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MEASUREMENT OF THE TEMPERATURE DEPENDENCE
OF HELIUM ION MOBILITIES IN HELIUM

by

Paul Louis Patterson

NOTICE

This report is identical to a thesis which was approved by the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Department of Physics and Astrophysics, 1966.

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Paul Louis Patterson

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Measurement of the Temperature Dependence of Helium Ion Mobilities in Helium

Thesis directed by Dr. Earl C. Beaty, Lecturer

The mobilities of helium ions in helium are measured using a double shutter drift tube similar to that employed previously by Beaty and Patterson. Data are obtained at temperatures of 300°K, 248°K, 196°K, 150°K, and 75.9°K. There are observed three helium ion species, He⁺, He₂⁺, and He₃⁺. The identities of the He⁺ and He₂⁺ are well established by numerous experiments done previously at room temperature. The existence of the He₃⁺ ion has not been reported previously. It is observed to be formed by means of a reaction of the He₂⁺ with the gas at low temperatures. Between 110°K and 160°K, there is observed an equilibrium reaction between the He₂⁺ and the He₃⁺. At temperatures lower than about 100°K, the formation of He₃⁺ is so fast that no trace of He₂⁺ can be seen without heating the ions slightly by means of an applied electric field. The direct observation of this He₂⁺ – He₃⁺ conversion is made possible by a cooling scheme which allows the mobility spectrum to be monitored continuously while the temperature of the apparatus decreases steadily.

The He⁺ mobilities measured here are found to be in better agreement with detailed theoretical treatments than the previously
reported measurements of Chanin and Biondi. The He$_3^+$ mobility at 75.9°K is consistent with qualitative predictions based on treating molecular ions in their parent gases as ions in unlike gases. For He$_2^+$, this usual theory of ions in unlike gases has been known for several years to be inadequate for explaining the experimental He$_2^+$ mobility. The measurements reported here suggest that the reason for the failure of the usual theory is that it neglects the symmetry in the He$_2^+$ - He interaction. A resonant rearrangement of the He nuclei between the free atom and molecular ion systems is proposed to explain the anomalously low He$_2^+$ mobility.
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CHAPTER I

INTRODUCTION

The experimental study described in this paper concerns the measurement of the temperature dependence of helium ion mobilities in helium. In order to better understand the objectives of this work, this introduction begins with a discussion applicable to ion mobility studies in general. Fundamental concepts are discussed in Section I-1, general features of mobility theory are described in Section I-2, and the specific case of helium ion mobilities is discussed in Section I-3.

I-1. Fundamental Concepts

In the absence of external force fields, a group of ions immersed in a neutral gas diffuses through the gas randomly due to the thermal agitation of the system and the density gradient of the ions. Under conditions where the ion density is much smaller than the gas density, ion-neutral collisions predominate over ion-ion collisions in determining the behavior of the ions. When a weak, uniform, and static electric field is applied, the random motion of the ions is altered to some extent. Between collisions with gas particles, the ions are accelerated along the field direction, thereby gaining energy from the applied field. Upon collisions,
some of this "field energy" is lost to the gas particles, and the
direction of motion of the ions is changed in a random manner. The
net result is an ionic motion consisting of a preferential drift
along the field direction, superposed upon the random thermal
motion. If the electric field is very weak—such that the field
energy of the ions is much smaller than their thermal energies—
then the drift velocity \( v \) acquired by the ions is proportional to
the field strength \( E \). The constant of proportionality is called
the ion mobility.

The mobility of an ion depends upon the ion-neutral interaction
forces that prevail, as well as the composition of both ion and gas
particles. The important feature of mobility (or ion swarm) studies
is that they provide a means of examining ionic motion in gases
under nearly thermal equilibrium conditions. Such studies can
yield valuable information on ion-neutral scattering events in the
very low energy region which is inaccessible to beam techniques.
Furthermore, mobility experiments can serve as a method of deter-
mining the types of ions that can be present under conditions
similar to those encountered in a variety of other gaseous elec-
tronics experiments, or in natural environments such as the earth's
upper atmosphere. In this latter respect, ion mobility studies
compliment mass spectrometer investigations which are generally
limited to lower pressures and to ion species that are stable
enough to survive the acceleration required of them.
Expressed simply as the ratio \( v/L \), the mobility constant is inversely proportional to the gas density \( n \). It is the usual convention to normalize the mobility \([i.e., (v/L)(n/n_o)]\) to a standard gas density \( n_o \) of \( 2.69 \times 10^{19} \) particles/cm\(^3\). (This is the density of an ideal gas at a pressure of 760 Torr and a temperature of 273°K.) It is important to point out that this is only a normalization with respect to density, and the temperature to which the normalized mobility refers is the temperature at which its value is measured or for which it is calculated. The ratio \( n/n_o \) can be expressed in terms of the more familiar experimental quantities, pressure \( p \) and absolute temperature \( T \). Consequently, throughout this paper the expression which will be used for the mobility constant \( K \) is,

\[
K = \frac{(v p_o)}{(E760)},
\]

where \( p_o = p273/T \). With \( v \) expressed in units of cm/sec, \( E \) in volts/cm, and \( p_o \) in Torr, the units on \( K \) are cm\(^2\)/(volt-sec).

The ratio \( E/p_o \) which occurs in equation (1) can be shown\(^1\) to be the parameter which determines the field energy of the ions.

The mobility of an ion has been defined to be the constant of proportionality between the drift velocity and the electric field in the limit of weak electric fields. When the field energy of the ions is no longer negligible compared to their thermal energy, the drift velocity may exhibit something other than a linear dependence on \( E/p_o \). In this case, the quantity \( K \) as defined by equation (1)
is no longer a constant. Nevertheless, it is common practice to still refer to \( K \) as the ion mobility. This practice will be followed throughout this paper.

At a given temperature, experimental results are usually displayed in the form of plots of \( K \) versus \( E/p_0 \). In most cases, \( K \) is found to be independent of \( E/p_0 \) at very low \( E/p_0 \) values, while at higher values it exhibits a characteristic \( E/p_0 \) dependence. The shape of this dependence is determined by the nature of the scattering forces and their dependence on the ion-neutral interaction energies. Qualitatively, variations in \( E/p_0 \) are expected to affect \( K \) in a manner analogous to changes in the gas temperature \( T \). Both \( E/p_0 \) and \( T \) are parameters which determine the interaction energy for the ion-neutral collisions. However, variations of \( E/p_0 \) affect only the ions, while variations of \( T \) affect both ions and gas particles, and a quantitative relationship between these two parameters is difficult to establish. In determining the dependence of \( K \) on interaction energies, it is experimentally much easier to vary \( E/p_0 \) than \( T \), but from a theoretical standpoint \( T \) is the more useful variable. From a given plot of \( K \) versus \( E/p_0 \), the mobility which is quoted in the literature for that ion-gas combination is always the value of \( K \) extrapolated to zero \( E/p_0 \).
I-2. General Features of Mobility Theory

The theoretical description of the phenomenon of ionic drift consists of two basic parts. First, gas kinetic theory must be employed to relate the mobility constant $K$ to a parameter which describes the individual ion-neutral scattering events that take place. This important parameter is the diffusion (or momentum transfer) cross section $Q_d$. Secondly, the cross section $Q_d$ itself needs to be related to the relevant scattering forces between ions and neutral particles.

The rigorous kinetic theory of gases is based upon the knowledge of the distribution function $f_i(x, v_i, t)$. This function represents the number of particles of the $i$th species which at time $t$ lie in a unit volume element about the point $x$ and which have velocities within a unit range about $v_i$. When the system is in complete equilibrium (i.e., no gradients in composition, velocity, or temperature), then $f_i(x, v_i, t)$ reduces to the well-known Maxwellian velocity distribution. When the system is not at equilibrium, the distribution function satisfies the Boltzmann transport equation. For a system which differs only slightly from equilibrium, the distribution function is nearly Maxwellian, and the Boltzmann equation can be solved by a perturbation method developed by Chapman and Enskog. 2

For the situation of interest here—that of ions immersed in a gas—the ion density is assumed to be sufficiently small so that
the Maxwellian distribution of the gas particles is not disturbed. The problem, then, is to solve the Boltzmann equation for the distribution function of the ions. When the drift motion of the ions is small compared to their thermal motion (i.e., in the limit of weak electric fields), the velocity distribution of the ions is again nearly Maxwellian, and the results of the Chapman-Enskog theory can be employed.

There is a close similarity between the phenomena of ionic drift and ionic diffusion. The mobility constant $K$ is related to the diffusion coefficient $D$ through the expression,

$$K = \frac{(eD/kT)(p_o/760)}{\epsilon},$$
(2)

where $e$ is the ionic charge, $k$ is the Boltzmann constant, and $T$ is the gas temperature. This equation is commonly known as the Einstein relation. In general, equation (2) is not exactly correct, but it is a very good approximation in the limit of zero $E/p_o$. For the diffusion coefficient $D$, the Chapman-Enskog theory gives the expression,

$$D = \left[\frac{3}{16(n_1 + n_2)}\right] \left(\frac{2\pi kT}{\mu}\right)^{1/2} \left[\frac{(1 + \epsilon)}{\langle Q_d \rangle}\right],$$
(3)

where $n_1$ is the ion density, $n_2$ is the gas density, $\mu$ is the reduced mass of the ion-gas particle combination, and $\epsilon$ is a small positive correction term which is usually neglected. (Exact calculations of $\epsilon$ have been carried out by Dalgarno and Williams for the general case of interaction potentials of the form $1/r^n$, where
\( R \) is the ion-neutral separation. Under certain circumstances, \( \epsilon \) can be of the order of a ten per cent correction, but in most cases it is much smaller. In particular, \( \epsilon \) vanishes completely for \( n = 4 \). The quantity \( \langle Q_d \rangle \) is an average diffusion cross section defined by the expression,

\[
\langle Q_d \rangle = \frac{1}{2} \int_0^\infty x^2 Q_d(x) \exp(-x) \, dx ,
\]

where \( x = (\mu g^2)/(2kT) \) and \( g \) denotes the relative velocity. Since the ion density \( n_1 \) is usually much smaller than \( n_2 \), equation (3) is normally used in the form in which both \( \epsilon \) and \( n_1 \) are missing. Equations (2) and (3) can be combined to give the relation,

\[
K = \frac{2.10 \times 10^4}{\langle Q_d \rangle} \left( \frac{1}{\mu T} \right)^{1/2} \text{ cm}^2/(\text{volt-sec}) ,
\]

where \( \mu \) is measured in atomic mass units, \( T \) in \(^\circ \text{K} \), and \( \langle Q_d \rangle \) in units of \( \pi a_o^2 \).

Equations (4) and (5) provide the required relationship between the mobility \( K \) and the diffusion cross section \( Q_d \). These equations are given by the Chapman-Enskog theory which presumes a nearly Maxwellian velocity distribution for the ions. Therefore, for comparison with values of \( K \) obtained from these equations, the relevant experimental \( K \) is that value extrapolated to zero \( \text{E}/\text{p}_o \). Some of the other assumptions of the Chapman-Enskog theory are that only binary collisions are important and the ion-neutral interaction
force is spherically symmetric. The latter limitation means that in the strict sense, the Chapman-Enskog theory is applicable only to monatomic ions and gas particles, since no allowance is made for the internal degrees of freedom of molecules. However, as a first approximation for molecular systems, the theory can still be used by employing spherically symmetric interactions obtained by averaging over all molecular orientations.

The ion-neutral scattering problem can be formulated in terms of a projectile of mass \( \mu \) and velocity \( g \), interacting with a fixed center of force (see Nott and Massey\(^5\)). The diffusion cross section, then, is given by the expression,

\[
Q_d = 2\pi \int_0^\pi I(\theta) (1-\cos \theta) \sin \theta \, d\theta , \tag{6}
\]

where \( I(\theta) \) is the differential cross section for the elastic scattering of the projectile through an angle \( \theta \) by the interaction potential \( V(R) \). Using the method of partial waves,\(^5\) quantum mechanical expressions for \( I(\theta) \) and \( Q_d \) can be derived, thereby relating these cross sections to the potential \( V(R) \), the relative velocity \( g \), and the reduced mass \( \mu \). If the scattering event is viewed classically rather than quantum mechanically, then \( Q_d \) can be expressed in the form,

\[
Q_d = 2\pi \int_0^\infty (1-\cos \theta) \, b \, db . \tag{7}
\]
In equation (7), \( b \) is the impact parameter which is defined to be the closest distance of approach of the two particles if there were no interaction. The classical scattering angle \( \theta \) can be replaced by an expression containing the quantities \( V(k), b, \mu, \) and \( g. \) Of course, the classical description of physical phenomena is merely an approximation to the correct quantal description. The classical treatment of scattering prescribes a well-defined trajectory and scattering angle to the projectile. In a quantal analysis, the projectile is represented by a wave packet which spreads as it travels through space, and the quantum mechanical uncertainty in the projectile's position is measured by the de Broglie wavelength 
\[ \lambda = \frac{\hbar}{\mu g}, \]
where \( \hbar \) is the Planck constant. The quantal and classical descriptions of scattering are essentially identical if:
(a) the de Broglie wavelength of the projectile is small compared to the extent of the interaction force; (b) the angle of scattering is not obscured by the spread of the wave packet. For the calculation of \( Q_d \), the contribution of small angle scattering (condition (b)) is minimal because of the occurrence of the \((1-\cos \theta)\) factor. If the arithmetic mean velocity of a Maxwellian distribution is used for the projectile velocity \( g \), the de Broglie wavelength of the projectile becomes,
\[ \lambda = 51.8/\sqrt{\mu T} \quad a_o, \quad (8) \]
where the unit \( a_o \) is the first Bohr radius of the hydrogen atom, and \( \mu \) and \( T \) are measured in atomic mass units (amu) and \( ^\circ K \), respectively. Equation (8) shows that the de Broglie wavelength
consideration becomes more important the lighter the particles and the lower the temperature. In addition, there are certain ion-gas combinations in which symmetries between the interacting particles produce an interaction which can only be described quantum mechanically.

