we can see that the first part is the same for both the 2s and 2p states. The second half is then merely a process involving the Coulomb excitation of H atoms by Ar^+ projectiles. If the ratio between the excitation probabilities for the 2p and 2s states is the same for ions as it is for electrons (about 5 or 3 to 1 according to Fite and Brackmann,[29] Fite Brackmann, Hummer, and Stebbings[30] and Lichten and Schultz[9]), then the ratio of the low energy 2p cross section maxima to the 2s should be of this order The experimental results have this property.

Although the above ideas are largely conjectural, they give a qualitative and consistent explanation for the appearance of the structure in the measured cross sections.

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[29] W. L. Fite and R. T. Brackmann, Phys. Rev. **112**, 1151 (1958).

[30] W. L. Fite, R. T. Brackmann, D. G. Hummer, and R. F. Stebbings, Phys. Rev. **124**, 2051 (1961).

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Mobilities and Reaction Rates of Ions in Helium*

E. C. Beaty and P. L. Patterson†
Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado

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The mobility of He^+ ions in helium gas was measured, the result being 10.40±0.10 (cm^2/V-sec). The He^+ ions were observed to react with the helium gas, the attachment frequency being $[1.08\pm0.05]\times10^{-31}$ n^2(sec^{-1}), where n is the gas density in atoms/cm^3. This value of the attachment frequency is roughly compatible with the theoretical estimate of Bates and with the mass-spectrometric measurement of Phelps and Brown for the rate of the three-body attachment reaction producing He_2^+. The mobility of the product ion, He_2^+, was found to be 16.70±0.17. This mobility is compatible with recent ambipolar diffusion coefficient measurements on cold afterglows, where the identification of the ion is confirmed by the spectroscopic observations of Kerr. This mobility is inconsistent with the widely quoted value of Biondi and Chanin and with the theoretical analyses of Geltman and Dalgarno. Mobility determinations were also made on another ion, which is possibly what Biondi and Chanin called He_2^+. The actual identity is unknown, the ion possibly being He^{2+}, possibly a contaminant.

I. INTRODUCTION

MOBILITIES of ions in gases have been studied for a long time with many confusing and contradictory conclusions. The mobilities are of widespread and continuing interest for two reasons. As a transport coefficient, the mobility constant is useful in certain applications where drift or diffusion is the principal mechanism for the loss of ionization. Also, the mobility constant provides an experimental measure of the effects of elastic scattering at thermal energies. Secondly, mobility studies provide a means of distinguishing the types of ions that are present in a relatively high-pressure gas. The existence of ionization in a low-temperature gas is an unstable state with the ions being neutralized either by free electrons, ions of the opposite charge, or at the solid surfaces. During the time required for this neutralization to occur the ions can react with the gas, the products in general having a different mobility. Mass spectrometers are capable of identifying the ions positively; however, it is necessary to extract the ions from the gas and accelerate them. Studies using mass spectrometers, even while having interpretation problems of their own, are being used to supplement mobility studies in supplying information on the chemical history as ions approach equilibrium in a gas.

Helium is in many ways the simplest of the gases, and accordingly, it has received a great deal of study in drift tubes, in afterglows, and in mass spectrometers. As new information has come in over the years the apparent understanding has oscillated wildly from poor to good and back again.

Electron impact in helium gas can produce only two kinds of ions, He^+ and He^{2+}. He^{2+} converts to He^+ rather rapidly by charge transfer, and the He^+ attaches to form He_2^+. It is almost certain that He^+ does not have excited states which can survive more than a few gas kinetic collisions. Thus, in pure helium gas, the ionic chemistry is expected to be very simple. The trouble is associated with the fact that small traces of contaminants become strongly preferentially ionized by charge transfer. The subject of this paper is a study of the behavior of a small density of helium ions as they approach thermal equilibrium.

II. DEFINITIONS AND CONVENTIONS

In accordance with traditional usage, ionic mobility is here defined as the ratio of the drift velocity, v(cm/sec),

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† Members of the National Bureau of Standards group of the Joint Institute for Laboratory Astrophysics and associated with the Department of Physics and Astrophysics, University of Colorado, Boulder, Colorado.

to the electric field, E(V/cm). With this definition the mobility is approximately inversely proportional to the gas density. In order to facilitate comparison, mobilities are normalized to standard density, and the mobility constant, K, is defined by: $(v/E)(n/n^*)$ where n is the gas density (atoms/cm^3) and n^* is the standard density. For convenience, density is commonly expressed in pressure units, i.e., $p_0=p(273/T)$ is a measure of density. The standard density used, here and generally in the recent literature, corresponds to $p=760$ Torr and $T=273$°K. In these terms the mobility constant is expressed as $K=(v/E)(p_0/760)=(v/E)(p760)(273/T)$.

For the densities of interest here, the individual ions interact principally with one gas atom at a time. The mobility depends on the masses of the ions and gas atoms, and on the interaction between them. The extent of the interaction in collisions depends on the energy of the collisions. The two parameters which characterize the velocity distribution of the ion-atom collisions are the temperature of the gas and the ratio E/p_0. In order to compare experimental measurements of mobility with the usual calculations based on kinetic theory, it is necessary to extrapolate the measurements to $E/p_0=0$.

Treated as first-order departures from thermal equilibrium the phenomena of diffusion and drift in a weak force field are closely related. The diffusion coefficient D is related to the low-field mobility constant by

$$K=ep_0D/760kT, \qquad (1)$$

where e is the ionic charge, k is the Boltzmann constant, and T is the absolute temperature.

III. HISTORICAL DEVELOPMENT

In 1930, Tyndall and Powell[1] published a paper reviewing the state of mobility determinations prior to that date and describing a new apparatus which removed many of the known problems. They concluded that the interpretation of all previous data was subject to doubt because of impurities in the gas samples used. They pointed out several mechanisms which cause impurities to become preferentially ionized. Also, they pointed out that some of the more common contaminants attach to ions, forming clusters. (This is the principle of operation of the Wilson cloud chamber for instance.) Using the new apparatus with renewed attention to the contaminant problem Tyndall and Powell measured the mobility of helium ions in helium. Using a radioactive source to produce ionization in the helium gas, they found several ions with mobilities in the range 6–16 (cm^2/V-sec). The relative abundances depended on the prior history of the gas and could be varied widely. Since the highest mobility was substantially higher than those from previously reported measurements, and since the theoretically expected value for the mobility of He$^+$ in He was even higher[2] (25) they believed that their highest value (16) was characteristic of He$^+$ and that the lower values were due to impurities.

In 1931, Tyndall and Powell[3] reported further improvements in their apparatus and in their purification techniques. The new value they reported for the mobility of He$^+$ in He was 19.9. Hasse and Cook,[4] however, repeated the calculation based on kinetic theory, this time including charge exchange. The new theoretical value was also 19.9. This striking agreement between theory and experiment did not last long, however. In 1933, Massey and Mohr[5] calculated the mobility of He$^+$ in He using quantum mechanics, reporting a value of 11.

In 1935, Tyndall and Pearce[6] reconfirmed the 1931 experimental value (19.9) and reported the temperature variation of mobility, showing it to be essentially independent of temperature from about 500°K down to about 200°K. Below 200°K the mobility went down, reaching 16.5 at 20°K.

The discrepancy between theory and experiment remained unresolved for many years. In 1946, Meyerott[7] proposed that the experimental value referred to He$_2^+$ and, in 1949, Biondi and Brown[8] reported ambipolar diffusion coefficient measurements indicating a mobility of 12.5. Biondi and Brown concluded that the 1930 results of Tyndall and Powell were correct for He$^+$ and that perhaps their 1931 results were due to He^{2+}.

