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STUDIES OF IONS IN PLASMAS EXCITED AT MICROWAVE AND HIGH FREQUENCIES

by

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DEDICATION

This is dedicated to my mother, Mrs. Stella Studniarz, for many reasons.
The author would like to express his most sincere thanks to Professor J. L. Franklin, in general for all he has done in making this a reality, and specifically for his clear insights and unparalleled guidance particularly during the crucial periods of this work. Professor Franklin's vigorous interest was a continual source of inspiration to the author.

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CHAPTER I

INTRODUCTION

This study is directed to ion molecule reactions that occur in microwave and high frequency electrodeless discharges. The techniques used to study ion molecule reactions in plasmas of electrodeless discharges up till now have not been well established. This is due in part to the relatively large number of plasma variables (ambipolar diffusion coefficient, positive ion mobilities, electron energy distribution, etc.) most of which are interrelated and dependent on the discharge conditions. For example, a change in gas pressure in a discharge vessel can change the relative ionic composition of the plasma by producing:

1. A change in the electron energy resulting in a new fragmentation pattern.
2. Increased formation of product ions through ion molecule reactions.
3. A change in the positive ion ambipolar diffusion coefficient.

Thus in order to begin this study, it was necessary to establish the dependence of the energies of the electrons and positive ions on the various discharge conditions.

The theoretical calculation of the electron energy distribution was initiated in 1913 by Pidduck (1) after Townsend (2) showed in 1912 that the average energy of the electrons present was greater than that of the gas. Since then numerous calculations have appeared (3-15). No attempt will be made here to review completely the work done in the calculation of the electron energy distribution. An excellent chronological
development along with the description of the calculation of the energy
distribution is given by Loeb (16). It will only be mentioned that the
best known calculations of the energy distribution are the Druyvestyn
distribution (4) for D. C. fields and the Margenau distribution (12) for
alternating electric fields. These two distributions are equivalent in
form for the case of zero oscillation frequency. J. A. Smit (9) made the
first successful derivation of the electron energy distribution that
considers inelastic impacts under conditions for D. C. fields. Hartman
and Margenau (12-13) in working out the breakdown definition for
electrodeless discharges derived the electron energy distribution for
electrodeless discharges in which ionization impacts occurred. Thus a
realistic electron energy distribution can be calculated in principle for
high frequency discharges from considerations of electron dynamics;
however mathematical complexities are such that it has only been solved
for a few inert gases (He, Ne) for which a linear variation of ionization
cross section with energy is approximately true.

The energies of the electrons in gases were measured as long ago as
1912 by J. S. Townsend (2) and more recently by numerous other workers
(17-29). Most of these energies (velocities) were measured to obtain or
supplement mobility, diffusion, or Townsend gas breakdown data. For this
reason, the experiments usually employed D. C. electric fields. Thus,
relatively few measurements of the electron energies in high frequency
plasmas have been reported. For this reason, when the functional
dependence of the electron energies in these systems on the various
discharge conditions are needed one usually resorts to laboratory
measurements.
The classical tool for measuring the electron energy distribution, the Langmuir single probe, requires modification for use in electrodeless discharges since no reference electrode is available. The usual experimental practice is to place a very large electrode in the plasma as a reference electrode and apply a potential between it and the small probe. The electron temperature is obtained from the collected current versus the applied potential trace (30). This is discussed in the Appendix, part c.

The symmetric floating double probe of Johnson and Malter (31) is more suited for electrodeless discharges, especially those involving decaying plasmas. This is due to its small physical size and its low current drain from the plasma. This method differs from the former method in employing two identical small electrodes. The electron temperature is obtained from the collected current versus the applied potential trace (24). A triple probe has been developed (32) that possesses certain advantages over the single and double probes. For a discussion of the triple probe and the earlier methods for determining the electron energy distributions in electrodeless discharges, along with their advantages, assumptions, and limitations, the reader is referred to reference (32).

A considerable amount of work was done to obtain the electron energy distribution in our electrodeless discharge from Langmuir single probe (LSP) studies. Some of the results of this study are given in the Appendix. This method was discontinued in favor of the retarding potential grid technique described below. Although the latter method requires somewhat more apparatus, it yields data not yet attainable from
wire probes. Specifically, the positive ion energy distribution in these plasmas cannot be obtained from LSP data (33). The assumptions and errors in interpretation of LSP data are discussed in detail by L. B. Loeb on page 361-371 in his book (16).

Recently, J. Y. Wada and H. Heil (34) used an energy spectrometer, which employed retarding potential grids, to study extensively the electron energy spectra (distribution) in discharges used for optical lasers. Their energy spectrometer was capable of an energy resolution for electrons of 0.01 eV (35). Energy spectrometers have the advantage of giving the positive ion energy spectra, from which a detailed description of the negative ion energy spectra that covers the probe surface can often be constructed (36).

In this study we report the electron and positive ion energy distributions, and plasma-probe potentials that were obtained by the retarding potential grid method. The sampling process is also discussed because of its fundamental significance in a study of the ion-molecule reaction kinetics in these systems. The pressure range in the energy distribution studies was 0.055-1.0 Torr and the range of input power to the resonant cavity was 5-100 watts.

Although the physical properties of plasmas have been investigated extensively, the knowledge of ionic chemical reactions occurring in steady state plasmas has advanced relatively little since J. J. Thompson first investigated the ions formed in a D. C. discharge in 1921 (37). This is the result of the complexities involved in obtaining a representative sample of the ionic composition of steady state discharges. Of the plasma systems open to investigation at relatively high pressures
only flames have received considerable attention (38). Mass spectrometric sampling of the positive column (39-46), the negative glow (47-48), the Faraday dark space (49), and the cathode region (50-51), of D. C. discharges has met with some success, yielding information on ion molecule reactions and other rate processes occurring in these systems. However, only one recent investigation of ion molecule reaction rates in a steady state high frequency electrodeless discharge has been reported (52).

High frequency plasmas have the advantage of not introducing an additional electrode other than the sampling probe and thus minimize the disturbance to the plasma. However, some of its other properties differ from those of a D. C. discharge and make interpretation of the data difficult. The most disturbing of these from our viewpoint is that the walls of the vessel containing the high frequency plasma are more negative with respect to the plasma than those in the positive column of low voltage D. C. discharges (49). This is a result of a higher electron energy in high frequency plasmas that produces stronger electric fields near the walls and probe orifice. It is ionic processes caused by these electric fields that make it difficult to obtain a representative sample of the plasma and it is these complexities that make interpretation of the experimental data uncertain. It was in part for this reason that the mean electron energy and the plasma-probe potentials were measured by the authors (53).

The sampling of high frequency plasma of nitrogen has been investigated by D. K. Böhme and J. M. Goodings (54-55) using a mass spectrometer in conjunction with double and single electrical probes.
Their results indicate that ion generation processes and ion-molecule collisions occurring in the sheath may strongly influence the composition of the sample extracted. Some evidence was given that the ionic composition extracted from a nitrogen plasma was dependent on the potential applied to the metallic sampling probe. However, they were limited by their pumping speeds to pressures less than 30 microns.

H. Lob (56) made a thorough study of one particular sampling arrangement by observing the energy spread of the ions emerging from the sampling leak. In his experiments ion formation by charge exchange in the sheath, charge exchange in the extraction channel, and secondary electrons released from the metal surfaces of the extraction channel were all observed under the various experimental conditions which he employed. These effects of the sampling channel are not surprising since the ionic mean free path was of the order of a millimeter at the pressures he employed (0.05 Torr) and the channel depth was $2\frac{1}{2}$ mm. The channel depth in our experiments was maintained as small as possible (0.025 mm) to avoid the channel effects described by Lob.

Initial attention of the kinetic study was focused on discharges of methane. The reactions of various positive ions with methane have been investigated by numerous workers (57-64) using ion sources other than gaseous discharges. The most definitive study of methane was made by Field and Munson (65) who were able to reach a pressure of 2 Torr using a high pressure electron impact ion source in their mass spectrometer. The reaction of methane ion and the fragment ions of methane with methane are now well established. Therefore the methane system was a suitable system in which to begin a kinetic study.
CHAPTER II

EXPERIMENTAL

a. Retarding Potential Grid Operation

The electrodeless discharge was driven in most of the experiments on energy distribution by a 2450 megacycle magnetron (medical diathermy unit) that supplied a maximum of 100 watts to an Evenson Cavity (National Bureau of Standards, number 5), (66). The forward and reflected microwave power were measured by reading a Micromatch power meter in the tuning transmission line connecting the oscillator and the discharge tube. The geometric relationship of the cavity, the input wave, and the sampling probe is presented in Figure 1A. This was the most common sampling arrangement. Different regions of the discharge plasma were sampled along the axis of the discharge flame by moving the resonant cavity along the cylindrical discharge vessel.

The positive ions and electrons in the plasma effused from a fast flow system into a high vacuum ($10^{-5} - 10^{-7}$ Torr) through a conical brass probe that had a sampling orifice of 0.5 mm or less diameter in the plane forming the top of the cone section (Figure 1A, B). The depth of the sampling orifice (lip of the orifice edge) is 0.1 mm or less and beveled to minimize collisions with the inside surface of the probe channel (Figure 1B). The probe is held at ground potential.

The experimental arrangement of the retarding potential grid system is shown in Figure 2. The retarding potential grid arrangement was designed by Professor P. K. Ghosh (67). In order to minimize the
FIGURE 1A

Geometric relationship of:

a. Resonant cavity  
b. Power meter  
c. Power generator  
d. Sampling probe

FIGURE 1B

Enlarged cut-away view of the sampling probe orifice showing the details of its construction.
FIGURE 2

Diagram of retarding potential grids and their relationship to the quadrupole mass filter.

A. X-Y recorder.
B. Quadrupole mass filter.
C. Electron Multiplier.
angular spread of ions and electrons before the collector, all the grids are placed 3 mm apart except grids 2 and 3, which are 1 mm apart. The grids were constructed of gold plated high transmission wire mesh. This mesh had an optical transparency of at least 85% as measured by an optical photometer.

The charged species present in the vicinity of the probe aperture are shielded from stray fields which may originate in the retarding grid envelope by grid number 1 which remained at ground potential. This grid also served to drain off any space charge that might build up due to the retardation of ions or electrons. A variable retarding potential is applied to grids 2 and 3. With this double retarding grid, the potential on grid 4 was varied between 0 and 180 volts without any observable effect on the energy distributions. It will be evident subsequently from the method of treating the data that the contact potentials between the brass sampling probe and the various grids does not effect the measurement of the energy distributions and will not enter into the expression for the mean energy. The contact potential between the various grids was removed by gold plating them. A potential is applied to grid 4 and Faraday cup sufficient to repel the undesired species and to collect the desired species. This potential ranged from +180 volts to -180 volts. The electron and positive ion current to the Faraday cup was measured by a Keithley picoammeter (Model 417). In a typical experiment for positive ion energies, grid 1 is grounded and grid 4 and the Faraday cup are 180 volts below ground. The retarding potential is referred to the sampling probe. The integrated energy distributions were obtained from a continuous plot of the retarding potential versus the transmitted
current by an X-Y recorder.

The energy resolution is limited in part by the coarseness of the wire mesh. This is the result of the variation of potential across the individual mesh openings. The effect of the variation in potential across the openings in the mesh on the energy resolution has been calculated by H. Heil (35) for the form of the potential across the openings given by V. K. Zworykin, et. al., (68). H. Heil traced several critical trajectories across the mesh openings. His results show that this effect introduces a relatively small error in these experiments and so is neglected here.

It is pertinent to consider whether a significant proportion of the electrons collected were formed by collision of high velocity ions with the interior walls of the probe. From an examination of the discolored portion of grid number 1 it was evident that the only collision with the probe walls occurred inside of the shallow cylindrical lip of the probe, an aperture 0.5 mm in diameter and less than 0.10 mm in depth (see Figure 1B). About 15-20% of the entering ions might be expected to strike the interior surface of this port (69). Not over one electron would be ejected per wall collision and the ions causing the electron ejection would probably be neutralized and so not be collected. Thus, wall collisions should not have affected the distribution measurements of positive ions. The number of total electrons collected was always some 10 to 100 fold greater than the ions so the secondary electrons resulting from walls collisions would amount to no more than 0.2 to 2.0 per cent of the electrons collected. This is within the reproducibility of our measurements and so can be ignored. It should be emphasized that
the case considered is the most unfavorable one applicable to our conditions. Actually Echme and Goodings (29) have shown that with a sampling aperture such as ours, the ions enter the sampling aperture with a large velocity component normal to plane of sampling aperture. Thus there would be fewer collisions with the interior probe walls than the above estimate would indicate. Some possible disturbing effects arising during the passage of an ion through the sampling channel are discussed in detail by M. Pahl (70). Three sampling probes, with the same probe orifice areas, were constructed with three different conical heights, constituting a variation of cone height by a factor of two, and three sampling probes were constructed of brass, gold plated aluminum, and stainless steel. No significant variation of the electron current, positive ion current, or their ratios, or the electron energy distributions could be attributed to these different sampling probes. The experimental data were reproducible on sweeping the spectrum backward or forward. No significant problems of stability were present. However, the mean electron energy appeared to be slightly dependent on the conditions of the discharge tube. A freshly prepared discharge tube gave mean energies about 4 eV higher than normal. After approximately one hour of discharging no changes in mean energy were observed with time. This could be due to a change in wall potentials produced by a thin layer of metal (translucent at first) sputtered from the probe which in turn could change the diffusion rates. It will be shown that the diffusion controlled electron temperature theory (71) gives values of the mean electron energy that are in reasonable agreement with the experimental values (Chapter V, part b and Table II).
The pressure in the discharge tube was measured by a thermocouple
gauge (Veeco Model DW-1M) and a Pace pressure transducer (Model P7D)
calibrated against a McLeod gauge to give the direct readout of the
pressure on a digital voltmeter.

The metastable species and the ultraviolet radiation present in the
beam are able to pass through the retarding potential unaffected and
register as a positive ion current at the negatively biased collector.
Since this background was constant and relatively small, no attempt was
made to shift the collector out of the path of the ultraviolet radiation.