For many ion-neutral encounters, the dominant scattering potential \( V(R) \) is that due to the attraction of the point charge of the ion and the induced dipole of the neutral. This polarization potential is characterized by a \( 1/R^4 \) dependence which is unique in several respects. For this potential form, the correction factor \( \varepsilon \) in equation (3) vanishes, and also equation (2) (the Einstein relation) is exact. Langevin,\(^6\) in 1905, combined this attractive potential with a hard sphere repulsion and derived a classical expression for the ion mobility. In the limit of \( 0^\circ K \), the classical interaction is a pure polarization, and the Langevin limit for the mobility is,

\[
K = \frac{35.9}{\sqrt{\mu a}} ,
\]

where \( a \) is the polarizability of the gas in units of \( a_0^3 \), and \( \mu \) is in amu. This equation has subsequently been verified by the quantum mechanical calculations of Dalgarno, McDowell, and Williams.\(^7\) Equation (9) shows that the pure polarization interaction produces a mobility which is independent of the charge state of the ion and of the gas temperature \( T \). These two features are unique for the \( 1/R^4 \) potential, while the dependence on \( 1/\sqrt{\mu} \) is predicted by classical theory for all interactions. The importance of the
pure polarization interaction is that it is a very long range interaction, and at low temperatures the ion-neutral scattering is determined primarily by the forces at large separations. Hence, it is expected that most mobilities will ultimately conform with the classical pure polarization behavior provided sufficiently low temperatures can be reached before quantum modifications become important. The quantum modifications cause the mobility to oscillate with decreasing temperature about the classical value.  

By combining equations (5) and (9), an expression for \( Q_d \) can be obtained for the case of a pure polarization potential. Then, the quantity

\[
 b_p = \left( \frac{Q_d}{\pi} \right)^{1/2}
\]

can be used as a measure of the extent of the interaction. A comparison of \( b_p \) with the deBroglie wavelength given in equation (8) can yield an estimate of the temperature at which quantum effects become significant. The temperature where \( \lambda = b_p \) is given by the relation,

\[
 T = \frac{25.1}{a\mu^2} \quad ^\circ K .
\]

For the favorable case of protons in helium, equation (10) gives the numerical value of \( 28^\circ K. \)

A pure \( 1/R^4 \) potential is of course an idealized case, and a more realistic potential should contain a short range repulsion and higher order long range terms as well. Langevin chose a hard
sphere repulsion for his calculations, but more recent studies of molecular structures suggest that an exponentially varying repulsion is more appropriate. The higher order long range terms are obtained by expanding the interaction of the two charge clouds of the ion and gas particle into its various multipole attraction components. Hence, a general form for \( V(R) \) is,

\[
V(R) = A \exp(-\gamma R) - B/R^4 - C/R^6 + \text{(higher order terms)} \quad (11)
\]

The \( 1/R^6 \) term includes contributions due to the point charge-induced quadrupole and induced dipole-induced dipole interactions of the ion and neutral particle. Terms of higher order than \( 1/R^6 \) can usually be neglected.

The principle effect of the additional terms in \( V(R) \) is that they cause the ion mobility to have a temperature dependence, in contrast to the temperature independent property of a pure \( 1/R^4 \) potential. For a general potential of the form \( V(R) = C/R^n \), the temperature dependence of the mobility is given by,

\[
K = \text{constant} \quad T^{2/n-1/2} \quad (12)
\]

Equation (12) shows that for potentials falling off more rapidly than \( 1/R^4 \), the mobility becomes an inverse function of \( T \). Whereas classical theory predicts the pure polarization interaction prevails at very low temperatures, at very high temperatures the dominant interaction is produced by the short range repulsion. Hence, in the high temperature region the mobility decreases steadily with increasing temperature, the specific temperature dependence being
sensitive to the exact nature of the repulsive forces. At intermediate temperatures there occurs a cancellation of the short and long range forces, so that as $T$ increases the mobility is expected to actually increase above the polarization value before ultimately decreasing due to the repulsive forces. The higher order attraction forces—such as the $1/R^6$ term in $V(R)$—affect the low temperature behavior of the mobility and can cause the mobility to pass through a slight minimum before rising to the maximum created by the long and short range cancellation effects. It follows from this discussion that measurements of the variation of ion mobilities with temperature can yield valuable information on the unknown parameters occurring in equation (11).

The theory that has been described so far agrees reasonably well with experimental observations, at least for the case of ions in unlike gases. In the case of ions moving in their parent gases, symmetries between the interacting ion and neutral systems can produce interactions which are purely quantum mechanical in nature. A particularly important interaction of this type is the resonant charge exchange that occurs for ionic structures which differ from the neutral particles only by having one less electron. In such a system, the electronic energy of the separated particles is independent of whether particle $A$ is neutral and particle $B$ is ionized or particle $A$ is ionized and particle $B$ is neutral. This twofold degeneracy of the system at infinite internuclear separations gives rise to two possible modes of interaction at smaller separations. Hence, there are two interaction potentials to
consider—two \( V^+(R) \) symmetric in the nuclei, the other \( V^-(R) \) antisymmetric. The two energy states corresponding to these potentials are just those which occur in the theory of the molecular ion formed by the colliding ion and neutral particle. After the collision has taken place, it is impossible to distinguish between an elastically scattered ion and an atom which has lost an electron, so the description of the collision needs to take into account the possibility of charge exchange. The quantum theory of the process was originally described by Massey and Mohr\(^8\) in a calculation of the mobility of \( \text{He}^+ \) ions in \( \text{He} \). In more recent semiclassical treatments by Holstein\(^9\) and Dalgarno,\(^10\) the nuclear motion is treated classically in terms of the impact parameter \( b \). A critical impact parameter \( b_c \) is found such that for \( b>b_c \) the probability of charge transfer falls off rapidly, while for \( b<b_c \) the probability oscillates between unity and zero, giving an effective probability of \( 1/2 \). The charge transfer cross section, then, is given by the expression,

\[
Q_t = \frac{\pi}{2} b_c^2.
\] (13)

The diffusion cross section is related to the charge transfer cross section through the relation,\(^11\)

\[
Q_d = 2(Q_t + Q_p),
\] (14)

where \( Q_p \) represents the long range polarization contribution to the scattering. While at room temperature \( Q_p \) is usually small compared to \( Q_t \), the relative importance of \( Q_p \) increases as the
temperature decreases, and at very low temperatures the classical approximation to $\eta_d$ is just the Langevin limit discussed before.

The charge transfer cross section decreases slowly as the temperature increases, so that the temperature dependence of the mobility is determined primarily by the $T$ factor which occurs explicitly in equation (5). Therefore, for ions which are subject to resonant charge transfer with the gas particles, the mobility is expected to decrease monotonically with increasing temperature. This variation with temperature differs from that described previously for ions in unlike gases.

Strictly speaking, the Chapman-Enskog solution of the Boltzmann equation is only applicable to the case of vanishing electric field. Several attempts have been made to find expressions for the ion mobility under conditions where the electric field is not vanishingly small. According to the theory of Kihara, the mobility can be expressed as a power series,

$$K = K_0 + K_2 L^2 + K_4 L^4 + \ldots,$$

where the coefficients $K_m$ are complicated functions of collision integrals. (These coefficients have been written out by Mason and Schamp.) For a pure $1/R^4$ interaction, the dependence on field strength vanishes, again demonstrating that this particular potential produces a mobility which is independent of the ion-neutral interaction energy. In the case of high values of $E$, Wannier has represented the particles as rigid spheres and finds that for this model the mobility varies as $1/(E/E_0)^{1/2}$ and is independent of
temperature. While Wannier's predictions are supported by several experimental studies of ions moving in their parent gases, it is generally true that quantitative comparisons of experimental $E/p_0$ dependences with theory have not been made. Kihara's theory does produce some interesting qualitative predictions of the variation of $K$ with $E/p_0$ as compared to the variation of $K$ with temperature. At any given temperature $T_o$, if $dK/dT|_{T=T_o}>0$, then $K$ is predicted to initially increase with increasing $E/p_0$; if $dK/dT|_{T=T_o}<0$, $K$ initially decreases with increasing $E/p_0$; and if $dK/dT|_{T=T_o} = 0$ (corresponding to a maximum or minimum in $K$), $K$ remains constant over a wide range of $E/p_0$. 
I-3. Ion Mobilities in Helium

Helium is, in many respects, the simplest of all gases. Hence, from the standpoint of testing the theory of ion mobilities, experiments in helium can be of great value. The situation of interest in this thesis is that of helium ions moving in their parent gas. Since a large quantity of mobility data already exists at room temperature, the main purpose of the experiment is to provide additional measurements at temperatures other than $300^\circ$K. In particular, the data reported here covers the temperature range of $76^\circ$K to $300^\circ$K.

In a study of the motion of helium ions in their parent gas, an important experimental difficulty encountered is that the helium gas has to be extremely pure. Because of the high ionization potential of helium, helium ions rapidly undergo a nonresonant charge exchange reaction with impurity particles. Thus, unless the impurity concentration is quite small, it is difficult to avoid the situation in which all of the ions present are impurities rather than helium ions.

Even in pure helium gas, there are several ion species that can be formed. Using a mass spectrometer, Madson, Oskam, and Chanin\(^{15}\) (MOC) recently identified three helium ions that are present at room temperature under conditions commonly encountered in mobility experiments. These species are the monatomic ion $\text{He}^+$ and two forms of the diatomic
ion \( \text{He}_2^+ \). One of the forms of the molecular ion is undoubtedly the ground state \( \text{He}_2^+ (^2\Sigma_u^+) \), and Beaty, Browne, and Dalgarno\(^{16}\) (BBD) have suggested that the other form is the metastable state \( \text{He}_2^+ (^4\Sigma_u^+) \). The \( \text{He}^+ \) can be formed in an ion source by electron impact or by a collision of two metastable \( \text{He} \) atoms. (The ion sources used in mobility experiments usually produce large concentrations of excited and metastable \( \text{He} \) atoms as well as ions and electrons.) The ground state \( \text{He}_2^+ \) can be formed by a collision of excited and ground state \( \text{He} \) atoms (the Hornbeck - Molnar process), or by the three body attachment reaction,

\[
\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}.
\]  

(BBD have suggested that the metastable \( \text{He}_2^+ \) can be formed from the interaction of \( \text{He}^+ (^1\Sigma_g^+) \) with \( \text{He}(^2\Sigma_g^+) \).

The mobilities found by MOC were about 10 cm\(^2\)/(volt - sec) for \( \text{He}^+ \), and 16 and 20 cm\(^2\)/(volt - sec) for the two forms of \( \text{He}_2^+ \). According to the interpretation of BBD, the mobility of 16 corresponds to \( \text{He}_2^+ (^2\Sigma_u^+) \), and the mobility of 20 corresponds to \( \text{He}_2^+ (^4\Sigma_u^+) \). These mobilities are in good agreement with the more precise values of 10.4, 16.7, and 19.6 reported previously by Beaty and Patterson\(^{17}\) (BP) for an experiment which did not include a mass analysis. While BP could not identify their ion with the mobility of 19.6, they did present convincing arguments for the identification of the other two ions as \( \text{He}^+ \) and \( \text{He}_2^+ (^2\Sigma_u^+) \). The measurements of MOC and BP provide a good illustration of the way in which these two types of experiments
compliment each other. The importance of the experiment by HOC is that it associates positive identifications of the ions with some rather crude mobility values. On the other hand, experiments such as that of BP provide quite precise determinations of the mobilities, but the identities of the ions has to be inferred from their behavior under varied experimental conditions.

Prior to the work of BP, only two ion species had been observed at any one time in helium mobility experiments. It was recognized early in the history of such experiments that both He\(^+\) and He\(_2\)\(^+\) were likely to be produced, both presumably in their ground states. However, a conflict developed over the identification of the He\(_2\)\(^+\) ion. Biondi and Chanin\(^{18}\) in 1954, reported a mobility of 20.3 for an ion they thought to be He\(_2\)\(^+\). This agreed with a previous value of 19.9 reported in 1931 by Tyndall and Powell\(^{19}\) and also was considered to be in reasonable agreement with Geltman's\(^{20}\) theoretical value of 22.9. In more recent experiments, however, a mobility of about 16.5 has been attributed to He\(_2\)\(^+\).\(^{17,21,22}\) A feature in common among these later experiments was that they employed a cataphoresis tube as a means of purifying the helium gas. This device was known\(^{23,24}\) to be particularly effective in separating out other rare gas impurities from the helium. Hence, it was concluded that the earlier data had actually referred to an impurity ion. This contention was supported by the observation that there were present several impurity ions with mobilities near 20 prior to cataphoretic cleaning of the gas.
In the work of BP, the reaction (16) was studied in some detail, and measurements of its rate coefficient were used to support the contention that the ion with the mobility of about 16.5 was indeed the ground state $\text{He}_2^+$. With the recent work of MOC and BBD, it now appears that the early mobilities near 20 could have referred to the metastable $\text{He}_2^+$. MOC showed that conditions in the ion source played an important role in determining whether both forms of $\text{He}_2^+$ could be observed simultaneously. This provided a plausible explanation of why one type of $\text{He}_2^+$ was observed in some of the experiments, and the second type was observed in others.