Hornbeck,[9] in 1951, apparently resolved the controversy. In his studies of transient currents in a pulsed Townsend discharge he showed that two kinds of ions were present simultaneously. He further showed that they were not doubly charged and that they were not due to impurities. Also, Horbneck and Molnar[10] showed, using a mass spectrometer, that He$_2^+$ could be formed under conditions similar to those existing in the pulsed Townsend discharge tube. The Hornbeck mobility determinations were not very precise, particularly for He$_2^+$, the points on his graph being spread between 17 and 20 at $E/p_0=10$. These results seemed consistent with the experimental values reported by Tyndall and Powell at $E/p_0=1$. Hornbeck's data on the mobility of He$^+$ were consistent with the calculation of Massey and Mohr, and with the measurements of Biondi and Brown.

Phelps and Brown,[11] also in 1951, reported an extension of Biondi and Brown's measurements. They used

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[1] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) **A129**, 162 (1930).

[2] H. R. Hassé, Phil. Mag. **1**, 139 (1926).

[3] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) **A134**, 125 (1931).

[4] H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

[5] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **A144**, 188 (1934).

[6] A. M. Tyndall and A. F. Pearce, Proc. Roy. Soc. (London) **A149**, 426 (1935).

[7] R. Meyerott, Phys. Rev. **70**, 671 (1946).

[8] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[9] J. A. Hornbeck, Phys. Rev. **84**, 615 (1951).

[10] J. A. Hornbeck and J. P. Molnar, Phys. Rev. **84**, 621 (1951).

[11] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

a mass spectrometer to analyze the ions which came out of the afterglow into a differentially pumped chamber. The mass spectrometer showed that He_2^+ was indeed produced. By studying the time dependences of the various constituents of the afterglow, they deduced a value for the rate of conversion of He^+ into He_2^+. The reaction was presumed to be a three-body reaction of the form

$$He^+ + 2He \rightarrow He_2^+ + He. \qquad (2)$$

The attachment frequency α was assumed to be expressed in the form

$$\alpha = \beta n^2 \qquad (3)$$

and β was assigned the value $63\pm14\times10^{-33}$cm^{6}sec^{-1}. The mobility of He^+, deduced from this analysis, was 13.0±0.5. This was judged to be in good agreement with Massey and Mohr. This value for the rate of reaction (2) at the pressures used in the measurements by Tyndall is so high that they could not have possibly observed He^+ ions. Similarly, the lifetime of He^+ at most of the pressures used by Biondi and Brown is too short to permit measurement of the diffusion coefficient.

Geltman[12] made a theoretical study of the mobility of He_2^+ in He, computing quantum mechanically the interaction potential between the ion and the atom. The mobility values determined from this potential were somewhat higher than the experimental results of Tyndall and Pearce, and Hornbeck; however, he found that by empirically changing the potential by a small amount, the theoretical mobilities agreed rather well with the experimental ones at 300°K.

Biondi and Chanin,[13] in 1954, reported measurements of mobilities of ions in all the rare gases at 300°K, and, in 1957, they reported extension of these measurements to other temperatures. Their measurement technique was similar to that used by Hornbeck, the principal difference being the means of producing the ions. Whereas Hornbeck used an electron avalanche, stimulated by a light flash, Biondi and Chanin used a high-voltage spark. They made no effort to identify the ions beyond trying to certify that their gas was pure helium, and noting that their mobility values were consistent with those of Hornbeck and Phelps and Brown. The values reported for the mobilities of He^+ and He_2^+ at 300°K, extrapolated to $E/p_0=0$, were 10.5 and 20.3, respectively.

More recent calculations of the He^+ mobility by Lynn and Moiseiwitch[14] in 1957, and by Dalgarno[15] in 1958, have improved the agreement between theory and experiment for this ion. Dalgarno in an extensive review concluded that the mobility of He_2^+ in He should be similar to the mobility of an impurity ion of similar mass. In more detail he concluded that the mobility at low temperatures was 18.6 and at room temperatures somewhat higher. This conclusion was consistent with Geltman's result as well as with the available experimental data for He_2^+ at room temperature.

The happy state of having the experimental results of the several investigators agree with each other and with theoretical expectations did not last long. The first evidence of substantial disagreement came in analogous studies in argon. While Biondi and Chanin considered their results on He_2^+ to be in agreement with Hornbeck's, their results on Ar_2^+ were in substantial disagreement. Beaty[16] using a copy of Hornbeck's apparatus showed that Hornbeck's argon data could be reproduced and extended somewhat, emphasizing the reality of the discrepancy. Using a completely different apparatus Beaty[17] later showed that, using a spark source of ions, Biondi and Chanin's data could be reproduced simultaneously with those of Hornbeck. Meanwhile, Oskam[18] reported afterglow studies in helium yielding a mobility of 17.3, the ion presumably being He_2^+.

In all of these measurements nothing was done to identify the ions beyond trying to certify that the gas was pure and comparing with mobility theory. Kerr[19] and co-workers have conducted a long series of measurements, not yet fully published, in which they studied the optical spectrum from a decaying helium plasma while siumltaneously observing the electron density. Impurities which were preferentially ionized were also preferentially excited. Using the intensity of the optical spectrum as a measure of the extent of impurity ionization, they proceeded to apply purification devices to clean the gas. They found that the most effective way to clean helium was to run a cataphoresis discharge[20] at pressures greater than 15 Torr. Using the pure gas, analysis of the decay constants led to the conclusion that two distinguishable kinds of ions were present with mobilities of 10.6 and 16.2. Kerr concluded that these mobilities were associated with He^+ and He_2^+, respectively. Other measurements[21] have yielded similar mobilities in helium purified in a similar way.

This paper supports the major conclusions of Kerr and Oskam. It is a more complete documentation of information previously reported informally.[22]

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[12] S. Geltman, Phys. Rev. **90**, 808 (1953).

[13] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954); L. M. Chanin and M. A. Biondi, *ibid.* **106**, 473 (1957).

[14] N. Lynn and B. L. Moiseiwitsch, Proc. Phys. Soc. (London) **A70**, 474 (1957).

[15] A. Dalgarno, Phil. Trans. Roy. Soc. (London) **A250**, 428 (1958).

[16] E. C. Beaty, Phys. Rev. **104**. 17 (1956).

[17] E. C. Beaty, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1961), Vol. I, p. 183.

[18] H. J. Oksam, Philips Res. Rept. **13**, 401 (1958).

[19] D. E. Kerr and C. S. Leffel, Bull. Am. Phys. Soc. **7**, 131 (1962); (private communication, 1963).

[20] R. Riesz and G. H. Dieke, J. Appl. Phys. **25**, 196 (1954); A. L. Schmeltekopf, Jr., *ibid.* **35**, 1712 (1964).

[21] H. J. Oskam and V. R. Mittelstadt, Phys. Rev. **132**, 1435 (1963); F. E. Niles and W. W. Robertson, J. Chem. Phys. **40**, 2909 (1964).

[22] P. Patterson and E. C. Beaty, Bull. Am. Phys. Soc. **7**, 635 (1962).

