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The Drift Velocities of Molecular and Atomic Ions in Helium, Neon, and Argon

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Drift velocity measurements as a function of E/p_0 , the ratio of field strength to normalized gas pressure, are presented for atomic and molecular ions of He, Ne, and A in their respective parent gases. Identification of the molecular ions is based upon the time resolution of the apparatus and the dependence of ion concentration on pressure, applied voltage, and gas purity. Extrapolation of the low field measurements to zero field yields mobility values for atomic ions, $\mu_0(\text{He}^+) = 10.8$ cm²/volt sec, $\mu_0(\text{Ne}^+) = 4.4$, and $\mu_0(\text{A}^+) = 1.63$ in good agreement with theory: Massey and Mohr compute $\mu_0(\text{He}^+) = 11$, and Holstein gives $\mu_0(\text{Ne}^+) = 4.1$ and $\mu_0(\text{A}^+) = 1.64$. Drift velocity data at low field for the molecular ions agree within experimental error with data of Tyndall and Powell (He), and Munson and Tyndall (Ne and A), which they assigned to atomic ions. A qualitative description in terms of ion-atom interaction forces is given for the observed field variation of the atomic ion drift velocities up to high E/p_0 .

THE drift velocity of positive ions and its variation with the electric field are fundamental in any discussion of a gaseous discharge in which positive ions are an important carrier of current. From the viewpoint of more fundamental theory, drift velocity measurements provide information on the interaction forces between an ion and an atom as well as on the kinetic theory of ion motion in a gas at high fields, where the velocity distribution of the ions is not Maxwellian.

In this paper measurements are presented on the drift velocity of both molecular and atomic ions of helium, neon, and argon in their respective parent gases. Arguments for the identification of the ions are given, and it is shown that, as a result of this identification, good agreement results between theory and experiment for the drift velocities of both species of ions in all three gases. It is concluded that in some cases earlier workers incorrectly identified molecular ions as atomic ions. A mechanism of formation of the molecular ions that is consistent with the experiment is discussed briefly, as is the drift velocity variation of the atomic ions at high fields.

IDENTIFICATION OF MOLECULAR AND ATOMIC IONS

A method has been described¹ for measuring the drift velocity of positive ions in the parent gas by direct

¹ J. A. Hornbeck, Phys. Rev. **83**, 374 (1951).

observation of the ion transit time between parallel plate electrodes in a uniform field. The experiment consists of measuring the time at which a sharp break occurs in the transient current following the release of a short (0.1 μ sec) pulse of photoelectrons from the cathode of a Townsend discharge tube. An experimental transient current pattern, reproduced from a photograph of a cathode-ray-tube trace, is shown in Fig. 1. This pattern is typical of all three noble gases for $E/p > 50$ volts/cm-mm Hg, where E is the electric field strength and p is the gas pressure.

If two species of ions are formed during the photoelectric pulse, two current breaks should occur. These will be resolved if the transit times for the two ions differ by more than about ten percent. Figure 2 is a transient current pattern in argon at lower E/p showing the presence of two different ions. Similar patterns are obtained in helium and neon. In each case, the ion that is found only at low E/p has the shorter transit time, i.e., it gives the first break in Fig. 2.

We identify the slow ion as the ordinary atomic ion of the parent gas (He^+ , Ne^+ , A^+) because it is easily formed by electron impact over a wide range of E/p . Formation of He^{++} , Ne^{++} , and A^{++} can be ruled out since both breaks are observed when the total voltage across the tube is less than the appearance potentials for these ions.

This leaves two reasonable hypotheses as to the

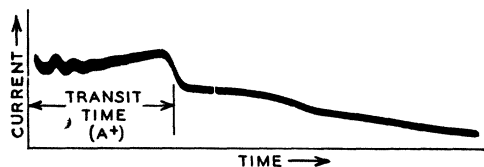


FIG. 1. Oscillogram of transient current in argon. The sharp drop in current occurs at the time for one ion transit between the parallel plate electrodes. This and similar patterns in helium and neon are found for $E/p > 50$ volts/cm-mm Hg.

identity of the fast ions: (1) impurity ions, and (2) molecular ions (He_2^+ , Ne_2^+ , and A_2^+). Low E/p should favor ionization of an impurity atom relative to the main gas constituent, in general, because of the lower ionization potential of most non-rare-gas atoms. Both low E/p and high pressure favor the production of molecular ions in the formation process discussed below. The choice between these hypotheses must be made on the basis of experimental evidence.