With the apparent existence of two types of $\text{He}_2^+$, some explanation is needed for the fact that they have quite different mobilities. Dalgarno\(^{10}\) has suggested that a diatomic ion in its parent atomic gas can be treated as an ion in an unlike gas. Then, the theory described in I-2 predicts that $K$ starts out at the Langevin limit at very low temperatures; perhaps passes through a slight minimum as $T$ increases; rises up to a maximum as $T$ increases further; and eventually decreases steadily at very high $T$. For "non-helium" ions moving in helium, it has been found that at 300°K the mobility is somewhat higher than the Langevin limit, and the maximum in the mobility has not yet been reached. For ground state $\text{He}_2^+$ at room temperature, the $E/p_o$ dependence of $K$ found by BP suggests that the $\text{He}_2^+$ mobility also has not yet reached it maximum as a function of $T$, but the zero field value is about 16.5 which is lower than the Langevin
limit of 18.6. Hence, the theory for ions in unlike gases does not adequately explain the experimental mobility for $\text{He}_2^+ (^{2}\Sigma_u^+)$ . It now appears that a plausible explanation of the inadequacy of the theory is that there actually is a certain symmetry present in the $\text{He}_2^+ - \text{He}$ system. BBD pointed out that the resonant process,

$$\text{He}(1S) + \text{He}_2^+ (^{2}\Sigma_u^+) \rightarrow \text{He}_2^+ (^{2}\Sigma_u^+) + \text{He}(1S), \quad (17)$$

could account for the small mobility of $\text{He}_2^+ (^{2}\Sigma_u^+)$. Furthermore, the mobility of the metastable $\text{He}_2^+ (^{4}\Sigma_u^+)$ would be expected to be somewhat higher since it is not subject to the resonant interaction (17). Indeed, if the interpretation of BBD is correct, then the mobility of $\text{He}_2^+ (^{4}\Sigma_u^+)$ is about 20 and this value is consistent with the theory for ions in unlike gases.

A principle objective of this experiment was to obtain some measurements of the $\text{He}_2^+ (^{2}\Sigma_u^+)$ mobility as a function of temperature. Previous measurements of the temperature variation of the $\text{He}_2^+$ mobility can be found listed in the literature, but these measurements all referred to the ion which has the mobility of about 20 at room temperature. In view of the evidence now available, this ion appears to have been either an impurity, or the metastable $\text{He}_2^+ (^{4}\Sigma_u^+)$. No theory yet exists for $\text{He}_2^+ (^{2}\Sigma_u^+)$ which takes into account the resonant process (17). If such a theory is to be developed, it would be of great value to have available measurements of the temperature dependence
of the mobility in order that the dependence of the scattering on interaction energy might better be understood. Furthermore, if it can be firmly established that process (17) is indeed important in helium, then it might be expected that analogous processes occur in other gases as well.

A second objective of this experiment was to obtain measurements of the \( \text{He}^+ \) mobility as a function of temperature. It has already been mentioned that \( \text{He}^+ \) is subject to the resonant charge exchange process

\[
\text{He}^+(1^2S) + \text{He}(1^1S) \rightarrow \text{He}(1^1S) + \text{He}^+(1^2S) \quad .
\]

This process causes the mobility of \( \text{He}^+ \) to decrease monotonically with increasing temperature, and at 300\(^\circ\)K it is approximately half its Langevin value. Experimental values\(^{17,18,21,25} \) for the \( \text{He}^+ \) mobility at room temperature are in excellent agreement with theoretical predictions.\(^{8,10,26,27} \) At other temperatures, there are available several calculations,\(^{10,26,27} \) so that there now exist theoretical values for the \( \text{He}^+ \) mobility for temperatures ranging from 0\(^\circ\)K to 5000\(^\circ\)K. Up to now, these predicted mobilities have been compared with the experimental results of Chanin and Biondi\(^{28} \) at the temperatures of 77\(^\circ\)K and 195\(^\circ\)K. However, the agreement between experiment and theory is less than satisfactory, partly because of the lack of precision in the measured values. In this experiment, more precise measurements of
the He\textsuperscript{+} mobility were sought, as well as additional measurements at temperatures intermediate between those used by Chanin and Biondi.
CHAPTER II

EXPERIMENTAL METHOD

II-1. Principles of the Experiment

There are basically two quite different types of experiments that have been used in the past to determine ion mobilities. In one method, the gas contained in a microwave cavity is initially broken down by the application of a pulse of power. Then, by a variety of analysis techniques, the decay of electrons and ions in the after-glow is monitored as a function of the time elapsed since the initial power pulse. One of the parameters determined from such an analysis is the ambipolar diffusion coefficient which can be related to the ion mobility by means of the Einstein relation (equation (2)).

The second method involves a direct measurement of the drift velocity \( v \), and equation (1) is then used to obtain the mobility. This is the method that was used in this experiment. Determination of the drift velocity is achieved by measuring the average time required for the ions to travel a fixed distance under the influence of a uniform electric field. The drift tube technique employed here was originally used by Tyndall and Powell,\(^{19}\) and more recently has been used by Beaty and Patterson.\(^{17}\) The fixed distance is defined at either end by an electrical shutter. Outside this drift region are an ion source at one end and an ion collector at the other end. The
shutter nearest the ion source serves to define a group of ions which is allowed to enter the main drift region. The ions then drift through the tube to the vicinity of the second shutter. If this second shutter happens to be open at the time the ions reach it, then they pass through and are collected on the ion collector. The data obtained consist of the tabulation of the current to the collector as a function of the time delay between the openings of the two shutters.

The drift tube method of determining mobilities has several advantages over the microwave cavity method. In the first place, the drift tube method is concerned only with the motion of ions through a neutral, unexcited gas. The microwave cavity method, on the other hand, deals with an afterglow in which ions and electrons as well as excited and metastable atoms are all present. Hence, it is necessary to take into account a number of production and loss mechanisms for the charged particles in order to obtain a value for the ambipolar diffusion coefficient. The drift tube technique has the additional advantage that the electric field in the drift region can be varied so as to provide values of \( K \) as a function of \( E/p_0 \).
II-2. The Mobility Tube

The mobility tube and its method of operation are modeled after that used by Beatty and Patterson.\textsuperscript{17} Fig. 1 shows a schematic drawing of the tube and its associated electronics. The electrodes are numbered below the tube schematic at the points where the connections to the electronics are indicated. Starting at the ion source (electrodes 19 and 20), the ions drift from left to right, terminating their motion at the ion collector (electrode 1). The main drift region lies between electrodes 4 and 14, with the electrode pairs 3 - 4 and 14 - 15 forming the electrical shutters on either end. Electrodes 5 - 13 act as guard rings to help maintain a uniform electric field in the drift region. There is an additional electrode pair 17 - 18 which can be used as a third shutter if it is required. The instances when this third shutter is useful will be mentioned later.

The overall geometry of the mobility tube is cylindrical, and it is constructed in two sections. The collector end of the tube (electrodes 1 - 16) is mounted on one stainless steel flange, and the source end (electrodes 17 - 20) is mounted on another flange. Photographs of the collector and source ends are shown in Figs. 2 and 3, respectively. These two sections are assembled into opposite ends of a 10.2 cm diameter stainless steel tube which forms a vacuum tight enclosure for the electrode assemblies. The assembled tube is shown in
Figure 2. Photograph of electrode assembly mounted on collector end of mobility tube.
Figure 3. Photograph of electrode assembly mounted on source end of mobility tube.
Figure 4. Photograph of assembled mobility tube.
Fig. 4. At the top of this tube is a port which provides a connection to a vacuum and gas handling system.

The principle structural components in the mobility tube are the electrodes, and these consist of circular plates of the form shown in Fig. 3. Each of these plates is constructed from 0.025 cm advance sheet metal, and is pressed into a three dimensional form for added mechanical strength. In the center of each plate, a large hole is punched out, and it is through this hole that the ions pass when all the plates are assembled. The total diameter of the plates is 7.78 cm, and the offset center portion of the plates has a diameter of 5.72 cm. The center hole diameter in most of the plates is 2.86 cm, with the most important exceptions being in electrodes 3 and 4 where the center hole diameter is 2.22 cm. The reason for having the center hole smaller in these two electrodes will be discussed later. Around the outer perimeter of each plate is a series of 15 small holes through which pass the electrical leads (encased in ceramic tubing) to the various plates. Also along this outer perimeter are three mounting holes for the support rods which are used to hold the stack of plates together. All the electrodes are gold plated in order to prevent the formation of dielectric residues which could produce undesirable surface potentials.

In order to control the motion of the ions, the electrode structure contains a total of eight grids. In Fig. 1, these grids correspond to electrodes 2, 3, 4, 14, 15, 16, 17, and 18. Each grid consists of a
parallel array of 0.0025 cm tungsten wires stretched across the center hole of an electrode plate. The wires were put under a slight tension and then spot welded individually to the plate. The top electrode in Fig. 3 has one of these grids, but the wires are too fine to be seen in the photograph. In the cases where two grids were used to form an electrical shutter, an attempt was made to align the wires of one grid directly behind the other in order to improve the ion transmission through the shutter. The determination of the spacings between wires in a grid involved a consideration of two factors. One of the purposes of the grids is to shield the electric field on one side of the grid from the electric field on the other side. For this purpose, it is advantageous to have the wires spaced as close as possible. On the other hand, it is most desirable that the wires be spaced far enough apart that a reasonable transmissivity of ions is achieved. The transmissivity of the ions is a difficult thing to estimate quantitatively, so the approach employed here was to use the maximum wire spacing consistent with the desired amount of shielding. The "shielding power" of an infinite grid of parallel wires placed at a distance c from a conducting plate is discussed in Morse and Feshbach, Methods of Theoretical Physics, page 1237. Most of the irregularities in the field due to the grid structure occur within distances comparable to the grid wire spacings a. The shielding power of the grid is strongly dependent on the ratio c/a. For the potentials normally used in the mobility tube, it was determined that a c/a ratio of about 4 provided
an adequate amount of shielding. The spacings actually used in the shutters (electrodes 3 - 4, 14 - 15, and 17 - 18) were 0.200 cm between grids, and 0.041 cm between wires in each grid. For electrode 16, the spacing to adjacent grids was 1.000 cm, and the spacings between grid wires were 0.081 cm. For electrode 2, the spacings to adjacent electrodes were 0.400 cm and the wire spacings were 0.081 cm.

Using alumina spacers, the set of electrodes 2 - 16 is stacked together on three ceramic insulated metal rods which are secured at electrode 16 by threaded boron nitride caps. At the other end, the support rods are fastened to a stainless steel support ring which in turn is bolted to a stainless steel flange. The ion collector (electrode 1) and a portion of its electrical shield are fastened directly to this same flange in such a manner than when the support ring and its stack of electrodes is lowered into place, electrode 2 becomes electrically connected to the shield about the collector. In a similar manner, electrodes 17 - 19 are fastened to another support ring, and this assembly fits down over electrode 20 and is bolted to an opposing flange. Nominal spacings of electrodes are: 1 - 2, 0.4 cm; 2 - 3, 0.4 cm; 3 - 4, 0.2 cm; 4 - 14, 1.0 cm between adjacent electrodes; 14 - 15, 0.2 cm; 15 - 16, 1.0 cm; 16 - 17, 1.0 cm; 17 - 18, 0.2 cm; 18 - 19, 1.0 cm.

The actual drift distance between electrodes 4 and 14 was measured with a vernier height gauge, and was found to be 9.98 ± .01 cm between the plane of the grid wires on 4 and that on 14. Where the electrode spacing is 1.0 cm, circular metallic bands are
added between adjacent electrodes as shown in Fig. 2. Each of
des these bands is electrically connected to the lower numbered plate,
and it fits around the outer perimeter of the plate, lying just
inside the ceramic spacers and insulators. The purpose of these
bands is to shield the ceramics from direct exposure to the center
portion of the tube where the ions move. In addition, the bands
provide a better definition of the boundary conditions seen by the
ions, especially in the main drift region.