IV. APPARATUS

The apparatus consists of a cylindrical double shutter drift tube mounted on a Pyrex vacuum and gas handling system. The drift tube was similar in design to that used by Tyndall, *et al.*[1,3,6]

Both the drift tube and the associated electronics are illustrated in Fig. 1. At the bottom is a pictorial drawing of the tube. The electrodes are numbered in the center of the illustration where connections to the electronics are indicated. Electrodes 3–16 are made from 0.025-cm advance using a single die. Each had a 2.2-cm-diam hole in the center and twelve small holes around the edge. Each of these electrodes has an offset pressed into the edge to provide mechanical strength. The set was stacked with Pyrex spacers and held together by ceramic insulated metal rods run through four of the small holes. The other eight small holes were used to thread wires and ceramic insulators for the electrical connections. Electrodes 3–4 and 14–15 were each covered by wire gauze knitted from 0.0025-cm tungsten, so that each of the pairs formed a shutter. This electrode structure was supported by spot welding electrode 3 to a metal cylinder which was strapped to a re-entrant glass stem. The electrical connections (shown schematically) to these electrodes were brought through the vacuum wall as tungsten wires mounted on glass stems shown at the right end of the tube.

The ion source and the ion collector were mounted on Kovar tubes, with the tubes also serving as an electrical shield. Ions were produced by striking a discharge between a Kovar wire (electrode 18) and the cylindrical can (electrode 17). A Pyrex funnel, strapped in place, served to confine the discharge to the vicinity of the opening in the can. The most serious noise in the measurements was generated in the discharge and coupled to the detector via a photoelectric effect. In order to minimize this problem, the discharge was pulsed. Enough ions could be obtained by taking those which diffused out through the grid in electrode 17. In order to further reduce the photoelectric effect the ion collector was made of a piece of the knitted tungsten used in the shutters.

Bias potentials for the electrodes were supplied by a set of regulated electronic power supplies as illustrated at the top in Fig. 1. The C supply providing the field for the drift space, was limited by drift tube breakdown to less than about 300 V. The B and D supplies providing the reverse fields for the two shutters were usually set to 2.5 V.

A pair of pulse generators, one positive and one negative, were capacitively coupled to the electrodes of the drift space. A negative pulse opened the shutter nearest the ion source and a positive pulse opened the other one. Neither of the pulses changed the field in the drift space.

A cycle of operation was begun by triggering a pulsed power oscillator (20 Mc) which drove the discharge. An electronic delay triggered the negative pulse generator sometime during the afterglow. Another electronic delay, this one with a calibrated control, triggered the positive pulse generator. The repetition rate could be arbitrarily chosen and was generally 100–1000 cps. An electrometer was connected to the ion collector electrode to measure the average current.

Because of the high-ionization potential of helium,

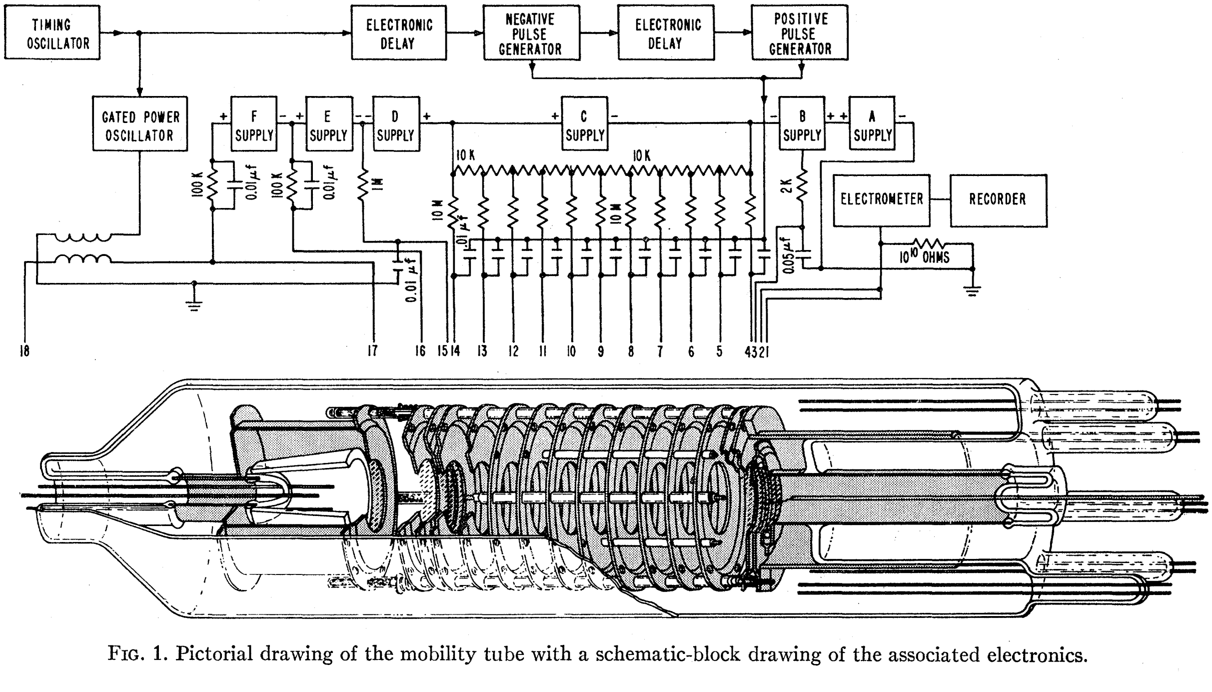

FIG. 1. Pictorial drawing of the mobility tube with a schematic-block drawing of the associated electronics.

charge exchange with all impurities is exothermic. In order to prevent contamination of the helium by the background gas, the tube was evacuated (10^{-9} Torr) and extensively outgassed. The rate of rise of background pressure after seal-off was generally about 10^{-6} Torr per day. Reagent grade commercial gas was admitted to the tube through a bakeable metal valve. The gas was purified by a cataphoresis discharge.[20] A description of the effects of purification is given in Sec. VIII.

The pump used was a mercury diffusion pump. Pressure was measured by either a mercury manometer (3–30 Torr) or a mercury McLeod gauge (0.1–7.0 Torr).

V. ANALYSIS

The experimental data consist of measurements of the charge $q_e(t_i)$, collected during the opening of the second shutter, t_i being the time delay between the two shutter openings. Interpretation of these data in terms of mobilities and reaction rates requires comparison of $q_e(t_i)$ with a theoretical function. When only one kind of ion was present, the experimental function was found to be approximately symmetric about a single maximum. The time-of-flight could be taken as that at which the maximum appeared and mobility could be easily calculated. Isolation of the contribution to $q_e(t_i)$ from the ions produced by a reaction in flight requires a more complex analysis. The equations used, together with an explanation for how these equations are supposed to describe the relevant aspects of the physical problem, are given below.

