ions and electrons. The relationship which describes this is known as the Saha equation.

With this information the recombination-rate coefficient could be found by simple division of the two sets of data, but in practice it was found that the electron temperature had to be determined, for evaluation of the Saha equation, and consequently the recombination-rate coefficient. Investigators have assumed that, in the experimental regions described by this report, the electron and neutral temperatures were equal. As a part of this work, this assumption was proven false by both theoretical and experimental analysis. This theoretical analysis was extended to the evaluation of the electron-energy-distribution function, in order to establish the validity of some of the measurements reported.

This method was applied to the helium afterglow at a pressure of 44.6 Torr and over an electron-density range of $10^{11}$ to $10^{12}$ cm$^{-3}$. Under these conditions the minority ion, He$^+$, recombination was determined.

To support the measurement technique, two additional measurements of the recombination-rate coefficient were made under conditions where there was previous data available for comparison. These two measurements were made for the majority ion, He$^+_2$, at 44.6 Torr and the majority ion, He$^+$, at 1.86
Excellent agreement was found between this work and that of the other investigators.

The minority ion recombination at 44.6 Torr was found to be in good agreement with the collisional-radiative recombination theory of Bates, Kingston and McWhirter, but in very poor agreement with the theoretical work of Bates and Khare for neutral stabilization. Strong evidence is presented that this theory does not apply to the recombination of the helium atomic ion.
A STUDY OF MINORITY ATOMIC ION RECOMBINATION
IN THE HELIUM AFTERGLOW

DISSERTATION

Presented to the Graduate Council of the North Texas State University in Partial Fulfillment of the Requirements

For the Degree of

DOCTOR OF PHILOSOPHY

By

William E. Wells, Jr., B.A., M.A.
Denton, Texas
August, 1972
The work of this dissertation, A Study of Minority Atomic Ion Recombination in the Helium Afterglow, overlaps a similar study which followed this by Drs. H. S. Hicks and R. Burton, who extended the methods described here to situations where the molecular ion is the minority ion. A common problem to both of these studies was the verification of the techniques of measurements by the evaluation of the majority ion recombination. The author would like to thank these two for their able assistance and in some instances for the use of their measurements.

The author would like to acknowledge the guidance, advice and many helpful discussions generously given by Dr. C. B. Collins, of The University of Texas at Dallas, who was the research professor for this dissertation.

Je remercie chaleureusement l'équipe française du Service de Physique Atomique, C.E.N.-Saclay, qui m'aide beaucoup.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFACE</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
<td>vi</td>
</tr>
<tr>
<td>Chapter</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. THE HELIUM AFTERTGLOW</td>
<td>4</td>
</tr>
<tr>
<td>III. COLLISIONAL-RADIATIVE RECOMBINATION</td>
<td>14</td>
</tr>
<tr>
<td>IV. EFFECTS OF METASTABLE POPULATIONS ON THE ELECTRON ENERGY BALANCE AND DISTRIBUTION FUNCTION DURING THE AFTERTGLOW</td>
<td>22</td>
</tr>
<tr>
<td>V. PREVIOUS MEASUREMENTS</td>
<td>49</td>
</tr>
<tr>
<td>VI. A MODEL INDEPENDENT MEASUREMENT OF THE RECOMBINATION RATE COEFFICIENT</td>
<td>55</td>
</tr>
<tr>
<td>VII. EXPERIMENTAL METHODS</td>
<td>60</td>
</tr>
<tr>
<td>VIII. EXPERIMENTAL RESULTS AND ANALYSIS</td>
<td>86</td>
</tr>
<tr>
<td>IX. CONCLUSIONS</td>
<td>129</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>131</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Tabulation of Rate Constants Used in Chapters III and IV and the Sources for Their Values</td>
<td>26</td>
</tr>
<tr>
<td>II. Gas Impurities in the 44.6 Torr Helium Afterglow Cell</td>
<td>64</td>
</tr>
<tr>
<td>Figure</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Energy Level Diagram of Helium</td>
</tr>
<tr>
<td>2</td>
<td>Rates of Stabilization Versus Electron Density for He⁺ and He₂⁺</td>
</tr>
<tr>
<td>3</td>
<td>Calculation Scheme for the Partition of Energy</td>
</tr>
<tr>
<td>4</td>
<td>Energy Transferred to a Maxwellian Electron Distribution by the Relaxation of a Non-Maxwellian Electron</td>
</tr>
<tr>
<td>5</td>
<td>Relaxation Time for a Non-Maxwellian Electron</td>
</tr>
<tr>
<td>6</td>
<td>Three Examples of the Electron Energy Distribution Function</td>
</tr>
<tr>
<td>7</td>
<td>Theoretical Electron Temperatures Versus Electron Density</td>
</tr>
<tr>
<td>8</td>
<td>Theoretical Electron Temperatures Versus Pressure</td>
</tr>
<tr>
<td>9</td>
<td>Comparison of Theoretical and Experimental Electron Temperatures</td>
</tr>
<tr>
<td>10</td>
<td>Comparisons of Radiation Temperature to Electron Temperature</td>
</tr>
<tr>
<td>11</td>
<td>Selected Prior Measurements of the Recombination Rate Coefficient of He₂⁺</td>
</tr>
<tr>
<td>12</td>
<td>A Representational Diagram of the Gas Handling System</td>
</tr>
<tr>
<td>13</td>
<td>A Drawing of the Quartz Afterglow Cell</td>
</tr>
<tr>
<td>14</td>
<td>A Block Diagram of the Photon Counting and Data Acquisition System</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>15. A Block Diagram of the 36 GHz Microwave Interferometer and Data Acquisition System</td>
<td>72</td>
</tr>
<tr>
<td>16. A Block Diagram of the Logical Functions Needed for Positive-Negative Signal Separation</td>
<td>76</td>
</tr>
<tr>
<td>17. A Block Diagram of the Initial Signal Processing of Electron Density Measurements</td>
<td>79</td>
</tr>
<tr>
<td>18. A Block Diagram of an X-Band Microwave Radiometer</td>
<td>83</td>
</tr>
<tr>
<td>19. Electron Temperatures as Measured by a Microwave Radiometer at Pressures of 10 to 80 Torr</td>
<td>88</td>
</tr>
<tr>
<td>20. Spectral Intensities of the N^3P \rightarrow 2^3S Series for a Period of 0.025 to 0.825 msec in the Afterglow</td>
<td>93</td>
</tr>
<tr>
<td>21. Spectral Intensities of the N^3P \rightarrow 2^3S Series for a Period of 0.025 to 8.025 msec in the Afterglow</td>
<td>95</td>
</tr>
<tr>
<td>22. Photon Emission Rate from the Atomic Helium Transition 18^3P \rightarrow 2^3S</td>
<td>98</td>
</tr>
<tr>
<td>23. Indications of Electron Temperature for 0.025 to 0.825 msec in the Afterglow</td>
<td>101</td>
</tr>
<tr>
<td>24. Electron Temperature as a Function of Time at 1.86 Torr</td>
<td>103</td>
</tr>
<tr>
<td>25. Electron Temperature as a Function of Time at 44.6 Torr</td>
<td>105</td>
</tr>
<tr>
<td>26. Comparison of Experimental Temperature Results</td>
<td>107</td>
</tr>
<tr>
<td>27. Photon Emission Rates at 44.6 Torr from the N^3D \rightarrow 2^3P</td>
<td>109</td>
</tr>
<tr>
<td>28. Intensity as a Function of Wave Length of an Atomic Line at 5015 Angstroms</td>
<td>111</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>29. Total Photon Emission Rate from Atomic Helium Transitions to the N = 2 Level</td>
<td>113</td>
</tr>
<tr>
<td>30. Electron Densities as a Function of Time</td>
<td>115</td>
</tr>
<tr>
<td>31. Recombination Rate Coefficient of He(^+) as a Function of Electron Density</td>
<td>118</td>
</tr>
<tr>
<td>32. Recombination Rate Coefficient for He(^+) as a Function of the Logarithm of ((G/300)^{-4})</td>
<td>120</td>
</tr>
<tr>
<td>33. Emission of Selected Features of the He(_2) Spectrum as a Function of Time</td>
<td>123</td>
</tr>
<tr>
<td>34. Photon Counting Rates as a Function of Time for Emissions from the Saha Region</td>
<td>126</td>
</tr>
<tr>
<td>35. Recombination Rate Coefficient as a Function of Electron Density</td>
<td>128</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

The study of electron-ion recombination was first begun by Thomson and Rutherford in the late nineteenth century. From that time to the present, it has been a fundamental study in atomic and molecular physics.

Only recently has an understanding of the basic constituent processes involved in this phenomena been developed and models constructed to represent the recombination. However, because of the difficulties involved in making independent measurements of all the parameters of the total recombination process, most of the measurements involve the use of the models dictated by the processes. Naturally, the accuracy of such measurements is limited by the accuracy of the models used.

This work describes a direct measurement of the recombination rate coefficient utilizing a nearly-model-independent method. This work provides the first unbiased representation of the recombination of both majority and minority ion concentrations.

During the course of this research, it was discovered that the energy balance of the electrons in the presence of the processes associated with the recombination yields
electron temperatures which can greatly affect the recombination. Both theoretical and experimental evidences of this fact are presented here.

Helium provides a natural medium for the study of the recombination of electrons and ions. Its structure, surpassed in simplicity only by hydrogen, presents a simple spectrum for analysis. Unlike hydrogen, helium's lowest energy state is that of an atom, rather than a molecule, and it does not react to form stable molecules. For these reasons, it was chosen as a suitable gas for this recombination study.

Being the inverse of ionization, electron-ion recombination is an exothermic reaction which can be best observed in an energetically isolated system. For this reason, the afterglow period of a plasma discharge is the optimum time to observe the electron-ion recombination. During this period there are no external sources of energy which result in excitation or ionization. Any ionizations or excitations which occur in this period must be from internal sources which are associated with the recombination processes. Within a very short time at the beginning of the afterglow the electron temperature thermalizes to a value dictated by the thermal energy balance. It is a unique temperature which is controlled by the afterglow parameters and not a function of external conditions.
A brief description of the recombination processes in helium and the definitions of the pertinent parameters of the afterglow can be found in Chapter II. A discussion of the collisional radiative recombination theory is presented in Chapter III. The theory of electron temperature, along with calculations of the thermal economy and the electron energy distribution function for the helium afterglow are the subjects of Chapter IV. Some of the more interesting previous measurements of the recombination rate coefficient in helium are presented in Chapter V.