The evidence at hand is the following: (1) The double break effect is observed to be reproducible in magnitude with different gas samples and different vacuum procedures. (2) Samples of the gases used, which were purchased as spectroscopically pure, have been sealed off from the experimental tube and subjected to mass spectrometer analysis. No impurities have been detected by this instrument, which had a sensitivity limit of 0.005 percent. (3) Flashing additional Ba-Mg getters in a tube filled with gas that had been sampled and analyzed in no way affected the observed pattern. (4) The residual gas pressure after exhaust of the tube and prior to the introduction of the gas was probably less than the ionization gauge reading of 2×10^{-8} mm Hg. This evidence suggested strongly that impurities in the gas could not account logically for the presence of the fast ion. We conclude that molecular ions, which are known to exist,² are formed quite easily at low E/p and moderate pressure.

The sharpness of the current break associated with the molecular ions restricts severely the number of

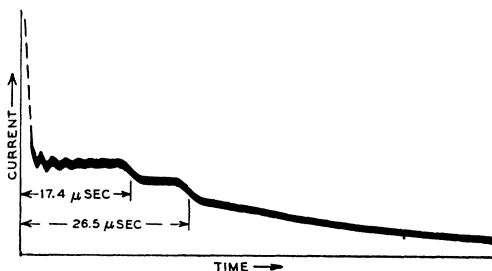
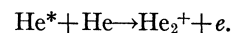


FIG. 2. Oscillogram of transient current in argon at low E/p ($p_0 = 5.13$ mm Hg, $E/p_0 = 36.6$ volts/cm-mm Hg). The current breaks at $17.4 \mu\text{sec}$ and $26.5 \mu\text{sec}$ indicate the presence of two ions of different transit times. The broken line at the start of the trace indicates the current due to the short photopulse that initiated the transient current. Similar oscillograms with two current breaks are found in helium and neon at low E/p .

² O. Tüxen, Z. Physik **103**, 463 (1936).

mechanisms one might advance to account for their formation. As shown in Fig. 2, the time width of the two breaks is about the same, and this has been ascribed¹ to diffusion. From the width of the current break we conclude that the molecular ions are formed within about one microsecond, or less, after the initial photopulse. This rules out a process such as a three-body collision³ between an atomic ion and two neutral atoms forming a molecular ion and, in general, a higher speed neutral atom; this process would smear out both current breaks, and also a longer time would be required before a three-body collision is very likely. Because of the time restrictions, the only reasonable process appears to be a collision between a neutral atom and an atom He^* raised to a high-lying excited state (by electron impact during the photopulse) before the excited atom decays; for example,



Here e stands for the liberated electron. The excited state involved cannot be a metastable state, as proposed by Arnot and M'Ewen⁴ in the case of helium, because of the known long lifetimes of metastable atoms in the rare gases. The lifetimes of the states in question, therefore, are about 10^{-7} sec or less. Thus on the time scale of this experiment, the molecular ions observed are probably formed as fast as the atomic ions. Mass spectrometer studies that support the formation process discussed above are presented in the following article in this issue.

GENERAL DRIFT VELOCITY MEASUREMENTS

Experimental data on the drift velocity of atomic ions are given in Fig. 3. Here on a log-log scale we plot the drift velocity v as a function of E/p_0 . The normalized pressure is defined as $p_0 = 273p/T$, where p is the measured gas pressure and T is gas temperature, in our case $\approx 300^\circ\text{K}$. Three regions are readily identified in Fig. 3. At high E/p_0 , v approaches tangency to a straight line of slope $\frac{1}{2}$ indicating $v \propto (E/p_0)^{\frac{1}{2}}$. At low E/p_0 , v approaches tangency to a line of slope 1, indicating $v \propto E/p_0$. A transition region at intermediate E/p_0 connects the high and low field regions.