The differential equations used to describe the volume effects are as follows:

$$\frac{\partial}{\partial t}\rho_1(\mathbf{r},t)=D_1\nabla^2\rho_1(\mathbf{r},t)-K_1\nabla\cdot[\mathbf{E}(\mathbf{r},t)\rho_1(\mathbf{r},t)]-\alpha\rho_1(\mathbf{r},t),$$

$$\frac{\partial}{\partial t}\rho_2(\mathbf{r},t)=D_2\nabla^2\rho_2(\mathbf{r},t)-K_2\nabla\cdot[\mathbf{E}(\mathbf{r},t)\rho_2(\mathbf{r},t)]+\alpha\rho_1(\mathbf{r},t). \quad (4)$$

In these expressions, the subscripts distinguish the two different kinds of ions, one being He^+ and two, He_2^+. The symbols, D, K, $\mathbf{E}$, α, ρ, refer to diffusion coefficient, mobility, electric field, attachment frequency, and ionic density. The space and time coordinates are indicated by $\mathbf{r}$ and t. If $\alpha=0$ the two Eqs. (4) become identical except for the subscripts. The solutions below can be used for an arbitrary number of additional ions which do not react. These equations are applicable only for small departures from thermal equilibrium. More explicitly, the equations are valid only when (1) the density of gas is very much larger than the density of ions and is constant in space and time; (2) the density of ions does not change significantly in the distance of one mean free path; (3) the temperature of the gas is uniform in space and time and the velocity distribution of the ions departs from a Maxwellian at the same temperature only in the respect of a local displacement of the origin in the velocity space; (4) ions of type one (He^+) react with the gas to produce ions of type two (He_2^+), but the reverse reaction does not occur; (5) all ions are singly charged, so that conservation of charge implies conservation of numbers of ions.

A cylindrical coordinate system is most convenient for describing the boundary conditions presented by the drift tube. With the coordinate axis coincident with the tube axis, the origin was chosen as the center of electrode 4. The tube was designed to make the electric field uniform and directed along the axis. Actual departures from uniformity could not be determined. Including even small departures from uniformity in the equations leads to severe mathematical complications. Accordingly, the electric field, and therefore the drift velocity, were taken as constant and directed toward the negative z direction. No experimental information was available on how the density might depend on θ. Symmetry of the electrode system does not necessarily insure symmetry of the densities; however, with the symmetrical boundary conditions the effect of diffusion is to decrease any asymmetries which might be created in the ion source. Furthermore, it is reasonable to expect that even in the ion source the densities were only weakly dependent on θ.

Since the final results are insensitive to errors in the description of the θ dependence, one of the chosen boundary conditions was that the densities are independent of θ.

If Eqs. (4) are multiplied by $2\pi r$ and integrated from $r=0$ to $r=r_0$, they can be expressed in the form

$$\frac{\partial Z_1(z,t)}{\partial t}=2\pi D_1\left[r\frac{\partial\rho_1(\mathbf{r},t)}{\partial r}\right]_{r=r_0}+D_1\frac{\partial^2 Z_1(z,t)}{\partial z^2}+v_1\frac{\partial Z_1(z,t)}{\partial z}-\alpha Z_1(z,t), \quad (5)$$

$$\frac{\partial Z_2(z,t)}{\partial t}=2\pi D_2\left[r\frac{\partial\rho_2(\mathbf{r},t)}{\partial r}\right]_{r=r_0}+D_2\frac{\partial^2 Z_2(z,t)}{\partial z^2}+v_2\frac{\partial Z_2(z,t)}{\partial z}+\alpha Z_1(z,t), \quad (6)$$

where

$$Z_1(z,t)=2\pi\int_0^{r_0}\rho_1(r,z,t)rdr,$$

$$Z_2(z,t)=2\pi\int_0^{r_0}\rho_2(r,z,t)rdr.$$

The data were analyzed using functions derived with the assumptions that the square brackets of (5) and (6) can be represented by

$$
\begin{aligned}
&2\pi\left[r\frac{\partial\rho_1}{\partial r}\right]_{r=r_0}=-\gamma Z_1(z,t)\,,\\
&2\pi\left[r\frac{\partial\rho_2}{\partial r}\right]_{r=r_0}=-\gamma Z_2(z,t)\,,
\end{aligned}
\tag{7}
$$

where γ is independent of z and t. Justification of this assumption is considered below.

Solution of (5) and (6) requires adoption of boundary conditions. This means approximating the effects of the shutters by some simple models. A detailed description of the densities in the neighborhood of the shutters is impossible but fortunately is not necessary. The irregularities caused by the structure of the grids extends into the drift space for a distance comparable with the spacing of the grid wires. This distance is small compared with the length of the drift volume. The densities in almost all of the drift volume are insensitive to whether the shutters are on. The model adopted for the second shutter is that electrode 4 is a complete absorber of ions at all times. This requires that Z_1 and Z_2 tend to zero as z approaches zero. The charge collected during the shutter opening, duration τ_2, was represented by

$$
q_t(t_i)=\int_{t_i}^{t_i+\tau_2-\delta_2/v_1}D_1\left[\frac{\partial Z_1(z,t)}{\partial z}\right]_{z=0}dt+\int_{t_i}^{t_i+\tau_2-\delta_2/v_2}D_2\left[\frac{\partial Z_2(z,t)}{\partial z}\right]_{z=0}dt\,,
\tag{8}
$$

where δ_2, the width of the second shutter, is introduced to account for the small time-of-flight across the shutter.

Since this model is impenetrable, its use for the first shutter leads to a trivial result. The model adopted was that the first shutter was nonabsorbing at all times, but that at time $t=0$ (the time of opening) the distribution of ions could be accurately enough represented by

$$
\begin{aligned}
f_1(z)=Z_1(z,0)&=\frac{N_1}{v_1\tau_1-\delta_1}\,, && d+\delta_1<z<d+v_1\tau_1\,,\\
&=0\,, && \text{otherwise};\\
f_2(z)=Z_2(z,0)&=\frac{N_2}{v_2\tau_1-\delta_1}\,, && d+\delta_1<z<d+v_2\tau_1\\
&=0\,, && \text{otherwise}.
\end{aligned}
\tag{9}
$$

τ_1 is the duration of the gating pulse, δ_1 is the width of the shutter, and d is the distance between electrodes 4 and 14. N_1 and N_2 are amplitude coefficients which represent the number of ions which pass through the first shutter. Equations (5) and (6) can be more easily solved for the current to the collector, as expressed in (8), than for the variables $Z_1(z,t)$ and $Z_2(z,t)$. The solution for arbitrary $f_1(z)$ and $f_2(z)$ is:

$$
I_1(t)=D_1\left[\frac{\partial Z_1(z,t)}{\partial z}\right]_{z=0}=\frac{\exp(-\alpha t-\gamma D_1t)}{(4\pi D_1t)^{1/2}}\int_{-\infty}^{\infty}\exp\left(-\frac{(x-v_1t)^2}{4D_1t}\right)\frac{xf_1(x)}{t}dx\,,
\tag{10}
$$

$$
\begin{aligned}
I_2(t)=D_2\left[\frac{\partial Z_2(z,t)}{\partial z}\right]_{z=0}&=\frac{\exp(-\gamma D_2t)}{(4\pi D_2t)^{1/2}}\int_{-\infty}^{\infty}\exp\left(-\frac{(x-v_2t)^2}{4D_2t}\right)\frac{xf_2(x)}{t}dx+\frac{v_2\alpha}{2(v_2-v_1)}\exp\left(-\frac{\alpha v_2t}{v_2-v_1}\right)\\
&\times\int_{-\infty}^{\infty}\left\{\exp\left(\frac{sx}{b}\right)\left[\operatorname{erf}\left(\frac{x+v_2{}^*t}{(4D_2t)^{1/2}}\right)-\operatorname{erf}\left(\frac{x+v_1{}^*t}{(4D_1t)^{1/2}}\right)\right]+\exp\left(-\frac{sx}{b}\right)\left[\operatorname{erf}\left(\frac{x-v_2{}^*t}{(4D_2t)^{1/2}}\right)-\operatorname{erf}\left(\frac{x-v_1{}^*t}{(4D_1t)^{1/2}}\right)\right]\right\}\exp\left(\frac{x}{b}\right)f_1(x)dx\,,
\end{aligned}
\tag{11}
$$

where

$$
v_1{}^*=v_1s\,;\quad v_2{}^*=v_2s\,;\quad s=\left[1+\gamma b^2+\frac{2\alpha b}{v_1-v_2}\right]^{1/2};\quad b=\frac{2D_1}{v_1}=\frac{2D_2}{v_2}\,.
$$