In Chapter VI the philosophy of the model independent measurement of the recombination rate coefficient is discussed in detail. The techniques of spectroscopic and microwave measurements used for the evaluation of the recombination rate coefficient, electron density, and electron temperature are described in detail in Chapter VII. The experimental results and the analysis of the data are found in Chapter VIII. Perhaps the most important chapter, Chapter IX, contains the conclusions of this research.
CHAPTER II

THE HELIUM AFTERGLOW

A plasma may be created by the imposition of an electric field on a region containing neutral atoms, thereby ionizing a significant fraction of them. Although helium is normally monatomic, after an electric field is discharged through the gas and ionization has occurred, helium molecular ions, as well as helium atomic ions, are formed. The molecular ions are formed by the three body reaction,

$$\text{He}^+ + \text{He} + X \rightarrow \text{He}_2^+ + X$$ (1)

where X is a third body necessary for the conservation of energy. This reaction is very probable during the afterglow, especially at high neutral particle densities where the third body may be a neutral atom. The diatomic ion produced in reaction (1) can build up significant densities, and by the reaction

$$\text{He}_2^+ + \text{He} + X \rightarrow \text{He}_3^+ + X$$ (2)

form a tri-atomic ion. Oskam has measured the relative concentrations of these three ions under varying conditions, and only the atomic and diatomic ions are important at the gas temperature and pressures of this experiment.
All three of these ions are subject to recombination. The atomic ion, having no simpler species to which it can dissociate during the recombination process, forms a neutral atom, usually in a highly excited state. The statistical culmination of collisional and radiative processes subsequently relaxes the atom to a state where it has a very low probability of re-ionization. This type of recombination is termed collisional radiative recombination, and is discussed in detail in Chapter III. The diatomic ion in process (1) is formed with approximately 2.4 eV of excess energy as can be seen in Figure 1. This energy has the highest probability of creating vibrational excitation in the diatomic molecule. These vibrational levels are also shown in Figure 1. In the recombination process these higher vibrational levels can dissociate into an excited atom and a ground state atom, as has been evidenced by the measurement of the inverse processes of associative ionization by Robertson and Wellenstein.\(^2\) This process is of the form

\[ \text{He}_2^+ + e \rightarrow \text{He}^* + \text{He} \]  

and is called dissociative recombination. In the lowest vibrational state (\(v = 0\)), dissociation is not possible and the process of recombination must be similar to that of the atomic ion except for the exceptions cited in Chapter III. Thus, there are two types of recombination possible for the
Figure 1

An energy-level diagram of mono-atomic, di-atomic, tri-atomic and quadri-atomic helium. The energy scale is in units of electron volts. The excited states are labeled in spectroscopic notation.
Fig 1
of the two, the dissociative recombination has by far the largest rate coefficient. Ten years ago\textsuperscript{3} this process was felt to be firmly established as the principal mode of recombination for the diatomic molecule, but the experimental and theoretical evidence\textsuperscript{4} of the last ten years indicates that dissociative recombination is only a small perturbation term to the recombination which is basically collisional-radiative.

Since there are no known bound neutral states for the two remaining ions shown in Figure 1, He\textsubscript{3} and He\textsubscript{4}, their recombination must be some form of dissociative recombination; but since, as was stated above, their densities are negligible under the conditions of this work, their recombination was not considered.

For each state, \( n \), of excitation of the atom or molecule a probability of ionization, \( P_n \), can be assigned, which will increase with \( n \) because of the lower amount of energy required to achieve ionization. The probability of capture into a state \( n \), \( R_n \), is also an increasing function of \( n \). The number of captures into state \( n \) is

\[
I_+ = R_n [\text{He}^+], \quad (4)
\]

and the number of ionizations out of the state \( n \) is

\[
I_- = P_n [\text{He}(n)]. \quad (5)
\]
Near the ionization limit these rates become very large and the populations of the excited states in this region are self-adjusting to satisfy an equilibrium, with continuum. Saha derived the thermodynamic equilibrium relationship based on Boltzmann's work which relates the population of an excited state, \( q \), to that of the continuum, and is in the case of \( T_e \neq T \)

\[
[\text{He}^+(q)] = [\text{He}^+][e] \frac{g(q)}{g^+g_e} \left( \frac{2\pi mkT_e}{q^2} \right)^{-3/2} e^{U_q/kT}
\]

for the mono-atomic ion, where \( g^+ \), \( g_e \), and \( g(q) \) are the statistical weights of the ion, electron and excited neutral atom, respectively. The mass of the electron is represented by \( m \) and Boltzmann's constant by \( k \). \( T_e \) represents the electron temperature and \( T \) is a distribution temperature which is between \( T_e \) and \( T_g \). The ionization energy of the state \( q \) is \( U_q \). This equation is very important in the study of recombination because it relates the population of an excited state to that of the continuum states.

As an excited state is relaxed to the ground state, it can undergo several transitions to intermediate states before making the final transition to the ground state. These transitions can be either radiative or collisional. Because of the selection rules for radiative transitions in the mono-atomic system, there are only six series of transitions to the \( n = 2 \) level. The \( n = 2 \) level is important in this work because it is the state where the atom or
molecule can be considered to be recombined, and it is the level where the metastable states of both the atom and the molecule are found. These series of transitions are

\[ n^1P + 2^1S, n^1D + 2^1P, n^3P + 2^3S \]
\[ n^1S + 2^1P, n^3S + 2^3P, n^3D + 2^3P \]  

A similar set of transitions exists for the molecule but are much more complicated because of the rotational and vibrational structure of the molecule. The collisional transitions are much less probable at the lower principle quantum levels than the radiative transitions because of the larger energy differences between levels. This is illustrated by numerical examples in Chapter VI.

Three metastable states are found in the atomic and molecular structure of helium. In spectroscopic notation these are \( 2^1S, 2^3S, \) and \( 2^3I \). It should be noted that in Figure 1 the ground state is not shown and these metastable states are of the order of 20 eV above the ground state. The energy of these states and the fact that they are metastable make these states very important in the afterglow decay. For the purposes of this chapter, only the \( 2^3S \) state will be discussed and it will be symbolized by \( M \). This state, as well as the other two, are discussed in more detail in Chapter IV. Because of the large densities which can be built up in a metastable state, the charged state interactions which are normally negligible become significant sources of
ions and energy for the afterglow through

\[ M + M \rightarrow \text{He}^+ + \text{He} + e(15 \text{ eV}) \]  
(8)

and

\[ M + e + \text{He} \left( \frac{1}{2} S \right) + e(19.8 \text{ eV}) \]  
(9)

Both of the processes above are important in the energy balance for the electrons, because of the large amounts of energy imparted to the electrons. In the mutual collision process (8) one of the two metastables is relaxed to the ground state, but the other is re-ionized thus creating a new candidate for recombination. It should be emphasized that this process is not considered to be a part of recombination.

The ground state for both the atomic and molecular systems is the atomic He \( \left( \frac{1}{2} S \right) \), because the ground state for the molecule is dissociative to this state.

In laboratory afterglows contained in cells of finite size, the densities of the constituent species must decay to zero at the walls. This forces a non-uniform density, and unless the afterglow is completely uniform so that no density gradient exists, the ions and electrons diffuse from the regions of high density to a lower density region. Because of the electric forces which exist between the charges, they do not diffuse at their individual rates. Schottky\(^6\) has shown the electrons and ions to diffuse at the same rate,
even though they have different mobilities, $k$, and diffusion coefficients, $D$. Schottky found the diffusion of both could be described by a common ambipolar diffusion coefficient

$$D_a = \frac{D^+ k^- + D^- k^+}{k^+ + k^-}$$

(10)

where the + and - superscripts refer to the positive and negative ions, respectively. In some of the experiments described in Chapter V, this process is extremely important, because all afterglows evolve eventually to the point where they are controlled by diffusion, and experiments which monitor the removal of electrons monitor only the diffusion after this point.

In the foregoing discussion the assumption of an afterglow in pure helium was inherent, but in reality no gas is completely pure. In the case of helium, impurities are particularly dangerous because of the very high ionization potential. Through the very efficient processes of charge exchange and excitation transfer, an excited or ionized helium atom may lose its excitation to an impurity atom. If the purity of the helium is not extremely good, the impurity ions may be of the same order or larger than the helium ions. Of course, measurements under these conditions are useless. The purity of the gas and the methods of purification used in this work are described in Chapter VII.
It is the intent of this brief review to provide a global view of the helium afterglow so that the following chapters can be placed in context as encountered.
CHAPTER III

COLLISIONAL RADIATIVE RECOMBINATION

In 1962 Bates, Kingston and McWhirter realized that for the recombination of a non-dissociating ion both collisional and radiative processes were important. Calculations were made on a model which provided for an initial capture,

\[ \text{He}^+ + 2e \rightarrow \text{He}^*(p) + e \]  \hspace{1cm} (11)

and

\[ \text{He}^+ + e + \text{He}^*(p) + h\nu \]  \hspace{1cm} (12)

where \( p \) is the principal quantum number and \( h\nu \) is the energy liberated by radiation and equals the energy difference between the states \( \text{He}^+ \) and \( \text{He}^*(p) \). Although the state, \( p \), can be any level, the highest probabilities are for the largest values of \( p \). Thus most of the captures are in the very high quantum levels of the Saha region described in Chapter II. The reaction (11) is also very probable in the inverse sense, and the Saha equilibrium is established mainly by the two processes indicated in this reaction. Electrons in these Saha levels are relaxed further by the processes.
\[
\text{He}^* (p) + e \leftrightarrow \text{He}^* (q) + e \quad (13)
\]

and

\[
\text{He}^* (p) \rightarrow \text{He}^* (q) + \nu \quad (14)
\]

where \( p > q \). The flux of relaxing atoms is the net resultant of these two processes acting on the equilibrium populations of the Saha region. Because the rates of processes (11) and (12) are much faster than the net result of (13) and (14), the equilibrium is virtually undisturbed by this flux in the quasi-steady-state approximations. It is this flux which is the rate limiting step in the recombination.