The designs of the ion collector and the ion source actually
depend to some extent on each other. The principle source of noise
in the experiment is generated in the discharge and is coupled to
the collector via a photoelectric effect. Photoelectrons leaving
the collector produce the same polarity signal as arriving positive
ions, so that the ion signal is superposed upon the photoelectric
signal. The ion source is operated by striking a point to plane
discharge between electrodes 19 and 20. The discharge is produced
by a pulse of high voltage applied to electrode 20 from the output
of a trigger transformer. In addition to ionizing the gas, the
discharge produces many photons, and these can cause photoelectric
emissions from metallic surfaces on down the tube. One of the
reasons for pulsing the discharge is to help minimize this photo-
electric emission. An additional advantage of using the pulsed
discharge is that it produces a minimal amount of heating of the
gas inside the tube. This is of particular importance in this
experiment, especially at the lower temperatures. In order
to further reduce the photoelectric effect at the collector,
Beaty and Patterson used a collector constructed of wire mesh. A different approach is used in this experiment. Instead of a mesh, the collector used here is a solid plate. However, back at the ion source, an optical baffle is introduced in an attempt to cut down on the light emitted. In Fig. 1, this baffle is represented by the two dashed lines which comprise part of electrode 19. The actual appearance of part of this baffle can be seen in Fig. 3. The baffle consists of two of the perforated plates of the type shown in Fig. 3. These plates are spaced a distance of 0.2 cm apart and are aligned so that the holes in one overlap the closed spaces in the other. Although an acceptable level of photoelectric signal was achieved at the collector, the optical baffle was only partially successful in that a sizeable number of photoelectrons were still emitted from surfaces upstream from the collector. In fact, some mobility data were taken using only ions produced in the electrode 15 - 17 region by photoelectrons racing back toward the ion source. Under more normal operating conditions, however, ions produced directly in the ion source were used. After the initial discharge pulse, there are no externally applied fields between electrodes 19 and 20, or for that matter between the two plates in the optical baffle. Hence, ions which do get out into the electrode 18 - 19 region, have either diffused out of the ion source or have been forced out by space charge. Obviously, then, only a small fraction of the ions produced by the discharge are actually used, but these are sufficient since only a small ion concentration is desired anyway.
Bias potentials for the electrodes are supplied by the set of regulated power supplies A - I shown in Fig. 1. With the exception of the shutter regions, the polarities of all the biases are such that the positively charged ions travel from left to right in Fig. 1. The biases in the shutter regions are in the reverse direction so that the shutters are normally closed to the passage of ions. Each shutter can be opened at some appropriate time by applying a square voltage pulse to one of the grids in the shutter pair. In order to open shutters 14 - 15 and 17 - 18, the voltage pulse is capacitively coupled to electrodes 15, 16, and 17. A negative pulse opens shutter 17 - 18 and a positive pulse opens shutter 14 - 15. By having these pulses coupled to all three electrodes 15, 16 and 17, the bias field between electrodes 15 and 17 is not disturbed. In order to open shutter 3 - 4, a negative voltage pulse is applied to electrode 3. This distorts the field in the region between electrodes 2 - 3 to some extent, but the bias in this region is sufficiently high that ions still move through to the collector. The bias potentials in the shutter regions are 4 V, and the pulse amplitudes are 8 V. Therefore, when the shutters are closed they have a reverse field of 20 V/cm across them, and when they are open they have a field of 20 V/cm in the forward direction. Electric fields used in other regions are: 18 - 19, 2 - 20 V/cm; 16 - 17 and 15 - 16, 5 - 20 V/cm; 4 - 14, 3 - 30 V/cm; 2 - 3, 50 V/cm bias and 30 V/cm when the pulse is applied on electrode 3; 1 - 2, 50 V/cm.
In order to obtain precise measurements of mobilities, it is essential that the field in the drift region be reasonably uniform. In this apparatus, the main drift region is the cylindrically shaped volume defined by the center holes in the stack of plates 4 - 14. The field in this region is produced by applying the output voltage of power supply D across electrodes 4 and 14. This voltage is measured to an accuracy of 0.1 per cent by means of a differential voltmeter. As mentioned before, electrodes 5 - 13 act as guard rings to prevent the warpage of field lines in the drift region. Potentials for these guard rings are derived from a stack of 0.5 per cent, 10 K resistors across the output of the D supply. Nominally, the field between adjacent guard rings is the same magnitude as that in the center of the tube, and is directed parallel to the tube axis. However, the design of the electrode assembly, as well as structural uncertainties, cause deviations from the nominal values. At the outer perimeter of the electrode plates, the circular band which shields the ceramics produces a distortion of the field lines. This distortion decreases in magnitude as the distance from the tube axis is decreased. At the outer edge of the cylindrical drift region (i.e., at the edge of the center holes in plates 5 - 14), this distortion still amounts to about a 2 per cent effect. Although this source of non-uniformity in the field could have been made negligible by using a slightly smaller diameter for the center hole, there is another source of non-uniformity which is independent of the size of the center hole. Because of the
finite thickness of the electrode plates, and the structural uncertainty in their spacing, the field between adjacent guard rings can be as much as 5 per cent higher than its nominal value. Hence, the field near the outer perimeter of the cylindrical drift region can be non-uniform to the extent of several per cent. In order to discriminate against ions which move in this non-uniform portion of the field, the center hole in electrode 4 (at the end of the drift space) has a smaller diameter than those electrodes which precede it. In other words, ions which have moved along the outer perimeter of the drift region are simply not recorded on the ion collector.

The method of operation of the mobility tube will be described first for the case where electrodes 17 - 18 are not used as a shutter. In this case, there is a forward bias applied across this electrode pair, and the electronic delay 1 and the first negative pulser are not included in the timing sequence shown in Fig. 1. A cycle of operation begins with the triggering of the transformer which supplies the discharge pulse to the ion source. Ions then diffuse out of the ion source and drift to the vicinity of electrode 15 under the influence of the applied fields. The electrode 15 - 19 region can be termed a "thermalizing" region in which the ions are allowed to come into thermal equilibrium with the gas. At some time after the discharge pulse, the electronic delay 2 causes the positive pulser to be triggered. This opens shutter 14 - 15 and allows a pulse of ions to enter the drift region. The width of this ion pulse is approximately equal to the width of the voltage pulse minus the transit time of the
ions across the shutter. After drifting through the main drift space, the ions are either neutralized at electrode 4 (when shutter 3 - 4 is closed) or pass through the open shutter 3 - 4 to be recorded on the ion collector. Shutter 3 - 4 is opened when electronic delay 3 triggers the second negative pulser in Fig. 1. The width of this negative voltage pulse is approximately equal to that of the positive pulse used to open shutter 14 - 15. A quartz crystal timing oscillator serves to calibrate the delay 3 as well as to establish the basic rate of repetition of each cycle of operation. In this experiment, the repetition rate is 100 cps.

At the ion collector, the average current is measured by means of an electrometer and a $10^{10}$ ohm resistor to ground. The output of this electrometer is sent to a recording device along with the time delay 3. Delay 3 is arranged so that it can be scanned either continuously or in digital steps. For the continuous scan, the collector current is recorded on one axis of an X-Y recorder and the time delay on the other axis so as to produce a plot of current versus time. For the digital scan, each time delay and the corresponding current are recorded on a punched paper tape for future analysis by a computer. Accurate mobilities can be determined from both the X-Y recorder plots and the digital data, but the digital data can be subjected to a more detailed analysis when the computer is used. The principle reason why much of the data in this experiment is in the form of X-Y recorder plots is that these can be accumulated in much less time than is required for the digital data. This feature is particularly useful in this experiment,
especially in instances when it is difficult to maintain a fixed
temperature for any length of time.

When electrodes 17 - 18 are used as a third shutter, there are
in effect two drift tubes placed end to end. In this case, the cycle
of operation includes the electronic delay 1 and the first negative
pulser. The pulse from this negative pulser opens shutter 17 - 18 at
the time delay 1 after the discharge pulse. Shutter 14 - 15 is then
opened at a time delay 2 after the opening of shutter 17 - 18, and the
rest of the tube operates as described before. In order that ions pass
through shutter 14 - 15 to get into the main drift region, delay 2
must coincide with the ion time of flight through the electrode 15 - 17
region. This feature is particularly useful when there are several
ion species present, and one of these species is converting to another
by means of a reaction. Because the various ion types have different
time of flights through the initial drift section, it is possible to
select delay 2 in such a way that only one ion species at a time enters
the main drift section. Both this three shutter mode of operation and
the two shutter mode are employed in gathering data in this experiment.
II-3. Data Analysis

A typical plot of current versus time delay is shown in Fig. 5. There is only one ion species represented in this particular plot. If the ions simply drifted without diffusing, then the observed ion current would be triangular in shape as shown in the upper left of Fig. 5. (This triangular shape is obtained if the voltage pulses on shutters 3 - 4 and 14 - 15 are approximately equal in width. If the widths of these pulses differed appreciably, then the shape without diffusion would be trapezoidal.) Diffusion causes the triangular current distribution to be smeared out somewhat. The ion mobility is determined from such a plot by extracting from it the time delay $t_p$ corresponding to the peak in the ion current. Then, the actual time of flight of the ions through the drift region is given by $t_f = t_p - \frac{1}{2}t_s$, where $t_s$ is the time of flight of the ions across the two shutter regions. Depending on the field used in the drift region, the magnitude of the shutter correction can amount to as much as a 3 per cent adjustment of the time $t_p$. This shutter correction is determined empirically by varying the pulse width on one shutter while holding the pulse on the other shutter fixed. The amplitude of the ion peak is then plotted as a function of each pulse width, and extrapolation to zero amplitude gives a value for the transit time across each shutter. Once the time of flight $t_f$ is known, then a knowledge of the pressure, temperature, and electric field in the drift region, allows the mobility to be calculated by means
Figure 5. Graph showing experimental ion current distribution for a single ion species.
of equation (1). This is the method used to deduce mobilities from data which is in the form of X-Y recorder plots.

From the width of a current distribution such as that shown in Fig. 5, it is possible to deduce an effective diffusion coefficient for the ions. This is one of the parameters that is readily obtained from a computer analysis of data in digital form. It has already been mentioned in Section I-2 that the mobility and the diffusion coefficient are related by means of the Einstein relation. Nevertheless, simultaneous measurements of these two quantities can prove useful in checking the performance of the drift tube. For example, Beaty and Patterson \(^7\) found that if the ion density is too high, then space charge effects cause an additional broadening of the current distribution, and the effective diffusion coefficient is somewhat higher than the value given by the Einstein relation. Also, it is expected that as \(E/p_0\) is increased, the effective diffusion coefficient again tends to become larger than the Einstein value due to electrical "heating" of the ions. No attempt is made in this experiment to determine the diffusion coefficient from the X-Y recorder data.

When there are more than one ion species present, the mobility spectrum becomes more complex as indicated in Fig. 6. Experimental data is again represented by points in this plot. The continuous curves are the results of computer calculations, and they illustrate how the composite experimental current distribution is broken up into four parts. The plot in Fig. 6 contains three current peaks similar to that shown in Fig. 5. Each of these peaks corresponds to a different
Figure 6. Graph showing the ion current distribution for three ion species and an ionic reaction. The points are experimental data and the solid curves are calculations whose sum provides a best least squares fit to the data.
ion species which has been created upstream from the drift region and which has traversed the entire drift space intact. The ion of highest mobility lies on the far left, and that of the lowest mobility on the far right. In addition to these current peaks, there is an approximately exponential distribution of ion current due to an ionic reaction occurring in the drift region. In this reaction, some of the slowest ion species are converted in flight to the ion species of intermediate mobility. (The specific reaction illustrated here is reaction (16).) The residual current, then, is due to ions which traverse part of the drift space as one ion species, and the rest of the drift space as another ion species.

The relatively complex situation illustrated in Fig. 6 is a typical example of a case where the three shutter mode of operating the tube proves useful. Any one of the three ion species shown in Fig. 6 can be selected to be analysed by itself. Hence, it is possible to display either of the two faster ion species as a single ion peak similar to that shown in Fig. 5. If only the slowest ion is selected to be analysed, then the corresponding data would show only that ion peak plus the current contributed by the reaction. In this manner, then, the composite current distribution shown in Fig. 6 can be broken up and analysed part by part.

Beaty and Patterson\textsuperscript{17} have described in detail the analysis scheme whereby the continuous curves in Fig. 6 are generated. In general terms, the analysis involves the computation of a theoretical function which is compared with the experimental data. The theoretical
function is the result of an effort to describe the relevant processes occurring in the drift region—namely, diffusion, drift, and possibly reaction. Variable parameters which are included in this theoretical function are: the mobilities and diffusion coefficients of each ion species; the number of ions of each kind which are let in at the source end of the drift region; and the reaction rate for any reaction that is present. These parameters are varied so as to produce the best least-squares fit of the theoretical function to the experimental data.

