Mobilities and Reactions of Ions in Argon*

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(Received 27 January 1967)

The development of an ion-drift cell using mass analysis has enabled the measurement of mobility and identification of six ions in argon. Reduced mobilities of 1.40, 1.95, and 2.40 have been obtained for Ar^+, Ar_2^+, and Ar^{++} in the pure gas, allowing positive identification of ions observed in early experiments by Hornbeck, Biondi, and Beaty. Also, mobilities are obtained for H_3^+, ArH^+, and Kr^+ formed in mixtures of argon with hydrogen and krypton. To determine mobilities in argon, three separate experiments using (1) a conventional parallel-plate ion-drift tube, (2) a modified pulsed Townsend discharge with mass analysis, and (3) a gated Tyndall technique with mass analysis were performed to permit comparison with previous experiments.

INTRODUCTION

THE study of the mobility of ions and how it depends upon electric field, pressure, and temperature is basic to the understanding of gaseous conduction. Since ion-atom collision theory is well advanced at least for simple systems, information can be obtained about the interaction forces from ion-mobility studies in an energy range difficult to achieve by other techniques such as beams.

Because of experimental difficulties, research in this field has had to rely on indirect methods to determine the ionic species present. Consequently, instead of yielding information on basic interactions between particles, the results of basic collision theory (such as Langevin's) have been used to identify the charge carriers. In fact, consistency with this theory and others has often been the central support in interpreting the results of an experiment. In view of this fact, it is not surprising that in early studies charge-carrier species have been misidentified. Processes such as charge exchange upon collision, ion-atom interchange, clustering, and other collision reactions often make identification of ions in this way difficult or impossible.

In this paper measurements of the mobility of the three ions in pure argon are presented. Both the Townsend and Tyndall techniques were used. The mobilities are compared with theory, but the central novelty of this research is that ion identification is made directly by withdrawing the ions from the gas at pressures up to 10 Torr and simultaneously measuring the ion mass and drift velocity or mobility. Mass analysis of the ions present in argon, and reported here, demonstrates that conflicting experimental values previously reported for the mobility of the Ar_2^+ ion result from the different manner in which the ions are produced and measured in the several experiments. Ion mobilities in mixtures of krypton and hydrogen with argon are also presented.

EXPERIMENTAL TECHNIQUES

Experiments to measure ion mobilities are performed in this research by using a variety of ion sources and drift cells—the choice depending upon the electron energy required to produce the desired ion. The two basic techniques with mass analysis are described briefly below.

Pulsed Townsend Discharge

In the pulsed Townsend technique[1,2] (non-self-sustaining discharge) ions are formed under conditions of controlled field strength nearly unaffected by reactions which can produce ions upon surfaces. Such reactions were found to be significant with glow sources in this work. The basic pulsed Townsend technique, including mass analysis to allow ion identification,[3,4] is illustrated in Fig. 1. For certain purposes a second grid is placed in the drift space. A full analysis[5] has been obtained which describes the ion distribution in the cell as a function of time after the initial charge multiplication. The effects of diffusion of the ions during transit, space-charge broadening, and the γ process which produces secondary electrons at the cathode have been obtained there theoretically and compared with experiment. In operation a short-duration spark rich in ultraviolet produces an avalanche of electrons in the drift space between grid 1 and the cathode when the cell is operated in its conventional manner.[2] Grid 2 is not used in this case. A series of transient currents comprising the several ions formed flow in the tube subsequently. A slit in the anode 1 cm long and 0.0025 cm wide allows ions to drift out of the cell for mass analysis. Any effect which the draw-out field produced by the ion lens has upon the ions is studied by plotting ion current as a function of draw-out field as the latter is reduced to zero. To date no such effects tending to alter the ions have been observed. Also collisions made by the ions within the field-free region provided by the stray-field shield severely defocussed them, removing them from

* This work was supported by Contract DA-30-069-AMC-333(Y) with the NIKE-X Project Office.