By using the four processes above, Bates, Kingston and McWhirter calculated the populations of each level in a hydrogenic approximation using the semi-classical cross-sections of Gryzinski. From these populations they calculated the rate of production of ground state helium by radiative and collisional de-excitations from all excited states. Thus,

\[
\frac{d[\text{He}(1^1S)]}{dt} = \frac{d[\text{He}^+]}{dt} \Bigg|_{\text{Rec.}} = a[\text{He}^+][e] \quad (15)
\]

where the brackets refer to densities and the subscript Rec. restricts that quantity to the portion due to recombination. In this manner the recombination rate coefficient, \( a \), was calculated as a function of ion densities. In the Bates,
Kingston and McWhirter work they assumed excited state interactions,

$$\text{He}^*(p) + \text{He}^*(q) \rightarrow \text{He}^+ + e + \text{He}$$

(16)

were negligible. In general this is true, except in the case of the metastable states where large populations can build up and processes such as (8) and (9) are quite efficient. Stevefelt\(^9\) has shown that these processes of metastable ionization and the recombination into metastable states produce a coupling between ions and metastables, which significantly affects the measurement of recombination.

The utility of having a recombination rate coefficient which is unique and not a function of external experimental parameters, such as cell size and discharge conditions, has led to the general acceptance of considering metastable-metastable ionization as a separate process not to be included in recombination. This is because the initial metastable densities are controlled by the discharge conditions used to establish the afterglow, and can take considerable time to be brought into equilibrium in the afterglow. At late times in the afterglow the loss of metastables is controlled by diffusion to the walls of the cell. Thus, the inclusion of this process in recombination leads to experimental values which can vary from experiment to experiment and are very difficult to compare to theory.
Under this definition recombination can be considered to be complete at the $n = 2$ level.

Although the above discussion has been for the atomic helium ion, the same type description can be made for the molecular ion.

Bates and Khare\textsuperscript{10} examined the case of very low electron densities and high neutral pressures, where the influences of the neutral atoms become important by the processes

$$\text{He}^+ + e + \text{He} \leftrightarrow \text{He}^*(p) + \text{He} \tag{17}$$

and

$$\text{He}^*(p) + \text{He} \leftrightarrow \text{He}^*(q) + \text{He}. \tag{18}$$

In considering this, it was assumed all collisions were possible and that they could be described classically.

Collins\textsuperscript{11} calculated the recombination rate coefficient considering processes (11), (12), (13), (14), (17) and (18) for the atomic ion, and Deloche\textsuperscript{12} made a similar calculation for the molecular ion. These two calculations are presented in Figure 2, in terms of a stabilization rate, $S$, which is defined in terms of the recombination rate coefficient to be

$$S = \left( \frac{\hbar^2}{2\pi mkT_e} \right)^{-3/2} g^+ g_e a \tag{19}$$

At the higher electron densities the recombination has the characteristics of pure collisional radiative recombination,
A graph of the functional dependence of the electron-ion recombination rates of $\text{He}^+$ and $\text{He}_2^+$, as predicted by the theory of collisional-radiative recombination. The curves are labeled as atomic and molecular recombination, respectively.
STABILIZATION RATE COEFFICIENT (sec$^{-1}$)

EFFECTIVE RECOMBINATION RATE COEFFICIENT (cm$^3$ sec$^{-1}$) AT 300°K

Fig 2
and at the lower electron densities there is very little electron density dependence which is characteristic of neutrally assisted recombination. The differences between the two calculations are due primarily to the difference of mass of the two recombining ions.

As was stated before, Bates and Khare assumed that all collisions were possible. This, however, requires a short examination. In the case of the atomic system, the stabilization by a neutral atom must take place within the potential energy structure of the diatomic molecule. This means that the collision must proceed along a potential energy curve and then, via a curve crossing, must convert to a new potential energy curve which then dissociates to a lower state of excitation, with the change of excitation energy being transferred to the neutral. The calculations of the potential energy curves of the helium molecule by Mulliken indicate no curve crossings. This places considerable doubt on the neutrally assisted superelastic relaxations of the excited atom.

In the case of the diatomic ion,

\[ \text{He}_2^+ + e + \text{He} \leftrightarrow \text{He}_2^*(p) + \text{He} \]  \hspace{1cm} (20)

and

\[ \text{He}_2^*(p) + \text{He} \leftrightarrow \text{He}_2^*(q) + \text{He} \]  \hspace{1cm} (21)
proceed within the triatomic potential energy structure of the He₃ molecule. Since there are no known bound states for this molecule and because of the possibility of large dynamic terms due to the vibrational and rotational structure of He₄, the assumption of "all collisions possible" may be more valid.

In the following chapters the measurement of the recombination rate coefficient will be compared to the theory presented here.
CHAPTER IV

EFFECTS OF METASTABLE POPULATIONS ON THE ELECTRON ENERGY BALANCE AND DISTRIBUTION FUNCTION DURING THE AFTERGLOW

Bates and Kingston\textsuperscript{14} considered the energy balance under conditions where the only source of energy was due to the release of energy in the recombination process of Bates, Kingston and McWhirter (see reference 7) and the drain of energy due to electron-neutral collisions. Ingraham and Brown\textsuperscript{15} later included the effects of the metastable populations through the reactions

\[ \text{He}(2^3S) + \text{He}(2^3S) \rightarrow \text{He}^+ + \text{He} + \text{e}(15 \text{ eV}) \]  \hspace{1cm} (22)

and

\[ \text{He}(2^3S) + \text{e} \rightarrow \text{He}(1^1S) + \text{e}(19.8 \text{ eV}) \]  \hspace{1cm} (23)

The values of energy shown within the brackets are the maximum energies which can be transferred to the electrons. Ingraham and Brown calculated the average energy for process (22) would be 9 eV, because some of the energy would be transferred to the heavy particles, and assumed that all of this energy would then be assumed by the background electron gas by
Miller, Verdeyen and Cherrington\textsuperscript{16} pointed out that experiments\textsuperscript{17} have shown that in reaction (22) almost all of the energy is transferred to the ejected electron and that at higher pressures there would be a competition between (24) and

\[ e(\varepsilon_1) + He(\varepsilon_2) + e(\varepsilon_1 - \Delta\varepsilon) + He(\varepsilon_2 + \Delta\varepsilon) \]  

(25)

for the energy of the non-maxwellian electron. Thus, there should be a partition of this energy between the background electrons and neutrals. Miller, Verdeyen and Cherrington estimated that this partition would be proportional to the weighted ratio of their collision frequencies. Certainly this is a more valid assumption than that of Ingraham and Brown for higher pressures, but it is still inaccurate as is shown in this chapter.

This theoretical investigation assumes that the dominant ion is He\textsuperscript{2+}, and calculations are made for pressures between 10 and 80 Torr.

The metastables He(2\textsuperscript{1}S), He(2\textsuperscript{3}S) and He\textsubscript{2}(2\textsuperscript{3}Σ) can be sources of energy for the electrons by (22) and (23), plus

\[ He(2\textsuperscript{1}S) + He(2\textsuperscript{1}S) \rightarrow He^+ + He + e(16.6 \text{ eV}) \]  

(26)

\[ He\textsubscript{2}(2\textsuperscript{3}Σ) + He\textsubscript{2}(2\textsuperscript{3}Σ) \rightarrow He^+ + 3He + e(11.3 \text{ eV}) \]  

(27a)

\[ \rightarrow He\textsubscript{2}^+ + 2He + e(13.7 \text{ eV}) \]  

(27b)
\[ \text{He} (2^1S) + e \rightarrow \text{He} (1^1S) + e (20.6 \text{ eV}) \]  
\[ \text{He}_2 (2^3\Sigma) + e \rightarrow 2\text{He} (1^1S) + e (17.9 \text{ eV}) \]

and, in addition, the cross-reaction between two different metastable species can occur.

A very efficient process for depletion of the He(2^1S) population is

\[ \text{He} (2^1S) + e + \text{He} (2^3S) + e (0.79 \text{ eV}) \]

which forms a conversion of He(2^1S) to He(2^3S).

Energy is also released by the processes of recombination discussed in Chapter III. At each level in the relaxing atom there is a competition between the electron and neutral relaxation processes. Only that energy which is released directly to the electrons should be considered. The rate coefficient for this is taken from the work of Berlande et al., because that measurement separates the recombination rate coefficient into electron stabilized and neutrally stabilized components.

The energy sink or cooling is primarily due to electron neutral collisions,

\[ \text{He} (\varepsilon_1) + e (\varepsilon_2) \rightarrow \text{He} (\varepsilon_1 + \Delta \varepsilon) + e (\varepsilon_2 - \Delta \varepsilon) \]

where

\[ <\Delta \varepsilon> = \frac{2m}{M} (<\varepsilon_2> - <\varepsilon_1>) \]
but can be augmented by thermal conductivity and diffusion.

All of the rate coefficients for the above processes are contained in Table I together with the references for their values.

The lack of knowledge of the distribution of the metastables, either theoretically or experimentally, forces the adoption of a model where only one metastable state is considered. Although the calculations themselves are readily adaptable to the inclusion of all the metastable states, if their relative populations were known. Even though there is no measurement of the relative populations, the large densities found by Cheret and Lambert for the He(2^3S) indicate that this population may be dominant in this work. Under this assumption, processes (22), (23), (24), (25) and recombination are considered in this calculation. The other processes are either negligible or not appropriate to the one metastable assumption.