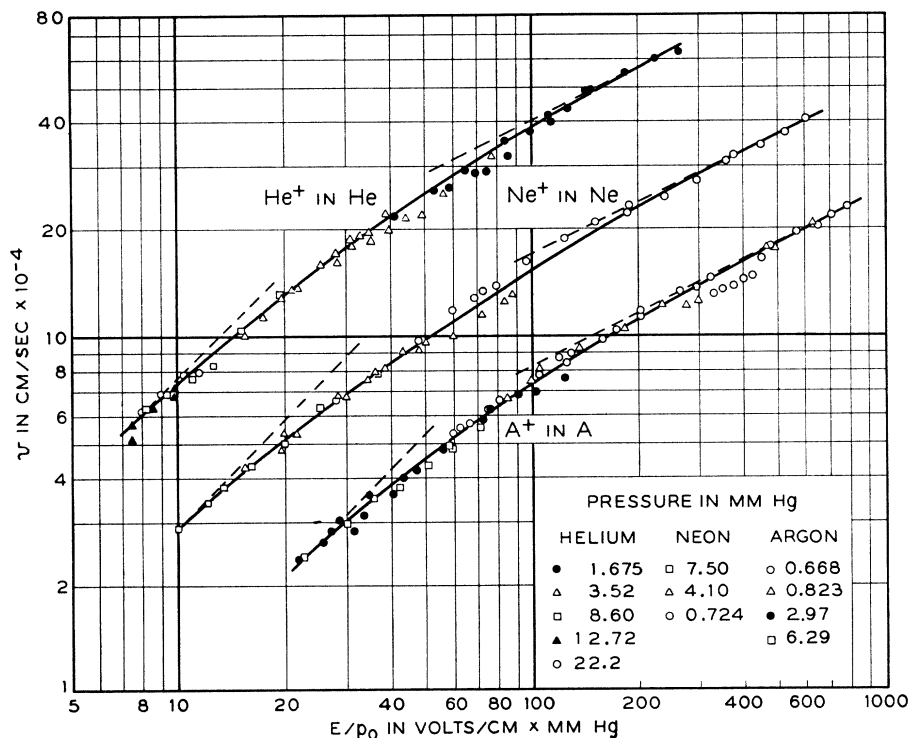
A qualitative explanation of these regions can be given in terms of the ion-atom interaction forces and the velocity distribution of the ions, factors that we shall now consider in a short digression. The major interaction forces⁵ are: (a) gas kinetic repulsion, (b) polarization attraction, and (c) symmetry forces. We shall assume that gas kinetic repulsion can be accounted for by a model in which the ions and atoms are hard elastic spheres whose closest distance of approach is fixed by the sum of the radii of the colliding particles.

³ Molecular ions can probably be produced in this way at higher gas pressure.

⁴ F. L. Arnot and M. B. M'Ewen, Proc. Roy. Soc. (London) **A171**, 106 (1939).

⁵ Van der Waals attraction can probably be ignored here.

FIG. 3. The drift velocity of atomic ions in helium, neon, and argon as a function of E/p_0 . The broken lines at the left of each experimental curve have slope = 1, whereas the broken lines at the right have slope = $\frac{1}{2}$.



Polarization attraction arises because an ion induces a dipole moment on a neighboring atom and thus attracts it. The magnitude of this force is directly proportional to the polarizability of the gas and inversely proportional to the fifth power of the separation of the particles. Massey and Mohr⁶ have pointed out that symmetry effects, which arise on account of the identity of the cores of the atomic ion and gas atom, include what we may call resonance attraction and resonance repulsion together with charge exchange, i.e., the shuttling of an electron back and forth between the ion and atom during a collision. For helium they show that the symmetry forces vary rapidly in a short range and therefore are somewhat similar to gas kinetic repulsion although of longer range.