Experiments performed on plasmas excited at 50 megacycles are also
discussed. The electrical circuitry of this oscillator was designed by
W. Fitzsimmons and R. Eyerly, Jr. (Physics Department, Rice University)
and constructed in this laboratory. The plasma was visibly stable and
the discharge vessel remained near the ambient temperature under normal
operation (low power). Under normal operation the discharge was visibly
weaker than that produced by the microwave generator; however, at the
highest output powers the high frequency oscillator was capable of
maintaining discharges with visible emission intensities equivalent to
that produced by the microwave generator. Primary interest in the energy
distribution studies was focused on the discharges produced by the
microwave generator (medical diathermy unit) in part due to its
widespread use in research laboratories as a high intensity source of
microwaves.

b. Mass Spectrometric Operation

The instrument used for mass analysis in this work was a
quadrupole mass spectrometer originally described by Paul et al. (72). The mass spectrometer was designed and built by Professor Ghosh et al. in this laboratory for specific use with electrical discharges. Several distinct operating characteristics make it well suited for this purpose:

a. The high transmission efficiency for ions which is nearly 100% at low resolution.

b. The kinetic energy discrimination of ions is minimal.

c. The resolving power is easily varied.

d. No stray magnetic fields are present that might disturb the plasma.

e. It is capable of operating at considerable residual pressure in the analyzer, allowing the plasma to be sampled at relatively high pressures.

The quadrupole rods were 20 inches in length and the mass spectrometer was operated at a frequency of 1 megacycle with a variable voltage for scanning between 1 and 80 amu at a maximum design resolution of 1 in 500. The resolving power was usually set at a low value of about 1 in 40 in order to:

a. Minimize the effect of mass discrimination present at high resolution.

b. Maximize the transmission efficiency.

An R. C. A. Model C60130 electron multiplier was used at the exit aperture of the mass analyzer and was connected to a Model 417 Keithley fast electrometer and then to an Electro-Instruments Model 520 X-Y recorder.

A drawing of the essentials of the apparatus is shown in Figure 3.
FIGURE 3

Schematic diagram of the quadrupole mass filter and associated apparatus.

1. Discharge vessel.
2. Plasma sampling probe containing the sampling leak.
3. Accelerating or grounded grid.
4. Retarding grids.
5. Shield - grid.
6. Focusing lens.
7. Quadrupole mass filter.
In normal mass spectrometric operation an accelerating-focusing voltage in the range of -20 to -100 volts is applied to grid 3 and/or focusing lens 6 while grids 4 and 5 are grounded.

The majority of the experiments on mass spectrometric sampling of plasmas was performed on discharges maintained by the 50 megacycle oscillator previously described. This largely resulted from the convenience afforded by its use. The 50 megacycle oscillator was easily coupled (either inductively or capacitively) to the plasmas contained in vessels of widely differing dimensions and geometries. Although the microwave generator could be coupled to the plasma in discharge vessels with the different geometries and dimensions employed here, the time and expense involved in constructing the special resonant cavities would have largely limited the number of experiments performed.

Due to the importance of the sampling process and also since the probes used in the mass spectrometric studies differ to some extent from those used in the energy distribution study (described previously), the probes used in this section will be described below.

Improved techniques resulting from experience in constructing sampling probes enable them to be produced for the mass spectrometric study with sampling channel depths as thin as 0.025 mm.

The sampling probe contained an aperture of 0.5 mm or less in diameter in the flat part forming the top of the cone section of the probe.

Probes were employed that were planar such that the ions leaked directly into the vacuum envelope containing the focusing lenses and then to the mass filter. Along the same lines, ions were also
extracted from a plasma through a hole that formed part of the walls of a cylindrical discharge vessel. No essential differences in results were observed between these probes and the conical probes.

Care was taken to make the depth of the channel of the sampling orifice much less than its diameter. The depth of this channel in all the probes employed in mass spectrometer study ranged from 0.025 to 0.125 mm except for probes constructed from glass in which the channel depth was approximately 0.2 mm.

The ions were sampled through a hole in the walls of a cylindrical and of a spherical discharge vessel and also along the axis of a cylinder as illustrated in Figure 1. (The oscillator was capacitively coupled to the gas by rings in the case of the spherical discharge vessel.) Sampling probes constructed of different materials were tried. Glass, gold plated aluminum, brass, and stainless steel were used. No variations in results could be attributed to these different probes. However, probes with small orifice diameters appear to disturb the plasma the least in that the results obtained by smaller diameter probes appear to be the most reproducible and the least sensitive to the experimental discharge conditions, e.g. power input. The orifice diameter used in the probes in most of the experiments was 0.25 mm.

The pressure in the mass analyzer was in the range of $10^{-5}$ to $10^{-7}$ Torr.

The power dissipated by the coils is in the range of 5 to 50 watts. This estimate is obtained from the current and voltage across the coils on the discharge vessel.

Matheson gases were used in these experiments. The carbon dioxide
was "Bone Dry" grade of stated purity of 99.8%. The ammonia was "Anhydrous" grade (99.99%) and the methane was research grade (99.99%). The Neon was research grade of stated purity 99.995% and the Helium and Argon were "High Purity" grade of stated purity 99.995%. These gases were used without further purification.
CHAPTER III

GENERAL THEORY OF ELECTRODELESS DISCHARGES

Presented below are some equations pertinent to the discussion presented in the following sections. These equations are presented in order to illustrate the magnitude of important experimental variables and to present briefly a few basic equations and concepts used in a study of electrodeless discharges. Equations presented below were taken from several recent review articles (73-75).

a. Electrical Properties of High Frequency Electrodeless Discharges

Collisionless electron motion in an alternating electric field, $E = E_0 \cos \omega t$ is given by equation 1 below:

$$\frac{dv}{dt} = \left( \frac{eE_0}{m_0} \right) \cos \omega t$$

where $e$ and $m_0$ is the electron charge and mass, respectively; $\omega$ is $2\pi f$ cps, and $v$ is the electron velocity. Integration of equation 1 with $v = 0$ at $t = 0$ gives the electron velocity, $v$, as equation 2.

$$v = \left( \frac{eE_0}{m_0} \right) \sin \omega t$$

For $E_0 = 200$ volts/cm and $f = 2450$ megacycles, which are approximately the values produced by the medical diathermy units (75), the maximum oscillation velocity is $2.3 \cdot 10^7$ cm/sec.

Integration of equation 2 with the limits $x = 0$ at $t = 0$ gives the oscillation amplitude as equation 3. The $x$ is the displacement from zero.
\[ x = -\left(\frac{eE_0}{m_0 \omega^2}\right) \cos \omega t \]

The maximum oscillation amplitude is 0.015 mm for the above values of \( E_0 \) and \( f \). Taking the elastic cross section of Argon (\( \sigma = 1.14 \times 10^{-16} \text{ cm}^2 \)) at an energy of five volts (76) as representative of the order of magnitude of the electron elastic collision cross section, the pressure at which the oscillator frequency equals the collision frequency is approximately 0.5 Torr. Thus, this work was done between the extremes usually described, i.e., many oscillations per collision or many collisions per oscillation.

The rate of energy picked up from the field, the power, is given by:
\[ P = eE_0 \vec{v}_z = (eE_0/m_0 \omega) \cos \omega t \sin \omega t \]
(The \( \vec{v}_z \) is the z component of the electron velocity.), which it is noticed can be negative as well as positive. The integrated \( \sin \omega t \cos \omega t \) product for the total power delivered over a complete cycle is zero, indicating that there is no net transferral of energy from the field in the absence of collisions. This is the result of the fact that in the absence of collisions the electrons oscillates 90 degrees out of phase with the field. However, an electron oscillating in an alternating field and undergoing elastic impacts will be accelerated during a portion of its cycle and deflected by collisions in another portion. Energy parallel to the field can be converted into energy perpendicular to the field by deflection through elastic impacts. However, the electric field will continue to give the electron kinetic energy parallel to the field. The potential energy of the field is thus pumped from electron kinetic energy parallel to the field to kinetic.
energy in all directions. It is collisions of this type that lead to the well known Druyvestyn distribution \((14)\) of electron energies. The motion of an electron undergoing elastic collisions in an AC field can be written by adding a collision term, \(\bar{Z} \text{ sec.}^{-1}\), that describes the average loss of electron velocity, \(\bar{v}_z\), in the direction of the field (z-direction) as given in equation \(4\).

Solving equation \(4\) for \(v_z\) and substituting \(v_z\) into \(\bar{F} = e \bar{E} \bar{v}_z\) yields

\[
\frac{d\bar{v}_z}{dt} = \left(\frac{eE_0}{m_e\omega}\right) \cos \omega t - \bar{Z} \bar{v}_z
\]

equation \(5\) for the average power, \(\bar{P}\), delivered over one cycle. The \(N_e\)

\[
\bar{P} = \frac{N_e e^2 E_0^2}{Z m_e} \left(\frac{Z^2}{Z^2 + \omega^2}\right)
\]

is the electron number density.

For electron densities greater than \(10^9\) electrons/cc and at constant pressure, some evidence is available that \(E_0\) in equation \(5\) is constant \((77-78)\). This implies that the electron energy is constant and that the electron densities increase with increased power (equation \(5\)).

Equation \(5\) does not consider inelastic collisions and the variation of the collision cross section with velocity, both of which are usually appreciable. However, it does show directly the role of collisions in converting electrical energy into electron kinetic energy in electrode-less discharges.

b. Plasma-wall Potential

The positive ions and electrons in a plasma diffuse to the walls of the containing vessel and recombine there. Initially, the electrons,
because of their higher energy and lower mass diffuse out more rapidly than the positive ions leaving behind a positive space charge. It is assumed here for simplicity that no massive negative ions are present. The case for ambipolar diffusion in the presence of negative ions is discussed in the Appendix. This space charge retards the diffusion of the electrons and accelerates the diffusion of the ions. The result is that the plasma potential is higher than that of the walls. The electron loss from the plasma continues to build up the positive space charge until arrival rates of the electrons and the positive ions to the walls are equal. This is ambipolar diffusion. The plasma-wall potential produced by this space charge is calculated below. A Maxwellian velocity distribution is assumed to be present.

The flow of charged particles to the walls can be written (79):

\[ \Gamma_\pm = \frac{\nu}{4\pi} \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} d\phi \sin \theta \cos \theta \exp(-r/\bar{r}) \]

where \( \exp(-r/\bar{r}) \) is the probability of a particle traveling a distance \( r \) without being scattered. The \( r \) has the cartesian coordinates \( x, y, \) and \( z. \) The \( n(r) \) is the variation of the particle density with distance from the walls. \( \Gamma_\pm \) is the electron or positive ion flux; \( \bar{V} \) is the mean velocity. Other terms have their usual meaning and are further defined by Figure 4. The \( n(r) \) is expanded in a Taylor series below and terms higher than the first are neglected. This is equivalent to assuming the

\[ n = n_0 + \left( \frac{\partial n}{\partial x} \right)_0 x + \left( \frac{\partial n}{\partial y} \right)_0 y + \left( \frac{\partial n}{\partial z} \right)_0 z + \cdots \]
FIGURE 4

Spherical coordinate system and solid angle.
particle gradient for a few mean free paths as negligible. Carrying out the integrations in equation 6 yields the current densities for the positive ions and electrons as:

\[
\begin{align*}
    \Gamma_+ &= \frac{1}{4} n_+ \overline{v}_+ \\
    \Gamma_- &= \frac{1}{4} n_- \overline{v}_- \exp\left(-eV_w/E_-\right)
\end{align*}
\]

The exponential term in equation 7 does not appear in equation 6. This term represents the fraction \(\exp(-eV_w/E_-)\) of the electrons able to surmount the wall potential and strike the walls.

Setting \(\Gamma_+ = \Gamma_-\) in the steady state, rearranging and taking the logarithms gives the plasma-wall potential as equation 8.

\[
\begin{align*}
    V_w &= \frac{\overline{E}_-}{2e} \ln\left[\frac{\overline{E}_- M_+}{\overline{E}_+ m_e}\right] \\
    \frac{\overline{V}_+^2}{\overline{V}_-^2} &= \frac{\overline{E}_- M_+}{\overline{E}_+ m_e}
\end{align*}
\]

For \(\overline{E}_- = 10\) eV, \(M_+ = 40\) amu, \(m_- = 1/1860\) amu, and \(\overline{E}_+ = 0.1\) eV, the plasma-wall potential is obtained from equation 8 as 80 volts.

c. Diffusion

The positive ion and electron loss can be shown to occur by diffusion to the container walls with subsequent wall recombination for the densities normally found in our discharges. The mean time for diffusion to the walls in our discharges is on the order of one microsecond. The calculation for the diffusion times appears in Chapter V, part g.

Taking the volume electron and positive ion radiative recombination coefficient, \(a\), measured by Kasner and Biondi (80) for the reaction:

\[
N_2^+ + e^- = N_2 + h\nu
\]
as representative of the order of magnitude for the process, the time when \( n = \frac{1}{e} \cdot n_0 \) is obtained from equation 9 for \( n_0 = 10^{10} \) electron/cc as \( 0.6 \cdot 10^{-3} \) second. The \( n_0 \) is the electron density at \( t = 0 \).

\[
\frac{1}{n} - \frac{1}{n_0} = \alpha \tau
\]

Since this time is two or three orders of magnitude larger than the diffusion time, we conclude that electron and positive ion loss in our plasmas occurs mainly by diffusion to the walls with subsequent recombination there.

If only electrons are present in a neutral gas they diffuse as any other gaseous component resulting in a current flux given by Fick's First Law of Diffusion.

\[
\vec{I} = -D_\text{e} \nabla n_\text{e}
\]

where \( n_\text{e} \) is the number density of electrons, \( D_\text{e} \) is the free diffusion coefficient of the electrons through the gas, and \( \vec{I} \) is the electron flux. If an electric field of intensity \( \vec{E} \) is applied, the electron flux will then contain an additional mobility term:

\[
\text{(11a) } \vec{I} = -D_\text{e} \nabla n_\text{e} - \mu_\text{e} n_\text{e} \vec{E}
\]

The relative magnitude of the first and second terms on the right side of equation 11a determines if the electron motion is diffusion dominated or field dominated.