The energy balance is formed by

\[
\frac{3}{3t} \left( \frac{3}{2} k T_e N_e \right) = - \frac{2m}{m_{He}} k_{eo} \frac{3}{2} k (T_e - T_0) N_e \quad \text{electron-neutral}
\]

\[+ \frac{1}{2} \beta M^2 \Delta \epsilon'_{MM} \quad \text{metastable-metastable}
\]

\[+ \gamma_{MN_e} \Delta \epsilon'_{se} \quad \text{metastable-electron}
\]

\[+ k_e N_e^2 \Delta \epsilon_r \quad \text{Recombination} \quad (33)
\]
<table>
<thead>
<tr>
<th>Process</th>
<th>Rate Constant</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter III</td>
<td>( \alpha = \alpha_2 + k_e n_e + k_{He} n_{He} ) with: ( \alpha_2 = 5 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} ) ( k_e = 2.7 \times 10^{-9} T_e^{-9/2} \text{ cm}^6 \text{ sec}^{-1} ) ( k_{He} = 2 \times 10^{-27} \text{ cm}^6 \text{ sec}^{-1} )</td>
<td>collisional-radiative recombination (see references 12-18)</td>
</tr>
<tr>
<td>(22)</td>
<td>( \beta = 1.8 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>Phelps and Molnar(^{20}) Collins(^{21})</td>
</tr>
<tr>
<td>(23)</td>
<td>( \gamma = 7 \times 10^{-11} T_e^{1/2} \text{ cm}^3 \text{ sec}^{-1} ) for ( T_e &lt; 2000^\circ \text{k} )</td>
<td>deduced by detailed balance from the work of Schultz and Fox(^{22})</td>
</tr>
<tr>
<td>(24)</td>
<td>( k_{ee} = 7.7 \times 10^{-6} \varepsilon^{-3/2} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>Delcroix(^{23}) Spitzer(^{24})</td>
</tr>
<tr>
<td>(25)</td>
<td>( k_{eo} = 3.7 \times 10^{-8} \varepsilon^{1/2} \text{ cm}^3 \text{ sec}^{-1} ) for ( \varepsilon &lt; 3 \text{ eV} ) ( 6.5 \times 10^{-8} \text{ cm}^3 \text{ sec}^{-1} ) for ( \varepsilon &lt; 3 \text{ eV} )</td>
<td>analytical approximation of the values of Brown(^{25})</td>
</tr>
<tr>
<td>(26)</td>
<td>( \beta = 1.8 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>assumed to be equal to the rate of process (22)</td>
</tr>
<tr>
<td>(27a) ( b) )</td>
<td>( \beta = 4 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>Phelps(^{26}) Collins (see reference 21)</td>
</tr>
<tr>
<td>(28)</td>
<td>( \gamma = 7 \times 10^{-11} T_e^{1/2} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>assumed to be equal to the rate of process (23)</td>
</tr>
<tr>
<td>(29)</td>
<td>( \gamma = 7 \times 10^{-11} T_e^{1/2} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>assumed to be equal to the rate of process (23)</td>
</tr>
<tr>
<td>(30)</td>
<td>( \delta = 3.5 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1} )</td>
<td>Phelps (see reference 26)</td>
</tr>
</tbody>
</table>
where \( k \) = Boltzmann's constant, \( Ne \) = electron density, 
\( m \) = electron mass, \( T_e \) = electron temperature, \( M \) = metastable density, \( M_{He} \) = mass of He and the rate coefficients, \( k_{eo} \), 
\( \beta \), \( \gamma \), and \( k_e \) are defined in Table I.

Because most of the results in Table I are only valid 
when the electron energy distribution function is maxwellian, 
equation (33) will only be valid under the same condition.

Processes (22) and (23) produce very energetic electrons 
which for the purpose of this discussion will be referred to as "hot." These hot electrons are too energetic to be con-
sidered part of the maxwellian distribution, and will undergo reactions (24) and (25) in the process of being thermalized. 
Only the energy which is transferred to the background maxwellian electrons should be considered in equation (33).

Although each of these processes is well known indivi-
dually, their simultaneous action must be considered. To do 
this the collision processes will be examined. Process (25) 
is a binary process and has discrete collisions. For 
mathematical convenience (24) is calculated as a binary process, but in reality, because of the long range inter-
actions of the electrons, the hot electron interacts with 
all of the electrons within its Debye sphere. If this 
sphere is sufficiently populated, the loss process is a continuous rather than discrete process. Figure 3 depicts 
the calculation scheme for the simultaneous action of these 
two processes. An electron is produced at some energy, \( \varepsilon_0 \),
Figure 3

Calculation scheme for the partition of energy of a hot electron interacting with maxwellian electrons and background neutrals.
Calculation scheme for the relaxation of non-maxwellian electrons of energy $E_0$

1- Loss of energy due to collisions with maxwellian electrons

$$\Delta E_{ee} = v_{ee} \left[ E(t) - \frac{3}{2} k T_e \right] \Delta t \quad ; \quad \Delta t = \frac{1}{v_{eo}}$$

2- Loss of energy due to a collision with an atomic neutral

$$\Delta E_{eo} = \frac{2m_e}{M} \left[ E(t) - \Delta E_{ee} - \frac{3}{2} k T_o \right]$$

Partition of energy by the relaxation of a non-maxwellian electron:

- to the maxwellian electrons $\rightarrow \sum_n \left( \Delta E_{ee} \right)_n$
- to the neutrals $\rightarrow E_0 - \sum_n \left( \Delta E_{ee} \right)_n$

Fig 3
and has a continuous loss of energy to the maxwellian electrons, until it is interrupted by a collision with a neutral. After this, it suffers the continuous loss process again until the next collision with a neutral, with the time interval between neutral collisions being the reciprocal of the electron-neutral collision frequency, $v_{eo}$. The partition of energy into the maxwellian electrons is simply

$$\Delta \varepsilon_{ee} = \sum_{n=0}^{nt} (\Delta \varepsilon_{ee})_n$$

where $(\Delta \varepsilon_{ee})_n$ is the energy lost to the maxwellian electrons between the $(n-1)^{th}$ and the $n^{th}$ collisions with neutrals, and $nt$ is the total number of collisions.

The results of this calculation are shown in Figure 4 for a maxwellian distribution of electrons at 300°K. In this figure the parameter, $N_e/P$, is the ratio of the electron density, cm$^{-3}$, to the neutral density in terms of pressure, Torr. It is interesting to note that the energy transferred to the electrons is independent of the kind of metastable considered for the lower values of the ratio $N_e/P$. In this region the approximation of only one metastable is quite valid, for it is not the type of metastable which is important here, but the total density of metastables.

In this same calculation, the relaxation time for a hot electron can be determined by
Figure 4

Energy transferred to a maxwellian electron distribution by the relaxation of a non-maxwellian electron.
Heating of a maxwellian distribution due to a non maxwellian electron

Fig 4
The relaxation time, \( \tau \), cannot be represented in terms of the ratio \( N_e/P \) like the partition of energy. The relaxation times for several examples are shown in Figure 5. The initial energy of the electron is 20 eV and the electron and neutral gases are at 300°K. The results of this yield not only the total relaxation time, but also incremental relaxation times. With the knowledge of the incremental relaxation times and the concept of particle conservation the population of an energy increment can be calculated by

\[
[n_i] = \tau_i \left[ \frac{[n_{i-1}]}{\tau_{i-1}} + \frac{1}{2} \frac{M^2}{\tau_{i-1}} \delta(\varepsilon_i-15) \right] + \gamma \delta(\varepsilon_i-19.8),
\]

where \([n_i]\) is the population density of the energy increment, \(i\), and \(\tau_i\) is the relaxation time from increment \(i\) to \(i+1\). The first term within the brackets on the right hand side is the flux of particles into increment \(i\) from increment \(i-1\). The second term is a dirac delta function production of electrons at 15 eV by process (22), and the last term is the dirac delta function production of process (23). These populations are perturbations to the maxwellian distribution. Three examples of the energy distribution function calculated by equation (36) are shown in Figure 6. The total distribution
Figure 5

Relaxation time for a non-maxwellian electron.
Relaxation time for a non Maxwellian electron

Fig 5
Figure 6

Three examples of the electron energy distribution function. The total electron energy distribution is the sum of the two curves shown for each condition. The incremental energy size for this calculation was $10^{-3}$ eV.
Electron Density per 10^3 eV Energy Slice (eV/cm^3) vs. Energy (eV)

- n_e = 1 x 10^12 cm^-3
- n_e = 5 x 10^11 cm^-3
- n_e = 1 x 10^11 cm^-3

10 Torr
40 Torr
40 Torr
function is

\[ f = f_{\text{max}} + \Delta f \]

where

\[ f = \] the energy distribution

\[ f_{\text{max}} = \] a maxwellian distribution function

\[ \Delta f = \] the perturbation due to the relaxation of non-maxwellian electrons.

In the three examples presented, the metastable density is assumed equal to the electron density.

With the results of this calculation equation (33) can be evaluated because the validity of the maxwellian energy distribution is known and the values of the \( \Delta e \) can be determined from Figure 4.

Because of the large rates of the terms in equation (33), the assumption of a quasi-steady-state equilibrium for temperature can be made. The left hand side of (33) can be written as

\[ \frac{3}{\beta t} \left( \frac{3}{2} k N_e T_e \right) = \frac{3}{2} k N_e \frac{\partial T_e}{\partial t} + \frac{3}{2} k T_e \frac{\partial N_e}{\partial t} \]  \hspace{1cm} (38)\]

where the second term on the right hand side is the mean energy gained or lost by the change in the electron density, and the first term is equal to zero with the quasi-steady-state assumption for temperature,
\[ \frac{\partial T_e}{\partial t} = 0 \]  \hfill (39)

The solution of (33), (38) and (39) gives the equilibrium electron temperatures shown in Figures 7 and 8, as functions of pressure and electron density for several values of metastable densities.

For a comparison of the theoretical temperatures with experimental values the absolute metastable densities must be known. Both can be found in the literature only in one case (see reference 16). This is for 10 Torr and electron densities between $10^{11}$ and $10^{12}$ cm$^{-3}$. In Figure 9 these data are compared to the theoretical results of this work and the results of Miller, Verdeyen and Cherrington (see reference 16) which are described at the beginning of this chapter.

The effects of the non-maxwellian part of the electron energy distribution function are a function of the energy dependence of the quantity being examined. In Chapters VII and VIII the experimental measurements of the electron radiation temperature are described. Thus in this chapter it is useful to examine the effect of the non-maxwellian distribution function on this measurement.