The first terms on the right of Eqs. (5) and (6) account for the rate of loss of ions due to diffusion across the boundary $r=r_0$. The densities for $r<r_0$ are greatly affected by the detailed nature of this flow. However, the immediate interest is in the effect on (10) and (11). The effect of radial diffusion on the He$^+$ is to reduce the number of ions which get through to the collector, with the fractional reduction being slightly greater for those ions which are late in arriving. The losses by radial diffusion for the electric fields used is small enough to

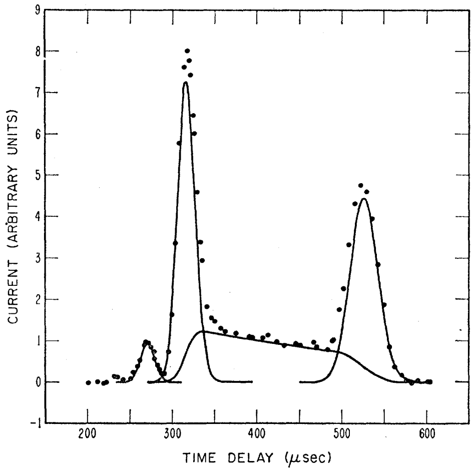

FIG. 2. Sample plot of the current to the ion collector versus the time delay between the gating pulses. Gas conditions: $p_0=3.15$ Torr; $E/p_0=2.46$ V/cm-Torr; $T=305$°K. Experimental data are shown in dots. The continuous curves were calculated using $K_1=10.22$, $K_2=16.95$, $K_3=19.82$ cm²/V-sec, $\beta=1.12\times10^{-31}$ cm⁶/sec.

cause the error in the drift velocity to be quite small. Since the diffusion coefficient is proportional to the mobility, the radial diffusion loss per unit distance travelled is approximately independent of mobility. If an absorbing wall is assumed to exist at $r=r_0$, the radial dependence can be expressed as a factor which is a sum of Bessel functions. The higher order terms decay more rapidly with time so that the radial dependence tends toward $J_0(ar)$ where $a=1.834(\text{cm}^{-1})$. For this lowest diffusion mode, Eqs. (7) are an accurate representation with $\gamma=2.93$ cm^{-2}. This is the value used for γ in most of the analysis. As a check selected samples of data were analyzed with $\gamma=0$ and $\gamma=5.86$. The variation in reaction rate produced by this change was less than 2%.

Using (8), (9), (10), and (11), a set of values for $q_t(t_i)$ were computed for comparison with $q_e(t_i)$. As a measure of the departures of the calculated and measured functions, the quantity

$$\epsilon=\sum_{i=1}^{j}[q_t(t_i)-q_e(t_i)]^2$$

was used, j being the number of observations. A minimum in ϵ, considered as a function of K_1, K_2, α, N_1, and N_2 was sought. The numerical procedure was to choose values for K_1, K_2, and α, calculate the coefficients of N_1 and N_2 in (9), then determine the values of N_1 and N_2 which minimize ϵ. The process was systematically repeated for different values of K_1, K_2, and α, always searching for the set which produced the lowest value of ϵ.

Figure 2 shows a sample set of data where the $q_e(t_i)$ are indicated by the dots. The continuous curves are the results of calculations. Three kinds of ions are observed, two which do not react with the gas. The fastest ion showed no sign of being involved in a reaction, and its curve is calculated using Eq. (10) with $\alpha=0$.

VI. RESULTS

Figure 3 shows the mobility spectrum of helium as a function of E/p_0. Approximate pressures are indicated by the symbol coding. This graph includes data on only those ions which were not removed by the cataphoresis cleaning process. The ion of lowest mobility is He$^+$. Identification of the ion is made, in this case, by comparison with calculations based on the kinetic theory of mobilities, using quantum mechanical momentum transfer cross sections. These data are consistent with the data on helium previously reported by Hornbeck, Biondi and Chanin,[13] Kerr *et al.*[19], and Oskam *et al.*[18,21] It is inconsistent with Phelps and Brown[11] if their limits of uncertainty are respected. The most likely explanation of the discrepancy is the assumption that Phelps and Brown were optimistic in the assignment of uncertainties.

The ion with the intermediate mobility is the one of most interest. There are several indications that this ion is the one which is characteristic of thermal equilibrium in pure helium at pressures above about 1.0 Torr, and accordingly it is presumed to be He$_2^+$. This interpretation is considered in more detail later. The mobilities reported here are in good agreement with those deduced by Oskam,[18,21] Kerr,[19] and Niles and Robertson[21] from their extensive analyses of the very late afterglow in helium.

The fastest ion has the characteristic of being unstable, at least in our afterglow. Data could be obtained with our apparatus only at the lower end of the available

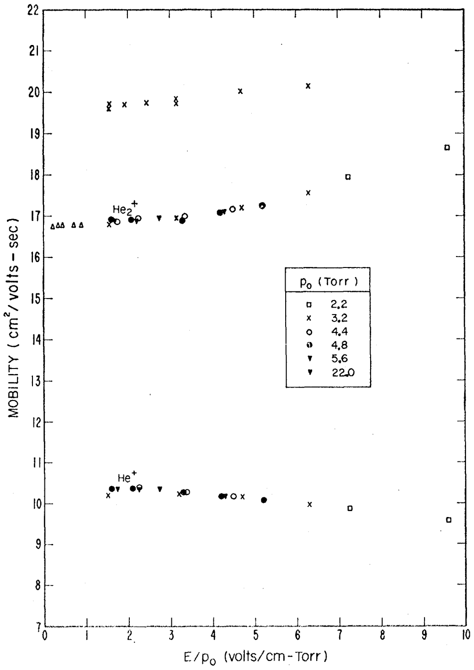

FIG. 3. Graph showing the spectrum of mobilities found in helium plotted as a function of E/p_0.

pressure range, and there only by sampling the ions from the plasma very shortly after the breakdown. The values of the mobilities agree rather well with some reported by Biondi and Chanin.[13] The value of the mobility extrapolated to zero E/p_0 is 19.6±0.3 which does not agree with the extrapolation of Biondi and Chanin. Biondi and Chanin assumed that they were measuring mobilities of He_2^+. There is no proof that these data are related to the ion studied by Biondi and Chanin. Helium gas, as supplied to us by a standard commercial source, contains impurities which yield several ions with mobilities in the range 20–25. The rather special conditions which we required to produce this ion were similar to those which Biondi and Chanin used. Although it seems unlikely that this ion is He_2^+, the actual identity is quite uncertain. The set of data displayed in Fig. 2 was chosen to show this "third ion." In general, conditions were chosen so that it was not present. Lack of identification of this ion has no bearing on the measurements of either the mobilities or the reaction rates of the other ions.

The range of pressures of helium which could be used with this apparatus was about 2–22 Torr. Over this entire pressure range, He_2^+ was more abundant than He^+. At the upper end of this range the only ion present was He_2^+. At the lower end, enough He^+ could be introduced into the drift space to permit observation of the effect of attachment in flight. While the mobility determinations could be made using a rather crude analysis, confidence in the attachment frequency determination required a detailed investigation.