In a steady state gas discharge the electrons will produce ions and these also will diffuse to the walls through the neutral gas and respond to the same electric fields. The flow of positive ions to the
container walls will therefore be given by an expression similar to equation 11a.

\[(11b) \quad \Gamma_+ = -D_+ \nabla n_+ + n_+ \mu_+ E_+ \]

The positive sign in the second term indicates that the positive ions will diffuse in the direction of the field.

Combining equations 11a and 11b to eliminate the electric field intensities, taking \(n_- = n_+\) and \(\Gamma_- = \Gamma_+ = n_+ v_+\) and mobility, \(\mu\), to be independent of the electric field strength, gives for the diffusion velocity, \(v\):

\[(12) \quad v = -\left(\frac{D_- \mu_- + D_+ \mu_+}{\mu_+ + \mu_-}\right) \frac{\nabla n}{n} \]

and therefore the ambipolar diffusion coefficient is:

\[(13) \quad D_\alpha = \frac{D_- \mu_- + D_+ \mu_+}{\mu_+ + \mu_-} \]

where \(\mu_\pm\) is mobility and \(D_\pm\) are free diffusion coefficients defined by 10. Ambipolar diffusion thus is a device to avoid the use of the electric field intensity and was introduced by W. C. Schottky (81) in 1924 in an analysis of the positive column of D. C. discharges.

The magnitude of the ambipolar diffusion coefficient in terms of the free diffusion coefficient can easily be seen. Taking \(\mu_- \gg \mu_+\) and \(\frac{D}{\mu} = \frac{kT_+}{e}\) (82) we obtain the approximate expression:

\[(14) \quad D_\alpha \approx \left[1 + \frac{T_-}{T_+}\right] \]

Therefore, for \(kT_- = 10\) eV and \(kT_+ = 0.1\) eV, the ratio of \(D_\alpha\) to \(D_+\) will be on the order of 100.
The above discussion is limited to the case of one positive ion species and no massive negative ion species present. The expression for the ambipolar diffusion coefficient when negative ions are present (83), when more than one positive ion is present (84), and when the mobility varies with the electric field intensity (85), has been worked out. The reader is referred to the respective references for the conditions and discussion.

d. Electron Density

The variation in the electron density across an infinitely long cylindrical discharge tube of radius R can be calculated by equating the electron loss and electron production processes occurring in annular elements across the discharge tube in the steady state (86). The result is given by equation 15 for the case when the only electron loss is by diffusion to walls with subsequent recombination there. (The q is rate of production of electrons per second per electron.) The solution is a zero order Bessel function, \( J_0 \).

\[
(15) \quad \frac{d^2n}{dr^2} + \frac{1}{r} \frac{dn}{dr} + \frac{q_n}{D_a} = 0
\]

diffusion to walls with subsequent recombination there. (The \( q \) is rate of production of electrons per second per electron.) The solution is a zero order Bessel function, \( J_0 \).

\[
(16) \quad n(r) = n_0 J_0 \left( r \sqrt{\frac{q}{D_a}} \right)
\]

For the case \( n_0 = 0 \) at \( r = R \) the variation in density with radius is given by equation 17.

\[
(17) \quad n(r) = n_0 J_0 \left( r / \Lambda \right) \quad \Lambda = \frac{R}{2.404}
\]

The \( \Lambda \) is the characteristic diffusion length for an infinite
cylinder.

The variation in the electron density across the discharge tube calculated from equation 17 for cylindrical vessel with a radius of 0.5 cm is illustrated in Figure 5.
FIGURE 5

The radial variation of electron density
in a cylindrical discharge vessel.
$R_o = 0.5 \text{ cm}$
CHAPTER IV

DATA EVALUATION OF ENERGY SPECTRA

Typical experimental electron and positive ion energy spectra are shown in Figure 6. These curves give the integrated translational energy distributions of the electrons and positive ions in the beam issuing from the sampling probe orifice. It is seen from Figure 6A that the walls of the sampling probe (and its orifice) are covered by a negative sheath such that the positive ions experience an accelerating electric field and therefore the electrons experience a retarding field on effusing through the orifice of the sampling probe. In this case the full accelerating potential (sheath potential) corresponding to the sharp break in the positive ion energy spectrum in Figure 6A is 39 volts.

The experimental current-voltage traces were evaluated for the electron energy distributions, positive ion energy distributions, and the sheath potentials by the methods described in their respective sections in this Chapter.

a. Electrons

The field gradient produced by the negative sheath causes the probe orifice to behave as a single aperture electrostatic lens. However, only the electrons with the specified velocity vectors in the solid angle subtended by an element of orifice area and with energies greater than the corresponding sheath potential (eV_s) effuse through the sampling probe and are collected, since the electrons experience a retarding field on effusing through the sampling probe orifice.
FIGURE 6

Representative energy spectra:

A. The transmitted positive ion current versus the retarding potential.
B. The transmitted electron current versus the retarding potential.
Electrons entering the electric field of the aperture lens along the symmetry axis of the field emerge with energy components parallel to the symmetry axis of the field decreased by the amount $eV_s$ while the radial component of energy is unchanged.

Electrons entering the field off the symmetry axis of the field emerge with energy components parallel to the symmetry axis decreased by the amount $eV_s$. However, the radial component of energy undergoes a change, the magnitude of the deflection depending on the velocity of the electron and the distribution of the potential in the vicinity of the probe aperture. For hemispherical equipotential surfaces concave toward the plasma, the electrons are focused on an axial line and not at a point (55). In the absence of space charge, the electrons emanate from focal points on this line with a variety of angle of divergence. The electrons diverging from focal points with angular specific energy distribution a considerable distance from the collector on the axial line might cause the loss of these electrons to the inside walls of the sampling probe. This could result in the preferential collection of the electrons with specific kinetic energies. This description is only qualitative because the exact three dimensional form of the distribution of potential in the vicinity of the probe aperture is not known. However, the absence of the loss of electrons with angular specific energy distributions was verified by applying an accelerating potential (0-100 volts) to grid 1 (Figure 2). In this manner the electrons could be drawn out to the collector before they are lost to the walls. The absence of a significant increase in electron current demonstrated that no preferential collection of electrons of a specific kinetic energy
occurs. Consequently, the electrons emerging from the field of the sheath have energy components normal to the plane of the sampling probe aperture that are representative of the corresponding energy components they had before entering the sheath decreased by $eV_s$. This is important since it is these energy components that are retarded by the retarding potential grids in measuring the electron energy distributions.

A typical experimental electron energy spectrum is given in Figure 6B. The experimental current-voltage trace gives the integrated energy distribution function of the translational energy components of collected electrons normal to the plane of the retarding grids. This distribution function was related to the distribution in the plasma by an analysis of the effusion process presented below.

The origin of a spherical coordinate system shown in Figure 4 with polar angle $\Theta$ and azimuthal angle $\phi$ is placed in the plane defined by the orifice of the sampling probe with the $z$ axis normal to that plane. For an isotropic velocity distribution, $f(v)$, in the plasma, the number of electrons, $n$, effusing from an electron gas of density $N$, through a probe aperture of area $A$ per unit time with velocities between $v$ and $v + dv$ in the direction $\Theta$ and $\phi$ is known to be (87);

$$dn(v, \Theta, \phi) = \frac{NV_f(v)\sin\Theta\cos\Theta d\Theta d\phi dvda}{4\pi}$$

(18)

We change equation 18 to obtain the velocity components parallel and perpendicular to an axis normal to the retarding grid plane ($z$-axis):

$$dn(v_\parallel, v_\perp) = \frac{1}{2V}NAf(v)\frac{V_\parallel V_\perp}{V_\parallel V_\perp}dv_\parallel dv_\perp$$

(19)

Integration of equation 19 for a Maxwellian distribution yields the
desired integrated energy distribution function given by equation 20.

\[
\frac{n(E_i)}{n_0} = \exp \left[ -\frac{E_i}{\bar{E}_-} \right]
\]

\(\bar{E}_-\) is the mean electron energy, \(E_{i\parallel}\) is the retarding potential, and \(n_0\) is the number of electrons striking the collector at \(E_{i\parallel} = 0\).

The mean electron energy is then obtained from the slope of a plot of the \(\ln(n)\) versus the retarding potential (see Figure 12).

Although the above derivation applies to low pressures where effusive flow prevails, the relationship 20 appears to hold at all pressures up to 1 Torr. Thus, the experimental results show no evidence that hydrodynamic flow effects the energy distributions of collected ions even at the highest pressures employed.

b. Positive Ions

A representative experimental positive ion current-voltage trace is shown in Figure 6A. The experimental (integrated) positive ion translation energy spectrum is adequately interpreted on the basis of conventional Langmuir probe theory (88). This assumes that ion production and charge exchange in the sheath can be neglected. In that case the distribution function for positive ion translational energies is displaced along the energy scale by the amount of the sheath potential. It is evident from the experimental trace (Figure 6A) that while the distributions are displaced significantly along the energy scale and the overall drop in the positive ion current occurs sharply, the initial decrease in ion intensities is more gradual than expected on the basis of the above interpretation. A possible explanation for the soft corner
is the presence of a large sheath r.f. potential resulting from electron oscillation in the input r.f. field. Calculation of the energy gain from the field averaged over one half cycle (Chapter III, part a) shows that the electron will gain a few tenths of an electron volt for a peak r.f. field strength of 100 volts/cm (89) and this would be superimposed on their random energies of about 15 eV. The ions will respond slowly to the oscillating fields and therefore undergo approximately 10 oscillations of sheath r.f. potential on passing through the sheath when the sheath oscillates at 2450 megacycles and will undergo less than one oscillation in the case of the 50 megacycle discharge. However, the experimental positive ion energy spectra for discharges at the two frequencies are similar. In addition, slightly more rounding is observed at the lower powers and considerably more rounding is observed at increased pressures (see Figure 7). This rounding is similar to that observed by J. Y. Wada and H. Heil (34) for the positive ion energy spectra in the positive column of D. C. discharges in the same pressure range. Therefore, we conclude that the r.f. sheath potential makes only a small contribution to the soft corner and instead this is attributed to ion production in the sheath. Because of this the sheath potential was measured from the inflection point on the experimental curve. The sheath potentials measured from the inflection point represents values for a collisionless sheath. Theoretical calculations (33,90) show that the wall potential does not drop sharply to zero, but rather asymptotically approaches zero on receding from the walls. Therefore, we cannot be certain whether the positive ions with energies beyond the inflection point gain this additional increment of energy from the fields produced.
FIGURE 7

Energies of the positive ions extracted from a plasma of air excited at microwave frequencies for six different pressures showing increased ion production in the sheath with increased pressure at the higher pressures.

A. .067 Torr  D. .338 Torr
B. .098 Torr  E. .633 Torr
C. .127 Torr  F. 1.130 Torr
by the walls to maintain the ambipolar diffusion of the charge carriers, or whether they gain this energy from a deep penetration into the plasma of a weak field from the probe sheath. However, due to the narrow distribution of positive ion energies, the sheath potentials measured from the inflection point differ from the maximum ion kinetic energy spread by less than 5\% (see Figure 6) except at low power or long distance from the cavity where the sheath thickness permits enough collisions to alter the distribution of energies, giving a wider energy spread and an erroneously high mean energy. The positive ion energy distribution was obtained from an analysis of the currents of ions appearing with energies greater than \( eV_s \). These ions are believed to enter the sheath with their translational kinetic energies and fall through the full collisionless sheath potential. The analysis of the experimental curve for the positive ion energy distribution was carried out in the same manner as for the electrons. The result is given by equation 21 for the case of a Maxwellian distribution of positive ion energies in the plasma.

\[
\begin{align*}
\frac{n_i(eV_{\parallel})}{n_{i0}} &= \exp \left[ -\frac{eV_{\parallel} - eV_s}{E_+} \right]
\end{align*}
\]

The mean positive ion energy was obtained from the slope of \( \ln(n_i) \) versus \( e(V_{\parallel} - V_s) \). An example of such a plot is given in Figure 15.

Most of the positive ions formed in the sheath are formed on the plasma side of the sheath since they appear with energies only slightly less than the full sheath potential. Using a symmetric change exchange cross section of \( 20 \cdot 10^{-6} \text{ cm}^2 \) (91) and sheath thickness of 0.03 mm (Chapter V, part a), our calculations show that charge exchange can be
neglected below a pressure of approximately 0.5 Torr; consequently, these currents are attributed to ionization by electron impact in the sheath. Since these ions are formed with near thermal energy and are immediately drawn out of the sheath to the walls (or through the probe aperture) by the field of the sheath, the shape of the positive ion energy spectrum below the sheath potential provides information from which the ion formation at various points in the sheath can be determined. The method which was used is given below.

The ion production rate, \( R_p \), in the plasma was calculated from the known ionization efficiencies (92) and the measured electron energy distribution. The ionization varies in front of the wall as the electron velocity groups moving up the sheath potential lose their kinetic energy.

The fraction of the electron density able to surmount potential \( V \) in the electric field of the sheath is given by equation 20. The positive ions collected from the probe edge of the sheath to potential \( V \) in the sheath is then given by equation 22.

\[
I(V) = \int Ex \exp \left[ - \frac{eV}{E} \right] \, dx
\]

\( A \) = unit area on the wall
\( E \) = mean electron energy
\( e_o \) = electron density in the plasma
\( x \) = distance in front of the sampling probe.

The electric field of the sheath was mapped for plane parallel geometry of equipotential surfaces in front of the sampling probe orifice by finding a function, \( dx = f(V) dV \), that produces the experimental ion arrival rates for each potential \( V \) in the sheath. On the
basis of the above discussion, equation 22 permits calculation of:

1. The collisionless sheath depth.

2. Potential in the sheath as a function of distance normal to the sampling probe orifice. Results are given in Chapter V, part a.