By using the distribution functions calculated here, the radiation temperature can be calculated by

\[
t_R = -m \int_{0}^{\infty} \frac{\sigma(v)}{\sigma(v)} \frac{df(v)}{dv} v^{4} dv \]  \hfill (40)
Figure 7

Theoretical electron temperatures versus electron density, at constant metastable densities, for different pressures.
THEORETICAL ELECTRON TEMPERATURE VS ELECTRON DENSITY AT CONSTANT METASTABLE DENSITIES FOR DIFFERENT PressURES

Fig 7
Figure 8

Theoretical electron temperature versus pressure for several values of electron and metastable densities.
THEORETICAL ELECTRON TEMPERATURE VS PRESSURE FOR SEVERAL VALUES OF ELECTRON AND METASTABLE DENSITIES
Figure 9

Comparison of theoretical electron temperatures to experimental measured values at a pressure of 10 Torr. Plots are experimental results given by Verdeyen et al. (see reference 16). Bars are experimental results obtained at Saclay by Deloche, Monchicourt and Wells using an X-band radiometer. The dotted line represents the theoretical model of Verdeyen. The dashed line represents the theoretical model of Wells for Verdeyen's experimental data.
Electron temperature (°K)

Electron density \((10^{11} \text{ cm}^{-3})\)

Fig 9
No effect of radiation damping is taken into account, because it is not only a function of the distribution but also of the radiation frequency. Figure 10 shows an indication of the deviation from maxwellian \( \frac{T_r - T_e}{T_e} \) as a function of electron density for equal electron and metastable densities, with pressure as a parameter. Again, exact knowledge of the metastable densities is necessary before the distribution function and its effect on a given parameter can be determined. However, for the reasonable assumption of equal electron and metastable densities it has been shown that elevated electron temperatures during the afterglow should be expected for electron densities between \( 10^{11} \) and \( 10^{12} \) cm\(^{-3} \).
Figure 10

The effects of the deviation of the energy distribution function on the radiation temperature of an afterglow for two maxwellian electron temperatures of $300^\circ$ and $500^\circ$K.
\[ T_R = \text{Radiation temperature of } f_0 + \Delta f \]
(Bremsstrahlung electron - neutral):

\[
kT_R = -m \frac{\int_0^\infty \sigma(v)f(v)v^5dv}{\int_0^\infty \sigma(v)f(v)v^4dv}
\]

\[ f(v) = f_0(v) + \Delta f(v) \]

\[ T_e = \text{Temperature of } f_0 \]

**Fig 10**
CHAPTER V

PREVIOUS MEASUREMENTS

Measurements of the rate of recombination of electrons with helium ions have spanned a period of more than twenty years with a considerable lack of convergence. Only the limiting conditions of low neutral gas density and high electron density where the dominant ion is He$^+$ have allowed measurements$^{27-30}$ which have been brought into reasonable agreement with theory (see reference 7).

While the most probable cause of variance has been the stringent experimental criteria which must be met to establish sufficient gas purity (see Chapter II), recombination control of the loss process, and the dominance of one type of ion, a group of past measurements remain which are difficult to fault on technique. These criteria will be discussed briefly in this chapter. Figure 11 illustrates a group of such measurements. The references for these measurements are found noted in parentheses.

The ion densities, with the information of Chapters II, III and IV, can be represented by a set of three coupled differential equations,

$$\frac{d[\text{He}^+]}{dt} = D_1a \gamma^2[\text{He}^+] - a_1[\text{He}^+][e] - \Gamma[\text{He}^+] + \frac{1}{2}BM^2$$  \hspace{1cm} (41)
Figure 11

A graph of selected prior measurements of the recombination rate coefficient for He$_2^+$ ions with electrons as a function of electron density. In parentheses is indicated the reference number of source material.
\[
\frac{d[He^+_2]}{dt} = D_2aV^2[He^+_2] - \alpha_2[He^+_2][e] + \Gamma[He^+] \tag{42}
\]
and
\[
\frac{d[e]}{dt} = D_{1,2}aV^2[e] - \alpha_1[He^+][e] - \alpha_2[He^+][e] + \frac{1}{2}M_2 \tag{43}
\]
where the subscripts 1 and 2 pertain to the atomic and molecular ions, respectively, and the other terms have been previously defined.

As can be seen from the above equations, the change in ion population is not easily related to the recombination process, but these equations can be greatly simplified by the selection of experimental conditions. When the pressure is significantly below 3 Torr, the dominant ion in the afterglow is usually assumed to be He^+. This assumption simplifies to two simpler differential equations, which still require precise knowledge of the remaining concentrations and processes. At pressures significantly above 3 Torr the dominant ion should be He^+_2, and at these pressures some assumptions about the importance of diffusion of the ion species can be made. With these simplifications it still remains a difficult task to resolve the electron recombination rate coefficient from the measurement of electron removal in a helium afterglow.

The measurements by Berlande, Cheret, Deloche, Gonfalone, and Manus (see reference 18), are the most sophisticated of
the measurements based on electron removal, and are the only ones to indicate the electron density dependence of the recombination rate coefficient. In these measurements Berlande et al. assumed the dominant ion to be \( \text{He}^+ \) at pressures between 10 and 100 Torr, and used the model of collisional-radiative recombination with neutral stabilization discussed in Chapter III. They used an expansion of the recombination rate coefficient such that

\[
\alpha = \alpha_o + k_e[e] + k_{\text{He}}[\text{He}]
\]  

(44)

Here \( \alpha_o \) is the rate coefficient for radiative recombination, \( k_e \) is the rate coefficient for a three-body process with electrons and \( k_{\text{He}} \) is the rate coefficient for a three-body rate coefficient with a neutral as the third body. By using this model they made measurements of the electron density at pressures between 10 and 100 Torr so that assumptions about the dominance of the processes could be made, and by a process of computer curve fitting they were able to determine the values of the rate coefficients of equation (44). The main criticisms that can be made about this work are that the electron temperature was assumed to be 300°K, and the effects of metastable-metastable ionization may have been underestimated.

The measurement made by Kerr used a technique similar to the one described in this work, but he had to make
assumptions about the dominance of the ions, and did not have equipment available with sufficient sensitivity to gather enough data to define the measurement well.

The last experiments to be discussed here are those of Johnson and Gerardo,\textsuperscript{32} who heated the electron density thereby changing the relative populations of ions and electrons to metastables and observed the return to equilibrium. Because the experiment is somewhat crude and their assumptions not completely valid, the values they obtained cannot be considered to be definitive, but their work has merit because it is the only measurement of the He\textsuperscript{+}\textsubscript{2} to directly consider the metastable-metastable ionization.
CHAPTER VI
A MODEL-INDEPENDENT MEASUREMENT OF THE
RECOMBINATION RATE COEFFICIENT

In the collisional-radiative recombination theory, described in Chapter III, many captures occur into the high quantum levels, but only those which are stabilized by relaxation to low quantum levels contribute to the net recombination. The measurement technique, to be described in this chapter, monitors such radiative relaxations to the n = 2 principal quantum level. At this level the internal energy of the atom is low enough to be considered stable.

The loss of atomic ions due to recombination alone is

$$\frac{d[He^+]}{dt} \bigg|_R = -\alpha[He^+][e] \quad (45)$$

but this loss of ions is in turn equal to

$$\frac{d}{dt} [He^+] \bigg|_R = \frac{d}{dt} [He(2)] + \frac{d}{dt} [He(1)] \quad (46)$$

the production of ground state and n = 2 level atoms. To avoid double counting the production term for [He(1)] must exclude any production which has resulted from the n = 2 level. The n = 2 level must be considered because of the large population concentration which can exist in the $2^3S$
or $2^1S$ metastable states. The production of these stabilized atoms may be written in terms of the relaxations to have the $n = 2$ level as

$$\frac{d[\text{He}(2)]}{dt} + \frac{d[\text{He}(1)]}{dt} = \sum_{n=3}^{\infty} I(n, 2) + \sum_{n=3}^{\infty} \left[ k_{2n}^2 [\text{He}(2)] + k_{2n}^1 [\text{He}(1)] \right] [\text{He}(n)]$$

where the $k_{2n}^2$ and $k_{2n}^1$ are the rate coefficients for superelastic relaxations due to collisions with electrons and neutrals respectively. Only the first term on the right side of equation (47) is important. The justification for the deletion of the remaining terms is given below.

Radiative transitions to the ground state were not measured, because this radiation is imprisoned in the plasma and only a small amount escapes. A photon released by a relaxation to the ground state is exactly the amount of energy required to raise a ground state neutral to the energy state previously occupied by the relaxed atom. Since the cell contains primarily neutral atoms in the ground state, there is a high probability of reabsorption of the photon. The newly excited atom has a probability of decaying to the ground state by another path. The probability of escape depends on the neutral density and the geometry of the cell. Holstein$^{33}$ has developed a procedure for calculating this probability of escape. Based on this method, Frost and
Phelps calculated the transition probability for a cylinder 3.0 mm in diameter and a pressure of 1 Torr. This value was \(0.527 \times 10^{-3} \text{ sec}^{-1}\). In the case of this experiment, the cell diameter is 10.2 cm in diameter and has a pressure of 1.6 to 44.6 Torr. Both of these larger parameters would present reductions in the escape probability for the ground state transitions in the experiment described herein. However, using the above as a limit, less than 0.003% of the transitions to the ground state take place by direct radiative transitions and escape the cell.

As shown in reaction (13), nonradiative transitions to the \(n = 2\) level are possible. But, these non-radiative transitions are improbable at low principal quantum numbers. The rate coefficient calculated (see reference 8) for the electron-collision superelastic de-excitation rate, reaction (13), for the \(n = 3\) to \(n = 2\) levels of helium, is \(6 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}\). At maximum electron densities, characteristic of the early afterglow, the non-radiative rate of relaxations is limited to \(5 \times 10^3 \text{ sec}^{-1}\). The radiative rate for the same transition quoted by Niles is \(13 \times 10^6 \text{ sec}^{-1}\). Since the most probable non-radiative transition to the \(n = 2\) level, the one with least energy transfer, is from the \(n = 3\) level, the ratio of these two rates can be considered as an upper limit for all transitions. Computing in this manner, less than 0.05% of the relaxations to the ground state could proceed by the non-radiative superelastic de-excitation process.
Since the preponderance of transitions to the \( n = 2 \) level can therefore be assumed radiative, the monitoring of the radiation from the afterglow gives an accurate indication of the recombination events per unit time. Thus, equation (46) becomes

\[
\alpha_{[\text{He}^+][e]} = \sum_{n=3}^{\infty} I(n,2) \tag{48}
\]

The product density is given by the Saha equation, (6), and can be used to simplify equation (47) to

\[
\alpha = \frac{g(q)}{g^+_e} \left( \frac{2\pi mkT_e}{q^2} \right)^{-3/2} e^{Uq/kT} [\text{He}^*(q)]^{-1} \sum_{n=3}^{\infty} I(n,2) \tag{49}
\]

The population of \([\text{He}^*(q)]\) can be determined by

\[
[\text{He}^*(q)] = \frac{I_{2,q}}{A_{2,q}} \tag{50}
\]

where \( I_{2,q} \) is the intensity of radiation from a transition from the state, \( q \), to a particular \( n = 2 \) state, and \( A_{2,q} \) is the transition probability such a transition can take place. By combining equations (48) and (49), \( \alpha \) can be determined from measurable quantities as

\[
\alpha = \frac{g(q)}{g^+_e} \left( \frac{2\pi mkT_e}{q^2} \right)^{-3/2} e^{Uq/rT} I_{2,q}^{-1} \sum_{n=3}^{\infty} I(n,2) \tag{51}
\]
The above description has been for the measurement of the atomic ion recombination. In principle the same type of measurement can be performed for the molecular ion, but in practice, because of the more complex structure of the diatomic molecule, absolute evaluations of the molecular recombination rate coefficient are not possible at this time. The partition functions for the near continuum Saha levels are not known, thus exact evaluations of the molecular Saha equations are not possible. But, relative measurements can be made for the technique described here, and the functional form of the recombination rate coefficient determined. A scale factor for this result can be found from a similar analysis to those described in Chapter V. This was done for the high pressure case and is described in Chapter VIII.
CHAPTER VII
EXPERIMENTAL METHODS

In this chapter, the experimental methods for the spectroscopic measurements of the plasma radiation, measurements of the electron density, and the determination of electron density are discussed.