The drift space used in this experiment differs slightly in design from that used by Beatty and Patterson,2 so a small modification needs to be included in the analysis scheme. Beatty and Patterson showed that the ion current \( I \) is proportional to

\[
I \propto \int_{0}^{r_{0}} \rho(r, z, t) r \, dr,
\]

where \( \rho \) is the ion density and \( r_{0} \) is the radius of the cylindrical drift region. (In this experiment, \( r_{0} = 1.43 \, \text{cm} \).) Assuming the lowest diffusion mode prevails, the radial dependence of the ion density tends toward the zeroth order Bessel function \( J_{0}(a r) \), where \( a = x_{1}/r_{0} \) and \( x_{1} \) is the first root of \( J_{0}(x) \). (In this experiment, \( a = 1.683 \, \text{cm}^{-1} \).) This gives,

\[
I \propto \frac{a}{a^2} \int_{0}^{x_{1}} J_{0}(x) \, dx.
\]
However, not all of this current is recorded on the collector in this experiment. As was pointed out in Section II-2, the shutter at the collector end of the drift space has a smaller center hole than the electrodes which precede it. Hence, the ion current collected in this experiment is given by,

$$I' \propto \frac{1}{a^2} \int_{r'_0}^{x_1 r'_0 / r_0} J_0(x) \, dx,$$

where $r'_0 = 1.11 \text{ cm}$ which is the radius of the center hole in the last shutter. Using a property of Bessel functions,

$$\int_{0}^{\infty} J_0(x) \, dx = y J_1(y).$$

This gives the relation,

$$I = \left[ \frac{r_0 J_1(x_1)}{r'_0 J_1(\frac{x_1 r'_0}{r_0})} \right] I' = 1.255 I'. \quad (19)$$

The current $I$ is calculated by the computer program, while $I'$ is the current measured at the collector. Hence, in order to compare the experimental and theoretical currents, the measured $I'$ is multiplied by the numerical factor shown in equation (19).
II-4. Vacuum and Gas Handling Systems

As has been pointed out previously, the helium gas used in this experiment must be extremely pure. Therefore, the mobility tube is connected to an ultra-high vacuum system in order that the walls of the system can be thoroughly outgassed before helium is let in. Fig. 7 shows a schematic diagram of this vacuum system which is comprised primarily of stainless steel and pyrex glass components. The ultra-high vacuum portion of the system is bakeable, and is enclosed by the dashed line in Fig. 7. At either end of the mobility tube are vacuum seals which are particularly critical in that they must withstand both high temperature bakeouts and immersion in low temperature refrigerant baths. Each of these seals consists of a gold "O" ring squashed between mating stainless steel shear-seal flanges. The total volume of the vacuum system is about 4 liters, and the pumping action is provided by an 8 liter/sec ion pump. Pressures less than $10^{-4}$ Torr are measured by means of an ion gauge. For this experiment, the vacuum system was baked at the relatively low temperature of 150-200°C for about 4 or 5 days, and the ultimate pressure reached was about $4 \times 10^{-9}$ Torr. A more important indication of the cleanliness of the system is the rate at which the pressure rises when the system is isolated from the ion pump. This rate is measured using the ion gauge operated intermittently and at very low emission current in order to minimize its pumping effect. The rate of rise was found to be about $10^{-5}$ Torr/day.
Figure 7. Schematic diagram of vacuum and gas handling systems.
Once the system itself is cleaned, there remains a problem of providing a sufficiently pure sample of helium gas. The gas used in this experiment is obtained commercially in a two liter pyrex flask, and is claimed to be spectroscopically pure. However, this commercial gas is not pure enough, and it is subjected to further purification using a cataphoresis tube.\textsuperscript{23,24} The cataphoresis technique simply consists of striking a glow discharge between two electrodes separated by a fairly long piece of glass tubing. Impurities in the gas are preferentially pumped by this device to the vicinity of the cathode. Although the exact pumping mechanism is not clear, it would seem that a plausible explanation for helium is that collisions of helium ions with impurity atoms cause the impurities to become ionized and to be dragged toward the cathode. The efficiency of the cataphoretic cleaning process depends strongly on the facility with which impurity particles diffuse from various parts of the system to the vicinity of the cataphoresis tube. In this experiment, the cataphoresis tube is found to be efficient if operated at a pressure between 15 and 20 Torr. A sample of helium at a pressure in this range is let into the system and is cleaned by operating the cataphoresis tube for at least 24 hours. Then the cataphoresis tube is isolated from the system, and mobilities can be measured either at the same gas pressure or at any lower pressure. For each gas sample, all mobility measurements are obtained within a 24 hour period after the cataphoresis tube is isolated from the system. Then the system is
evacuated again, a fresh supply of helium is let in, and another cleaning process is started.

The contamination rate of $10^{-5}$ Torr/day seems to be just on the borderline of being acceptable. At a pressure of 1 Torr this gives an impurity buildup of 1 part in $10^5$ per day, and at 10 Torr it is 1 part in $10^6$ per day. It is observed that at pressures greater than 10 Torr, a very clean mobility spectrum can be maintained throughout the duration of mobility measurements. However, at lower pressures there are small traces of impurities present, although these tend to disappear as the tube is refrigerated.

One of the important parameters needed for determining mobilities is the gas pressure. In this experiment, pressures in the range of 1 - 20 Torr are measured by means of a capacitance manometer. This device makes possible the measurement of the pressure of the pure gas without introducing any liquids such as oil or mercury into the clean system. The capacitance manometer is a nulling instrument in which the pressure on the "clean" side of a metal diaphragm is balanced by an adjustable pressure on the "dirty" side. Shown at the lower right in Fig. 7 is the setup used to adjust and measure the pressure on the "dirty" side of the capacitance manometer. The pressure can be increased by letting in dry air from a low pressure ballast tank, or decreased by pumping via a mechanical roughing pump. An aneroid manometer provides a rough estimate of the pressure, and precision measurements are obtained by means of a quartz Bourdon gauge or a
mercury manometer. In this experiment, the precision mercury manometer was used primarily to calibrate the Bourdon gauge. The Bourdon gauge was then relied upon to determine the pressure on the "dirty" side of the capacitance manometer.

The combination of the Bourdon gauge and the mercury manometer provided the capability of measuring pressures to within an uncertainty of $\pm 0.01$ Torr. However, due to an erratic behavior of the capacitance manometer, the accuracy realized in this experiment was more like 1 or 2 per cent of the pressure being measured. At least part of the trouble with the capacitance manometer appeared to be due to the buildup of contaminants in its critical components (presumably on the "dirty" side of the diaphragm). This caused the instrument to indicate a null when there was still a small pressure differential across the diaphragm. The magnitude of this zero offset appeared to increase as the contamination of the instrument grew worse, and in the very worst cases it amounted to about 0.2 Torr. Late in the course of the experiment, the capacitance manometer was subjected to a mild bakeout which seemed to rectify the situation. Most of the data in this experiment was obtained under conditions where the pressure measurements were reliable to within the 1 or 2 per cent uncertainty limits mentioned above.
II-5. Refrigeration Technique

The refrigeration container for the mobility tube is shown in Fig. 8. It consists of two styrofoam boxes, one inside the other, and each fitted with a lid. A uniform low temperature environment for the mobility tube is achieved by filling the inner styrofoam box with a fixed temperature refrigerant bath. Baths used in this experiment are dry ice-ethanol (196°C), ethanol-liquid $N_2$ slush ($\sim$150°C), and liquid $N_2$ (75.9°C). The dry ice-ethanol and the liquid $N_2$ baths are quite uniform in temperature, and their temperature remains fixed for long periods of time. The temperature of the ethanol-liquid $N_2$ slush, however, is both less uniform and less stable with time. Electrical leads to either end of the mobility tube are sealed from the bath liquid and are carried out through the lids of the styrofoam boxes. Also shown in Fig. 8 are the locations of three copper-constantan thermocouples which are taped to the stainless steel mobility tube in order to monitor its temperature. Extending out the top of the refrigeration container is a 1 inch diameter pyrex tube which connects to the vacuum system.

The mobility tube and the rest of the vacuum system define a closed volume of gas. Upon cooling a part of this volume, the pressure in the entire system decreases. Assuming the total gas volume $V$ can be broken up into a volume of gas $V_T$ at temperature $T$, and a volume $V_R$ at room temperature (300°C), then the
Figure 8. Schematic diagram of refrigeration container for mobility tube.

x MARKS LOCATION OF THERMOCOUPLE
pressure in the system can be related to the temperature of the cooled portion. When the entire system is at 300°K, the pressure is given by,

$$p_R = \frac{(Nk300)}{V},$$

where $N$ is the total number of gas particles. When a portion of the system is cooled, then the pressure is given by,

$$p_T = \frac{(N_Rk300)}{V_R} = \frac{(N_TkT)}{V_T},$$

where $N_R + N_T = N$ and $V_R + V_T = V$. Combining these relations in such a way as to eliminate the particle numbers, the following equation is obtained:

$$\frac{p_R}{p_T} = \frac{V_R}{V} + \left(\frac{V_T}{V}\right)\left(\frac{300}{T}\right). \quad (20)$$

Hence, according to this equation, a plot of $p_R/p_T$ versus $300/T$ should be a straight line. Some experimental data are shown in Fig. 9. These experimental points are scattered more than they should be in view of the estimated accuracy in determining pressures and temperatures. The reason for their scatter appears to go back to the original assumption that the volume can be broken up into a part $V_R$ and a part $V_T$. There is, of course, not an abrupt change from the cool to hot portions of the system, but rather there is a somewhat undefined transition region. If the experimental data are looked at in greater detail, it appears that $V_R/V$ and $V_T/V$ have a dependence on the pressure. For any given $p_R$, for example, the data available indicate that a straight line
Figure 9. Graph showing the dependence of measured pressures on the temperature of the mobility tube.
dependence of $\frac{P_R}{P_T}$ on $300/T$ is followed reasonably well. Multiplying equation (20) by $T/300$, the following relation is obtained:

$$\frac{P_{OR}}{P_{OT}} = \frac{V_T}{V} + (\frac{V_R}{V})(T/300),$$

(21)

where $P_{OR} = 273P_R/300$ and $P_{OT} = 273P_T/T$. This equation shows that the quantity $P_0$ increases as the temperature of the mobility tube decreases. This is a consequence of the fact that only a portion of the system is cooled. The quantity $P_0$ is sort of a measure of the gas density. If the entire system were cooled, then $P_0$ would remain the same at all temperatures. However, since only part of the tube is cooled, the density in the cold portion increases at the expense of the density in the warm portion.

In addition to using refrigerant baths, another scheme of cooling is employed in this experiment. Between the inner and outer styrofoam boxes is a gap of about 1/2 inch. By filling only this gap with liquid $N_2$, there is achieved a gradual cooling of the mobility tube by means of cold $N_2$ vapor which gets through several holes punched in the lid of the inner box. The tube can be cooled down by this method from room temperature to about 100°K in about 4 hours. (Even when a refrigerant bath is used, the tube is cooled initially by this method in order to minimize the thermal shock on the system.) In order to obtain mobility measurements, this cooling of the tube can be halted at almost any temperature by judiciously varying the level of the liquid $N_2$ and
the frequency of replenishment. When the cooling process is so
terminated, there are three criteria that are invoked to determine
when thermal equilibrium is satisfactorily established. First, it
is required that the temperature variation of the mobility tube be
reasonably small for the duration of any measurements; second, it
is required that the three thermocouples indicate that the
temperature is approximately the same at their three locations;
and third, it is required that the pressure variation is sufficiently
small during any measurements. The second of these criteria becomes
increasingly hard to meet as the temperature decreases, and at
temperatures of about 100°K there can be as much as a five per cent
difference in the temperatures read by the three thermocouples. The
mean of the three thermocouple readings is used for the temperature
in the calculation of mobilities. During the course of any set of
measurements, the variation of the mean temperature with time is
generally no larger than the uncertainty due to the nonuniformity.
The variation of the gas pressure with time serves as an indication
of when the gas inside the mobility tube reaches equilibrium.
Again over the duration of any measurements, the time variation of
the pressure is generally of the same magnitude as the uncertainty
(about one or two per cent) in measuring the pressure. Once the
approximate desired temperature is reached in the overall cool down
cycle of the tube, it takes from one to two hours more for the three
criteria to be satisfied.

The cold $N_2$ vapor cooling scheme is used to obtain data at
temperature intervals of about 50°K in order to supplement the
data obtained with the refrigerant baths. However, the most important feature of the \( N_2 \) vapor cooling scheme is that it provides a means whereby the mobility spectrum can be continuously monitored while the tube gradually cools. In the past, all experiments on the temperature dependence of mobilities have employed the refrigerant bath technique. Generally it is assumed that the same ions are observed in the various baths as were observed at room temperature. However, this is a hazardous assumption since unknown ion conversion reactions might very well occur between the various bath temperatures. In fact, some mobility data can best be explained by postulating the occurrence of ion clustering at low temperatures. In order to be certain of the identity of the ions in the low temperature baths, it is essential that the mobilities be traceable almost continuously from the room temperature values. The \( N_2 \) vapor cooling scheme makes this possible in this experiment.
CHAPTER III

DATA

III-1. Room Temperature Measurements

Many accurate measurements of helium ion mobilities already exist at room temperature, so the primary purpose of such measurements in this experiment is to check the performance of the mobility tube. Since the design of this tube is essentially the same as that used by Beaty and Patterson, their data is singled out for comparison with measurements obtained here. Fig. 10 shows a plot of \( K \) versus \( E/p_0 \) where the data of Beaty and Patterson are represented by the solid lines. The ion of slowest mobility is \( \text{He}^+ \) and that of higher mobility is \( \text{He}_2^+ (\text{He}_u^+) \). Data obtained with this apparatus are represented by the two symbols "x" and "o". For the purpose of comparing with the solid lines, the "o" data can be neglected for reasons which will be explained later. The "x" data, then, do reasonably reproduce the Beaty and Patterson measurements. Most of these data are for the \( \text{He}_2^+ \) ion because it is the dominant ion over the entire range of pressures. The data shown in Fig. 10 provide sufficient evidence that the tube is operating correctly. For the remainder of this paper, the solid lines shown in Fig. 10 will be considered to represent the accurate room temperature mobilities.
Figure 10. Plot of Helium Ion Mobility Versus $E/p$ at 300°K.