The above discussion of the soft corner seems the most reasonable to us. The results will be substantiated by other methods when possible.
CHAPTER V

RESULTS AND DISCUSSION

a. Sheaths

The sheath thickness is the maximum depth from which ions are formed and collected with energies less than the collisionless sheath potential and was calculated from the measured ion arrival rates using the techniques described in Chapter V, part b. The approximate value of the sheath thickness in the experimental pressure range below 0.5 Torr is 0.03 mm. Due to the uncertainty in the electron concentration, which appears in the calculation, it is not possible at this time to follow quantitatively the functional dependence of the sheath thickness on the various experimental variables.

The potential in the sheath as a function of distance normal to the sampling probe orifice was qualitatively mapped from the measured ion arrival rates and equation 22 by assuming a plane parallel geometry of equipotential surfaces parallel to the orifice of the sampling probe. The result is shown by the solid curve in Figure 8 for Ne. The dotted line represents values extrapolated to small distances and expanded on the distance scale by a factor of 100. It is obtained by extrapolating the solid curve and does not represent experimental points. It is not feasible to map the potential in the sheath accurately as a function of distance normal to the sampling probe orifice since the distribution of the equipotential surfaces in front of the sampling probe is not quantitatively plane parallel geometry. However, it is seen from
FIGURE 8

Potential in sheath versus distance normal to the sampling probe orifice.
Figure 8 that most (85%) of the potential of the sheath is dropped in a region so near the walls that few ions are produced in that part of the sheath. Additional evidence for this is obtained from a study of ion molecule reactions and is presented in Chapter V, part 1. At higher pressures more low energy ions are indicated by the experimental trace because of the increased rates of charge exchange and ion production in the sheath. This results in increased rounding of the corner with increased pressure as shown in Figure 7.

In 1929 it was discovered by Tonks and Langmuir (93) that the electric field of the sheath penetrates beyond the sheath edge and into the plasma. (In classical probe theory it was assumed that collisions did not occur in the sheath, hence the entire sheath was considered collisionless.) This was again studied by Bohm, Burhop, and Massey (33) in 1949 and recently by Boyd (94), Wenzl (95) and Allen and Thonemann (96). The results described above are thus in agreement with the Langmuir theory of collectors in gaseous discharges in that the sheath penetrates into the plasma. Also, the form of the potential distribution shown in Figure 8 is in reasonable agreement in form with the theoretical prediction of Allen, Boyd, and Reynolds (97).

Ratio of electron flux to positive ion flux through probe orifice as high as 100 were observed. This might be attributed to the presence of a large r.f. voltage across the sheath rectified by the non-linear sheath characteristics. However, our data support the view that the r.f. sheath potential shows only a small effect (see Chapter IV, part b).

Since ambipolar diffusion of charge carriers to the walls of the containing vessel presumably occurs we attribute the large electron flux
to a local disturbance to the electric fields in the sheath produced by the grounded metallic probe and its orifice. This effect can be quite important to mass spectrometer sampling of ions from the discharge and is discussed in detail in Chapter V.

The experimental plasma-probe potentials were found to be less than the calculated wall potentials (98) by as much as 50 volts. The wall potential is the plasma-wall potential required to produce ambipolar diffusion and was calculated from the measured mean electron and positive ion energy and equation 23.

Sheath potentials were obtained as a function of pressure, input power, and probe position along the axis of the plasma flame. The sheath potentials decreased with increased pressure and with decreased power at low power. The sheath potentials were found to be slightly dependent on the region of the plasma flame sampled. A representative selections of results are shown in Figure 9, 10, and 11 respectively. The trends observed for the sheath potentials are discussed further in Chapter V, part c.

b. Electrons

The experimental electron energy distribution fitted the Maxwellian distribution function. An example of a plot to obtain the mean electron energy is given in Figure 12 for Helium. The electron energy distribution was obtained as a function of input power, pressure, and position along the axis of the discharge tube.

In order to ascertain whether the electrons are collected from the sheath or from the plasma, theoretical estimates of the ratio of the
FIGURE 9

Plasma-probe potential (sheath potential) versus the pressure.
FIGURE 10

Plasma-probe potential (sheath potential) versus the microwave power.
Sheath Potential (volts) vs Power Input (watts)

- Helium 370 microns
- Neon 165 microns
- Argon 75 microns
FIGURE 11

Plasma-probe potential (sheath potential) profile along the axis of the discharge tube. Distance is measured from the edge of the resonant cavity; +outside, -inside.
FIGURE 12

The logarithm of the transmitted electron current versus the retarding potential.
$\bar{E}_{(\text{-})} = 15.1 \text{ eV}$

HELUM
370 MICRONS
70 WATTS
electron current to positive ion current were made for the cases:

1. Electrons sampled from the sheath.
2. Electrons sampled from the plasma.

These calculations were based on the equation:

\[
\frac{I_1}{I_+} = \frac{\bar{v}_e}{\bar{v}_+} \exp \left[ -\frac{eV}{E} \right]
\]

(23)

derived from diffusion rates of electrons and ions (99), where \( V = 0 \) for sampling from the sheath and \( V = V_s \) for sampling from the plasma. The mean electron velocity, \( \bar{v}_e \), and mean positive ion velocity \( \bar{v}_+ \), were obtained from the measured mean electron and mean positive ion translational energy. A representative selection of results is listed in Table I. The calculated current ratios for sampling from the plasma are seen from Table I to give better agreement with the experimental values than the calculated ratios for sampling electrons from the sheath. Due to the approximate nature of the physical model, significantly better agreement would have to be considered fortuitous. We believe the agreement observed shows that the electrons are sampled mainly from the plasma. This conclusion is verified by mass spectrometric ion-molecule reaction rate data presented in the following sections.

The high sheath potentials result in sampling only the electrons in the higher energy tail of the distribution. An attempt was made to lower the sheath potential in order to observe a larger fraction of the energy distribution by introducing a large electrode into the plasma and applying a potential between it and the probe. The drop in the sheath potential was observed from the positive ion current-voltage trace. We found that appreciable drops in the sheath potentials could
### TABLE I

**EXPERIMENTAL AND CALCULATED CURRENT RATIOS AND ASSOCIATED DATA**

<table>
<thead>
<tr>
<th>Gas</th>
<th>$E(\text{+})$</th>
<th>$E(-)$</th>
<th>$V_s$</th>
<th>Sheath</th>
<th>Plasma</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>0.72</td>
<td>14.3</td>
<td>36</td>
<td>860</td>
<td>69</td>
<td>68.5</td>
</tr>
<tr>
<td>Ne</td>
<td>3.7</td>
<td>15.4</td>
<td>29.5</td>
<td>394</td>
<td>58</td>
<td>83.7</td>
</tr>
<tr>
<td>Ar</td>
<td>0.35</td>
<td>8.9</td>
<td>24</td>
<td>1376</td>
<td>84</td>
<td>36</td>
</tr>
<tr>
<td>Ar</td>
<td>0.70</td>
<td>11.5</td>
<td>23.5</td>
<td>1107</td>
<td>149</td>
<td>74.6</td>
</tr>
<tr>
<td>He</td>
<td>0.46</td>
<td>14.4</td>
<td>37</td>
<td>341</td>
<td>26</td>
<td>42</td>
</tr>
<tr>
<td>He</td>
<td>0.91</td>
<td>15.4</td>
<td>45</td>
<td>251</td>
<td>13.5</td>
<td>23</td>
</tr>
</tbody>
</table>

$I(-)/I(\text{+})$ was calculated for sampling from...
be obtained only by introducing a prohibitively large electrode. The large electrode produced a high current drain and, at high applied potentials, unstable tufts formed on the electrode. For a smaller reference electrode the drop in the sheath potentials was insignificant. This is the result of the relatively large area the sampling probe presents to the plasma. (Results obtained with a very much smaller sampling probe area are presented in the Appendix.) Consequently, usually less than 20% of the electron energy distribution was observed in these experiments as a result of the high sheath potentials. This may not be enough to ascertain the form of the entire energy distribution. Therefore, we claim here only that the observed distribution fitted nicely in most cases the Maxwellian distribution function.

The mean electron energy did not change with a power input variation of 10 to 100 watts. A representative plot is given in Figure 13. The upper limit of input power was set by the maximum output of the generator. The lower limit was the power input necessary to maintain the discharge in our system.

For comparison purposes, the mean electron energy was calculated from the radius of the discharge tube, the ionization potential of the noble gas, and its cross section by the theory presented by von Engel and Steenbeck (100). Equation 24 is the relation they derived relating

\[(24) \quad \left( \frac{eV_i}{E_-} \right)^{-\frac{1}{2}} \exp \left( -\frac{eV_i}{E_-} \right) = 1.16 \cdot 10^7 C^2 P^2 \]

the electron temperature to ionization potential of the gas, V_i, the gas pressure, P, the radius of the discharge tube, R, and the nature of the gas expressed by constant C. The constant C depends in part on the
FIGURE 13

Mean electron energy versus the microwave power input.
molecules ionization cross section and is given in Tables. This theory is based on diffusion controlled electron energy and as seen from equation 24 the input power does not appear in the calculation. The calculated and experimental values are given in Table II. The theory is seen to predict the correct order with the respect to energy, although the error is large in the case of Argon.

Also, the calculated mean energies decrease more rapidly with increased pressure than the experimental values. A possible explanation for this is that the boundary condition $n = 0$ at $r = R$ is not exact. This is discussed by Fowler (101).

The mean electron energy for several gases is given in Table III. The high mean electron energy and non-Maxwellian distribution of energy of $\text{SO}_2$ and $\text{H}_2\text{S}$ are construed as an abnormality and are discussed in the Appendix, part b.

The mean electron energy was found to remain constant on moving from 15 mm inside the cavity to 60 mm outside the cavity (usually a few mm from the visible flame edge) as shown in Figure 14. Although the points on the graph scatter somewhat, it is obvious no significant decrease in the mean electron energy occurs. In the case of Helium we were able to obtain data for the electron energy distribution outside the strongly glowing and decaying region of the visible plasma. For the Helium discharge, on receding from the visible flame edge (2 cm) into the nonglowing region, the mean electron energy decreased from 17 eV to 9 eV while the electron intensity decreased by a factor of nearly 1000. The mean electron energy decreased on receding farther down stream and the electrons appear to retain the Maxwellian distribu-
<table>
<thead>
<tr>
<th>GAS</th>
<th>CALCULATED</th>
<th>OBSERVED</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>12 eV</td>
<td>14.6 eV</td>
</tr>
<tr>
<td>Ne</td>
<td>19</td>
<td>15.4</td>
</tr>
<tr>
<td>Ar</td>
<td>5</td>
<td>11.7</td>
</tr>
</tbody>
</table>

*Experimental conditions are given in Figure 13.*
### TABLE III

**OBSERVED MEAN ELECTRON ENERGY FOR SEVERAL GASES**

<table>
<thead>
<tr>
<th>GAS</th>
<th>$\text{SO}_2$</th>
<th>$\text{H}_2$*</th>
<th>$\text{H}_2$*</th>
<th>$\text{H}_2$</th>
<th>$\text{CH}_4$</th>
<th>$\text{CO}$</th>
<th>$\text{O}_2$</th>
<th>$\text{NH}_3$</th>
<th>$\text{NO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRESSURE (microns)</td>
<td>1110</td>
<td>830</td>
<td>255</td>
<td>400</td>
<td>380</td>
<td>350</td>
<td>495</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>$E$, e.V.</td>
<td>44</td>
<td>38</td>
<td>15.0</td>
<td>13.6</td>
<td>14.0</td>
<td>14.2</td>
<td>14.9</td>
<td>15.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GAS</th>
<th>$\text{He}$</th>
<th>$\text{H}_2$</th>
<th>$\text{CO}_2$</th>
<th>$\text{Ar}$</th>
<th>$\text{N}_2$</th>
<th>$\text{Ne}$</th>
<th>$\text{Kr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRESSURE (microns)</td>
<td>500</td>
<td>2900</td>
<td>350</td>
<td>415</td>
<td>550</td>
<td>380</td>
<td>300</td>
</tr>
<tr>
<td>$E$, e.V.</td>
<td>15.6</td>
<td>17.0</td>
<td>17.2</td>
<td>17.8</td>
<td>19.0</td>
<td>21.1</td>
<td>18.5</td>
</tr>
</tbody>
</table>

**POWER APPROXIMATELY 70 WATTS**

*NON-MAXWELLIAN ENERGY DISTRIBUTION*
FIGURE 14

Mean electron energy profile along the axis of cylindrical discharge vessel for plasmas excited at microwave frequencies. Distance is measured from the edge of the cavity; + outside, - inside.
The graph shows the mean energy (eV) as a function of distance (cm) for two different gases: Neon 150 microns and Argon 75 microns. The energy values are measured at 70 watts of power. The graph indicates a nearly constant energy level for both gases across the distance range shown.
tion. Thermalization appears to be slight in this region, probably because some energy is received from the cavity even outside the visible region. The length of the discharge tube and the signal intensities prohibited sampling electrons farther than 30 mm from the visible flame edge. The low signal intensity prevented measuring the energy distribution of the positive ions outside the glowing plasma.

The variation of the mean electron energy with pressure at constant power is given in Table IV, for a Helium discharge excited at 2450 megahertz and 50 megahertz. Since we were unable to measure the power delivered to the discharge for the 50 megahertz oscillator we cannot be sure the power delivered to the plasma remained constant with increased pressure. However the power dissipated by the coil was maintained constant. This power was measured by the current-voltage product across the coil and is not necessarily equal to the power coupled to the plasma.

The mean electron energy in the plasma of discharges excited at the two different frequencies are not appreciably different although the decrease in the mean electron energy with increased pressure is larger for the 50 megahertz discharge as seen from Table IV.