Included in this report are additional measurements of electron density, which are not described in this chapter. These measurements were performed by colleagues of the author, for this study, but do not represent the work of the author. Since sufficient descriptions of the methods are available in the literature, it will not be repeated here.

As was mentioned in Chapter II, the purity of the gas used in experiments such as this is extremely important to the validity of the experiment. The gas handling system used for the majority of the measurements is shown in Figure 12. The prime purpose of this system was to introduce a very pure low neon content gas into the system, perform additional purification of the gas by cataphoretic pumping,\textsuperscript{36} and control and measure the pressure of the gas in the cell. Because at the high pressure of 44.6 Torr a pressure of approximately 100 Torr was required in the
Figure 12

A representational diagram of the gas handling system.
Fig 12
device used for cataphoretic pumping, temperatures dangerous to the glass developed. To ameliorate this situation, a special glass jacket was constructed around the tube, and water was allowed to flow through it, thereby cooling the walls of the tube. Table II lists the impurities, as determined by spectroscopic analysis of their radiation, at 44.6 Torr.

A cylindrical quartz cell, 17.5 cm in length and 10 cm in diameter, depicted in Figure 13, was used to contain the afterglow. Tantalum electrodes were used in the cell to create the discharge. A low level pulse generator synchronized to a data acquisition system was used to trigger a high voltage pulse generator. In standard operation at the high-pressure the helium discharge was created with 5000 volts for 10-μsec 16 times per second.

Figure 14 shows a block diagram of the photon counting and data acquisition system used to obtain the spectroscopic data. In the visible region, the spectrometer used was a Czerny-Turner .75 meter tandem spectrometer with the grating blazed at 5000 Å. In quartz ultraviolet of the spectrum, data was acquired with a .75 meter Czerny-Turner spectrometer with a lower blaze angle for the grating. An EMI 6256S photo-multiplier was utilized to detect the photons passed by the spectrometer in the visible and ultraviolet regions, and an EMI D224B photomultiplier was used in the infrared regions. After amplification of the output pulses, they
TABLE II
GAS IMPURITIES IN THE 44.6 TORR HELIUM AFTERGLOW CELL

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Observation Wave Length In Angstroms</th>
<th>Ratio of Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO⁺</td>
<td>4274.3</td>
<td>No Trace</td>
</tr>
<tr>
<td>H</td>
<td>4861.3</td>
<td>.02</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>4278</td>
<td>No Trace</td>
</tr>
<tr>
<td>Ne</td>
<td>5850</td>
<td>.017</td>
</tr>
</tbody>
</table>

*The intensity of the impurity was compared to the peak intensity of the 4650-Angstrom helium molecular band, by forming a ratio. The ratio of the background intensity to the peak intensity of the 4650-Angstrom helium molecular band was .01.*
Figure 13

A drawing of the quartz afterglow cell used in the recombination rate coefficient measurements in helium.
Fig 13
Figure 14

A block diagram of the photon counting and data acquisition system.
Fig 14
were processed by an adjustable discriminator which was optimized for maximum signal detection and dark current rejection. A programmable data acquisition system then accumulated the conditioned pulses, in phase increments of time width determined by the program. The system could accommodate a maximum of 500 frames of data per afterglow cycle. The framing scheme utilized for the high pressure part of the experiment was nineteen 10-μsec frames, followed by ninety-six 25-μsec frames, and then one hundred twenty 500-μsec frames. This scheme, with short frames during the early time periods and long frames during the late time periods, allowed adequate time resolution when the count rates were high, and the slope of the data was large. Poorer time resolution occurred where time resolution was not as important, but total counts accumulated in a frame were important in order to minimize statistical errors. In the late time regions, the slope was low and slowly changing; therefore, time resolution was not as important.

The number of photon counts in each frame was converted to a photon count rate by an on-line digital computer. The last 5-msec of data, corresponding to approximately 60-msec into the afterglow, were averaged together to form a base line reference. The data was then adjusted to this base line. Using standard statistical methods, the number of counts in each frame was used to calculate the standard deviation of the data.
The measurement of electron density was made by use of a microwave interferometer. The interferometer is a system which splits radiation from a common source into two paths. One path is used as a reference and the other is transmitted through the cell. The two paths are rejoined and their energy fed to a common detector. With the plasma in an unionized state the two path lengths are made equal. Then, when the plasma is ionized, the increase in dielectric constant will produce a change in phase for one of the paths but not for the other. This phase difference is detected by a change in power at the detector. But, the ionization causes scattering of the microwaves, and this also appears as a decrease in detected power. This attenuation can be evaluated by measuring the decrease in output power when the microwave energy is transmitted only through the cell path. A functional block diagram of the microwave part of the microwave interferometer system is shown in Figure 15. Precision attenuators are provided in each path so the two paths can be equalized in power. A reference cell is in the reference path for two purposes. One, it is desirable to have the only difference between the two paths the existence of the ionized media in the signal path. If the two paths are exactly equal, then not only are the two in phase but have traveled the same number of wave lengths. When the two signals have the same number of wave lengths in each path, then changes in the microwave frequency will not change the phase balance of the
Figure 15

A block diagram of the 36 GHz microwave interferometer and data acquisition system.
Fig 15
interferometer. Second, since the first objective cannot be accomplished exactly, the reference cell can be used to produce small changes in effective path length by changing the pressure of the gas within the cell and thereby changing its dielectric constant. Thus, the cell will allow a small phase trim without creating a discontinuity in the path.

The gas that was chosen for this experiment was \( \text{CO}_2 \), whose dielectric constant change with pressure is well known.

The microwave source used for the experiment was a basic 18 GHz signal produced by a backward wave oscillator. This signal was then doubled in frequency to 36 GHz and then split into the two paths by a 3 db directional coupler. Slide screw tuners were provided in both paths to tune out any reflections in either path. After passing through the respective attenuators and cells, the paths were rejoined by another 3 db directional coupler. Another slide screw tuner was provided prior to the detector to eliminate any reflections at this point.

The analog signal which was produced by the crystal detector was proportional to the square of the power detected, if the power was not so large that the crystal would have been driven out of the square low response region.

In order to make the electron density data relatable to the spectroscopic data in computer analysis, the analog signal had to be converted to a digital signal. This was accomplished by use of an analog to digital converter which
in essence was a frequency modulatable oscillator. The converter used had a base level of zero frequency for zero voltage input and responded linearly to 1 KHz for inputs to ±1 volt. In the evaluation of signals with near zero voltage, the polarity of the signal had to be taken into account. The converter had not only the digital signal output but also a parity output.

Because both polarity signals must be evaluated, a scheme of accumulating positive signals on one cycle of the plasma and negative signals on alternate cycles was used. This could have been accomplished ideally by an alternate cycle gate, two threefold logical "and" functions and a logical "or" function as shown in Figure 16. In this arrangement, coincidence of the signal, S, with the parity, $P_+$, or complementary parity, $\bar{P}$, and the gate, $G_+$, or the complementary gate, $\bar{G}$, to produce positive signals, $S_+$, in the positive cycle and negative signals, $S_-$, in the negative cycle. Thus,

$$S \lor P_+ \lor G_+ = S_+$$

and

$$S \lor \bar{P} \lor \bar{G} = S_-$$

are the logical functions performed by the arrangement depicted in Figure 16.
Figure 16

A block diagram of the logical functions needed for positive-negative signal separation.
CRYSTAL → AMP

A/D

parity

COINC 3 fold

G

GATE

COINC 3 fold

OR

ON LINE COMPUTER

ADAC

timing pulse

Fig 16
Due to equipment limitations, a more complicated scheme had to be used. No modular logical "or" functions were available, but by using the relationship,

$$S_+ \land S_- = \overline{S}_+ \lor \overline{S}_-$$

and vetoing the gate generator, the same functions could be accomplished. This is shown in the functional block diagram in Figure 17. The signal processing can be traced by starting at the crystal detector. The interface amplifier which follows provides an impedance transform as well as an increase in gain. An additional three orders of magnitude gain is provided by the second amplifier. The amplified signal is then converted to a digital signal by the analog to digital converter which has two outputs, a digital signal output and a parity output.

The width of the digital pulses had to be adjusted to avoid ambiguous counting during the time frame changes in the automatic data acquisition system. This was accomplished by differentiating and clipping the positive voltage. The width of the pulse was reduced from 2 msec to 80 µsec. The circuit which produced the pulse modification also provided an impedance transform. The discriminator was used to provide two output signals. These signals were connected to the 2 fold and 3 fold coincidence modules. It was in these modules that the positive signals in the positive cycles and the negative signals in the negative cycles were
Figure 17

A block diagram of the initial signal processing of electron density measurements.
determined. In order to determine the positive signals in the positive cycle in this 2 fold coincidence module, a gate which was started by a timing pulse from the ADAC by a gate generator had to be produced. But, in order to not produce the negative signals during the positive gate, the gate had to be vetoed when the parity signal delivered a negative signal indication. The normal output of the coincidence module contained all the positive counts during the positive cycle, but to perform the local function (see reference 27), in the second 2 fold coincidence module the complement output was delivered to the second coincidence module.

The complement to the positive cycle gate could not be used because of the parity veto which would produce all negative signals during all cycles. So, another gate generator was used which was triggered by a pulse from the positive cycle gate generator which was produced at the end of its cycle. The output from this gate generator was delivered to the 3 fold coincidence module. This, together with the signal from the discriminator, and the parity input produced only negative signals during negative cycles. The complement of this output was checked for coincidence with the complement of the positive signal in the second 2 fold coincidence module, and the complement output was used to fire a Schmitt trigger. This signal was then processed the same as the optical signals in the ADAC and on-line computer.
In addition to the above signal processing, the microwave source had to be blanked once each cycle for reference purposes during the analysis. This was accomplished by a saw tooth signal triggered by the timing pulse from the ADAC, which generated a delayed pulse, which in turn set the output of the backward wave oscillator to zero for its duration.