Points represent measurements obtained with this apparatus.
Solid lines represent data of Beatty and Patterson.
There remain to be explained the data represented by the symbols "o" in Fig. 10. It was pointed out in Section II-4 that during the course of the experiment, there were some pressure measuring problems caused by the apparent contamination of the capacitance manometer. For the data represented by the symbols "o", the error in the pressures was particularly bad, and these data would normally be discarded. However, it is possible to use these room temperature data to deduce a pressure correction which can then be applied to similarly errant data at lower temperatures. As pointed out in Section II-4, the pressure error was in the form of a zero offset. For each "o" point shown in Fig. 10, the magnitude of this offset can be determined from the pressure adjustment needed to bring each point into coincidence with the accurate mobilities represented by the solid lines. Once this pressure offset is determined for a given gas sample at room temperature, the same correction can be applied to all pressure measurements on that gas sample at lower temperatures. This method of correcting the errant pressures has the effect of normalizing the low temperature data with respect to the correct mobilities at room temperature. As will be seen shortly, data normalized in this manner are in excellent agreement with other low temperature data obtained from accurate pressure measurements.

Before discussing data at other temperatures, it is helpful to review the main observations at room temperature. In this particular type of apparatus, the only ion observed at pressures greater than 6 Torr is the He$_2^+$ ion. This is because the He$^+$ ion takes
part in the three body attachment reaction (16), and at pressures greater than 6 Torr, this reaction is so fast that no \( \text{He}^+ \) ions survive to get into the main drift region. At pressures lower than 6 Torr, the reaction is slowed down sufficiently that both \( \text{He}_2^+ \) and \( \text{He}^+ \) can be observed. In addition to the \( \text{He}^+ \) and \( \text{He}_2^+ \) ion peaks, the low pressure mobility spectrum includes a current contribution due to the reaction. A spectrum of this type was shown previously in Fig. 6. The existence of the reaction (16) is the principle reason why the \( \text{He}^+ \) data do not extend to as low values of \( \frac{E}{p_0} \) as do the \( \text{He}_2^+ \) data in Fig. 10. The very low \( \frac{E}{p_0} \) data are obtained using relatively high pressures where only the \( \text{He}_2^+ \) ion is present. Fortunately, the \( \frac{E}{p_0} \) dependence of the \( \text{He}^+ \) mobility is flat enough that a reasonably accurate extrapolation of the mobility to zero \( \frac{E}{p_0} \) can still be made. The zero field mobilities obtained from the solid lines in Fig. 10 are 10.4 for \( \text{He}^+ \) and 16.7 for \( \text{He}_2^+ \). Beatty and Patterson also reported a third ion with a mobility of about 19.6 which is not shown in Fig. 10. This third ion is difficult to produce in this type of apparatus, and no effort is made to observe it in this experiment. The \( \text{He}^+ \) mobility is seen to decrease with increasing \( \frac{E}{p_0} \) in Fig. 10. This implies that at 300°C, the \( \text{He}^+ \) mobility has a negative slope as a function of temperature. This is in accord with the predictions of the resonant charge exchange theory for \( \text{He}^+ \) which was discussed in Section I-2. For the \( \text{He}_2^+ \) ion, the mobility increases with increasing \( \frac{E}{p_0} \), so the mobility-temperature dependence is expected to have a positive slope at room temperature.
III-2. Measurements at Temperatures Other than 300°K

Plots of $K$ versus $E/p_0$ are shown in Figs. 11-14 for the temperatures of 248°K, 196°K, 150°K, and 75.9°K. In these plots, the measured data are represented by the same symbols used in Fig. 10. Data obtained from accurate pressure measurements are represented by the symbols "x", and the symbols "o" refer to data which have been normalized according to the method described in the previous section. As an additional check on the validity of this normalization procedure, the correlation of pressure with temperature can be considered. It was pointed out in Section II-5 that for a given pressure $p_K$, the ratio $p_K/p_T$ follows reasonably well the predicted linear dependence on $300/T$. In all cases where the data were normalized in the manner described, the adjusted pressures fit the predicted pressure-temperature behavior much better than the original pressures. The scatter in the data shown in Figs. 11-14 is due primarily to pressure uncertainties, although at 150°K there is an additional two per cent uncertainty in the temperature.

At 248°K and 196°K, the observed mobility spectrum is similar to that at room temperature. The $\text{He}^+$ mobility is seen to increase with decreasing temperature, and the $\text{He}_2^+$ mobility decreases slightly. At lower temperatures, however, the $\text{He}_2^+$ ion is observed to take part in an ion conversion reaction resulting in
Figure 11. Plot of helium ion mobilities versus \( E/p \) at 2.48\( \times 10^4 \) Torr.
Figure 13: Plot of helium ion mobilities versus $E/p^0$ at 150$^\circ$K.
Figure 14. Plot of helium ion mobilities versus $E/p_0$ at 75.9 K.
the formation of a new ion species. This ion transition sets in at about 160°K, and is depicted in the series of current versus time delay plots shown in Fig. 15. These plots are obtained by using the N₂-vapor cooling scheme described in Section II-5. The temperatures shown are those recorded by one of the thermocouples attached to the mobility tube, and the actual temperature of the gas inside the tube probably lagged the indicated values by some small amount. Time intervals between adjacent plots ranged from five to ten minutes with the temperature decreasing with time. The gas sample used for these plots has p₀ = 11 Torr at 300°K. At this high pressure, only a single He₂⁺ ion peak is observed in the mobility spectrum. The electric field used for all the plots is 20 V/cm, so at room temperature the E/p₀ is about 1.8 V/(cm-Torr). As the tube is cooled, however, the E/p₀ decreases because p₀ increases as pointed out in Section II-5. If the mobility were constant, this increase in p₀ would cause the ion peaks to shift toward longer time delays as the tube cools. For the He₂⁺ ion, the mobility actually decreases with decreasing temperature, thereby adding a further shift toward longer times. The He₂⁺ peak shifted steadily in this manner from room temperature down to the first temperature shown in Fig. 15, and the trend continues down to about 160°K. At that temperature, the peak starts shifting toward shorter time delays, indicating that the mobility has started to increase with decreasing T at a faster rate than the p₀ increase. In addition to this movement in the opposite direction, the ion peak is noticeably
Figure 15. Plots of ion current versus time delay illustrating the conversion of $\text{He}_2^+$ to $\text{He}_3^+$ over the temperature range of 185\,°K to 108\,°K.
broadened. This behavior continues down to about $110^\circ$K, at which point the peak again becomes narrow and starts moving back toward longer times with decreasing temperature. This indicates that the increase in $p_0$ again dominates over the rate of change of the mobility with the temperature. The $^2\text{He}^+$ ion which enters this transition region at about $160^\circ$K has a mobility of about $16.0$, and the ion which emerges at about $110^\circ$K has a mobility of $18.5$ to $19.0$. In the transition region, the observation of a single, broad ion peak with a mobility between the two extremes indicates the existence of an equilibrium set up between the $^2\text{He}^+$ and the ion to which it converts. The shape of the ion current observed in this case can be contrasted with that shown previously in Fig. 6 for the $^2\text{He}^++^1\text{He}^+$ conversion reaction (16). The conversion depicted in Fig. 6 goes only in one direction, and the reactant and product ion peaks are clearly visible. In the situation shown in Fig. 15, the conversion goes in both directions, so there are no reactant or product ion peaks to be observed, but rather just a single peak at an intermediate mobility.

The ion species created from $^2\text{He}^+$ at low temperatures is believed to be $^3\text{He}^+$. (This identification is discussed in more detail later.) In the transition region between $110^\circ$K and $160^\circ$K, the equilibrium reaction that is observed is presumed to be,

$$\text{He}_2^+ + \text{He} \rightleftharpoons \text{He}_3^+. \quad (22)$$
The $\text{He}_3^+$ ion is stable only at low temperatures and at low values of $E/p_0$. The stabilization most probably occurs by a collision with a third body (i.e., another He atom). Shown in Fig. 16 are several current versus time delay plots which illustrate the breakup of this ion as $E/p_0$ is increased at $T = 75.9^\circ\text{K}$. These data are obtained by operating the mobility tube in the three shutter mode described in Section II-2. For the plots shown in Fig. 16, only the $\text{He}_3^+$ ion is allowed to enter the main drift region, and at low $E/p_0$ only a single ion peak is observed. As $E/p_0$ is increased, however, various stages of breakup are observed, and at $E/p_0 = 4.76$ most of the $\text{He}_3^+$ is reconverted into the $\text{He}_2^+$ ion. In this case of destruction of the $\text{He}_3^+$ ion by electrical heating, the distribution of the ion current in the transition region is quite asymmetric as compared to the symmetric peak observed (see Fig. 15) when the breakup is achieved by varying $T$ instead. A meaningful mobility cannot be deduced from such asymmetric current distributions.

There remains one feature of the plots in Fig. 16 that is unexplained. That is the appearance of a small current peak on the fast side of $\text{He}_2^+$ at the $E/p_0$ values of 4.04 and 4.76. It might be postulated that this peak simply refers to some $\text{He}_3^+$ remnants. However, the mobility is about 23 at an $E/p_0 = 4.76$, and this would require that the $\text{He}_3^+$ mobility rise rather abruptly with increasing $E/p_0$. An alternate explanation is that this fast current peak is due to yet another ion created from the electrical breakup of $\text{He}_3^+$. There are some data at slightly higher temperatures which tend to support this latter contention, but the
Figure 16. Plots of ion current versus time delay illustrating the break-up of He3 with increasing E/p at T = 75.9 K.
existing data are by no means sufficient to confirm this. Still another possibility is that the fast peak is some ion species created upstream from the main drift region. Although the tube is adjusted so that nominally only \( \text{He}_3^+ \) gets into the drift region, the mobility of the fast peak is close enough to that of \( \text{He}_3^+ \) that some of the fast ion species may also be getting into the drift region. There is a very small interaction between the field in the drift region and that in the shutter region, so it is possible that the transmissivity of the shutter could be enhanced for the fast ion as the field in the drift region is increased.

Some additional current versus time delay plots at 75.9 K are shown in Fig. 17. In this case, only the \( \text{He}^+ \) ion is allowed to enter the main drift region, and everything else that is observed is produced from the \( \text{He}^+ \) by means of a reaction. At the high \( E/p_0 \) of 4.53, the \( \text{He}^+ - \text{He}_2^+ \) three body attachment reaction \((16)\) is observed to take place. As \( E/p_0 \) is decreased, the \( \text{He}_2^+ \) in turn reacts in flight to form the \( \text{He}_3^+ \), so that there are observed the two reaction stages,

\[
\text{He}^+ + \text{He} + \text{He} \rightarrow \text{He}_2^+ + \text{He}, \quad (16)
\]

\[
\text{He}_2^+ + \text{He} \rightarrow \text{He}_3^+ + \text{He} \quad (23)
\]

(Again, the third body in equation \((23)\) is presumed to be necessary to stabilize the \( \text{He}_3^+ \).) At the low \( E/p_0 \) value of 2.26, the observed ion current shape is just that expected for a unidirectional
Figure 17. Plots of ion current versus time delay illustrating the ion conversions He$^+$, He$^+$, He$^+=\text{He}_2^+$, He$^+=\text{He}_3^+$ as a function of E/p$^0$. At T = 73.9 K, $p^0 = 4.88$ Torr, $T = 75.9$ K.
reaction beginning at He\(^+\) and terminating at He\(_3^+\). In other words, the rate of reaction (23) is at least as fast as that of (16) so that no He\(_2^+\) peak is built up. It is interesting to see that in the high E/p\(_o\) case, there is no evidence of that fast ion peak seen in Fig. 16. This may be due to the fact that the effect of increasing E/p\(_o\) is quite different for the two situations depicted in Figs. 16 and 17. In Fig. 10, an already existing He\(_3^+\) is broken up by the use of high fields, while in Fig. 17 the high fields simply act to inhibit the formation of He\(_3^+\) by means of reaction (23).

The ion mobilities extrapolated to zero E/p\(_o\) are indicated on each of the \( K \) versus E/p\(_o\) plots shown in Figs. 11-14. These values are also recorded in Table I. For He\(^+\), the extrapolation becomes increasingly difficult as the temperature decreases. It was already pointed out in connection with the room temperature measurements that the He\(^+\) mobility data extend only down to about E/p\(_o\) = 2 because of the He\(^+\) - He\(_2^+\) reaction (16). At room temperature, the extrapolation to zero E/p\(_o\) was still reasonably accurate because the He\(^+\) mobility had only a weak E/p\(_o\) dependence. However, as the temperature decreases, the E/p\(_o\) dependence becomes increasingly stronger. Although it is anticipated that the He\(^+\) mobility will eventually become independent of E/p\(_o\) at some low value of E/p\(_o\), for most of the data this flattening off of the He\(^+\) mobility was not yet achieved at the point where the data stopped. In order to extrapolate the existing data to zero E/p\(_o\), there are two extreme choices that can be
TABLE I. Zero field helium ion mobilities at various gas temperatures T. Mobilities are normalized to a standard gas density of $2.69 \times 10^{19}$ atoms/cm$^3$.