[1] R. W. Engstrom and W. S. Huxford, Phys. Rev. **58**, 67 (1940).
[2] J. A. Hornbeck, Phys. Rev. **83**, 374 (1951); **84**, 615 (1951).
[3] K. B. McAfee, Jr., and D. Edelson, Bull. Am. Phys. Soc. **7**, 634 (1962); Proc. Phys. Soc. (London) **81**, 382 (1963).
[4] K. B. McAfee, Jr., and D. Edelson, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases, Paris, 1963* (S.E.R.M.A., Paris, 1964), Sec. III, A3, pp. 299–304.
[5] D. Edelson, J. A. Morrison, and K. B. McAfee, Jr., J. Appl. Phys. **36**, 1682 (1964).

the beam. The mass analyzer discriminates very extensively against spurious ions produced anywhere along the beam trajectory. Mass analysis is accomplished by measuring the time required for the unknown ion to travel a measured distance in free flight after acceleration by a known potential. Detection of the ions is effected by an ion-electron multiplier with a response time of a few nsec.

Figure 2(a) shows the fit obtained between experiment and the theory of the pulsed Townsend current. It is particularly important that the full analysis be used to determine the transit time in this experiment, since nonsymmetrical diffusion effects[5] make the true transit time of the ions not coincident with the peak of the observed ion-current transient.

The scatter in the experiment results from the small number of ions observed, and it has been demonstrated that the distribution follows Poisson statistics. The usual counting rate approximates one or two ions per thousand sparks from the source, although meaningful

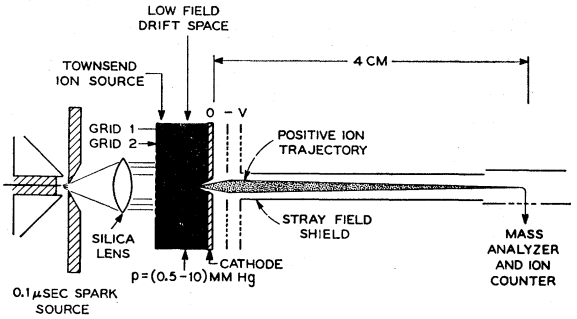

FIG. 1. Double-grid Townsend cell.

data can be obtained for far lower currents. Increasing the intensity of the light source is not feasible since space charge at higher ion densities has been shown to distort ion transients, particularly for low drift-cell voltages where the determination of mobility is most desired.

For low fields, when the total voltage across the Townsend cell is about equal to the gas ionization potential, the electrons emitted from the cathode cannot gain enough energy to form ions. It is then necessary to produce ions by some other method. The addition of a second grid (grid 2) about 1 mm behind the normal Townsend anode extended the usefulness of the Townsend technique to somewhat lower fields.

In one mode of operation, grid 2 is held at a high negative potential with regard to grid 1. Incident light generates photoelectrons from grid 2. These photoelectrons are accelerated in the high-field region between grid 1 and grid 2 and enter the Townsend drift space with enough energy to ionize the molecules of the gas. The advantage in this technique lies primarily in its ability to produce a large number of ions when the total voltage across the drift space is relatively small.

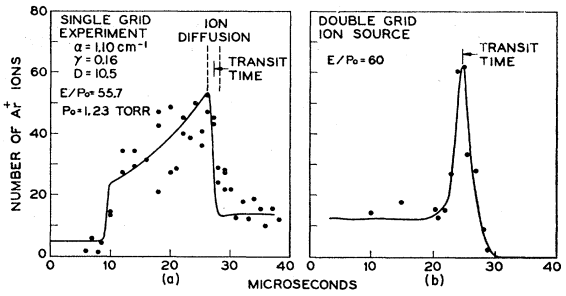

FIG. 2. Ar^+ pulsed Townsend current transients. Experimental points (•). Solid curve indicates theory of pulsed Townsend discharge including effects of diffusion and secondary processes, γ.

Moreover, since the ions are concentrated in a narrow space rather than being distributed across the drift space, the transit time of the ions involved is represented by a peak rather than a break in the ion-density curve. This can be seen in Fig. 2. Consequently, it is possible to determine the transit time of a particular ion with greater accuracy and for lower intensities.