The elastic sphere model gives a collision cross section that is independent of the velocity of approach of the colliding particles and also a constant mean free path between collisions. The cross section for polarization attraction⁷ is inversely proportional to the velocity of approach, which gives a constant mean free time between ion-atom collisions. As a whole, symmetry forces give a cross section that varies slowly with the relative velocity of approach of the ion and atom. No calculation of this variation in cross section is available in the literature. To the extent that this variation is small, a hard sphere model with its accompanying constant

mean free path may be assumed. The evidence from this experiment supports making this assumption, as we shall point out.

The velocity distribution function of the ions is Maxwellian at very low fields because of sufficient energy interchange with gas atoms. At very high field strengths, where thermal energy is negligible compared with the energy derived from the field, the distribution function is known, through the work of Wannier,⁸ only in the case of constant mean free time. Without knowing the distribution function explicitly, velocity averages have, however, also been computed by Wannier for the high field case in which the mean free path is constant. He finds in this case $v \propto (E/p_0)^{1/2}$, and he finds $v \propto E/p_0$ for the constant mean free time case. This last result is independent of the velocity distribution, i.e., applies regardless of the magnitude of E/p_0 . We also know⁹ that at very low fields the elastic sphere model by itself gives $v \propto E/p_0$. We are now ready to interpret the three regions in Fig. 3.

In the limit of high field and thus high velocity of approach, the cross section associated with polarization attraction becomes very small. The drift velocity should vary, therefore, as $(E/p_0)^{1/2}$ to the extent that symmetry effects and gas kinetic repulsion approximate the elastic sphere model. Experimentally we find no reason to dispute the hard sphere model although we recognize the limited range of the experiment. Theory aids us in estimating the relative contributions of gas

⁶ H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A144, 188 (1934).

⁷ The definition of this cross section requires especial care. It can be defined to a good approximation according to G. H. Wannier, private communication.

⁸ G. H. Wannier, Phys. Rev. 83, 281 (1951).

⁹ See H. R. Hassé, Phil. Mag. 1, 139 (1926).

kinetic repulsion and symmetry forces to the hard sphere cross section. Wannier⁸ has computed for the hard sphere model $v = 1.147(a\lambda)^{\frac{1}{2}}$ at high fields. Here a is the acceleration of the ion due to the electric field, and λ is the mean free path, i.e., $\lambda = 1/N\sigma_i$ where N is the gas number density and σ_i the hard sphere cross section. We have applied¹⁰ this formula to the data, Fig. 3, and obtained the values of σ_i given in Table I. For the gas kinetic cross section we may use published values of the viscosity cross section, σ_a , listed also in Table I. It is apparent that we should associate the hard sphere cross sections σ_i primarily with the symmetry forces.¹¹

As E/p_0 is decreased from the high field region, the situation changes in the following way: (1) the velocity distribution changes from a true high field distribution to a mixture of high field and temperature dependent distributions; (2) the polarization force becomes relatively more important, and, to the extent that this occurs, there results a distribution in which neither the mean free path nor the mean free time between collisions is constant; (3) and the cross section associated with symmetry effects may vary slowly, perhaps not significantly. These changes characterize the inter-

TABLE I. Hard sphere cross section σ_i and viscosity cross section σ_a .

| | $\sigma_i \times 10^{18}$ cm ² | $\sigma_a \times 10^{18}$ cm ² |
|--------|---|---|
| Helium | 54.3 | 14.9 |
| Neon | 65.2 | 21.0 |
| Argon | 134 | 41.7 |

mediate region of Fig. 3. Of the three effects, the velocity distribution change appears to be the most important because even in the low field case, as we shall see, the hard sphere cross section seems to be the major factor in determining the drift velocity.

As E/p_0 is decreased still further, the above mentioned changes continue, and we approach the low field region. Here the energy contributed from the field is small (and this need not be very small) compared with thermal energy, the velocity distribution becomes Maxwellian, and v must become proportional to E/p_0 because the field is so small. It was mentioned above that if scattering in this region were caused primarily by the polarization force, the mobility would be constant (or nearly so) for this reason alone, regardless of the field strength. The evidence in the following section on low field mobility suggests that this effect is not very important at room temperature. Again, to the extent

that polarization is important there will be a mixed constant mean free time and constant mean free path situation at low field.