Ion Mobility in cm$^2$/V-sec

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>He$^+$</th>
<th>He$_2^+$</th>
<th>He$_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300*</td>
<td>10.40±0.10</td>
<td>16.70±0.17</td>
<td></td>
</tr>
<tr>
<td>248</td>
<td>11.40±0.25</td>
<td>16.40±0.30</td>
<td></td>
</tr>
<tr>
<td>196</td>
<td>11.75±0.25</td>
<td>16.10±0.30</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>13.00±0.50</td>
<td>16.00±0.40</td>
<td>&gt;18.50</td>
</tr>
<tr>
<td>75.9</td>
<td>10.10±0.60</td>
<td>16.60</td>
<td>18.00±0.20</td>
</tr>
</tbody>
</table>

*Mobilities listed at 300°K are those reported by Beaty and Patterson. 17

considered. First, the mobility versus $E/p_0$ slope which exists at the point where the data stop can be assumed to persist down to zero $E/p_0$. A zero field mobility determined in this manner is expected to represent an upper limit. A lower limit on the mobility is obtained by assuming that the mobility becomes independent of $E/p_0$ immediately below the point where the data stop. The true mobility, then, is expected to lie somewhere between these two limits. For the He$^+$ mobilities listed in Table I, the estimated uncertainties generally coincide with these upper and lower limits on the extrapolation.
For He$_2^+$ and He$_3^+$, the extrapolations to zero E/p$_0$ are in somewhat better shape, both because the data extend to lower E/p$_0$ and because the dependence on E/p$_0$ is not as strong. Hence, the estimated uncertainties shown in Table I for these two ions reflect the scatter of the data rather than an uncertainty in the extrapolation. At both 150°K and 75.9°K, the He$_2^+$ data do not extend to very low E/p$_0$ because of the conversion to He$_3^+$. The He$_2^+$ mobility listed in Table I for 75.9°K is determined from data which extend only over the E/p$_0$ range of 4.5 to 6.0. These He$_2^+$ data are not sufficient to determine whether the mobility is really independent of E/p$_0$, so the zero field He$_2^+$ mobility at 75.9°K is listed without any estimate of the uncertainty. Only the data at 75.9°K actually refers to the pure He$_3^+$ ion. The high mobility data at about 18.5 in Fig. 13 corresponds to a broadened ion peak such as that observed in the transition region between the temperatures of 110°K and 160°K in Fig. 15. Since this current peak is produced by the He$_2^+ -$ He$_3^+$ equilibrium, its mobility is dependent on the gas pressure. For the data shown in Fig. 13, the 18.5 mobility refers to a p$_0$ of about 24 Torr. At lower values of p$_0$, the mobility shifts down toward the He$_2^+$ value, and at higher p$_0$ it shifts in the opposite direction.

Using equation (5) of this paper, an averaged diffusion cross section $\langle 0_d \rangle$ can be determined from the value of the mobility extrapolated to zero E/p$_0$. Listed in Table II are values of $\langle 0_d \rangle$ corresponding to each of the mobilities in Table I.
TABLE II. Averaged diffusion cross sections $\left\langle Q_d \right\rangle$ for helium ions at various temperatures.

$\left\langle Q_d \right\rangle$ in units of $\pi a_0^2$

<table>
<thead>
<tr>
<th>$T$ in °K</th>
<th>$\text{He}^+$</th>
<th>$\text{He}_2^+$</th>
<th>$\text{He}_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>82.4</td>
<td>44.5</td>
<td></td>
</tr>
<tr>
<td>248</td>
<td>82.7</td>
<td>49.8</td>
<td></td>
</tr>
<tr>
<td>196</td>
<td>90.3</td>
<td>57.1</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>93.3</td>
<td>65.6</td>
<td></td>
</tr>
<tr>
<td>75.9</td>
<td>106</td>
<td>88.9</td>
<td>77.3</td>
</tr>
</tbody>
</table>
III-3. Identification of the Low Temperature Ion Formed from $\text{He}_2^+$

It has been assumed in Section III-2 that the ion formed from $\text{He}_2^+$ at low temperatures is $\text{He}_3^+$. Since this apparatus does not include a mass spectrometer, a positive mass identification is not available. However, it is not evident that this ion could be identified even if there were a mass spectrometer attached to the system. It was pointed out previously that the $\text{He}_3^+$ is stable only at low temperatures and at low values of $E/p_o$. Hence, in order to see this ion, a mass spectrometer would have to be immersed in a refrigerant bath such as liquid $N_2$, and the ions would have to be extracted from the high pressure mobility section to the low pressure spectrometer without passing through a transition region of "high" $E/p_o$ (i.e., $E/p_o > 4 \text{ W(cm-Torr)}$ at $T = 76^\circ\text{K}$).

In this experiment, the identity of the $\text{He}_3^+$ ion is inferred from its behavior under varied experimental conditions. One of the possibilities that must always be considered in a helium experiment is that of an impurity ion. The vacuum and gas handling systems used to provide a clean gas sample were described in Section II-4. While some traces of impurities are observed at room temperature at the lowest pressures used (particularly $p_o = 2 - 5 \text{ Torr}$), at higher pressures the mobility spectrum is quite clean. (Contaminants in the gas produce a number of ion peaks with mobilities of about 20 and higher at room temperature.) The reason for believing that the
ion called $\text{He}_3^+$ is not an impurity is that it is observed to be formed over the entire pressure range of $p_o = 2 - 30$ Torr. In particular, at the higher pressures the single $\text{He}_2^+$ ion peak is seen to convert (see Fig. 15) to the single $\text{He}_3^+$ ion peak with no trace whatsoever of any additional peaks.

Assuming that the $\text{He}_2^+$ is indeed reacting with pure helium gas, there are two other observations which point to $\text{He}_3^+$ as the identity of the low temperature ion. First, it is demonstrated in the data shown in Fig. 16 that the low temperature ion can be broken up to reproduce the $\text{He}_2^+$ directly. This indicates that this ion is in fact comprised of some "cluster" about $\text{He}_2^+$ as opposed to an ion created by a charge exchange type of reaction. Secondly, it is indicated by the data in Fig. 17 that the rate of formation of the low temperature ion is at least as fast (and probably faster) as the $\text{He}^+ - \text{He}_2^+$ conversion. This particular point is difficult to understand in view of the cross sections listed in Table II. At 75.9°K, the $\text{He}^+$ interaction still has the largest cross section of any of the ion-neutral interactions. Hence, it is expected that the $\text{He}^+ - \text{He}_2^+$ conversion would have a higher rate than any other three body ion-neutral reaction in helium. Of course, if the $\text{He}_3^+$ could be stabilized without requiring the third body in reaction (23), then the $\text{He}_2^+ - \text{He}_3^+$ conversion would be via a two body reaction and this could be expected to go at a faster rate than the three body $\text{He}^+ - \text{He}_2^+$ reaction. In any case, the possibility is remote that the low temperature ion is some more
complex species such as $\text{He}_4^+$, since these species would have even
less chance of being formed from $\text{He}_2^+$ at a rate fast enough to
compete with the $\text{He}^+ - \text{He}_2^+$ reaction. In view of these
observations, then, it is difficult to imagine what the low
temperature ion could be if it is not $\text{He}_3^+$. 
CHAPTER IV

DISCUSSION OF DATA

IV-1. The He\(^+\) Mobility

The zero field He\(^+\) mobilities listed in Table I are plotted versus temperature in Fig. 18. Also shown in this plot are the previous measurements of Chanin and Biondi\(^{28}\) and the theoretical curve of Lynn and Moiseiwitsch.\(^{26}\) The data reported here at 75.9°K are about ten to fifteen per cent higher than Chanin and Biondi's data, although the \(E/p_0\) dependences of the mobility are about the same in the two experiments. In comparison with the calculations of Lynn and Moiseiwitsch, the results of this experiment roughly parallel the theoretical curve, but lie slightly higher over the entire range of temperature. More recent calculations of the He\(^+\) mobility by A. S. Dickinson\(^{30}\) are not yet published, but generally they run about three or four per cent above the Lynn and Moiseiwitsch curve, and thus are in excellent agreement with the values measured here.

The He\(^+\) - He system has been studied sufficiently in the past that it is now possible to subject the He\(^+\) mobility to a relatively thorough theoretical treatment. The general features of the theory of ions in their parent gases have already been discussed in Section I-2 of this paper. The He\(^+\) mobility is related to the
Figure 18. Plot of zero field mobility $K_0$ of $\text{He}^+$ as a function of gas temperature $T$. Included in this plot are previous experimental results of Chanin and Biondi (CB) and the theoretical curve of Lynn and Moiseiwitsch (LM).
The $\text{He}^+ - \text{He}$ diffusion cross section $Q_d$ by means of the kinetic theory solution of Chapman and Enskog. For the specific case of an $\text{He}^+ - \text{He}$ interaction, Dalgarno and Williams have calculated the correction $\epsilon$ in equation (3), and they find that it is always less than a one per cent correction at the temperatures of interest in this paper. The diffusion cross section can be readily deduced using standard methods if the interaction potential is known.

Hence, the principle theoretical problem is the determination of the interaction potentials. It was pointed out in Section I-2 that the symmetry of the $\text{He}^+ - \text{He}$ system gives rise to two interaction potentials. These are the $2^u_L$ and the $2^u_g$ potentials of $\text{He}_2^+$ which are supplemented at large internuclear separations by a long range polarization potential. The details of these interaction potentials constitute a principle difference between the calculations of Lynn and Moiseiwitsch and Dickinson.

The $\text{He}^+$ mobilities shown in Fig. 18 have a temperature dependence that is typical of ions which are subject to resonant charge exchange with the gas. If $Q_d$ is approximated by $2Q_t$ ($Q_t$ is the charge transfer cross section given by equation (13) in Section I-2), then the mobility is expected to follow closely a $T^{-1/2}$ dependence because $Q_t$ has a relatively weak energy dependence. However, the long range polarization becomes more important as the temperature decreases so that $Q_d$ deviates more and more from the pure charge exchange cross section. As a result, the mobility falls off from the $T^{-1/2}$ behavior by an increasing amount as $T$ decreases.
It was pointed out in Section III-2 that the He⁺ mobility has an increasingly strong dependence on $E/p_0$ as the temperature decreases. This appears to be correlated with the fact that the slope of the mobility-temperature curve is also increasing with decreasing $T$. Most of the He⁺ mobilities measured in this experiment were gathered between the $E/p_0$ values of 2 and 6. Over this $E/p_0$ range, the data could be reasonably well fit by a linear $K$ versus $E/p_0$ dependence. The slopes $dK/d(E/p_0)$ have approximately the same relative values at the various temperatures as the slopes $dK/dT$. Qualitatively, this correlation of the $E/p_0$ and $T$ dependences is in accord with the theory of Kihara mentioned in Section I-2.
IV-2. Mobilities of the Helium Molecular Ions

The zero field mobilities of \( \text{He}_2^+ \) and \( \text{He}_3^+ \) are plotted as a function of temperature in Fig. 19. Previous measurements of Chanin and Biondi\(^{28}\) and Tyndall and Pearce\(^{31}\) are also included in the plot. Although these previous measurements are listed in much of the literature as referring to \( \text{He}_2^+ \), they do not refer to the ground state \( \text{He}_2^+ (^2\Sigma_u^+) \). As was pointed out in Section I-3, the room temperature mobility of \( \text{He}_2^+ (^2\Sigma_u^+) \) is about 16.7 and not about 20.0. It is difficult to speculate as to what the ion in the earlier measurements was. However, the recent mass analysis by Madson, Oskam, and Chanin,\(^{15}\) along with the interpretation given by Beaty, Browne, and Dalgarno,\(^{16}\) suggests the metastable \( \text{He}_2^+ (^4\Sigma_u^+) \) as a possible identification of the ion with mobility about 20 at 300°K. Another possibility is that it was an impurity. The solid curve shown in Fig. 19 represents the only reported quantitative calculation of the \( \text{He}_2^+ \) mobility. Geltman's\(^{20}\) theoretical treatment of \( \text{He}_2^+ \) was by no means as refined as the \( \text{He}^+ \) theories described in the preceding section, and the comparison with experimental data is quite poor.

There do not exist any previous measurements of the temperature dependence of the \( \text{He}_2^+ (^2\Sigma_u^+) \) mobility for comparison with the values measured here. For the \( \text{He}_3^+ \), there have been no previous reports of its existence, although Geltman did suggest that the
Figure 19. Plot of zero field mobilities $K$ of helium molecular ions as a function of gas temperature $T$. Included in this plot are previous measurements by Chanin and Biondi\textsuperscript{28}(CB), and by Tyndall and Pearce\textsuperscript{31}(TP). Also shown is a theoretical curve by Geltman\textsuperscript{20} for the $\text{He}_2^+$ mobility. The Langevin limits for $\text{He}^+$, $\text{He}_2^+$, and $\text{He}_3^+$ are indicated at $T = 0^\circ\text{K}$.
decline of Tyndall and Pearce's mobilities with decreasing \( T \) indicated the possibility of ion clustering setting in at about 170°K. In fact, from the data shown in Fig. 19, it looks like both Tyndall and Pearce, and Chanin and Biondi had \( \text{He}_3^+ \) at 77°K. These previous measurements point out the necessity for being able to trace the mobilities almost continuously as a function of temperature in order to be sure of the ion identities at the lower temperatures. Chanin and Biondi, for example, connected their three points at 300°K, 195°K, and 77°K with a smooth curve, and they assumed that this curve represented the temperature dependence of the \( \text{He}_2^+ \) ion. However, on the basis of the observations in this experiment, it seems quite probable that their molecular ion at 77°K was in fact not the same ion species they observed at higher temperatures.