About 300 sets of data were recorded; however, most of these were not analyzed in the detail described in the previous sections. Most of the data were used to study qualitatively the behavior of the apparatus and the adequacy of Eqs. (10) and (11). At the higher pressures, 10–22 Torr, only He_2^+ was present. Furthermore, the range of E/p_0 available at these pressures was so low that the mobility was independent of E/p_0. Extensive tests were made to demonstrate that the mobility was independent of various parameters such as applied field, pulse widths, age of ions, power to the discharge, etc. All the mobility determinations were consistent with those displayed in Fig. 3. The best values for the extrapolations to zero field are He^+—10.4; He_2^+—16.7; third ion —19.6.

For most of the data the fit of Eqs. (10) and (11) was not very good if the diffusion coefficients were determined from (1). The difficulty was traced to the effects of space charge. Securing a comfortable signal-to-noise ratio had meant allowing the densities of the ions to get too large. For a symmetrical distribution of charge, the field at the center is zero. The first-order effect of the space charge is to broaden the distribution. Because the environment in the drift space was not symmetrical, the drift velocity might be expected to depend weakly on the ion density. The effects of space charge were synthesized in Eqs. (10) and (11) by using values of the diffusion coefficients which were larger than those given by Eq. (1). With this means of broadening, the equations could be fitted to the data even when space charge had a noticeable effect. By including the diffusion coefficient as one of the independent variables in minimizing ϵ it was possible to determine an "apparent" diffusion coefficient D^*. The data displayed in Fig. 2 have this defect.

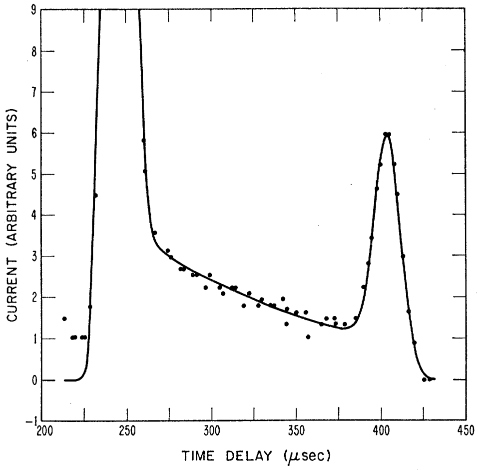

FIG. 4. Sample plot of the current to the ion collector versus the time delay between the gating pulses. Gas conditions: $p_0=4.99$ Torr; $E/p_0=3.15$ V/cm-Torr; $T=304°K$. Experimental data are shown in dots. The continuous curve was calculated to fit the data using $K_1=10.43$, $K_2=17.22$ cm²/V-sec, $\beta=1.08\times10^{-31}$ cm⁶/sec.

Extensive studies were made of D^* as a function of the number of ions in the cloud when only one species of ion was present. For all of these data the mobility was constant. The extrapolation of D^* to zero ion density is in good agreement with the value computed from (1). This agreement supports the conclusion that the approximations made in deriving (10) and (11) were valid.

Figure 4 shows a sample set of data as points and the function (8) which provided the best fit as the continuous curve. The number of He^+ ions was kept low by opening the first shutter for only a short time. This means of attenuation did not reduce the number of the faster He_2^+ ions nearly as much; hence, the peak in the current due to He_2^+ from the discharge is well off the graph. In the determination of the attachment frequency α, the current due to He_2^+ from the discharge was of no interest, the data being fitted solely to provide a basis for distinguishing the current of He_2^+ produced by a reaction of He^+. For the data in Fig. 4 it would have been adequate to discount completely the data points at values of t_i which gave a significant amount of He_2^+ from the discharge. At higher pressures application of such a data selection technique was not so clear-cut and might have influenced the results. The He_2^+ formed in the ion source was probably produced by the Hornbeck-Molnar[10] process, a two-body reaction involving a highly

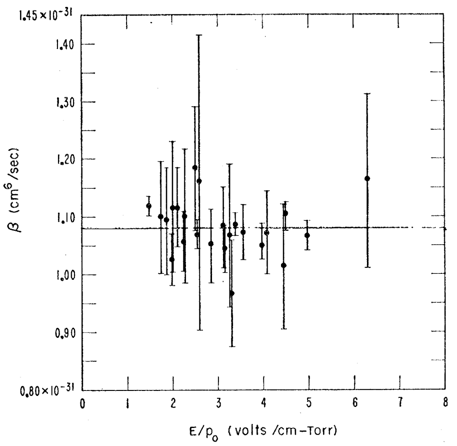

FIG. 5. Graph of the reaction rate coefficient for the attachment of He^+ in helium gas. The rate coefficient is plotted versus the ratio of electric field to gas density. The horizontal line corresponds to $\beta=1.08\times10^{-31}$ cm^6/sec.

excited atom. This process is not possible outside the discharge because of the absence of excited atoms.

The analysis sequence which was used with all the data was: (a) make a first approximation fit to that part of the scan $[q_e(t_i)]$ which only involved He^+ and He_2^+ produced from it by a reaction; (b) the results of this computation were subtracted from all the data leaving, to a moderate approximation, only the He_2^+ produced in the discharge; (c) fit Eq. (8) to the adjusted data with $N_1=0$, this time allowing the diffusion coefficient to vary [note that in the derivation of Eq. (8), N_1 is the assumed number of He^+ ions transmitted by the first shutter]; (d) subtract the last results from the original data and fit Eq. (8) to the readjusted data using $N_2=0$. Errors due to space charge were minimized by choosing a particular value for N_1, N_1^*, which corresponded to a small enough number of ions that increasing D over its normal value did not significantly reduce ϵ. Data scans taken with enough ions to cause N_1 to exceed N_1^* were rejected.

Having chosen a data analysis routine, the old data were set aside, new scans were taken with conditions carefully chosen to yield values of α. The drift velocity had to be chosen so that the fraction of He^+ ions which attached in flight was neither too high nor too low. The only bases used for rejecting the new data were: (1) The best value for N_1 exceeded the preset value N_1^* above which space charge effects were judged to be serious; or (2) the signal-to-noise ratio was so low that ϵ did not depend on α strongly enough to make the minimization meaningful. The acceptable range of N_1 was a factor of five. The results of this analysis are shown in Fig. 5, where the rate coefficient, β is plotted versus E/p_0.

Some of the data scans were much more useful in determining the attachment frequency than others. A measure of the statistical uncertainties could have been obtained by repeating the same data many times; however, this was judged to be not worthwhile. In order to provide a semiquantitative basis for comparing the relative uncertainties, each of the determinations was given a weight factor which was proportional to the number of He^+ ions present initially. Since the determination was imprecise if the reaction was either too strong or too weak, a further weight factor was applied to account for this effect. The weight factor was proportional to αt_1 if $\alpha t_1<1$ and proportional to $1/\alpha t_1$ if $\alpha t_1>1$, where t_1 is the time-of-flight of He^+. The error bars of Fig. 5 are inversely proportional to the weight factors. The average of all the data in Fig. 5 is 1.08×10^{-31} cm^6/sec, and the standard deviation is 0.06×10^{31}. Using the weight factors changes the average by less than 1% and reduces the standard deviation to 0.05×10^{-31}.

Figure 6 shows the rate coefficients β plotted as a function of p_0. At each of the pressures an average was computed using the weight factors described above. The error bars are an indication of the relative weights of the averages. The solid horizontal lines of Figs. 5 and 6 indicate $\beta=1.08\times10^{-31}$ cm^6/sec.