Tyndall Technique

Figure 3 shows schematically how the basic Tyndall technique is employed to determine mobilities at E/p_0 about equal to 5 V/cm Torr. The addition of mass analysis, however, significantly enhances the usefulness of the technique, since the rf ion source produces a variety of unpredictable species. Ions are continuously produced in an rf discharge in the ion source. Grid 1 shields the rest of the apparatus from stray rf fields. The ions drift through grid 1 under a constant field and are stopped by a gate formed by a small reverse field between grids 2 and 3, which are separated by about 1 mm. Between the source and the gate the ions make enough collisions to dissipate any excess energy they may have gained in the high fields of the source. At zero time, a square positive pulse of 1–5 μsec duration is applied to grid 2. A narrow pulse of ions is then caused to pass through the gate into the drift region. The magnitude of this pulse and voltage on grid 1 may be adjusted simultaneously with the drift field in such a manner that the field is constant not only in the drift region but as far back as grid 1. At some later time τ_1 the ions are drawn into the mass analyzer by a pulse

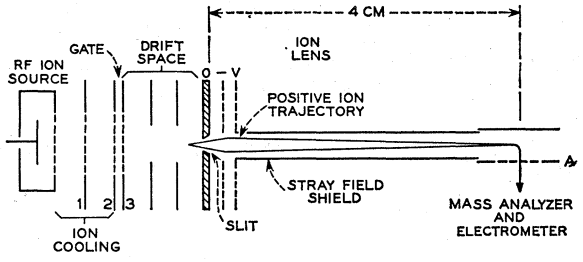

FIG. 3. Ion-drift spectrometer.

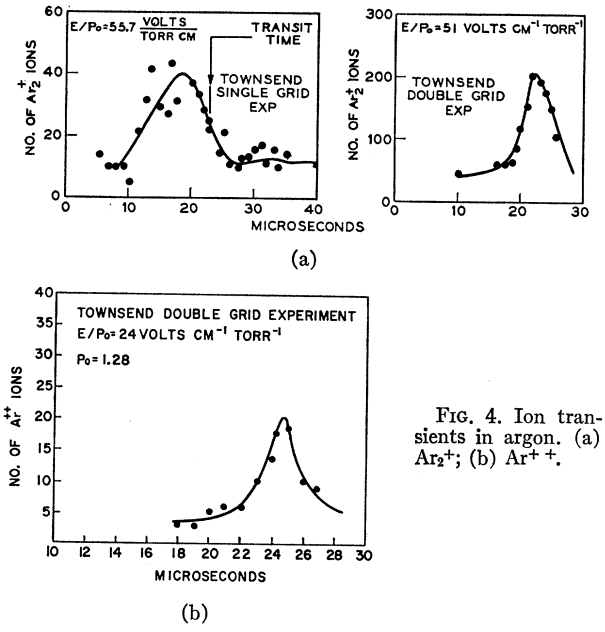

FIG. 4. Ion transients in argon. (a) Ar_2^+; (b) Ar^{++}.

at A. The number of ions of any one type is recorded as the time τ_1 is varied. The transit time τ across the drift space is determined by subtracting the time τ_2 from the slit to the analyzer from the time τ_1. τ_1 can be accurately calculated from the known voltages on the ion lens, but in practice a measurement is always made for confirmation.

In order to minimize losses by absorption on the grids, electroformed mesh was used for the grid material. The mesh has a transparency of 95% and is about 0.001 in. thick.

EXPERIMENTAL DATA

The data presented in this paper are derived from all three of the above-mentioned techniques. The choice of one technique over the others generally depends on the region of pressure and E/p_0 in which it is desired to work. The pressures used in ion extraction experiments ranged from 0.5–3 Torr. E/p_0, corrected to 0°C, ranged from 5–80 V/cm Torr.