It was brought to our attention after completing this work that it has been experimentally observed with a nanosecond oscilloscope that the power output from the magnetron (Raytheon, 2450 megahertz) is not a coherent wave (102), presumably because the output consists of rapid burst of power produced somewhat out of phase. A free electron subjected to this field might gain energy even in the absence of collisions, since it could be out of phase with the successive burst of power. However, the 50 megahertz oscillator produces a continuous power output,
### TABLE IV

**MEAN ELECTRON ENERGIES IN He DISCHARGES AT DIFFERENT PRESSURES**

<table>
<thead>
<tr>
<th>PRESSURE</th>
<th>MEAN ELECTRON ENERGY</th>
<th>PRESSURE</th>
<th>MEAN ELECTRON ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.388 Torr</td>
<td>14.5 eV</td>
<td>0.381 Torr</td>
<td>15.4 eV</td>
</tr>
<tr>
<td>.536</td>
<td>11.8</td>
<td>.535</td>
<td>14.6</td>
</tr>
<tr>
<td>.668</td>
<td>11.6</td>
<td>.650</td>
<td>13.5</td>
</tr>
<tr>
<td>.756</td>
<td>7.9</td>
<td>.750</td>
<td>12.9</td>
</tr>
<tr>
<td>.912</td>
<td>5.9</td>
<td>.928</td>
<td>11.3</td>
</tr>
<tr>
<td>1.514</td>
<td>6.3</td>
<td>1.530</td>
<td>10.7</td>
</tr>
</tbody>
</table>
as observed on an oscilloscope (Tetronix 540A) in this laboratory. The electron energy distributions observed in discharges maintained by either oscillator fitted the Maxwellian distribution function without large variations in the mean electron energy. Therefore, it appears that this effect is negligible under our experimental conditions.

c. Positive Ions

The positive ions were found to fit the Maxwellian energy distribution. An example of a plot to obtain the mean positive ion energy is given in Figure 15. The mean energy of the positive ions was studied as a function of the input power and mean energy profiles were obtained along the axis of the discharge tube.

The mean positive ion energy remained constant with decreased input power or increased distance from the resonant cavity except at the lowest power input or long distance from the cavity as shown in Figure 16 and 17 respectively. The increased mean positive ion energy at long distance from the cavity or low input power is reproducible. Theoretical calculations show that the sheath length increases with decreased densities (103). At the lowest densities (lowest powers or longest distance from the cavity) in these experiments the sheath length increases resulting in a widespread of ion energies. This is seen from Figures 16 and 17 to occur at the low powers and long distance from the cavity. In such cases, (low densities) we are unable to obtain data representative of the positive ion energies in the plasma. The functional dependence of sheath length on the positive ion and electron densities is discussed again in Chapter V, part j.
FIGURE 15

Logarithm of the transmitted positive ion current versus the difference between the retarding potential and the plasma-probe potential (sheath potential).
$E_+ = 3.1\, \text{eV}$
FIGURE 16

Variation of the mean positive ion energy with input microwave power to the resonant cavity: ○ Neon .165 Torr, ▲ Argon .080 Torr.
FIGURE 17

Mean positive ion energy profile along the axis of a cylindrical discharge vessel for a plasma excited at microwave frequencies. Distance is measured from the edge of the cavity; + outside, - inside.
These trends in the positive ion energies are consistent with the observed trends in the sheath potentials (Chapter V, part a). The sheath potentials are considered to differ from the wall potentials only in magnitude and hence are a function of the velocities of the electrons and positive ions. Since the mean electron velocity was shown to be independent of the position of the plasma sampled and the input power to the resonant cavity, the sheath potentials are expected to follow the mean positive ion velocities. Equation 25 gives the change in sheath potentials, \( \bar{V}_{s2} - \bar{V}_{s1} \), produced by the change in positive ion energy from \( \bar{E}_{+1} \) to \( \bar{E}_{+2} \) (104); where \( e \) is the charge on an electron. Thus, the sheath

\[
(25) \quad \bar{V}_{s2} - \bar{V}_{s1} = \frac{\bar{E}_-}{e} \ln \sqrt{\frac{\bar{E}_{+1}}{\bar{E}_{+2}}}
\]

potentials depend on the logarithm of the mean positive ion energy and hence decrease slowly with increased positive ion energy. This is seen to be the case by comparison of Figures 10 and 11 with Figures 16 and 17.

d. Electron and Positive Ion Densities

The electron and positive ion densities near the walls were estimated from the experimental ion and electron arrival rates to the probe orifice and the usual plasma effusion equation given previously as equation 7. Since, on the macroscopic scale the positive ion and electron densities in the plasma are nearly equal, we will use the term electron density here to refer to both the electron density and positive ion density.

The electron density range in the visible plasma was \( 10^8 - 10^{11} \) electrons/cc. The electron density in Helium in the nonglowing region
outside of and down stream from the visible plasma flame edge (2 cm) was approximately $10^6 - 10^7$ electrons/cc and appeared to decrease on receding farther down stream from the flame edge.

The densities were found to decrease on receding from inside the cavity to the region of the visible flame extending outside the cavity. The maximum extension of the flame outside the cavity was dependent on the pressure, the input power to the cavity, and the nature of the gas. The electron densities decreased with decreased power as shown in Figure 18. This plot is qualitative. Increased power increased the extension of the plasma flame outside the resonant cavity.

We have observed both the atomic and the diatomic ions of Helium in the visible plasma. At 70 watts input power to the cavity the absolute ion intensity of the Helium atomic ion decreased with increased pressure while the Helium molecule ion went through a maximum at approximately 0.3 Torr pressure. At the maximum the Helium diatomic ion constitutes approximately 30% of the ion intensity. We have observed both diatomic Argon and Neon ions.

e. Ion-Molecule Reaction

Initial experiments in a kinetic study of the positive ions were carried out on a methane high frequency (50 megacycle) plasma. The positive ion composition of the plasma was monitored as a function of the methane pressure in the discharge tube. It was found that a low power discharge minimized the deposit of carbonaceous material of the walls of the discharge tube thus permitting experiments to be performed. At low input powers a faint brown deposit was formed on the glass walls
FIGURE 18

Variation of the positive ion current to the probe orifice with microwave input power to the resonant cavity. The calculation of the density scaling (right side) was based on mass 20 and a mean energy of 0.5 eV.
only after at least four hours of discharging. This deposit could be removed by a vigorous discharge in oxygen.

As had been expected, the two principle ions in the methane plasma at low pressures are CH$_4^+$ and CH$_3^+$. Indeed, at low pressures they occur in very nearly the same relative abundances (~40 and 50% of the total ionization, respectively) as is observed in an ordinary mass spectrum of methane. With increasing pressure the intensities of these ions drop exponentially and simultaneously C$_2$H$_5^+$ and CH$_3^+$ intensities build up as seen from Figure 19. The general shape of the curves for the intensities of these four ions as a function of pressure are similar to those Field and Munson (65) obtained with a mass spectrometer ion source as a reactor. In pure methane the only reactions of CH$_4^+$ and CH$_3^+$ are

i. CH$_4^+$ + CH$_4$ = CH$_3^+$ + CH$_3$

ii. CH$_3^+$ + CH$_4$ = C$_2$H$_5^+$ + H$_2$.

These reactions are exothermic and have been observed to occur in other sources and the reaction cross sections (or rate constants) of the primary ions have been measured (63). Other ions of appreciable intensities (~2%) are C$_2$H$_6^+$, C$_2$H$_4^+$, C$_2$H$_3^+$, C$_2$H$_2^+$, and CH$_2^+$. The acetylene ion intensity is approximately 4% of the total ion intensity at the lowest pressure.

The sum of the relative intensities of the ionic reactants and products in reactions i and ii are approximately constant. Possible further reactions of the secondary ions CH$_3^+$ and C$_2$H$_5^+$ are given in Table V. It is seen from Table V that only reaction 13 is exothermic and therefore could be expected to proceed at a rate sufficiently rapid to be important. However, Field and Munson have shown that in pure
FIGURE 19

Relative positive ion intensities extracted from a plasma of methane excited at 50 mc versus the pressure in Torr.

\[ \Delta \text{CH}_4^+ \quad \Delta \text{CH}_2^+ \quad \bullet \text{CH}_3^+ \quad \bullet \text{C}_2\text{H}_5^+ \]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
<th>ΔHf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH_2^+ + CH_4</td>
<td>CH_4^+ + CH_4 + H</td>
<td>101 kcal</td>
</tr>
<tr>
<td>2. &quot; &quot;</td>
<td>CH_4^+ + CH_3 + H_2</td>
<td>100</td>
</tr>
<tr>
<td>3. &quot; &quot;</td>
<td>C_2H_5^+ + H_2 + H</td>
<td>83</td>
</tr>
<tr>
<td>4. &quot; &quot;</td>
<td>C_2H_5^+ + 2H_2</td>
<td>6</td>
</tr>
<tr>
<td>5. &quot; &quot;</td>
<td>C_2H_6^+ + 2H_2 + H</td>
<td>89</td>
</tr>
<tr>
<td>6. &quot; &quot;</td>
<td>C_2H_3^+ + 3H_2</td>
<td>62</td>
</tr>
<tr>
<td>7. &quot; &quot;</td>
<td>C_2H_2^+ + 3H_2 + H</td>
<td>151</td>
</tr>
<tr>
<td>8. &quot; &quot;</td>
<td>C_2H^+ + 4H_2</td>
<td>196</td>
</tr>
</tbody>
</table>
### TABLE V

**B. REACTIONS OF C₂H₂⁺ WITH METHANE AND THE ASSOCIATED HEAT OF REACTION**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>ΔH°</th>
</tr>
</thead>
<tbody>
<tr>
<td>9. C₂H₂⁺ + CH₄ = CH₄⁺ + C₂H₂</td>
<td>69 kcal</td>
<td></td>
</tr>
<tr>
<td>10. &quot; &quot; = C₂H₄⁺ + CH₄ + H</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>11. &quot; &quot; = C₂H₃⁺ + CH₄ + H₂</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>12. &quot; &quot; = C₃H₆⁺ + H</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>13. &quot; &quot; = C₃H₇⁺ + H₂</td>
<td>-16</td>
<td></td>
</tr>
<tr>
<td>14. &quot; &quot; = C₃H₆⁺ + H + H₂</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>15. &quot; &quot; = C₃H₅⁺ + 2H₂</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>16. &quot; &quot; = C₃H₄⁺ + 2H₂ + H</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>17. &quot; &quot; = C₃H₃⁺ + 3H₂</td>
<td>68</td>
<td></td>
</tr>
</tbody>
</table>
methane the $C_2H_7^+$ does not undergo further reaction with methane (pressure up to 2.0 Torr). Therefore we conclude that the product ions of reaction i and ii, $CH_3^+$ and $C_2H_5^+$, do not undergo further reaction with methane.

A few of the ion molecule reactions of the product ions of reaction i and ii with the neutral species (other than methane) probably formed and present in the discharge, e.g., $C_2H_2$, $C_2H_4$, etc., are exothermic and could have appreciable cross sections. Assuming equal relative collection efficiency of the primary ions at the different pressures employed, the approximately constant sum of the reactants and product for reactions i and ii indicates that further ion molecule reactions of $CH_3^+$ and $C_2H_5^+$ is insignificant for our discussion here. The relative intensities of the positive ions extracted from plasmas are in general similar to the results obtained by workers using mass spectrometer ion source as a reactor. That this is the case is surprising in view of the drastic differences in conditions and ion environment in the two ion sources. In particular it was expected that the ions sampled from a high frequency plasma would display reaction times considerably longer than the times of ions in the standard mass spectrometer ion source, in view of the size of the discharge vessel and the pressures employed.

This would seem to be the case especially for the ions that have relatively small ambipolar diffusion coefficients.

f. Reaction Time

The time scale for the reactions of the ions sampled from the plasma was obtained from the exponential decay of the primary ions with
increased pressure. The reaction rate constant-time product, \( kt \), is determined in the usual manner for the primary ions, i.e., from the slope obtained from a plot of the logarithm of the relative ion intensity versus the pressure in the discharge tube (105). This will be discussed extensively in Chapter V, part j. It was found that a plot of the logarithm of the primary ion intensity versus the pressure was linear in the low pressure region. At higher pressures, deviations from linearity were observed. This is the result of the fact that the ions do not asymptotically approach zero with increased pressure but rather approach a small constant value. This was generally the case and is presumed to be due to electron impact ionization of neutrals in the beam issuing from the probe orifice into the vacuum, particularly just after they enter the sampling probe orifice. When this small constant value is treated as the new zero the linearity of the semilogarithmic plots was satisfactory. An example of such a plot is given in Figure 20.

It is evident that the discharge mixes ions with different reaction times since the primary ions are formed by electron impact in the center of the discharge tube and up to the sampling orifice. (This is discussed in detail later.) Therefore, the time appearing in the \( kt \) product is an average time. Also the electric field strength is not constant on receding from the walls but probably decreases exponentially with increased distance from the walls. Thus the rate constant is taken as an average one, and would best be defined at some average electric field intensity. It will be shown that the electric field intensity in the region of the plasma where the observed ions originate is not drastically different from those employed by investigators using a mass
FIGURE 20

The logarithm of the per cent CH$_4^+$ versus the pressure for a methane plasma excited at 50 mc.
spectrometer ion source as a reactor. This is pertinent because some ion molecule reaction rate constants are a function of ion energy (106-108) and the majority of the rate constants reported in the literature (some of which will be used to interpret the gaseous discharge data) were obtained from normal electron impact sources. In mass spectrometer ion sources (field strength on the order of 10 volts/cm) the ions react with translational energies on the order of 1 eV or less in most cases.