Having explained qualitatively the E/p_0 variation of the atomic ion drift velocity, we now consider the low field variation separately.

DRIFT VELOCITY MEASUREMENTS AT LOW E/p_0

Experimental data on the drift velocity of atomic and molecular ions (in the parent gases) are given in Fig. 4 for the lowest range of E/p_0 reached in this experiment. The ordinate μ is the mobility, defined as the ratio of the drift velocity to the electric field at standard gas density. The experimental measurements of Tyndall and Powell¹² (helium) and Munson and Tyndall¹³ (neon and argon), assigned by them to the respective atomic ions, are shown for comparison. Also included in the figure are the low field (essentially zero-field) theoretical values^{6,14} for μ , which are based upon calculations that include charge exchange and the anomalous resonance interactions characteristic of the scattering of an atomic ion in the parent gas.

Two conclusions appear to be warranted from the data presented in Fig. 4. First, the measurements by the pulse technique on the atomic ions at low E/p_0 in each case are in agreement with the theoretically predicted "zero-field" mobility, μ_0 : extrapolation of the experimental curves to $E/p_0 = 0$ yields, $\mu_0(\text{He}^+) = 10.8$ cm²/volt-sec, $\mu_0(\text{Ne}^+) = 4.4$, and $\mu_0(\text{A}^+) = 1.63$, whereas theory predicts $\mu_0^6(\text{He}^+) = 11$, $\mu_0^{14}(\text{Ne}^+) = 4.1$, and $\mu_0^{14}(\text{A}^+) = 1.64$. Second, the measurements by the pulse technique on the molecular ions agree within experimental error with the measurements of Tyndall *et al.*, which they ascribed (quite understandably) to the atomic ions of the parent gases. Thus the long-standing discrepancy between theory and experiment as to the zero-field mobility of He^+ in helium apparently is resolved in accord with the suggestion of Meyerott¹⁵ that Tyndall and Powell incorrectly identified the ion measured in their apparatus. It is significant that reproducible results on the mobilities of ions in the parent rare gases are now being obtained; for not only the molecular ion measurements just mentioned, but also other measurements¹⁶ on $\mu_0(\text{He}^+)$ agree within experimental error with the data in Fig. 3.

In addition to the experimental error in measuring μ , another error arises in the predicted values of μ_0 from the present measurements because the correct procedure for extrapolating the data to zero field is not known. Some confidence in the simple method used

¹⁰ J. A. Hornbeck and G. H. Wannier, Phys. Rev. **82**, 458 (1951).

¹¹ This treatment of the high field case is somewhat similar to that of L. Sena, J. Phys. (U.S.S.R.) **10**, 179 (1946) because the mean free path is assumed to be (approximately) constant. Attributing the constant mean free path to charge exchange alone, as Sena did, is incorrect in principle. It leads to obvious mistakes in the conclusion one reaches regarding the velocity distribution of the ions, and it leads to a predicted collision cross section that is too small, although of the right order of magnitude.

¹² A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) **A134**, 125 (1931).

¹³ R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) **A177**, 187 (1940).

¹⁴ T. Holstein, private communication.

¹⁵ R. Meyerott, Phys. Rev. **70**, 671 (1946).

¹⁶ M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949). The identity of the ions in this experiment has not been established completely, however.

here can be obtained from reasoning based upon the Langevin mobility formula and a knowledge of the interaction forces between an ion and an atom. Because the Langevin formula will be of general use in our discussion, the assumptions behind it will be stated.