Pure Argon

The ion spectrum in pure argon shows three peaks at $M/e=20$, 40, and 80 which with little doubt must be interpreted as Ar^{++}, Ar^+, and Ar_2^+. The relative intensity of the ions varies widely depending on pressure and E/p_0, the ratio of field strength to pressure; this latter quantity is indicative of the average energy attained by the ions between collisions. Comparison of Figs. 2 and 4(a) shows a marked difference in the shapes of the ion transients for Ar^+ and Ar_2^+ obtained by the double-grid technique. The Ar^+ transient is a narrow, symmetrical peak showing somewhat of a tail at faster times [Fig. 2(b)]; by contrast the Ar_2^+ peak is broad and skewed with a steep rise and slower fall-off. Recent theoretical work[6] indicates that this arises because these ions are not drifting independently but are interconverting[7] by reacting with the neutral parent gas: $Ar^+ + Ar \rightleftarrows Ar_2^+$. Possibly a third body is involved. The curve shapes show that the ions initially injected into the drift space are largely Ar^+, some of which convert to Ar_2^+ during drift. There is a slight back reaction which produces the early time increase in the Ar^+ transient, but it is not sufficient to affect the symmetry of the main peak. The Ar_2^+ curve to be expected under these conditions would show a sharp rise corresponding to the transit time of ions formed at the start of the drift space followed by a gradually falling ramp toward the transit time of the slower ion. The rounding of the actual curve observed can be accounted for by diffusion. Reading the time of the peak as the transit time leads to high values, since diffusion of a skewed curve will shift the peak toward longer times. The exact transit time is, therefore, still somewhat uncertain, and scatter in the results is to be expected.

Figure 4(b) shows an example of the curve obtained for Ar^{++} with the double-grid Townsend tube at low E/p_0. The single-grid Townsend tube does not give Ar^{++} ion transients of measureable intensity because the total voltage across the single-grid tube is usually less than the ionization potential required to produce Ar^{++} in the range of E/p_0 required for comparison. At high E/p_0 (150 V cm^{-1} $Torr^{-1}$ or greater) Ar^{++} transients indicate that no interconversion reactions take place in the single-grid tube.

In order to compare results using the ion-spectrometer apparatus with determinations made previously using parallel-plate mobility tubes, measurements of Ar^+ and Ar_2^+ using the latter apparatus were repeated.

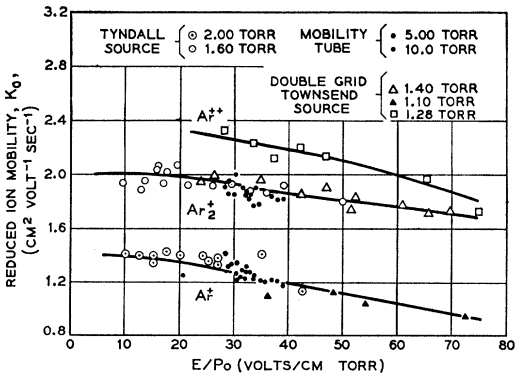

FIG. 5. Experimental mobilities in pure argon.

[6] D. Edelson and J. A. Morrison, Bull. Am. Phys. Soc. **11**, 69 (1966).

[7] Beaty has also suggested association reactions of this type, and the shape of the mass-analyzed ion transients argues strongly in favor of this possibility. [E. C. Beaty, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Munich, 1961* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 183.]

Of course, it is only possible to assume that the two breaks which are observed in the total current represent the two ions Ar_2^+ and Ar^+ when using the parallel-plate mobility tube. Figure 5 shows results of mobility determinations using the three methods. It will be observed that the three methods give fairly identical results, but as pointed out above, difficulty is experienced in ascertaining which point in the ion-current transient, determined with the mobility tube, is the correct value of the ion transit time.

Argon-Hydrogen Mixtures

Unless great care is used in the bombardment-cleanup of the copper grids used in the experiment, the presence of an ion at $M/e=41$ is observed, which has been shown by other experiments to be ArH^+. When

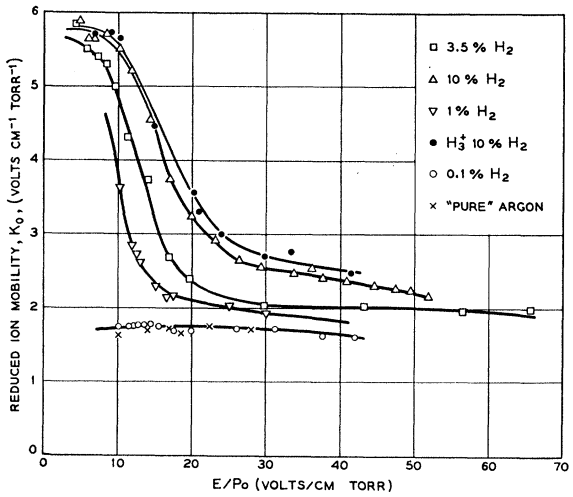

FIG. 6. Mobilities of H_3^+ and ArH^+ in argon-hydrogen mixtures (Tyndall source).

present, this ion complicates the mobility determination in argon because its mobility lies between that of Ar^+ and Ar_2^+. Unless mass analysis is employed, therefore, this ion will alter the shape of the current transient in a mobility tube and yield incorrect values for the transit time.

