Drift Velocities of Ions in Krypton and Xenon

ROBERT N. VARNEY
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received June 26, 1952)

Drift velocities and mobilities of ions of Kr and Xe in their respective parent gases have been measured over a wide range of values of E/p_0, the ratio of electric field strength to normalized gas pressure. Two ions appear in each gas identified as Kr^+ and Kr_2^+ in Kr and Xe^+ and Xe_2^+ in Xe. The relation that drift velocity varies as $(E/p_0)^{\frac{1}{2}}$ at high E/p_0 has been found to hold for the atomic ions and has been used to determine the equivalent hard sphere cross sections at high fields. The cross sections are 157×10^{-16} cm^2 for Kr and 192×10^{-16} cm^2 for Xe. The Langevin theory of mobilities gives excellent agreement with experimental results extrapolated to zero field strength provided that, in the theory, the hard sphere cross section is taken as large for the atomic ions and very small for the molecular ions. The range of the polarization forces is such as to render them insignificant in atomic ion collisions and of primary importance in molecular ion collisions.

THE work reported by Hornbeck[1] on drift velocities in helium, neon, and argon has been extended using the same equipment to include krypton and xenon. The technique described in the references is essentially a time-of-flight method. As reported by him, an oscilloscope pattern is obtained in which sharp steps appear at time intervals after the start of the sweep equal to the transit time for ions to cross from anode to cathode in the parallel-plate Townsend tube.

In Kr and in Xe, two steps appeared in the oscilloscope pattern for values of E/p_0 below 75 volts/(cm×mm Hg). (The symbol p_0 is used to indicate that pressure readings are adjusted to the value which would be produced by the same gas density at 0°C.) These two steps indicate the presence of two ions which are identified as the molecule ions Kr_2^+ and Xe_2^+ as the faster and the atomic ions Kr^+ and Xe^+, respectively, as the slower ions. The identification is supported by the further observation that the supposed molecular ions disappear at higher E/p_0 in accordance with the greater difficulty of producing these ions, the fact that they do have greater speed (see reference 1), and the mass spectrographic analysis by Hornbeck and Molnar[2] showing the presence of the molecular ions of these gases and the relative abundance of these ions and the atomic ions.

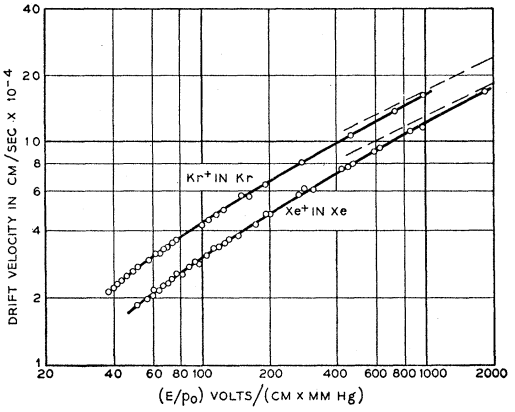

FIG. 1. The drift velocity of atomic ions in krypton and xenon as a function of E/p_0, log-log plot. The broken lines at the right of each curve have a slope of $\frac{1}{2}$.

In Fig. 1, the drift velocity is plotted against E/p_0 on a log-log scale for the atomic ions. The curves for both Kr and Xe approach slopes of one-half at high E/p_0 and tend toward slopes of unity at lower E/p_0. The slope of one-half at high E/p_0 has been predicted by Wannier and Hornbeck[3] on the basis of a hard-sphere model of the atom-ion collisions. (The use of the term "hard-sphere scattering" here simply means that cross sections are independent of velocity and that scattering is probably isotropic. It does not deny the possibility that scattering by charge exchange may in fact be occurring if that process satisfies the same criteria.) Application of their calculation to present drift velocity measurements leads to cross sections shown in Table I. The values for He, Ne, and A are added for reference.

The increase in the ion-atom cross section for krypton above the argon value may seem small, by contrast, for example, with the increase from neon to argon. It is of some interest to note that the atom-atom cross sections increase with atomic number in a similar way. Table II shows this comparison. The ratio of the two cross sections for each gas is given, and it is seen to vary over a very limited range for all the gases tested.

Figure 2 shows the values of the mobilities of the various ions observed. The mobility is defined here by the equation

$$\mu=(v/E)(p/760)(273/T).$$

The experiments were conducted at 27±1°C, and the mobilities are reduced to standard gas density by this definition. However, no correction is made for the direct influence of temperature on mobility other than through change of gas density.

The mobilities reported here for Kr^+ and Xe^+ are in excellent agreement with those of Tyndall and Mun-

[1] J. A. Hornbeck, Phys. Rev. **83**, 374; **84**, 615 (1951).

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

[3] G. Wannier and J. Hornbeck, Phys. Rev. **82**. 458 (1951).

TABLE I. Ion-atom and atom-atom cross sections.

Gas	Ion-atom cross section from drift velocity $\times 10^{16}$ cm^2	Atom-atom cross section from viscosity $\times 10^{16}$ cm^2
He	54	15
Ne	65	21
A	134	42
Kr	157	49
Xe	192	67

son.[4] This agreement is in contrast with the observations of reference 1 in which the results for the molecular ions of He, Ne, and A obtained in these laboratories coincided with Tyndall and Munson's reported values for atomic ions. The present agreement for Kr^+ and Xe^+ also concurs qualitatively with the observations of reference 3 that molecular ions are formed in relatively lesser number to atomic ions as the molecular weight increases and hence are less likely to appear and be mistaken for atomic ions.