The ADAC performed the same function as for the optical data. But the on-line computer program had to be modified to alternate the storage of the input signals into separate vectors corresponding to positive signals in positive cycles and negative signals in the negative cycle, since all signals are the same polarity in the counters of the ADAC. The computer had to store the data according to the cycle it was taken in, and negate one of the vectors. Then the two vectors were combined and processed.

When the pulse shift was determined from the law of cosines, the electron density was calculated from

$$[e] = \frac{2\varepsilon_0 mc\omega\Delta \phi}{e^2}$$  (52)

where $\varepsilon_0$ is the permittivity of free space and $m$ is the mass of an electron. $C$ is the speed of light, and $\omega$ is the angular frequency of the microwave radiation. $\Delta \phi$ is the phase shift measured, and $e$ is the charge on an electron.

The measurements of electron temperature were made by two methods: evaluation of the electron radiation temperature
by the measurement of the microwave radiation, and evaluation of the electron temperature by analysis of the radiation from the Saha levels and the continuum to a bound level. The experimental methods for the second of these techniques was the same as that described earlier in this chapter.

For the radiation temperature measurements, a cell size of 2 cm diameter and length of 30 cm was used. This was contained within an over-sized X-band waveguide, as shown in Figure 18. This figure also indicates the experimental arrangement for the measurement. The principle of this type measurement is well described by Bekefi,\(^{37}\) so only a brief description will be given here.

The radiation power produced by a perfect absorber is

\[ P = kTB \]  \hspace{1cm} (53)

where \( k \) is, again, Boltzmann's constant and \( T \) is the electron temperature and \( B \) is the bandwidth of the observation. When a radiation passes through an absorption of less than one, the equivalent temperature is given by

\[ T_R = (1-\alpha) T_0 + \alpha T_\alpha \]  \hspace{1cm} (54)

where

- \( T_R \) = the resultant temperature,
- \( \alpha \) = the absorption,
- \( T_0 \) = the original radiation temperature,

and

- \( T_\alpha \) = the temperature of the absorber.
Figure 18

Block diagram of an X-Band microwave radiometer.
MICROWAVE RADIOMETER (X Band)
Two paths for the radiation from the standard source can be traced in Figure 18 according to the circulation path of the switchable circulator. In one path the radiation from the standard source is transmitted directly to the detection system (mixer). In the other path the radiation is transmitted through the afterglow cell twice. The resultant radiation is given by (54) for this second path. In practice, the difference between the power of the radiation from these two paths and this difference is adjusted to zero by changing the equivalent temperature of the standard source. Under these conditions,

$$T_o = T_a$$  \hspace{1cm} (55)

The detection system used for these measurements allowed the observation during any 20 μsec in the afterglow.

The detection system consisted of a wide-band (1 GHz) double-side-band mixer followed by a 0.01 to 500 mHz amplifier. The bandwidth of this system and the low noise figure of 7.0 db allowed the resolution of temperatures within $10^0 K$ of the thermalization temperatures.
CHAPTER VIII

EXPERIMENTAL RESULTS AND ANALYSIS

The recombination rate coefficient, \( \alpha \), is a very sensitive function of temperature, as is shown later in this chapter. For this reason it is useful to consider the results of the electron temperature evaluations first.

As can be seen from equation (51), two temperatures must be determined for the determination of \( \alpha \): the distribution temperature, \( T \), and the electron temperature, \( T_e \).

The measurements of the radiation temperature described in the preceding chapter gives direct indications of the electron temperature if the electron energy distribution function is near maxwellian. The results of the theoretical analysis of Chapter IV indicate that it is reasonable to expect the energy distribution function to be near-maxwellian under the experimental conditions of this study. In Figure 19, the results of the radiation temperature as a function of electron density are presented.

The results of this measurement are somewhat surprising because for many years almost all investigators assumed the electron temperature to be equal to the gas temperature in these experimental regions. But, these results are in good agreement with the theoretical analysis of Chapter III.
Figure 19

Electron temperatures as measured by a microwave radiometer at pressures of 10 to 80 Torr.
Fig 19
Because the difference in cell size could cause some differences, by diffusion of metastables, between these results and the electron temperature of the afterglow in the larger cell size, an additional method was used to determine the temperature in the larger cell. By smoothing equation (6) and allowing the independent variable to be the ionization energy rather than the principal quantum number,

\[
\frac{d\{\text{He}(u)\}}{du} = \frac{\{\text{He}(U_q)\}}{\Delta U_q}
\]

(56)

where

\[
\Delta U_q = U_q - U_{q-1}
\]

By recognizing that the transition probability is approximately

\[
A_n(2,q) \approx q^{-3}
\]

(57)

then for large \(q\),

\[
A_n(2,q) = C\Delta U_q
\]

(58)

where \(C\) is an appropriate constant for scale. For conditions where

\[
\Delta U_s \ll kT
\]

(59)

the measured intensity \(I_n(2,U)\) is given by
\[ I_n(2,U) = G \int_{U}^{U+\Delta U_S} A_n(2,q(U')) \frac{d[H_\text{e}(U')]}{dU'} \, dU' \quad (60) \]

where \( G \) is the collection of geometric factors. The evaluation of (60) after consideration of (6), (58) and (56) is

\[ \frac{I_n(2,U)}{\Delta U_S} = C'e^U/kT \quad (61) \]

where \( C' \) is a collection of factors which do not depend on \( U \), and hence independent of the detected wavelength for any particular set of afterglow parameters. The distribution temperature appears as the inverse slope of the curve of the logarithm of the left-hand side of (61) when plotted as a function of ionization energy corresponding to the transition measured. The extension of the measurements to the continuum radiation from process (11) allows a similar evaluation of the electron temperature. Since the transition from discrete lines to continuum is smooth, the application of (61) to measurements spanning both sides of the ionization limit suffices to determine both \( T \) and \( T_e \).

The first of the two methods for optical determination of the electron temperature required the accumulation of photon counting rates as a function of wavelength for a constant value of experimental parameters. This was obtained with the use of a synchronous gate which passed photon counts
to the accumulating system during a relatively short time interval.

The lower curve of Figure 20 shows a typical example for a value of $\Delta U_s < \Delta U_g$ resulting in a well resolved spectrum of the $n\,P$ to $2\,S$ series for afterglow times of 0.025 to 0.825 msec. As can be seen, the discrete lines can be resolved only to a value of $q$ equal to 19 or 20.

The upper curve in Figure 20 illustrates the improvement obtained for the same data as the lower curve but with a larger value of $\Delta U_s$. It is interesting to note that the free bound continuum does not decrease with wavelength to the value of the "dark current" of the photomultiplier. In Figure 21, which concentrates on the high energy tail of the continuum, this is readily discernible. This could be due to the typical high energy tail of the electron energy distribution function calculated in Figure 6, but unfortunately it could also be due to the decay of fluorescence of the quartz window following irradiation by the vacuum ultra-violet emission from the active discharge. In any case, since the theory presented in Chapter III makes the basic assumption of a maxwellian distribution, adequate comparison between theory and experiment can only be made in this region. Thus, for this comparison, the high energy tail, whether due to fluorescence or the high energy perturbation of the distribution, must be subtracted to give recombination results due to a maxwellian distribution of electron energy.
Figure 20

Graphs of the intensities, as functions of wavelength in the spectral region continuing the ionization limit, of the \( n^3P + 2^3S \) series. Data is presented in terms of the total photon counts recorded during 300 repetitions of the period extending from 0.025 to 0.825 msec, from the end of the discharge pulse. Lower curve: \( \Delta U_s = 0.07 \) kT; Upper curve: \( \Delta U_s = 0.35 \) kT.
Fig 20
Figure 21

The same characteristics as the Figure 20. Total counts recorded for the period extending from 0.025 to 8.025 msec from the end of the discharge pulse. ΔUS = 0.70 kT.
Fig 21
A second and more convenient optical technique consists of comparing the total energy emitted in the states described by (6) and the radiation emitted from the population of a single state. When an integration of (6) is made from $U_q$ to infinity with the substitution of (61), the expression becomes

$$\left[ I_{n(2,q)} \right]^{-1} \int_{U_q}^{\infty} I_{n(2,U)} \, dU = \frac{kTq^3}{2R_y}$$

(62)

and can be used to continuously monitor $T$ as a function of the time varying experimental parameters. However, although less convenient, the first method provides better sensitivity and, hence, better signal-to-noise ratios.

The application of this second method required the measurement of the absolute intensity of a single line in the Saha region together with the total intensities of all of the members above that line in the Saha region. The data shown in Figure 22 are count rates for the $18^3P + 2^3S$ transition for 1.86 Torr. In this case, the horizontal dimension of the data blocks represents the uncertainty in time caused by the finite duration of each counting interval. Vertically, within each block has been indicated the mean counting rate for that time interval and limits representing that mean rate ± one standard deviation of the counting rate.
Graphs of the photon emission rate as a function of the time following the initiation of the discharge pulse for the atomic helium transition $^3P \rightarrow ^3S$, at 2624 Å and 44.6 Torr. Where resolved limits are shown representing the data ± one standard deviation.
In Figure 23, a typical example of this type of temperature determination is presented for 1.86 Torr. It can be seen here that 300°K is compatible with the inverse slope of the data plotted. The inferred temperatures for 1.86 Torr and 44.6 Torr are presented in Figures 24 and 25, respectively. These measurements at the high pressure can be compared with the radiation temperatures measured directly by the radiometer method in Figure 26. Also in this figure are the measurement results of several other authors. The excellent agreement between all of the measurements supports the conclusions of Chapter IV that the electron temperature should be a unique function of the afterglow parameters.

As stated previously, the total rate of photon relaxation to the n = 2 levels requires the observation of six different relaxation channels. One of these series is shown in Figure 27 for 44.6 Torr. To verify that these lines were free from any spurious contributions from the more abundant molecular bands, a profile of each important line was made from data taken at each of the measurement periods in the afterglow. A selection of this data is shown in Figure 28. The total photon flux rates for both pressures are shown in Figure 29.