In the Langevin theory of ionic mobility it is assumed (1) that the ions are hard, elastic spheres moving in a polarizable gas comprised of elastic spheres; and (2) that the velocity distribution function of both ions and gas atoms is Maxwellian and characterized by the gas temperature. In this model the interaction forces are polarization attraction and gas kinetic repulsion. For a given gas density and at low applied field (because of the assumption regarding the velocity distribution of the ions), the mobility of an ion in a gas depends, then, only upon the polarizability of the gas, the hard sphere collision cross section, and the gas temperature. We are not restricted, however, to interpreting the hard sphere cross section as originating from gas kinetic repulsion; it cannot be smaller than the hard sphere cross section associated with symmetry effects, which we derived from the high field data. It is this latter cross section we shall interpret as the repulsion cross section in the Langevin theory and see what information can be obtained.

According to Langevin's theory, one limiting value of the mobility, dependent only on the repulsion cross section, derives from the case in which polarization attraction is negligible compared with the repulsion cross section. As polarization becomes more important relatively, the mobility increases from this limiting value and passes through a maximum somewhat before the other limit is reached of a repulsion cross section negligible compared with the polarization effect. Substitution of the hard sphere cross sections, Table I, and published values of the polarizability of the gases in the Langevin formula yields, in Hassé's⁹ notation,¹⁷ $A\lambda$ values of about 0.7 for the three gases. This indicates that the atomic ion mobilities do not depend greatly upon the polarization force because the limiting values of $A\lambda$ are 0.75 for the case of negligible polarization effect and 0 for the case of negligible hard sphere scattering. The theory, in fact, predicts fairly satisfactorily the low field mobilities of the atomic ions. It gives $\mu_0(\text{He}^+) = 13.4$, $\mu_0(\text{Ne}^+) = 4.85$, and $\mu_0(\text{A}^+) = 1.67$. We conclude, therefore, that our interpretation of the symmetry forces as a hard sphere cross section is at least semiquantitative.

The results of the previous paragraph give us some confidence that the extrapolation of our data to zero field is not made through a maximum in the μ vs E/p_0 curve, which is found experimentally on occasion.¹⁸ On the basis of the Langevin theory such a maximum could exist at room temperature if, in decreasing E/p_0 at low field towards the region where μ is independent of E/p_0 ,

the major effect was to increase the predominance of the polarization scattering through lowering the mean velocity of approach of the particles, without altering much the velocity distribution of the ions. The result $A\lambda = 0.7$ which we obtained for the atomic ions indicates that at room temperature and essentially zero field the ions are in the region where hard sphere scattering is predominant, in fact sufficiently far from the maximum mentioned in the preceding paragraph that we need not worry about the extrapolation. We expect, then, as we extrapolate towards zero field that the mobility rises and becomes constant when thermal

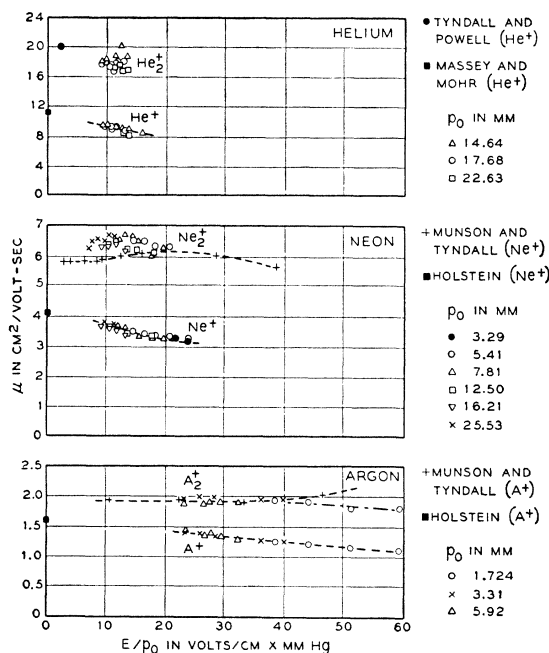


FIG. 4. The mobility at standard gas density, μ , of atomic and molecular ions in helium, neon, and argon as a function of E/p_0 . The data shown were taken from only those oscillograms like Fig. 2 in which two current breaks were observed. This restricts the range of μ for the atomic ions in this figure to that in which molecular ion data could be obtained. Note that the drift velocity data, Fig. 3, could be converted to mobilities and used to continue the above atomic ion data to higher E/p_0 . Theoretical calculations and experimental data of other investigators are included for comparison.

energy predominates sufficiently over the energy acquired from the field.