The reaction rate constant-time product, \( k_t \), for reactions of \( \text{CH}_4^+ \) and \( \text{CH}_3^+ \) in our methane plasma is \( 4.8 \cdot 10^{-16} \) cc/molecule and \( 5.0 \cdot 10^{-16} \) cc/molecule, respectively. These products were obtained from the decay of the primary ion intensity with increased pressure by the method described in Chapter V, parts j and f. It will be seen later that this method is equivalent to the method normally used in studying ion-molecule reactions in conventional mass spectrometer ion sources. The \( k_t \) product for reactions i and ii measured from the rate of appearance of the secondary ions (105) is in agreement with the above values that were obtained from the disappearance of reactant ions. The value of the \( k_t \) product obtained from the appearance of secondary ions \( \text{CH}_2^+ \) and \( \text{C}_2\text{H}_5^+ \) is \( 4.2 \cdot 10^{-16} \) and \( 3.9 \cdot 10^{-16} \) cc/molecule, respectively. The \( k_t \) product using a mass spectrometer ion source as a reaction is \( 20 \cdot 10^{-16} \) cc/molecule and \( 16 \cdot 10^{-16} \) cc/molecule (63) respectively. The average reaction time is calculated from the experimental \( k_t \) product and from the reported rate constants (63) for reactions i and ii. The value of the reaction time in the plasma is then \( 5 \cdot 10^{-7} \) sec. The reaction time in most mass spectrometer ion sources is on the order of 1-2 microseconds. Thus, the ions sampled from the discharge actually display reaction times
shorter than even those in a normal mass spectrometer ion source.

\[ g. \ \text{Region of the Plasma Sampled} \]

The residence time of the positive ions and electrons in the discharge is calculated below and compared with the reaction time observed and presented in the previous section. The positive ions and electrons diffusing to the walls of the discharge vessel have average diffusion times that depend on the ambipolar diffusion coefficient and on the dimensions and the geometry of the containing vessel. The average time, \( \bar{t} \), that an ion requires to diffuse to the walls can be calculated from the reported thermal ambipolar diffusion coefficient and the geometry of the containing vessel. The mean ion lifetime in our discharge vessels was calculated for Helium discharges by taking the ambipolar diffusion coefficient of He ion in Helium at 0.2 Torr as 2300 cm\(^2\)/sec at \( T = 300^\circ \text{C} \) (109). This thermal value of the diffusion coefficient is corrected to a mean electron energy of 10 eV, which is approximately the electron energy in our discharges (Chapter V, part b), by equation 14. With this correction the value of ambipolar diffusion coefficient is \( 3.45 \times 10^5 \) cm\(^2\)/sec.

The average residence time in the plasma, \( \bar{t} \), is obtained for an infinite cylinder of radius \( R \) from the ambipolar diffusion coefficient, \( D_a \), and the characteristic diffusion length for an infinite cylinder, \( L = (R/2.404) \), through equation 26 (110) below. We assume here that diffusion occurs only by the first diffusion mode. The average lifetime of a Helium ion in the plasma contained in a cylinder of radius 0.5 cm is then calculated to be approximately \( 1.3 \times 10^{-7} \) sec.
(26) $\Lambda_c^2 = D_a \cdot \bar{t}_c$

It should be pointed out here that the basis of the calculation is equation 14 which was derived through Einstein relation $\frac{D}{\mu} = \frac{kT}{\Theta}$ (82) and assuming the mobility, $\mu$, to be independent of the electric field strength (111). The minimum kinetic energy of a Helium ion needed to traverse one half of the radius of the discharge tube in $1.3 \cdot 10^{-7}$ sec. in the absence of collisions is 20 eV. The fields necessary to produce ions with this mean energy are quite high, and the approximations mentioned above are likely to break down. Also, weakly bonded molecules such as $N_4^+$ and $N_3^+$ probably could not survive such energetic collisions yet these are observed in the plasma. The case chosen above is actually an unfavorable one with respect to long reaction times in the discharge, since Helium ion has a relatively large ambipolar diffusion coefficient. Indeed if Argon ion were chosen in the example above the reaction times would be approximately a microsecond (112).

Nevertheless, on the basis of the calculation alone we cannot rule out the possibility that the reaction times observed in our experiments are controlled by the ambipolar diffusion coefficients.

In order to ascertain if the reaction times are ambipolar diffusion controlled, the geometry and dimensions of the discharge vessel was varied since the reaction times will follow the diffusion length according to equation 26 above.

To this end the ionic mass composition of a NH$_3$ discharge in a 1.0 cm diameter pyrex cylinder was monitored as a function of the
pressure. The tube was removed and a pyrex bulb was inserted that was spherical with a radius of 2.5 cm. The mass composition was again monitored as a function of the pressure. The plasmas in the cylinder and the bulb were sampled through a hole in the walls. The plasma completely filled the sphere and it was cigar shaped in the cylinder but of sufficient length to render end effects negligible. Under equivalent discharge conditions the ambipolar diffusion coefficient will be approximately the same, regardless of the geometry of the containers, since the mean electron energies will be nearly the same or show only a small variation with the characteristic diffusion length. The ratio of the average time an ion exists in a discharge, and therefore the average reaction time, would then be given by equation 27 below. Ion and electron wall recombination is assumed to be the only loss mechanism.

\[
\frac{\Lambda_s^2}{\Lambda_c^2} = \frac{D_a \bar{t}_s}{D_a \bar{t}_c} \quad \frac{\Lambda_s}{\Lambda_c} = \frac{R}{R_{2.4}}
\]

Thus there would be a ratio of 15:1 for the average reaction time, \(\bar{t}\), in these two geometries. The decay of \(\text{NH}_3^+\) with increased pressure is shown in Figure 21 for a \(\text{NH}_3\) discharge in both the spherical and cylindrical reactors. This is a representative result. The \(\text{NH}_3^+\) is seen to decay with nearly the same slope (and therefore the same reaction times) in both containers. This result is observed for the decay of other primary ions and sampling along the axis of the cylinder results in the same conclusions.

Since the reaction time is experimentally observed to be independent of the characteristic diffusion length and since the time scale for the decay of the reactive primary ions with increased pressure indicates
FIGURE 21

The logarithm of the per cent $\text{NH}_3^+$ versus ammonia pressure for $\text{NH}_3$ discharge in:

a. spherical bulb, $r = 2.5 \text{ cm}$, ○

b. cylinder, $r = 0.5 \text{ cm}$, 0
that the ions are not sampled much more than a few millimeters from the 
plane of the sampling orifice, we conclude that the ions observed 
originate only in a narrow region in front of the probe orifice.

The general result that the reactive ions form an appreciable part 
of the mass spectrum at the higher pressures (NH$_3^+$ and CH$_4^+$ constitute ~ 
10% of the total ion intensity at 100 microns pressure) is a good 
indication that the ion diffusing to the walls from deep in the plasma 
interior (particularly from the center of the large sphere) do not 
strike the probe orifice and are consequently not observed. The 
reactive ions (primary ions) will undergo reaction on nearly every 
collision with the neutrals. Thus, most primary ions formed many mean 
free paths from the wall will react to form stable product molecules 
before they can diffuse to the walls. Since the dimensions of the 
discharge vessel are a few orders of magnitude greater than the mean free 
paths, there would be a preponderance of stable product molecules arriv-
ing at the walls and the probe orifice. Their presence in the issuing 
ion beam would greatly lower the relative abundance of the observed 
reactive ions simply by dilution.

This preponderance of stable product molecules arriving at the 
walls and orifice of the probe is not observed. This is attributed to 
the disturbance of the electric fields near the walls by the probe and 
its orifice. This disturbance is believed to deflect the ions away from 
the orifice in the manner of an electric lens such that only the ions 
formed inside the disturbed region (lens) and near the orifice are 
collected and observed.
h. Ion Lens

The electric fields in the vicinity of the probe orifice that defocuses the positive ions will be referred to here as an ion lens. We attribute the source of the ion lens in part to the fact that the potential across the sampling probe orifice is less negative with respect to the plasma than the potential on the walls. This was reported previously (Chapter V, part a, b) and can be shown to be the case by comparison of the calculated wall potential (113) and the measured plasma-probe potentials. The plasma-probe potentials were measured by the retarding grid technique which has been described previously (Chapter V, part a). Since the measured potential across the probe orifice was as much as 50 volts lower than the calculated potential of the walls, the potential across the probe orifice is positive with respect to the wall potential. This produces equipotential surfaces concave toward the plasma (see also G. N. Spokes (114-115) and T. Kinbara, et. al. (116)).

The source of the ion lens could also be attributed in part to the plasma pressure. The plasma is pushed through the sampling orifice somewhat by the plasma pressure causing the potential across the probe to be concave toward the plasma. This bending of the equipotential surfaces away from the plasma will also have a focusing effect on the electrons and a defocusing effect on the positive ions. For additional discussion of the potential disturbance in front of the probe the reader is referred to reference 55.

In order to determine if a significant deflection of ions across the probe orifice could be produced by the fields available in the plasma, the trajectories (in the absence of collisions) of an ion of mass 40
were plotted for the case of equipotential surfaces shown in Figure 22. Justification of the magnitude of the electric fields used in constructing Figure 22 is given in Chapter V, part i. The equation for the equipotential surfaces to the left of the center of the orifice in Figure 22 can be given as:

\[ V = V_1 \exp(-bX) - V_2 Y \]

where \( b \) is a parameter that determines the rate of potential variation with distance across the orifice and has the values

\[ b = -\infty \quad X < 0 \]
\[ b = 28 \text{ mm}^{-1} \quad X > 0 \]

\( V_2 \) is a measured of the X component of electric field intensity and it is taken as 50 volts/cm. \( V_1 \) is the measure of the disturbance across the probe, and is taken as 0.50 volts. In view of the usual magnitude of the sheath potential (Table I), a disturbance of 0.5 volts represents only a few per cent of the total sheath potential.

Differentiation of equation 28 with respect to distance gives the X and Y components of the electric field intensity as equation 29 and

\[ (29) \left( \frac{\partial V}{\partial Y} \right)_x = E_y = -V_2 \text{ volts/cm} \]

and 30 below.

\[ (30) \left( \frac{\partial V}{\partial X} \right)_y = E_x = -bV_1 \exp(-bX) \text{ volts/cm} \]

Equations describing the motion in the X and Y directions as a function of time are obtained from \( f = ma \) and equations 29 and 30 above. The result is given by equation 31 and 32 below,
FIGURE 22

Hypothetical equipotential surfaces forming an ion lens in front of the probe orifice. The dashed lines are ion trajectories calculated from equations 31 and 32. The slanted lines across the probe orifice represent a region of high non-linear electric fields.
\[ t = \left[ \frac{2(Y - Y_0)M}{eV_2} \right]^{1/2} \]

\[ \sec^{-1}\left\{ \left( \frac{2eV_1}{M} \right)^{1/2} (2b^t) \exp\left( -\frac{1}{2} bX_0 \right) \right\} = \exp\left\{ -\frac{1}{2} (X - X_0) \right\} \]

where \( X_0 \) and \( Y_0 \) are the coordinates of the ion at its formation and \( e \) is the electron charge. The ion velocity is taken as zero at \( t = 0 \).

The ion trajectories given by the dashed lines in Figure 22 were plotted from equations 31 and 32. It is evident from Figure 22 that a considerable deflection of positive ions away from the probe orifice can occur. The area enclosed by the two dashed lines that intersect at the equipotential valley represents the maximum region of ion collection for this case and is seen to be a narrow region in front of the probe orifice. Although the case considered above is the simplest one for our discussion, it is presented to show that deflection of ions across the probe orifice can be produced by even relatively small variations in potential across the orifice.

1. Sheath Potential

The translational energy of the ion issuing from the sampling probe orifice is usually in the range of 30 to 80 eV (Table I and III). Ion-neutral collisions between species of this energy could result in considerable extent of reaction (both endothermic and exothermic) in the sheath which can cause interpretational complexities. Also, it is necessary to know at least the magnitude of the energy of the ions participating in the reactions under investigation since the reaction
cross section is a function of ion energy. Therefore, a qualitative
description of the variation of the potential with distance in front of
the sampling orifice is in order.

The experiments discussed in this section were done by the
retarding potential grid method. In this method, the relative intensi-
sities of the various ions were recorded as functions of the positive
potential applied to the retarding grids (Figure 2). The probe potential
is held at ground potential and the remaining experimental parameters
(pressure, power, etc.) are held constant. By this means the relative
intensities of the ions striking the probe orifice under fixed discharge
conditions were obtained as a function of the energy of the incident ions.
It was found that no variation in the relative ionic composition was
observed until the retarding potential approached within approximately
five volts of the plasma potential. A representative result is given in
Figure 23 for ions extracted from methane plasma. A change in the
relative mass composition was usually first observable at a potential
approximately five volts from the plasma potential (Figure 23). When
the retarding potential is made to approach the plasma potential
sensitivity becomes a problem. Therefore not much reliance is placed on
the points near the plasma potential shown in Figure 23.

Because of the sheath potential one might expect ions collected
from the region just in front of the probe orifice to be predominantly
primary ions of relatively low energy whereas those collected from a
greater distance would be mainly secondary ions and would possess con-
siderably more energy. Thus the relative ionic composition of the ion
beam emerging from the probe orifice will show a variation with ion
Relative intensities of:

a. CH$_4^+$, △; CH$_2^+$, ▲

b. CH$_3^+$, O; C$_2$H$_5^+$, ○

as a function of retarding potential for a methane plasma excited at 50 mc. The plasma-probe potential is 75-80 volts.
energy where a significant amount of ion molecule reaction occurs in the sheath. The variation of the relative intensities with translational energy will reflect the region where the ions are formed due to a difference in the reaction times at the various potentials in the sheath. However, no variation in the relative ion composition with ion energy was observed until the ion energy was within approximately five volts of the energy corresponding to the full sheath energy; therefore we conclude that no significant amount of reaction occurs near the walls in the high energy region of the sheath.

This is consistent with the theoretical calculations of J. E. Allen et al. (97). They showed that the positive ion current collected by a wire probe immersed in a plasma is determined mainly by the relatively weak electric field which penetrates beyond the sheath edge into the plasma.

This requires most of the sheath potential to be dropped in a region much less than a reaction mean free path (~0.01 mm) and near the plane of the sampling orifice such that the high energy ions escape into the vacuum chamber without undergoing further reaction. This sheath depth is seen to be consistent with that calculated and discussed earlier in Chapter V, part a. Since the sheath potentials observed are approximately 50 volts, the magnitude of the electric field intensity near the walls is estimated to be ~$10^4$ volts/cm. The remaining sheath potential is dropped on receding further into the plasma. For a collection distance of 1.0 mm and a potential drop of 5 volts, the average electric field intensity in the region where the observed ions react is then on the order of 50 volts/cm. This value was used as the Y component of the
electric field intensity in Figure 22.