Figure 6 shows the determination of the mobility of ArH^+. Also the mobility for H_3^+ in the mixture is plotted. For a mixture of 0.1% H_2 in Ar, the mobility of ArH^+ is not significantly different from the mobility of ArH^+ in argon gas under conditions where the hydrogen is present only to the extent of a few parts per million. Thus it is shown experimentally that the hydrogen partial pressure does not alter the ArH^+ ion mobility when hydrogen is present at concentrations less than about 0.1%. It is thus safe to conclude that the identity of the ion does not change during its passage through the drift tube. However, for higher levels of H_2 in Ar, the apparent ArH^+ mobility rises sharply below $E/p_0=30$ V/cm Torr to a limiting value of about

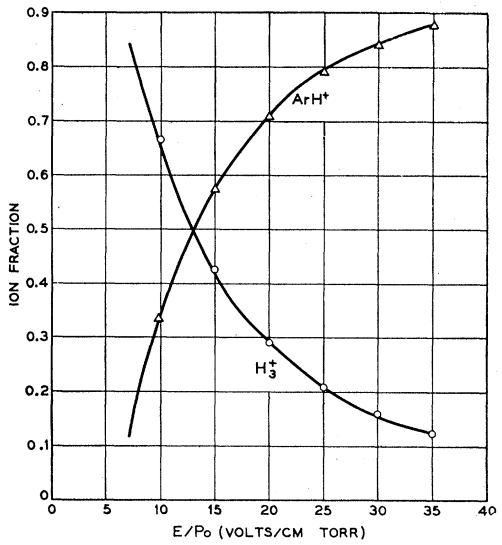

FIG. 7. Relative intensity of ArH^+ and H_3^+ in argon.

5.75 cm^2/V sec. In a mixture of 10% H_2–90% Ar, the arrival times of ArH^+ and H_3^+ are seen to be practically simultaneous. Further, Fig. 7 shows the variation in intensities of the two ions showing an inverse relationship between them.

Argon-Krypton Mixtures

Figure 8 shows mobility values obtained for $^{84}Kr^+$ ions in a 1% mixture with argon. No evidence of Ar_2Kr^+ or any other ions was found, and from the shape of the Kr^+ ion-transient curves, it is apparent that ion-molecule reactions are not occurring to any significant extent in the gas at the pressures and E/p_0 shown.

DISCUSSION

To determine zero-field mobilities from the experimental data shown, extrapolation to E/p_0 equal to zero is required from values of approximately five or slightly higher. It can be observed from the graphs that no significant change in ion mobility occurs below E/p_0 of approximately 25 except in the case of Ar^+ + and hydrogen-argon mixtures. From the measured velocity of Kr^+ at $E/p_0=8$ it can be determined that the ion

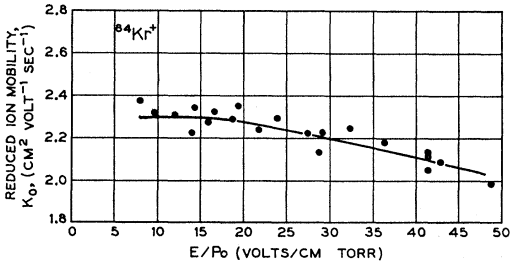

FIG. 8. Ion mobilities of krypton ions in argon.

TABLE I. K_0, reduced mobility of ions in argon (cm^2/V sec at $T=0°C$, $p=760$ Torr).

Ion	Experimental value[a]	Langevin polarization limit ($\epsilon-1=5.17\times10^{-4}$)
Ar^+	1.40±0.05	2.42
Ar_2^+	1.95±0.1	2.10
Ar^{++}	2.40±0.2	2.42
H_3^+	5.75±0.1	6.48
ArH^+	1.70±0.05	2.40
Kr^+	2.30±0.05	2.08

[a] A discussion of errors inherent in the experiment is contained in Appendix I.

drift energy is less than 0.008 eV, compared with the value of $kT=0.0256$ eV at the temperature employed. Thus it can be experimentally shown that the drift energy is smaller than the energy resulting from thermal agitation of the molecules, and no further change in measured mobility is to be expected as E/p_0 approaches zero.