It is pertinent that energy arguments alone suggest that at the lowest E/p_0 obtained experimentally we are very close to a true measurement of μ_0 because the energy of field origin is small. The recent theory of Wannier⁸ gives for the total mean energy of an ion in a gas whose temperature is T :

$$\text{Total energy} = mv^2 + \frac{3}{2}kT.$$

Here m is the mass of the ion and v its drift velocity. In helium, at $E/p_0 = 8$ volts/cm-mm Hg the "field" energy is already smaller than thermal energy since the field contributes about 3×10^{-14} erg while at room

¹⁷ The parameter λ has no connection with any mean free path.

¹⁸ See L. B. Loeb, *Fundamental Processes of Electrical Discharge in Gases* (John Wiley & Sons, Inc., New York, 1939), page 76.

temperature $\frac{3}{2}kT \simeq 6 \times 10^{-14}$ erg. All of the above considerations imply that the error introduced by the extrapolation may well be less than ten percent.

In contrast to the atomic ions, the molecular ion mobility results indicate that at room temperature polarization attraction dominates strongly over the hard sphere cross section, which we now interpret as arising from gas kinetic repulsion because of the absence of symmetry effects in this case. The Langevin formula in the polarization limit predicts $\mu_0(\text{He}_2^+) = 20$, $\mu_0(\text{Ne}_2^+) = 6.0$, and $\mu_0(\text{A}_2^+) = 2.1$. These values are so close to the experimental results, Fig. 4, *viz.*, $\mu_0(\text{He}_2^+) = 19$, $\mu_0(\text{Ne}_2^+) = 5.85$, and $\mu_0(\text{A}_2^+) = 1.9$, that the theory and experiment cannot be used reliably to obtain the values of the hard sphere cross sections of the molecular ion-atom collisions.

TEMPERATURE EFFECTS

It is apparent from this discussion that a further variation of mobility is to be expected if the temperature of the gas is decreased under low field conditions. This will further decrease the relative velocity of approach and make polarization attraction predominate for any ion at sufficiently low temperature. Thus, with decreasing temperature, the atomic ion mobility should increase, perhaps pass through a maximum at a low temperature, and approach the value one computes for the polarization force. These values are 22 for He^+ , 7.0 for Ne^+ , and 2.4 for A^+ .

We expect the molecular ion mobilities to behave quite differently as a function of temperature because the symmetry forces do not exist between a molecular ion and a gas atom, just as they are not present for alkali ions in the rare gases. With polarization attrac-

tion already predominant at room temperature, decreasing the temperature accentuates the predominance but there is not so far to go to reach the limit in which polarization alone is significant. Thus as the temperature is lowered, the atomic ion mobility should rise and eventually become larger¹⁹ than the molecular ion mobility, the difference in limiting values resulting only from the mass difference of the two ions. In each gas the mass factor amounts to $(3/2)^{\frac{1}{2}}$, in accord with the limiting values quoted above.

Additional measurements of ionic mobilities at lower temperature are needed to settle the accuracy of these conjectures. Temperature measurements²⁰ with alkali ions in the noble gases indicate that the physical interpretation may not be so simple as that given here. On the other hand, measurements at Bristol²¹ on the temperature dependence for the helium ion we believe to be He_2^+ , but identified as He^+ by Tyndall, show just the type of behavior one predicts for molecular ions by the arguments above.

ACKNOWLEDGMENT

The advice and support of my colleagues has proved invaluable in this investigation, particularly P. W. Anderson, W. C. Herring, J. B. Johnson, J. P. Molnar, and A. H. White. The explanation presented here of the variation of drift velocity with electric field has evolved primarily from numerous discussions with G. H. Wannier.

¹⁹ G. H. Wannier has pointed this out in a private communication.

²⁰ K. Hoselitz, Proc. Roy. Soc. (London), **A177**, 200 (1940).

²¹ A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, London, 1938), page 60.