The variation of the reaction rate constant for reactions i and ii have been measured as a function of the electric field intensity using a normal mass spectrometer ion source as a reactor (63). The reaction time of the methyl and methane ions in the same discharge of methane is expected to be almost the same since their masses differ by only 1 amu. The ratio of the methyl ion reaction rate constant, to that of the methane ion in the discharge is 1.04. This ratio is obtained from the ratio of the reaction rate constant-time product, $k_t$, given in Chapter V, part e. This permits, on examination of the variation of the reaction rate constant with electric field intensity (63), an assignment of the range of electric field intensity for the ions participating in the observed reaction. The range of electric field intensity corresponds to the error range for the rate constants. The average electric field intensity encountered by the ions undergoing reaction is then seen to be greater than 10 volts/cm but less than 80 volts/cm. This is seen to be consistent with that deduced from the retarding potential grid data presented previously in this section.

j. Functional Dependence of Reaction Times

In Chapter V, part e and g the reaction time was treated as invariant with pressure. In that case the disappearance of $A^+$ by the reaction iii

$$iii. \ A^+ + A = B^+ + C$$
is given by equation 33:

\[
(33) \quad \frac{dA^+}{dt} = -kA^+A^+
\]

which integrates to give equation 34:

\[
(34) \quad \ln \frac{A^+}{A^+_0} = -kAt
\]

where \(A^+_0\) is the concentration of \(A^+\) at \(t = 0\). The \(kt\) product is then given by the slope of the usual plot of the logarithm of the relative intensity of the primary \(A^+\) versus the gas density. Because the rate constants are not expected to vary significantly with increased pressure, changes in the reaction time with increased pressure would be given by the changes in the slope, i.e., \(kT\).

Since the slope was constant we conclude that the reaction time was invariant with pressure. In these experiments the pressure range represented a change in mean free paths by a factor of 200. Therefore, we also conclude that the reaction time is not dependent on the mean free paths. Instead we attribute the magnitude of the reaction time to the dimensions of the coulombic disturbance in front of the sampling probe.

The collected and observed ions originated within or about the ion lens and near the walls of the sampling probe. The distance from which the ions are collected from the plasma is taken as the distance that the coulombic disturbance (ion lens) penetrates the plasma and is not directly dependent on the gas pressure.

The distance that a coulombic disturbance penetrates the plasma is a function of the electron density and the electron energy. This
distance is calculated below for one hypothetical case. This calculation is given in essence by E. MacDaniel (117) and is included here only to illustrate the approximate collection distance for one particular case.

Consider a thin slab across the surface of the orifice of the probe that is negatively charged due to the net number density of electrons, \( N_e \), in it.

This charge density gives rise to a potential difference between the slab and its boundaries (the plasma) that is given by Poisson's equation for the electrostatic potential:

\[
(35) \quad \frac{d^2V}{dy^2} = \frac{N_e e}{\epsilon}
\]

where \( N_e \) is the net electron density and \( e \) is the electron charge. The \( \epsilon \) is the permittivity and is taken as that of free space. Equation 35 on integration gives equation 36 for \( V = 0 \) at \( X = 0 \).

\[
(36) \quad V = \frac{N_e e Y_0^2}{2\epsilon}
\]

We seek a value of \( Y_0 \), which gives rise to a change in potential energy, \( eV \), equal to the mean kinetic energy in one direction, \( \frac{1}{2} \). Equating the former to the latter and solving for \( Y_0 \) gives equation 37:

\[
(37) \quad Y_0 = \left[ \frac{eE}{N_e e^2} \right]^{1/2}
\]

which gives the approximate distance, \( Y_0 \), that a coulombic disturbance will penetrate into a plasma. Equation 37 is recognized as equivalent to the expression for the Debye length (118).

The electron and positive ion number density varies across the
discharge vessel and is believed to drop to zero at the surface of the walls or drop to zero at some small extrapolated distance beyond the walls (119). \( N_e \) in equation 38 is the net electron density in a volume element near the surface of the walls and is non-zero. If positive ion density in this volume is taken to be much less than the electron density, then \( N_e \) is on the order of the electron density in the plasma, i.e., \( 10^9 \) electrons/cc. For \( E_\perp = 12 \) eV and \( N_e = 10^9 \) electrons/cc, \( Y_0 \) is given by equation 37 as 0.8 mm.

Several systems were studied for which the ion-molecule reaction rate constants were previously investigated and now are well known. When possible, the previously reported reaction rate constants used here were obtained at ion energies corresponding to energies of the ions in the plasma. A plot of the \( kT \) product observed in these experiments versus the value of the rate constant is given in Figure 24. The \( kT \) product for point 7 in Figure 24 was taken from the decay of \( \text{H}_2 \) with increased pressure in an electrodeless discharge of hydrogen as reported by I. B. Ortenburger, et. al. (52). Ortenburger used a cylindrical discharge vessel with a diameter of 5 cm.

The scattering of the points in Figure 24 is due in part to the fact that the rate constants are a function of ion energy which we cannot control in our experiments. This scattering is also attributed to the fact that the time scale in the discharge system cannot be controlled and shows some variation from day to day. Due to the short reaction times, we were limited to fairly fast reactions. Unfortunately this limited the range of the reaction rate constants; however, a linear trend is evident in Figure 24. The slope of the straight line
FIGURE 24

Reaction rate constant versus the reaction rate constant-time product, kt.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{O}^+ + \text{O}_2 = \text{O}_2^+ + \text{O}$</td>
<td>123</td>
</tr>
<tr>
<td>2. $\text{O}^+ + \text{CO}_2 = \text{CO}_2^+ + \text{CO}$</td>
<td>123</td>
</tr>
<tr>
<td>3. $\text{CO}^+ + \text{CO}_2 = \text{CO}_2^+ + \text{CO}$</td>
<td>123</td>
</tr>
<tr>
<td>4. $\text{NH}_3^+ + \text{NH}_3 = \text{NH}_4^+ + \text{NH}_2$</td>
<td>121</td>
</tr>
<tr>
<td>5. $\text{CH}_4^+ + \text{CH}_4 = \text{CH}_5^+ + \text{CH}_3$</td>
<td>63</td>
</tr>
<tr>
<td>6. $\text{CH}_3^+ + \text{CH}_4 = \text{C}_2\text{H}_5^+ + \text{H}_2$</td>
<td>63</td>
</tr>
<tr>
<td>7. $\text{H}_2^+ + \text{H}_2 = \text{H}_3^+ + \text{H}$</td>
<td>52</td>
</tr>
<tr>
<td>8. $\text{C}^+ + \text{CO}_2 = \text{CO}_2^+ + \text{CO}$</td>
<td>123</td>
</tr>
</tbody>
</table>
$10^9 \text{ cc/molecule - sec.}$

$k t \cdot 10^{16} \text{ cc/molecule}$
corresponds to a time of $3.5 \cdot 10^{-7}$ seconds. This time is observed to be consistent with our interpretation that the observed ions originate in or about the ion lens of the probe orifice.

An alternate but equivalent description of the decay of the primary ions with increased pressure can be made through the reaction cross section and the collection distance. The collection distance here is the average distance the ions travel to the wall or probe orifice. The rate of decay of primary $A^+$ (reaction iii) with increased pressure is given in terms of the reaction cross section of $A^+$, $\sigma$, and the collection distance, $Y_0$, by equation 39:

\[(39) \frac{dA^+}{dY} = -\sigma AA^+\]

which integrates to:

\[(40) \ln \frac{A^+}{A_0} = -\sigma Y_0 A\]

Thus a plot of the left side of equation 40 versus the number density of neutrals, $A$, will have a slope of $Y_0$. Since $\sigma$, is not expected to vary significantly with increased pressure, although the change in pressure represents a change in mean free paths by a factor of approximately 200. The collection distance calculated from the experimental and the reported cross sections is given in Table VI for discharges of several gases. The collection distance is seen to be on the order of a millimeter.

Probes constructed of different materials and geometries (and also different orifice diameters) were used in an attempt to remove the effect of the lens but they were not completely successful. It appears that
### TABLE VI

**DISTANCE FOR ION COLLECTION**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Distance (mm)</th>
<th>Cross Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_4^+ + \text{CH}_4 ) = ( \text{CH}_2^+ + \text{CH}_3 )</td>
<td>1.1</td>
<td>63</td>
</tr>
<tr>
<td>( \text{CH}_3^+ + \text{CH}_4 ) = ( \text{C}_2\text{H}_5^+ + \text{H}_2 )</td>
<td>1.1</td>
<td>63</td>
</tr>
<tr>
<td>( \text{O}^+ + \text{O}_2 ) = ( \text{O}_2^+ + \text{O} )</td>
<td>1.63</td>
<td>120</td>
</tr>
<tr>
<td>( \text{NH}_3^+ + \text{NH}_3 ) = ( \text{NH}_4^+ + \text{NH}_2 )</td>
<td>.81</td>
<td>121</td>
</tr>
<tr>
<td>( \text{H}_2^+ + \text{H}_2 ) = ( \text{H}_3^+ + \text{H} )</td>
<td>2.3*</td>
<td>122</td>
</tr>
</tbody>
</table>

*Based on the calculated cross section (122) and experimental data reported by Ortenburger et al.*
small sampling probes with small orifice diameters disturbed the plasma the least. In fact, as stated previously, smaller orifice diameters gave longer reaction times which indicates increased collection of the ions from the walls and therefore less coulombic disturbance to the electric fields at the walls and also a more representative sample of ions arriving at the walls for the case of small orifice diameters.
CHAPTER VI

BIBLIOGRAPHY

12. H. Margenau, Phys. Rev. 69, 508 (1946); 73, 297 (1948).


24. E. Klarfeld, J. Techn. Phys. USSR 4, 44 (1937); 5, 725 (1938), (He, Ne, A, Kr, K, Hg).


67. P. K. Ghosh, India Institute of Technology, Campur, India.


76. R. B. Brode, Rev. Mod. Phys. 5, 257 (1033).


102. L. Hatfield, (private communication).


139. J. D. Cobine, Casecous Conductors, (McGraw-Hill Book Co., Inc.
New York, 1941) 134.

140. F. C. Chen, Plasma Diagnostic Techniques, edited by R. H. Huddles-
1965) 113.

141. R. Popovlar, Electrical Phenomena in Gases, (American Elsevier

142. N. A. Karpow, Elektrische Vorgange in Gase und im Vakuum,

143. R. Popovlar, Phenomenes Electriques Dans Les Gaz, (Donad, Paris,
1963) 255.


148. G. Wehner and G. Medicus, J. App. Phys. 25, 270 (1954); G. Wehner,


APPENDIX


The experimental trace of the current transmitted by the retarding grids versus the retarding potential gives the integrated energy distribution of the electrons in the beam issuing from the sampling probe orifice. This was discussed in Chapter IV, part a. This distribution function was related to the distribution function in the plasma by calculating the distribution of energy components normal to the plane of the retarding potential grids in terms of the distribution function in the plasma, \( f(v) \), since it is these energy components that are retarded. The result of such an analysis is given in Chapter IV, part a, for a Maxwellian velocity distribution in the plasma.

Equation 41 below is the form of the electron energy distribution derived by M. J. Druyvestyn (8) for D. C. fields and H. Margenau (12) for strong alternating fields.

\[
(41) \quad f(v) = Bv^2 \exp(-\alpha^2 v^4)
\]

In the following the distribution of the energy components normal to the plane of the retarding potential grids is calculated for the case of a velocity distribution in the plasma given by equation 41.

The analysis of the electron effusion process (Chapter IV, part a) yields equation 19 (reproduced below) which is a general equation for the velocity components parallel and perpendicular to an axis normal to the plane of the retarding potential grids. The \( f(v) \) is the velocity distribution function in the plasma.
\[(19) \quad \frac{dn(v_{\perp},v_{\parallel})}{N} = \frac{1}{2v^2} NAf(v) v_{\perp} v_{\parallel} dv_{\perp} dv_{\parallel} \]

In the following the constants (where possible) will be collected and expressed by a single symbol since they carry through the derivation and their values determined by normalization of the distribution function.

Substituting the distribution function expressed by equation 41 into equation 19 gives the electron velocity distribution in the beam as equation 42 below.

\[(42) \quad \frac{dn(v_{\perp},v_{\parallel})}{n_0} = A_0 \exp(-\alpha^2 v^4) v_{\perp} v_{\parallel} dv_{\perp} dv_{\parallel} \]

We change equation 42 to obtain a distribution of energies with

\[mv_{\perp} dv_{\perp} = dE_{\perp} \quad \text{and} \quad mv_{\parallel} dv_{\parallel} = dE_{\parallel} \quad . \quad \text{The result is given by equation 43.} \]

\[(43) \quad \frac{dn(E_{\parallel},E_{\perp})}{n_0} = A_0 \exp(-b^2 E^2) dE_{\perp} dE_{\parallel} \]

\[(44) \quad E_{\parallel}^2 + E_{\perp}^2 = E^2 \]

Since the parallel and perpendicular energy components exert their distributions independently, we can separate their distributions and formulate the integrals given by equation 45 below;

\[(45) \quad \int_0^{\infty} \frac{dn(E_{\parallel})}{n_0} \int_0^{\infty} \frac{dn(E_{\perp})}{n_0} = A_0 \int_0^{\infty} \exp(-b^2 E_{\parallel}^2) dE_{\parallel} \int_0^{\infty} \exp(-b^2 E_{\perp}^2) dE_{\perp} \]

which gives on integration equation 46.
\( \frac{n(E)}{n_0} = A_0 \left[ 1 - \text{Erf}(bE) \right] \)

Equation 46 is subjected to the normalization conditions:

\[ \frac{n}{n_0} = 1 \text{ at } E = 0; \quad \therefore A_0 = 1 \]

which yields equation 47.