Table I shows experimental mobilities of six ions observed in argon. Except in the case of Ar^{++} and H_3^+, no significant variation in K_0 for the ions between $E/p_0=25$ and the lowest values obtained is observed, so the values in the table represent averages in that range. They are considered to be very close to the exact zero-field mobilities. Only in the case of Ar^{++} is some change in mobility still occurring at the lowest E/p_0 employed, and this effect is reflected in the error indicated.

Figure 9 is a collection of experimental and theoretical determinations of mobilities in pure argon up to the present time. All previous measurements were made without ion identification and employed different experimental techniques. Measurements[5,7–10] in argon can be grouped around three separate curves which when extrapolated to $E/p_0=0$ yield reduced mobilities corresponding to those shown in Table II. It is apparent from examination of Fig. 9 that early conflicts of identification probably resulted from the different sources employed in those investigations. In early research efforts, the extent of argon purity is not known because mass analysis of the gas after the drift experiment was performed was not possible. Munson's increase in K_0 at $E/p_0=40$ V/cm Torr has not been repeated up to the present and must be regarded as an experimental artifact.

With the exception of Munson and Tyndall, all investigations have agreed that the ion A is Ar^+, and this fact is established conclusively in the present studies. Ion B is seen in the present studies by three separate techniques (see Fig. 5) and falls on the curves of Hornbeck and Beaty. Although it is evident from the shape of the transient (Fig. 4) that this ion is undergoing a reaction in transit, it must be identified as Ar_2^+.

Ion *C* at K_0, which is about equal to 2.4, lies somewhat beneath the curves of Beaty and Biondi. However, since mass analysis is employed, we conclude ion *C* should be identified as Ar^{++}. In order to verify this conclusion a search has been made for other ions in argon, such as Ar_3^+ or Ar_4^+, but no such ions have been observed using either Townsend or Tyndall sources.

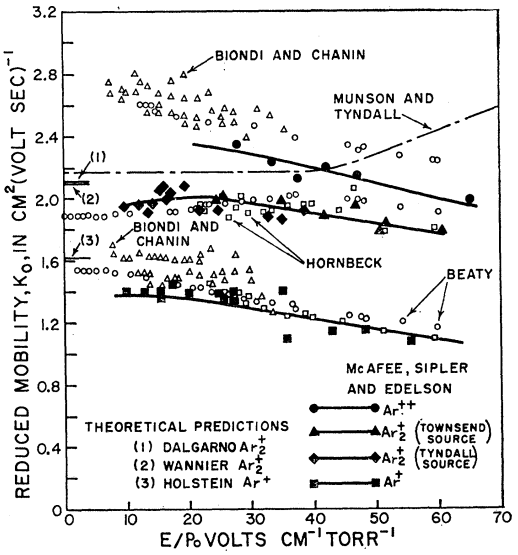

FIG. 9. Argon mobility. Comparison with previous measurements and theory.

The study of ion mobility of ArH^+ was made primarily because hydrogen present in electrode materials in very small quantity as an impurity is often the dominant charge carrier unless exceptional precautions (severe outgassing) are employed. It is important, therefore, to determine how the presence of this ion will affect mobilities obtained with conventional parallel-plate mobility tubes. Figure 6 illustrates that the apparent mobility of the ArH^+ ion is radically affected by the percentage of hydrogen gas present. It is obvious from the near coincidence of the upper two curves of this figure that a rapid exchange during the drift time is taking place between the two ions ArH^+ and H_3^+. From Fig. 7 it is seen that H_3^+ is the more stable charge

TABLE II. Extrapolated values of reduced mobility of ions in argon (cm^2/V sec at $T=0°C$, $p=760$ Torr).