One of the outstanding features of the \( \text{He}_2^+ \) mobilities measured here is their relatively small variation with temperature as compared to the behavior of the \( \text{He}^+ \) mobilities. At each temperature, the \( \text{He}_2^+ \) mobilities show a similarly weaker dependence on \( E/p_0 \) than did \( \text{He}^+ \). The \( \text{He}_2^+ \) mobilities are seen to decrease slightly down to about 150°K, and then possibly pass through a minimum, rising slightly at 75.9°K. As was pointed out in Section III-2, however, the \( \text{He}_2^+ \) data at 75.9°K are at relatively high \( E/p_0 \), and it is not evident that the value listed in Table I (and plotted in Fig. 19) is an adequate representation of the zero field mobility.
In some respects, the upturn in the \( \text{He}_2^+ \) mobility at low temperatures is supported by the \( E/p_o \) dependences shown in the plots in Figs. 11-14. First, all the plots down to 150°K show an eventual increase in the \( \text{He}_2^+ \) mobility with increasing \( E/p_o \). This behavior is consistent with the observed positive slope \( dK/dT \) over this temperature range. Secondly, the \( E/p_o \) dependence of the \( \text{He}_2^+ \) mobility does not appear to set in until higher and higher \( E/p_o \) values with decreasing temperature. This is consistent with a tendency of the slope \( dK/dT \) to decrease as the temperature decreases toward 150°K. Finally, the \( \text{He}_2^+ \) data at 75.9°K appear to be independent of \( E/p_o \), and if this is the case then the existing data should still provide a good value for the zero field mobility. Support for this independence of \( E/p_o \) comes from the data at 150°K where the \( \text{He}_2^+ \) mobilities are reasonably independent of \( E/p_o \) all the way up to an \( E/p_o \) value of 5.

The \( \text{He}_3^+ \) mobility is measured only at 75.9°K, but at that temperature it is seen to increase with increasing \( E/p_o \). This suggests that the \( \text{He}_3^+ \) has a positive slope \( dK/dT \) at 75.9°K, and this is further supported by the fact that the \( \text{He}_2^+ - \text{He}_3^+ \) "equilibrium" mobility at 150°K is greater than the pure \( \text{He}_3^+ \) mobility at 75.9°K.

Shown at the left of the plot in Fig. 19 are the classical Langevin limits for the \( \text{He}^+ \), \( \text{He}_2^+ \), and \( \text{He}_3^+ \) mobilities at 0°K. The disagreement of experiment with the conventional theory is
again demonstrated in the case of \( \text{He}_2^+ \) by the fact that the measured mobilities lie considerably below the \( \text{He}_2^+ \) Langevin limit. It was pointed out in Sections I-2 and I-3 that the theory of ions in unlike gases has generally been assumed to be applicable to \( \text{He}_2^+ \). This theory predicts that the mobility should be somewhat above the Langevin limit at temperatures greater than \( 0^\circ\text{K} \). A second point of disagreement with the existing theory is the fact that the \( \text{He}_2^+ \) ion is observed to convert to a heavier ion which has a higher mobility. This conflicts with the prediction that the mobility depends on \( 1/\sqrt{\mu} \) where \( \mu \) is the reduced mass of ion and gas atom. The most notable exceptions to this predicted mass dependence are the cases where symmetry effects such as resonant charge exchange are active. In contrast with \( \text{He}_2^+ \), the \( \text{He}_3^+ \) mobility is above its Langevin limit at \( 77^\circ\text{K} \), and so it is at least qualitatively consistent with the usual theory which neglects any symmetry effects (i.e., the theory of ions in unlike gases).

The shape of the \( \text{He}_2^+ \) mobility versus temperature dependence suggests one possible explanation of the anomalously low \( \text{He}_2^+ \) mobility. The observed \( \text{He}_2^+ \) mobilities do appear to turn back up toward the Langevin limit at very low temperatures. Also, the apparent minimum in the mobility is just what is expected if the interaction potential \( V(R) \) contains an important \( 1/R^6 \) term along with the \( 1/R^4 \) and repulsive terms. (See equation (11) for a general form of the interaction potential.) However, the coefficient of the \( 1/R^6 \) term would have to be unusually large
in order to drop the $\text{He}_2^+$ mobility to a value even below that of $\text{He}_3^+$. In addition, it would have to be assumed that such a large $1/R^6$ term does not occur for the $\text{He}_3^+ - \text{He}$ interaction. However, the most serious objection to this explanation is that it provides no reason why there are observed two forms of $\text{He}_2^+$ having quite different mobilities at room temperature. (The situation at room temperature was reviewed in Section I-3.)

An alternate explanation of the low $\text{He}_2^+$ mobility was suggested in Section I-3, and it invokes the resonant process,

$$\text{He}(1S) + \text{He}_2^+(2\Sigma_u^+) \rightarrow \text{He}_2^+(2\Sigma_u^+) + \text{He}(1S). \quad (17)$$

As in the case of the $\text{He}^+ - \text{He}$ interaction, the energy of the separated $\text{He}_2^+ - \text{He}$ system is degenerate in the sense that it is invariant to all possible permutations of the three helium nuclei among the separated molecular ion and free atom systems. However, the interaction of the $\text{He}_2^+$ and the He as they approach each other is not clear. Process (17) suggests the formation of a transient complex $(\text{He}_3^+)^*$ in which there exists some possibility of a rearrangement of the $\text{He}_2^+$ molecular bond before the complex breaks up. One of the difficult features to understand is how such a rearrangement of nuclei could occur since the $\text{He}_2^+ - \text{He}$ cross sections listed in Table II indicate that most of the scattering is at distances larger than the normal separation of the nuclei in $\text{He}_2^+$. 
The observations of this experiment tend to support the suggestion that the resonant process (17) is responsible for the low \( \text{He}_2^+ \) mobility. At temperatures between 110°K and 150°K, the association of \( \text{He}_2^+ \) with \( \text{He} \) is strong enough to give rise to an \( \text{He}_2^+ - \text{He}_3^+ \) equilibrium, and at lower temperatures all of the \( \text{He}_2^+ \) can be converted into a stable \( \text{He}_3^+ \). At these low temperatures, the \( \text{He}_2^+ - \text{He} \) scattering distances are also large, but it is still possible for the \( \text{He}_2^+ \) bonding to give way to an \( \text{He}_3^+ \) bond. It therefore seems plausible to imagine that at higher temperatures an \((\text{He}_3^+)\) transient complex can be formed such that a rearrangement of the \( \text{He}_2^+ \) molecular bond can occur before breakup. The observations in this experiment indicate that such a rearrangement likely becomes more probable as the temperature decreases. This would explain the decrease in the mobility with decreasing \( T \) down to about 150°K, although it is not quite clear why the mobility should then start rising at lower temperatures. A most attractive feature of this rearrangement mechanism is that it does provide an explanation for two \( \text{He}_2^+ \) ions of different mobility as was pointed out in Section I-3. The fact that the \( \text{He}_3^+ \) mobility is higher than that of \( \text{He}_2^+ \) suggests that \( \text{He}_3^+ \) is not subject to this rearrangement of nuclei, at least not to the extent that \( \text{He}_2^+ \) is.
CHAPTER V

SUMMARY OF RESULTS

The three ions studied in this experiment were \( \text{He}^+ \), \( \text{He}_2^+ \), and \( \text{He}_3^+ \). Their various interactions with the helium gas are collected and listed in the following scheme:

(a). \( \text{He}^+ + \text{He} \rightleftharpoons (\text{He}_2^+)^* + \text{He} + \text{He}^+ \);

(b). \( \text{He}^+ + \text{He} \rightarrow (\text{He}_2^+)^*, (\text{He}_2^+)^* + \text{He} \rightarrow (\text{He}_3^+)^* + \text{He}_2^+ + \text{He} \);

(c). \( \text{He}_2^+ + \text{He} \rightleftharpoons (\text{He}_3^+)^* + \text{He} + \text{He}_2^+ \);

(d). \( \text{He}_2^+ + \text{He} \rightleftharpoons (\text{He}_3^+)^* \);

(e). \( \text{He}_2^+ + \text{He} \rightarrow (\text{He}_3^+)^*, (\text{He}_3^+)^* + \text{He} \rightarrow \text{He}_3^+ + \text{He} \);

(f). \( \text{He}_3^+ + \text{He} \rightleftharpoons (\text{He}_4^+)^* \).

In this interaction scheme, the transient complex \( (\text{He}_n^+)^* \) is used to represent the ion \( \text{He}_{n-1}^+ \) and atom \( \text{He} \) when they are close enough to interact appreciably. This complex merely indicates that the ion and atom are temporarily associated through their interaction, and it in no way implies that \( (\text{He}_n^+)^* \) is some bound molecular state. Interaction (a) represents the elastic scattering and the resonant charge exchange which govern the motion of \( \text{He}^+ \) through the \( \text{He} \) gas. The resonant charge exchange accounts for the low mobility of \( \text{He}^+ \). This charge exchange process is resonant because the energy of the system after a charge exchanging collision is equal to the energy before the collision. The \( \text{He}^+ \) mobilities
measured in this experiment over the temperature range of 76°K to 300°K are in good agreement with detailed theoretical treatments.

In interaction (b), the transient \( \text{He}_2^+ \)\(^*\) collides with another He atom to produce a stable \( \text{He}_2^+ \) ion. This interaction is just the three body \( \text{He}^+ - \text{He}_2^+ \) attachment reaction (17). At pressures greater than 1 Torr, and at temperatures greater than about 160°K, the \( \text{He}_2^+ \) is the only chemically stable helium ion that is observed. (\( \text{He}^+ \) is chemically unstable since it is converting to \( \text{He}_2^+ \)).

Interaction (c) represents the elastic scattering and the rearrangement mechanism proposed to account for the low mobility of \( \text{He}_2^+ \). Since the rearrangement of nuclei yields a separated ion-atom system having the same energy as the initial system, the process is a resonant one. There is no existing theory which takes into account this rearrangement mechanism. It is interesting to compare interaction (c) with the reverse of interaction (b) (i.e., \( \text{He}_2^+ + \text{He} \rightarrow \text{He}^+ + 2\text{He} \)). There is no evidence that the reverse of (b) occurs, even at 300°K and \( E/p_0 \) values up to 10. This, of course, is just what might be expected since the reverse of (b) is not a resonant process.

Interaction (d) is the \( \text{He}_2^+ - \text{He}_3^+ \) equilibrium that is observed to exist between the temperatures of 110°K and 160°K. In this case, the \( (\text{He}_3^+) \)\(^+\) is presumed to be some activated form of \( \text{He}_3^+ \) which needs to dissipate some energy in order to become a stable \( \text{He}_3^+ \). Such a stabilization is represented in interaction
(e). At temperatures between 75.9°K and about 100°K, at pressures greater than 1 Torr, and at very low values of $E/p_o$, $\text{He}_3^+$ is the only chemically stable helium ion.

Finally, the interaction (f) is represented in the same format as the preceding interactions although it represents just the usual elastic scattering of $\text{He}_3^+$ and $\text{He}$. Symmetry effects appear not to be important (at least at 75.9°K) for $\text{He}_3^+$ since its mobility lies above that of $\text{He}_2^+$ and is consistent with the conventional mobility theory.

The various helium ion-neutral interactions listed above represent processes which might be expected to occur under similar conditions in other gases. Only in the case of the $\text{He}^+ - \text{He}$ interaction has there yet been developed a reasonably detailed theory. If adequate theoretical treatments are to be worked out for the other interactions as well, it is to be expected that they could most readily be developed for a simple gas such as helium. Such theories would undoubtedly contribute to a better understanding of ionic phenomena in all gases.

One of the most interesting interactions observed in this experiment was the conversion of $\text{He}_2^+$ to $\text{He}_3^+$ at low temperatures. There were no previous reports of the existence of this $\text{He}_3^+$ ion, although the results of this experiment indicate that it was probably present at 77°K in earlier helium mobility experiments. The direct observation of this $\text{He}_2^+ - \text{He}_3^+$ conversion was made possible by the cooling scheme which allowed the mobility spectrum to be monitored continuously as $T$ decreased. All
previous measurements of the temperature dependence of mobilities have employed the refrigerant bath method of cooling. However, the situation observed in this experiment was that the \( \text{He}_2^+ \) converted completely to \( \text{He}_3^+ \) over the temperature range of \( 110^\circ\text{K} \) to \( 160^\circ\text{K} \). This range of temperatures just happens to lie between the temperatures of the two most commonly used refrigerant baths (namely, liquid \( \text{N}_2 \) and dry ice-alcohol). In other words, this ion conversion might not have been detected if only refrigerant baths had been used. These observations suggest that previous mobility versus temperature measurements in other gases might well be re-examined for the possibility of ion conversion reactions similar to that observed here in helium.
BIBLIOGRAPHY