\( \frac{n(E)}{n_0} = \left[ 1 - \text{Erf}(bE) \right] \)

The constant \( b \) in equation 47 is not numerically the mean energy; however, it does determine it. \( E_\parallel \) is the energy component parallel to an axis (z-axis) normal to the plane of the retarding grid and \( \eta \) the electron current to the collector at \( E_\parallel = 0 \).

Equation 47 is the desired result; however in practice it is more convenient to use an approximate form. To obtain this we make the approximation (124):

\[ 1 - \text{Erf}(bE) = \frac{\exp(-b^2E^2)}{bE_\parallel \sqrt{\pi}} \]

Thus the current transmitted by the retarding potential grids is given approximately by equation 48 below.

\( \frac{n(E_\parallel)}{n_0} = \frac{\exp(-bE_\parallel)}{bE_\parallel \sqrt{\pi}} \)

We take the logarithm of both sides of equation 48. The result is given by equation 49.

\( \ln \left[ \frac{n(E)}{n_0} \right] = -b^2E_\parallel^2 - \ln b \sqrt{\pi} - \ln E_\parallel \)

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Since the square of the energy (first term, right side of equation 49) will change much more rapidly than the logarithm of the energy (last term, right side of equation 49), the last term on the right side of equation 49 can be neglected. On this basis, the logarithm of the current transmitted by the retarding potential grids versus the square of the total retarding potential will be nearly linear with a slope of $-b^2 (eV)^{-2}$ for the case of a velocity distribution in the plasma of the Druyvestyn form.

b. Abnormalities Observed in a Plasma of $H_2S$ and $SO_2$ Excited at Microwave Frequencies

The mean electron energies for fourteen different gases has been measured and presented previously in Table III. The mean electron energy range is seen from Table III to be 13-21 eV with the exception of the data for $SO_2$ and $H_2S$ which are seen to have abnormally high energies. A number of differences were observed for discharges in these gases. In all the gases except $SO_2$ and, in some cases $H_2S$, the electron energy distribution fitted the Maxwellian energy distribution. At higher pressures and electron densities the electron energy distribution in $SO_2$ and $H_2S$ fitted in form the Druyvestyn distribution (8) or (equivalently in certain cases) the Margenau distribution (12) derived for the case of strong alternating fields. The form of these energy distributions is given by equation 41 in the Appendix, section a. They are seen to be equivalent to the Maxwellian distribution except for the appearance of $v^4$ term in the exponent.

It has been shown previously (Appendix, part a) that the integrated energy distribution of the electrons in the issuing beam have the
approximate form:

\[(49) \quad \ln \left[ \frac{n(E_n)}{n_0} \right] = -b^2 E_n^2 - \ln b \sqrt{\Pi} \]

for a Druyvestyn distribution of velocities in the plasma. The constant \(b\) is related to the mean electron energy.

Equation 41 was found to be obeyed in discharges of the gases (SO\(_2\) and H\(_2\)S) that displayed abnormally high energies. The gas H\(_2\)S fitted nicely the Maxwellian energy distribution at low pressures and Druyvestyn distribution at high pressure as inferred from Table III. An example of a linear plot of the \(\ln(n_e)\) versus the square of the retarding potential is given in Figure 25 for our H\(_2\)S discharge.

Sheath potentials ranged from 5 to 80 volts and were pressure dependent.

The positive ion and electron densities (inferred from the magnitude of the beam currents) were a few powers of ten higher in discharges of SO\(_2\) and H\(_2\)S (at the higher pressures) than is usually observed in normal discharges. In addition, these densities went through a distinct maximum at about 0.8 Torr.

Since the power input (and power density) was nearly constant in these experiments and since the geometric relationship of the input microwave to the sampling probe was not altered during these experiments, the energy abnormality of the electrons cannot be attributed to increased strength of the electric field component of the input wave or its orientation relative to the orifice of the sampling probe. Since the electrons gain their energy from the oscillating electric field of the input wave through collisions (125), it might be thought that a
FIGURE 25

The logarithm of the electron current transmitted by the retarding grids versus the square of the applied retarding potential for H₂S plasma excited at microwave frequencies. The pressure is 0.725 Torr.
difference in collision cross section or polarity produced the
abnormalities by providing an abnormally efficient means of gaining
energy from the electric field. The collision cross section and
polarity is not abnormally large. Therefore, the following explanation,
based on the effect of negative ions on ambipolar diffusion rates, is
proposed to explain the above phenomena. The existence of the negative
ions of SO₂, i.e., SO⁻, S⁻ and O⁻ and H₂S, i.e., HS⁻, are well
established and have been investigated and observed by numerous
researchers (126-130).

The electron energy (in the positive column of D. C. discharges)
has been related to the ion or electron loss processes (131). In the
case where the sole positive ion or electron loss occurs by diffusion to
the walls, the electron energy is calculated simply by finding the
electron energy necessary to produce ions at a rate sufficient to
account for the diffusion loss. By this means the electron energy in
the positive column has been calculated from the radius of the discharge
vessel, the gas pressure, etc. Also it has been observed experimentally
for the positive column of D. C. discharges that the processes which
accelerate the electron or positive ion loss raise the electron
temperature (24,26).

This theory was extended by Holm (83) and Seeliger (132-133) to
include ambipolar diffusion in the presence of massive negative ions.
The ambipolar diffusion coefficient in the presence of negative ions is
given by equation 50 (134).

\[
(50) \quad \left( D_{a} \right)_{e} = (1 - 2\lambda) D_{+} \left( \frac{I_{e}}{I_{+}} \right) \quad \text{where} \quad \lambda = \frac{n_{-}}{n_{e}}
\]
The principle effect of the negative ions as seen from equation 50 is to accelerate the diffusion of the electrons.

Spencer-Smith (135) first reported in a study of the negative ions present in the positive column of a D. C. discharge of iodine that the electron temperature was large in the presence of negative ions. He found from probe measurements that the electron temperature in his positive column was about 13 eV.

In the plasma the low energy negative ions diffuse only with difficulty at the higher pressures against the electric field that produces the plasma-wall potential. The electrons diffuse out and leave behind the negative ions. In this manner the ionic concentration of the negative ions builds up in the plasma. This negative charge retards the diffusion of the positive ions in order to maintain approximate charge neutrality in the plasma. Thus, the electron, the negative ion, and the positive ion densities increase until the rate of the various volume ion destruction processes (ion-ion recombination, etc.) equals the rate of their production. The observed abnormally high electron and positive ion densities (inferred from the abnormally high current issuing from the probe orifice) can be explained on the basis of the above discussion.

It is mentioned here that the plasma-wall potential has been observed in our measurements to be as much as sixty volts less than that calculated on the basis of the measured electron and positive ion energies. The calculation assumes no massive negative ions are present. Due to the low plasma-wall potential and the high electron energy more than 60% of the electron energy distribution has been observed. As
stated previously, the integrated electron energy distribution had the form given by equation 51 below.

\[
\frac{n(E)}{n_0} = A \exp(-b^2 E^2)
\]

\(E(-)\) is electron energy; 
\(A\) is a constant.

At pressures above one Torr deviations from equation 3 were observed in that the experimental curves displayed an excess of electrons at the low energies (0-25 eV) and a deficiency at high energies (above 90 eV).

Thus, when the presence of negative ions is assumed the experimental data were in qualitative agreement with the diffusion theory of D. C. discharges and qualitatively with the theoretical calculations of Holm and Seeliger.

In order to obtain current multiplication, the fourteen dynodes of the electron multiplier must be a negative potential with respect to ground. Therefore, our mass filter cannot be used to mass analyze for negative ions without modification because our present amplifier cannot be floated appreciably above ground. Since up till now the positive ions were of sufficient interest, this instrument has been used exclusively for positive ion analysis.

c. Langmuir and Mott-Smith Probes

A Langmuir probe consisting of a very small silvered electrode and a large electrode were placed in the plasma of the electrodeless discharge (Figure 26A). A potential was applied across the electrodes (Figure 26A) and the current was recorded at each applied potential or
FIGURE 26

A. Schematic diagram of the Langmuir probe-sampling probe apparatus and associated electrical circuitry.

B. Current-voltage trace obtained by using the probe tip as a Langmuir single probe.
plotted continuously by an X-Y recorder. A schematic diagram of the electrode system and associated electrical circuitry is given in Figure 26A.

An experimental current voltage trace is presented in Figure 26B. The various regions of the current-voltage trace shown in Figure 26B have been labeled and are discussed below. The discussion that follows is given in essence in several books (136-143). The origin of the coordinate system in Figure 26B is point 0.

In steady state electric discharges ambipolar diffusion of the positive ions and electrons to the walls we presume occurs. Thus initially each electrode is at negative potential, $V_w$, with respect to the plasma. The fraction of the electrons in the plasma that are able to surmount this negative potential and strike the probe is $\exp(-eV_w/E_-)$ for a Maxwellian velocity distribution. When the potential applied, $V_{applied}$, to the probe is negative the total retarding potential for the electrons to strike the probe is $V_w + V_{applied}$ and the net current to the probe becomes more positive since fewer electrons have sufficient energy to surmount the retarding fields. This corresponds to region b-0 in Figure 26B. When the probe is made highly negative essentially all the electrons are retarded and only the positive ions are collected by the probe. This corresponds to region a-b. The current in this region is largely space charge limited and under the appropriate discharge conditions it is given by the Child-Langmuir Law (144).

When the potential applied to the probe is positive the electrons see a net retarding potential of $V_w - V_{applied}$ and the fraction of the total electrons able to strike the probe is then $\exp(-V_w + V_{applied})$ as
is evident from energy considerations. This corresponds to the region o-c in Figure 26B. Therefore as the applied potential becomes more positive a larger fraction of the total electrons strike the probe yielding increased electron current. The electron current increases in the usual exponential manner until the applied potential is equal to the plasma wall potential. At this point the Boltzmann relation no longer is valid because the retarding field vanishes. This corresponds to point c in Figure 26B. Region c-d the probe is at a positive potential with respect to the plasma. Thus the electron energy (temperature) can be determined from the slope of the usual plot of the logarithm of the electron current versus the applied potential. The results obtained from conventional wire probes indicated electron temperature of approximately 10 eV.

d. Plasma-Probe Potentials Measured by Langmuir Probe and Retarding Potential Grid Technique

The retarding potential grid apparatus discussed previously was used in conjunction with the Langmuir probe apparatus illustrated in Figure 26B to obtain data on the plasma-probe potentials. It will be evident that this apparatus permitted data to be obtained by these different techniques on precisely the same region of the plasma. The results are construed as a partial affirmation of the Langmuir probe theory for the one particular set of Langmuir probes. This work was undertaken before a similar paper, in which a similar apparatus was used, appeared in the literature (54-55). Some new results are presented here. A brief description of the new apparatus, that has not been previously

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described, will now be given.

The tip of the sampling probe (Figure 26B) contained the sampling leak. The tip was silvered about the orifice such that the leak itself could be used as an electrical probe. The total area of the silvered surface was relatively small—a few square mm. This tip was able to conduct current and was floated above ground by power supply b.

The ions striking the probe orifice issued into a vacuum envelope that contained the retarding potential grid apparatus (Figure 2).

Four sets of data were taken with this arrangement:

1. The probe tip was grounded and the energies of the positive ions issuing into the vacuum envelope were obtained by the retarding potential grid technique.

2. The retarding potential grids were grounded and the positive ions issuing into the vacuum envelope were collected as a function of the positive potential applied to the probe tip.

3. The probe tip was used as a Langmuir single probe. This operation was discussed in the Appendix, part c.

4. The applied probe potential was fixed at some positive potential and the energies of the positive ions issuing into the vacuum envelope were measured by the retarding potential grid technique in the usual manner.

A plot of the potential applied to the probe versus the plasma-probe potential for nitrogen is given in Figure 27. The curve is seen to give a straight line with a slope of unity in agreement with Langmuir probe theory. (We were unable to obtain data near the plasma potential due to the loss in sensitivity as the probe potential approached the plasma potential.) This has been reported previously (54-55) and this general method of lowering the plasma-probe potential has been used many times in the past (145-146). It is particularly useful in studies involving negative ions in electric discharges where a large negative
FIGURE 27

A plot of the potential applied to the sampling probe versus the plasma-probe potential (sheath potential).
potential barrier can block the sampling of the low energy negative ions.

Retarding Probe and Retarding Grid Operation

The following data are presented to illustrate the agreement obtained among the three methods of measuring the plasma-probe potential that were discussed previously. Each method is described briefly to facilitate the discussion.

First the retarding grids are held at ground potential and the positive ions issuing into the vacuum are collected on the Faraday cup and are measured as a function of the positive voltage applied to the probe (tip or orifice). The collected current versus the positive potential applied to the probe is given by the dashed-dotted line in Figure 28.

The dashed line is the retarding potential (grid) curve, taken under equivalent discharge conditions, and is included for comparison. The plasma-probe potential deduced from the retarding probe trace (dashed-dotted line) is seen to give good agreement with the plasma-probe potential deduced from the retarding potential trace. Differences in form of these traces is slight and is probably due to a disturbance of the charge densities and gradients in front of the probe orifice produced by the applied field.

The solid line in Figure 28 is a portion of a Langmuir probe curve (see Appendix, part c) also taken under nearly equivalent discharge conditions as the two traces discussed immediately above. It is seen from Figure 28 that the plasma-probe potential deduced from Langmuir probe theory is in good agreement with that obtained by the previously presented methods. The difference of a volt or two could be due to
Current-voltage traces giving the plasma-probe potential by three different techniques for 50 mc discharge in N₂, 35µ.

——— Retarding probe operation.

—— Retarding grid operation

—— Langmuir probe operation
slight difference in pressure. This was a reproducible result. Also, the break is much less distinct at higher pressures (200).

In general, the single probe current-voltage characteristics should be interpreted cautiously. In this case the probe passes nearly no current in the absence of an applied voltage to the probe—a good indication that both probes are at the same potential with respect to the plasma. This need not be the case. Errors in single probe and double probe techniques as well as interpretational difficulties are presented in several publications (147-152).