VII. THEORETICAL DISCUSSION

Using a general relation which is widely quoted,[5,12,14,23] the mobility of ions in a gas can be expressed in terms of an average diffusion cross section $\langle Q_d\rangle$ (in units of πa_0^2) as

$$K=\frac{2.71\times10^{-8}}{\langle Q_d\rangle}\left(\frac{1}{\mu T}\right)^{1/2}. \tag{12}$$

Q_d is averaged according to

$$\langle Q_d\rangle=\int_0^\infty v^5 Q_d(v)\exp\left(-\frac{\mu v^2}{2kT}\right)dv\,, \tag{13}$$

where v is the relative velocity of the collision and μ is the reduced mass. Q_d is given by Dalgarno[15] and others in terms of the classical differential cross section, and also in terms of the quantum-mechanical partial-wave phase shifts. The value of $\langle Q_d\rangle$ for He^+ in He (corresponding to $K=10.4$ at 300°K) is 82.6.

The drift velocity is determined as a balance between the acceleration of the charged particle by the electric field and a "drag" due to scattering collisions with the gas atoms. Charge transfer causes a scattering of the charged particle even if the relative motion of the nuclei is unchanged. In addition, there is some scattering due to forces which alter the relative motion of the colliding atoms. Lynn and Moiseiwitsch[14] show that the actual scattering contributes relatively little to $\langle Q_d\rangle$ for He^+ in He, except at low temperatures.

To a fairly good approximation, Q_d is expressed in terms of the charge transfer cross section by

$$Q_d=2Q_t. \tag{14}$$

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[23] T. Holstein, J. Phys. Chem. **56**, 832 (1952).

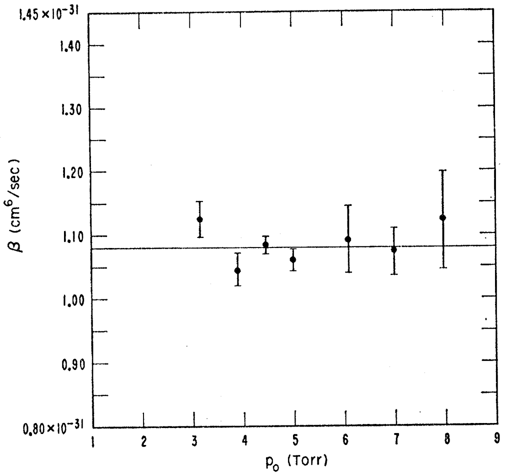

FIG. 6. Graph of the reaction rate coefficient for the attachment of He^+ in helium gas. The rate coefficient is plotted versus the gas density, p_0. The horizontal line corresponds to $\beta=1.08\times10^{-31}$ cm^6/sec.

The charge-transfer cross section is known to be insensitive to energy. Equation (14) yields a value $41\pi a_0^2$. Rapp and Francis[24] have recently surveyed the literature on charge transfer in He, and provide a graph which shows that the result above ($41\pi a_0^2$) compares favorably with the high-energy data using theoretical extrapolations.

The theoretical situation is not as clear for the mobility of He_2^+. For spherically symmetric ions (without resonance charge transfer), the scattering can almost all be accounted for by using only the polarization interaction. Computing the mobility with the polarization model requires only a knowledge of the bulk dielectric coefficient for the gas and the reduced mass of the colliding pair. For He_2^+ in helium, the mobility, according to this model, would be 18.6. The effect of an additional short-range repulsive interaction has been investigated for a few simple models.[4,25] The first-order effect of adding a repulsive term is to increase the mobility. At 300°K, the experimental mobilities of atomic ions in He are found to be somewhat greater than the mobilities calculated using only the polarization attraction. For instance, for Li^+ the ratio is 1.26 and for Hg^+, it is 1.21. For other atomic ions, the ratio is similar although generally higher. (See Dalgarno, McDowell, and Williams[26] for a review.) For He_2^+ the ratio is 0.9.

A spherical model including short-range repulsion can give a mobility less than 18.6, but only by also having the mobility be a decreasing function of temperature. Such a temperature dependence is almost certain to result in a similar E/p_0 dependence (such as that observed for He^+). However, the measured mobility of He_2^+ increases with E/p_0.

The fact that He_2^+ is a molecule with internal degrees of freedom makes Eq. (12) technically inapplicable. However, in a similar kinetic theory treatment of viscosity, the molecular structure does not have a large effect. Furthermore, the forces which scatter the ions are longer range than the forces between neutral particles. Using Eq. (12), a mobility of He_2^+ of 16.7 implies that $Q_d=44.5(\pi a_0^2)$. Such a large cross section implies that a large proportion of the scattering is with impact parameters larger than the separation of the nuclei in He_2^+. In this circumstance it is difficult to see how the molecular structure could have a substantial effect on the mobility. Thus, the experimental value for the mobility of He_2^+ has not been given an adequate theoretical treatment.

Bates[27] reported calculating the rate coefficient for the three-body attachment of He^+ using the Thomson recombination theory.[28] The result was reported by giving the lifetime of He^+ at 25 Torr as 10^{-5} sec. This corresponds to $\beta=1.6\times10^{-31}$ cm^6/sec which compares well with the experimental value of 1.08×10^{-31} cm^6/sec.

The details of Bates' calculation were not reported and are not clear. A plausible argument can be made relating the rate coefficient to the charge transfer cross section. The argument may not be independent of that due to Bates; however, it gives a useful insight into the mechanism of the reaction.

The usual treatment of charge transfer at moderate energies is to regard the nuclear motion as classical and to compute the probability of charge transfer as a function of impact parameter. The probability is small for large impact parameter rising to unity as the impact parameter is reduced. Further reduction of the impact parameter causes the probability to oscillate between unity and zero. The overall effect is approximated by considering the charge-transfer probability to be one-half for impact parameters less than b_c and zero for larger values. The charge transfer cross section is given by

$$Q_t=(\pi/2)b_c^2. \tag{15}$$

Using Eqs. (15), (14), and (12), the mobility can be expressed in terms of b_c. The value of b_c required to give a mobility of 10.4 for He^+ in He is $9.1a_0$. Collisions between He^+ ions and He atoms can be described by an electronic wave function which is a function of the internuclear separation and implicitly a function of time. The colliding system may be considered as two He^+ ions plus an extra electron. The eigenstates of such a system are the $^2\Sigma_g{}^+$ and $^2\Sigma_u{}^+$ states of He_2^+. At large values of the internuclear separation, the two molecular states are degenerate, and a superposition can be formed which describes a positive ion and a neutral helium

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[24] Donald Rapp and W. E. Francis, J. Chem. Phys. **37**, 2631 (1962).

[25] P. Langevin, Ann. Chim. Phys. **8**, 245 (1905).

[26] A. Dalgarno, M. R. C. McDowell, and A. Williams, Phil. Trans. Roy. Soc. (London) **A250**, 411 (1958).

[27] D. R. Bates, Phys. Rev. **77**, 718 (1950).

[28] J. J. Thomson, Phil. Mag. **47**, 337 (1924).

atom. As the nuclei approach each other slowly, the two molecular states cease to be degenerate. The wave function for the system is still a superposition of the molecular states; however, the relative phase becomes a function of time. The phenomenon can be qualitatively described as the transfer of the electron from one ion to the other and back again each time the relative phase goes through 2π. As the internuclear separation approaches b_c, the frequency of exchange becomes high enough to permit the system to be legitimately described as a molecular ion He_2^{+*}. Such a molecule has only a transient existence since it is not in any sense bound, this fact being indicated by the asterisk.