Group	K_0	Identification
A	1.4±0.15	Ar^+
B	2.0±0.1	Ar_2^+
C	2.4±0.2	Ar^{++}

[8] R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) **A177**, 187 (1940).
[9] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954); also L. M. Chanin and M. A. Biondi, *ibid.* **106**, 473 (1957).
[10] E. C. Beaty, Phys. Rev. **104**, 17 (1956); G. Jager and W. Otto, Z. Physik **169**, 517 (1962).

carrier at low E/p_0. Increasing E/p_0 above 15 drives the reaction toward ArH^+. The over-all equilibrium reaction can be written $H_3^+ + Ar = H_2 + ArH^+$.

Langevin Polarization Limit

In the absence of charge-exchange effects and ion or atom exchange or interchange upon collision, the Langevin polarization limit represents a true lower limit for K_0. Table I compares theory and experiment. Calculations of charge exchange effects by Holstein[11] have yielded good agreement for Ar^+. In the case of Ar_2^+, however, the measured mobility is slightly less than calculations by Wannier[12] and Dalgarno,[13] and also less than the polarization limit. This small discrepancy cannot be considered significant, however, until a complete analysis of the Ar_2^+ transient curve has been completed.

Since mobility given by the Langevin theory is independent of charge, the theoretical mobility in the polarization limit calculated for Ar^{++} is equal to that of Ar^+, that is, polarization-limit mobility is charge-independent. Within the experimental limits shown in Table I the experimental mobility obtained for Ar^{++} agrees with the polarization-limit mobility predicted for Ar^+ and Ar^{++}. The experimental value for K_0 obtained for Ar^+ is reduced greatly by the effects of charge exchange. A relatively small value for the cross section for the exchange of two electrons in argon is therefore indicated by the experiment.

For ArH^+ a large discrepancy between experiment and the polarization limit exists. Since colliding cores are not symmetrical in this case, effects of charge exchange must be small. It is possible, however, to evaluate the effect upon the Langevin mobility by assuming a 50% probability of proton exchange by a procedure suggested by Hassé.[14] Since the proton mass is a small percentage of the total, it cannot introduce a large error in the calculation by which Hassé estimated electron exchange. Such procedures reduce the polarization limit K_0 to 1.80 for ArH^+ compared with the experimental value of 1.70 ± 0.05.

[11] T. D. Holstein, J. Chem. Phys. **56**, 832 (1952).
[12] G. Wannier, Bell System Tech. J. **32**, 170 (1953); Phys. Rev. **83**, 281 (1951).
[13] A. Dalgarno, Phil. Trans. Roy. Soc. **A250**, 426 (1958).
[14] H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

APPENDIX: ACCURACY OF MEASUREMENT

The mechanical tolerances of the apparatus were determined to a precision of 0.0001 in. using the Townsend and Tyndall cell. Measurement of time was controlled to better than 0.1 μsec. Voltages were measured to better than 0.5%, and pressures were measured to about 3%. The pressure measurements were checked by several independent methods, and the 3% figure represents our estimate of the accuracy of these methods. In some measurements the pulse repetition rate was found to influence the shape of the ion-transient curves. This was ascribed to the influence of long-lived metastable argon atoms produced in the discharge and remaining in the drift cell until the next discharge. In such cases the data were taken at as low a pulse rate as was feasible. In the Tyndall cell the rf discharge was always adjusted so that source current was as small as possible. This is necessary to avoid production of large numbers of metastables and high-energy ions which will distort current wave forms as a result.

Care was taken to insure gas purity. High-purity cylinder gas was used, and the gas was passed through two liquid-nitrogen traps to eliminate any water vapor or mercury which might be present in the gas coming directly from the cylinder. The final determination of purity was made using the mass analyzer and separate electron gun to evaluate the purity of the argon after having flowed through the drift cell. It was found to contain less than 10 ppm impurities. The cell and spectrometer were baked to 150–200°C, and ultimate pressures were about 3×10^{-8} Torr. Nevertheless, with an rf discharge in the Tyndall cell, an ion at mass 41 was sometimes observed which was identified in further experiments as ArH^+. The ion ArH^+ was present in much greater proportions than molecular hydrogen in the argon. The ArH^+ intensity could, however, be reduced below the threshold of detection by thorough and prolonged bakeout and by ion bombardment of the grids. Measurements were made in a controlled-temperature room ($T = 298$°C).