The electron density was measured by the technique described in the preceding chapter at 44.6 Torr, and this, along with the electron density measurements at 1.86 Torr, are presented in Figure 30. At 1.86 Torr the measurements
Measurements, at the neutral pressure of 1.86 Torr, of the spectral intensities of the n$^3\text{P} \rightarrow 2^3\text{S}$ series per unit energy interval of ionization potential of the upper state. Where possible, energy intervals corresponding to discrete transitions have been labeled with the value of n of the upper state. Limits corresponding to the data ± one standard deviation have been shown. The temperatures corresponding to the reciprocal of the slope of the fitted linear approximation are indicated. Measurements are taken during the time interval (.025 -.825 msec) following the termination of the discharge pulse.
T = 300 °K

Fig 23
Figure 24

Electron temperature as a function of time following the initiation of discharge pulse. Temperatures derived from data taken at 1.86 Torr. Shaded data blocks results from application of equation (61), open data blocks from equation (62). In the latter case, the vertical dimensions of each block bound probable errors in temperature and contain the mean value.
Figure 25

Electron temperature as a function of time following the initiation of discharge pulse. Temperatures derived from data taken at 44.6 Torr and analyzed according to equation (62).
Fig 25
Comparison of results of temperature measurements from Collins et al., Deloche et al. (solid lines with experimental error bars), Miller, Verdeyen and Cherrington (x), and Delpech (|).
Fig 26

Electron Temperature (°K) vs. Electron Density (cm⁻³)

- 10.15 Torr
- 10 Torr
- 20.25 Torr
- 23 Torr
- 40.1 Torr
- 44.6 Torr

Fig 26
Figure 27

A graph of photon-emission rates at 44.6 Torr, in units of \( \text{cm}^{-3} \text{ sec}^{-1} \), from the \( n^3D \rightarrow 2^3p \) series, versus time in msec. Each level \( n^3D \) is labeled on the graph.
Figure 28

A graph of normalized intensity as a function of wavelengths of the 5 Å interval centered about 5015 Å. The data is repeated for the five successively later afterglow times indicated. Intensity limits representing data ± one standard deviation of the accumulated data are shown.
A graph, as a function of time following the initiation of the discharge pulse, of the total photon-emission rate from atomic helium transitions to levels having \( n = 2 \). The function with the steepest initial slope represents data at a neutral pressure of 44.6 Torr; the other curve, data at 1.86 Torr. At late times limits are shown representing the data \( \pm \) one standard deviation.
Fig. 29

ABSOLUTE TOTAL INTENSITY (photons cm\(^{-3}\) sec\(^{-1}\))

TIME (msec)

$10^{14}$

$10^{12}$

$10^{10}$

$10^{8}$

$0$ $5$ $10$ $15$ $20$ $25$
Figure 30

Electron densities as a function of time following the initiation of the discharge pulse. Upper curve: Data for a neutral pressure of 44.6 Torr. Lower curve: Data for 1.86 Torr.
Fig 30

ELECTRON DENSITY (cm⁻³)
were made by a more sophisticated system which utilized a 36 GHz Fabry-Perot interferometer which is described elsewhere. By combining the temperature and intensity data according to the methods of Chapter VI, the recombination rate was obtained for these two pressures. These results are presented in Figure 31 as a function of electron density. It should be re-emphasized that the data of this figure comprises a set of independent statistical averages for both ordinates and abscissas over the individual ranges of the experimental times. This is indicated qualitatively by the spacing between points.

The theory of Chapter III suggests a dependence of the rate coefficient on the inverse nine-halves power of the temperature. Because of this, the logarithm of $\alpha/[e]$ is plotted as a function of $T^{-4}$ for convenience in Figure 32. In this same figure, at the high temperature end are grouped the experimental results of Hinnov and Hirshberg (see reference 27) and measurements of Motley and Kuckes.

Quite good agreement is found in this figure between the 1.86 Torr values of this work, the high temperature results of the other authors, and the empirical straight line representing the approximation,

$$\alpha = 7.1 \times 10^{-20}[e] \left( \frac{T_e}{300} \right)^{-4.3} \text{cm}^3/\text{sec.}$$

(63)
Figure 31

A graph of the recombination rate coefficient of He$^+$ with electrons as a function of electron density. Measurements grouped to lower electron densities result from data taken at 1.86 Torr, as indicated. Those at higher electron densities result from data taken at 44.6 Torr, as marked.
Fig 31

RECOMBINATION RATE COEFFICIENT, $\text{He}^+$

$\text{cm}^3/\text{sec}$

$10^{-7}$

$10^{-8}$

$10^{-9}$

$10^{-10}$

$10^{10}$

$10^{11}$

$10^{12}$

$10^{13}$

ELECTRON DENSITY (cm$^{-3}$)

1.86 Torr

44.6 Torr
Logarithmic graph of the recombination rate coefficient for He$^+$ expressed as a three-body coefficient and plotted as a function of the logarithm of $(T/300)^{-4}$. Points represent the measurements at 1.86 Torr; open circles, the measurements at 44.6 Torr; x, the values of reference (27); and, +, the interpretations of reference (27) of the work from reference (39). The solid line corresponds to equation (63).
Fig 32

ELECTRON TEMPERATURE

THREE-BODY RATE COEFFICIENT (cm$^6$/sec$^{-1}$) vs $(300/T)^4$
This can be compared with the value of

\[ \alpha_{HH} = 7.8 \times 10^{-20} \ [e] \ (T_e/300)^{-4.5} \text{ cm}^3/\text{sec} \]  \hspace{1cm} (64)

calculated by Hinnov and Hirshberg from classical considerations.

The 44.6 Torr data lies somewhat below this line but parallel to it. This is probably due to the processes of associative ionization (3) which become more important at higher pressures.

If the pressure dependence of this process is represented by

\[ \alpha \propto (1+\nu P)^{-1}, \]  \hspace{1cm} (65)

then all of the data can be represented by

\[ \alpha = 8.1 \times 10^{-20} [e] \ (1+0.079P)^{-1} (T_e/300)^{-4.4} \text{ cm}^3/\text{sec}. \]  \hspace{1cm} (66)

As was stated in Chapter VI, this method of determination can also be applied to the molecular ion recombination with electrons. Unfortunately, because of the difficulties associated with the lack of knowledge of the molecular aspects of the He\textsuperscript{+} ion, only the functional form of the recombination rate coefficient can be determined directly. In Figure 33, the data from sample bands of the He\textsubscript{2} spectra are presented. It was found that all of the important bands decayed with the same time dependence. But, since the molecular structure is
Figure 33

Graph of the absolute intensities of emission of selected features of the He2 spectrum as a function of delay time following the initiation of the power pulse. At late times limits are shown representing the data ± one standard deviation. Above each curve is the nominal wavelength of the band represented in the graph by the P(4) line of the $4s^1\Sigma^+_{ug} \to 2p^1\pi_g$ (4720 Å) band, the Q(7) line of the $3p^3\Pi_g \to 2s^3\Sigma^+_{u}$ (4650 Å) band, and the R(1) line of the $5p^3\Pi_g \to 2s^3\Sigma^+_{u}$ (3350 Å) band.
Fig 33

PHOTON EMISSION RATE (sec\(^{-1}\) cm\(^{-3}\))

TIME (msec)
so vast, no attempt was made to measure the total photon flux rate to the $n = 2$ level. It was assumed, because of a large sample of such lines which all showed the same time dependence, that the total photon flux would have the same time dependence as one of the samples. The characteristics of the radiation from the Saha region are shown in Figure 34. The ratio of these two types of data yields the functional form of the recombination rate coefficient for the $\text{He}_2^+$ ion. This data was scaled by techniques similar to those presented in Chapter V. It should be emphasized that this scale is no better than that of the previous measurements. The results of this are shown in Figure 35, along with the data from Berlande, et al. (see reference 18). The pressure for this measurement was 44.6 Torr. Fairly good agreement is obtained between these two measurements and the differences most certainly lie in the temperature dependence of the rate coefficient, which has not been analyzed. This data is presented only to show that this technique for recombination rate coefficient measurement can be extended to the molecular ion, with good agreement with existing data. A more complete study of this is being performed by one of the author's colleagues at this pressure and 1.86 Torr, and in this study the temperature dependence and a more realistic evaluation of the scale factor for the functional form should be forthcoming.
Graph of the detected photon counting rate as a function of delay time following the initiation of the power pulse for the spectral features of He₂ having the nominal wavelengths indicated. At late times limits are shown representing the data ± standard deviation. The lower curve corresponds to the total intensity of the $16p^3\pi_g + 2s^3\Sigma_u^+$ (2953 Å) band. The upper curve represents the total intensity of the bands and continuum lying within the interval 2920-2930 Å and corresponds to $\Sigma_{n>24}^n p^3\pi_g + 2s^3\Sigma_u^+$. 
Fig 34
Figure 35

Graph of rate coefficients for the recombination of He$_2^+$ ions with electrons, as a continuous function of electron density, at a neutral helium pressure of 44.6 Torr. The scaled values resulting from this work are shown as rectangles bounded by the accumulated statistical errors of measurement and including the average values within each. For comparison, the results interpolated for the same neutral gas pressure from the measurements of the Saclay group (reference 18) are plotted without statistical error (solid curve), together with the predictions of theory (dashed curve) for a constant electron temperature of 300°K.
CHAPTER IX

CONCLUSIONS

It has been shown that the electron temperature under conditions such as those described herein is not, as it has often been assumed by investigators, equal to the gas temperature, but can be significantly elevated. This has probably been one of the most serious problems in helium afterglow work which has caused some of the erratic results.

With the knowledge of the electron temperature and the technique for the measurement of the recombination rate coefficient, the first measurements of the recombination rate coefficient were made where the ion is a minority ion. Excellent agreement was found with the theoretical model of Bates, Kingston and McWhirter (see reference 7), but no support for the neutral stabilization processes of Bates and Khare (see reference 10) was found for the atomic recombination. This is in agreement with the arguments of Chapter III. The recombination of the molecular ion is consistent with this model where it is more realistic to assume "all collisions possible."

As should be the case with all studies, this one has laid the foundations for several additional studies. Of these, the paramount ones are: a more complete analysis
of the molecular ion recombination, the extension of both
the atomic and molecular measurements to different pressures,
and the extension of the optical temperature measurements
to the determination of the electron energy distribution
function which, as was shown in Chapter IV, can become
extreme under certain experimental conditions. At present,
there is no good method for determining experimentally the
electron energy distribution function under such conditions.
REFERENCES


21. Collins and Hurt, 9th Conf. on Ionized Gases (Bucharest), 1969.