The density of He atoms in the neighborhood of He^+ ions will be affected by the forces between them, and it may be higher or it may be smaller than the density in other places. However, the detailed effect of such forces are unknown. It seems reasonable as a first approximation to assume that the density is not affected by the forces, yielding

$$\mathfrak{N}=(4\pi/3)b_c^3 n\rho, \tag{16}$$

where $\mathfrak{N}$ is the number density of He_2^{+*}, and as above n and ρ are the densities of He and He^+. Alternatively, the density of He_2^{+*} could easily be estimated using the known collision frequency if the lifetime were known. In the absence of detailed calculations, such lifetimes cannot be estimated any more precisely than the density.

In the same sense that the system of a helium ion and a helium atom can be considered as He_2^{+*}, it is reasonable to consider two helium atoms and an ion to be He_3^{+*} if the nuclei happen to be close enough together. The He_2^{+*} molecules are being continually created and destroyed; hence, the collision frequency with atoms does not strictly obey the usual gas kinetic laws. However, the error introduced by this approximation is probably small. Assuming that the cross section is πb_c^2 for forming He_3^{+*} from a collision between He_2^{+*} and He, the rate of formation of He_3^{+*} is given by the expression

$$F=\frac{16}{\pi\sqrt{3}}Q_t^{5/2}\left(\frac{2kT}{m}\right)^{1/2}\rho n^2. \tag{17}$$

The He_3^{+*} presumably has no bound states, and in any case, the energy is positive. Dissociation will be (almost always) into either $He_3^{+*}\rightarrow He_2^{+*}+He$ or $He_3^{+*}\rightarrow He_2^{*}+He^+$. He_2^{+*} and He_2^{*} are molecules in the sense that the nuclei are separated by a distance less than b_c. The atom (ion) which leaves the complex first will, on the average, be the one whose relative energy is highest. If the energy of relative motion of the two remaining nuclei (He_2^{+*}) is sufficiently small, the molecular ion may be bound.

If s is the fraction of He_3^{+*} which decays into bound He_2^+, the three-body attachment coefficient is

$$\beta=\frac{16s}{\pi}Q_t^{5/2}\left(\frac{2kT}{3m}\right)^{1/2}, \tag{18}$$

where m is the atomic mass.

To obtain the experimental value for $\beta(1.08\times10^{-31})$, s must have a value of about 4. Values larger than unity are impossible, by definition, 0.2 to 0.6 being reasonable estimates. The reason for Eq. (18) underestimating the rate coefficient is probably the neglect of the effects of interatomic forces on the motions when the ions and atoms are close together. The parameter b_c is rather well defined by the mobility; however, any error is amplified since it enters Eq. (18) raised to the fifth power. The combined errors can be reasonably assumed to account for the underestimate. Regarding Eq. (18) as qualitatively correct, the weak temperature dependence supports the experimental deduction that the rate is insensitive to E/p_0.

VIII. ANALYSIS OF UNCERTAINTIES

The physical quantities measured which most directly affect the determination of the mobility and attachment frequency are: the spacings of the electrodes; the relative potentials of the electrodes; the time between the gating pulses; and the temperature and pressure of the gas. The estimated uncertainties in these measurements are: spacings ±0.05 cm; potentials ±0.1 V; time intervals ±0.1 μsec; temperature ±0.1°C; and pressure ±0.02 Torr. The current to the collector and the time interval between gating pulses were recorded by a digital recording system with a three-digit capacity. The quantization involved in the digital recording provided the principal uncertainties in the relative measurements of both time and current. The time measurements were calibrated using a quartz oscillator, and a correction was applied to the digital data. The residual round-off errors were random and were substantially reduced by averaging. Round-off errors in the current measurements were masked by noise in the photoelectric current which was produced by light from the discharge. The absolute calibration of current measurements was unimportant.

By using more ions, the effect of noise could be suppressed; however, the space charge introduced caused the analysis to be subject to doubt.

The mobility determinations were not sensitive to either the noise or the space charge. The largest uncertainty in the mobility determination came from the assumed value for the length of the drift space. Whereas the spacings of the electrodes could be measured quite accurately, the holes in the grids caused a breakdown of the model used in deriving Eqs. (10) and (11).

The uncertainty in the attachment frequency determinations is difficult to judge. All the parameters going into the calculations were known well enough to permit an uncertainty as low as 1%. Also, using the standard statistical analysis the probable error of the mean of the data is less than 1%. However, confidence in the answer is not that high. For each of the sets of data, the computations were redone with $\beta = 1.08\times10^{-31}$ cm^6/sec and the original values of the other parameters. In all cases, the computations fit the data well, showing that the variations are not due to large systematic effects. Small systematic effects could not be studied, however. Systematic errors due to space charge, improper accounting for the r and θ dependences of the ion densities, were not investigated well enough to permit the over-all uncertainty to be less than 5%. A more detailed study of systematic errors would permit the methods used here to yield reaction rates with higher precision, possibly as high as 1%.

More important than the uncertainties of measurement is the question of accuracy of the interpretation of the data. The plausible argument which Dalgarno applied to argon (partially reproduced above) would rule out the possibility that the ion of mobility 16.7 is He_2^+. This interpretation is also inconsistent with the interpretation Biondi and Chanin put on their data. The identification made here of the ion of mobility 16.7 is based on the observation that it is produced from He^+ by a reaction with the gas. The observed attachment frequency is quadratic in the gas pressure, and is consistent with previous measurements[11,21,29] and theoretical estimates of the attachment frequency of the reaction (2). Two other hypotheses present themselves. One is that reaction (2) is followed by a reaction of He_2^+ with the gas. If such a reaction occurs at all, it must be either much faster or much slower than (2) at pressures in the range 3–22 Torr. The other possibility is that an impurity in the gas was responsible for the observed disappearance of He^+, the most likely reaction being charge transfer. The rate of such a reaction would depend on the concentration of the impurity. The cataphoresis discharge is known to change the concentration of at least some impurities, and it is not unreasonable to suppose that it might change the concentration of all impurities. It seems unlikely that the relevant impurity concentration should be even consistent in the different samples of gas, and surely it would not be such as to give the observed quadratic variation of the attachment frequency with pressure.

Running the cataphoresis discharge caused the ion source to stop producing certain ions and to produce others more efficiently (those whose mobilities are reported above). One explanation would be to assume that the cataphoresis discharge was increasing the concentration of some of the impurities and therefore accelerating the conversion to impurity ions. Evidence that this was not the case was obtained by observing the relative abundances of the ions coming from the afterglow as a function of the time since the spark. In gas known to be impure, the concentration of He_2^+ was observed to decrease rapidly while the concentrations of the ions called impurities increased. Running the cataphoresis discharge slowed and eventually stopped this conversion.

IX. CONCLUSIONS

The mobilities of He^+ and He_2^+ in helium were found to be 10.40 ± 0.10 and 16.70 ± 0.17 cm^2/V-sec, respectively. The He_2^+ was observed to be produced from He^+ by a three body reaction with a rate coefficient of $1.08\pm0.5\times10^{-31}$ cm^6/sec. The mobility of He^+ and the rate coefficient are theoretically reasonable; however, the mobility of He_2^+ has not been explained theoretically.

ACKNOWLEDGMENTS

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[29] F. E. Niles and W. W. Robertson, J. Chem. Phys. 40, 3568 (1964).