A comparison of the present results may be made with the Langevin theory of mobilities[5] in several ways, depending on the size of the hard sphere (range of repulsive forces) used. At one extreme, the formula gives a mobility based on polarization forces only, and in the other direction the influence of a large hard core on the scattering predominates. In the latter case, the calculation requires a cross section value which in the present paper is taken as in Table I from the high E/p_0 limit of hard-sphere scattering.

For the molecular ions, which have a small charge exchange cross section and whose mobilities are therefore likely to depend largely on polarization forces, the Langevin equation has been used in the form

$$\mu_0 = 0.5105\left(1+\frac{m_a}{m_i}\right)^{\frac{1}{2}} \Big/ [\rho(K-1)]^{\frac{1}{2}}.$$

Here m_a is the mass of the gas atoms, m_i is the mass of the ion, ρ is the gas density, and K is the dielectric constant. The experimentally observed mobility must be extrapolated to zero field for comparison with the theoretical value. The resulting comparison appears in Table III. For the atomic ions, the Langevin formula

TABLE II. Ratio of ion-atom to atom-atom cross section.

Gas	Ratio of ion-atom to atom-atom cross section
He	3.6
Ne	3.1
A	3.2
Kr	3.2
Xe	2.9

[4] A. M. Tyndall and R. J. Munson, Proc. Roy. Soc. (London) **A177**, 187 (1940).
[5] H. R. Hasse, Phil. Mag. **VII**, 1, 139 (1926).

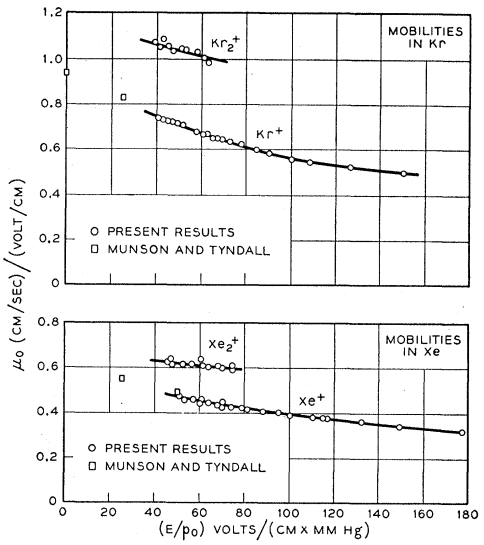

FIG. 2. The mobility at standard gas density, μ, of atomic and molecular ions in krypton and xenon as a function of E/p_0.

is taken as

$$\mu_0 = A\left(1+\frac{m_a}{m_i}\right)^{\frac{1}{2}} \Big/ [\rho(K-1)]^{\frac{1}{2}},$$

where A must be taken from Langevin's table as a function of a parameter

$$\lambda = 8\pi p\sigma^4/(K-1)e^2.$$

Here p is the gas pressure, $\pi\sigma^2$ is the experimentally determined hard-sphere cross section, e is the electronic charge, and K is again the dielectric constant. Using cross sections from Table I, the results shown in Table IV are obtained. The slightly less satisfactory agreement in Table IV compared with that in Table III is attributable to the somewhat too schematic nature of the Langevin theory.

In summary, the measurements have shown the existence of both atomic and molecular ions in krypton and in xenon, thus maintaining the same pattern previously found for helium, neon, and argon. The drift velocities for the various ions in their respective parent gases have been measured. For the atomic ions, the hard-sphere or equivalent charge exchange model of ion-atom interaction has been shown to apply at high E/p_0 values. For the molecular ions, the polarization forces between ion and atom primarily influence the drift rate. As in the case of the lighter rare gases, the molecule ions showed a higher drift velocity than the

TABLE III. Theoretical and experimental ionic mobilities.

Ion	Polarization mobility (Langevin)	Experimental mobility (extrapolated)
Kr_2^+	1.18 cm^2/volt-sec	1.1–1.2 cm^2/volt-sec
Xe_2^+	0.74	0.67–0.77

TABLE IV. Theoretical and experimental ionic mobilities.

Ion	Langevin mobility (hard sphere)	Experimental mobility (extrapolated)
Kr^+	1.01 cm²/volt-sec	0.9–0.95 cm²/volt-sec
Xe^+	0.77	0.6–0.65

atomic ions in agreement with the concept of weaker exchange forces. The cross sections for the atomic ion-atom collisions have been computed. They are some three times larger than the atom-atom cross sections. If the ion-atom collisions are largely charge exchange interactions, the large cross sections are in accordance with numerous direct measurements of this cross section (at higher energies) which show increasing size with decreasing energy.[6]

The writer is most indebted to Dr. J. A. Hornbeck for placing at his disposal the equipment designed and constructed for the earlier work on helium, neon, and argon. He is also pleased to acknowledge the assistance and the helpful suggestions of Dr. David J. Rose. Mr. F. D. Dolezal also assisted materially in the work of assembly and of taking of data. Dr. Hornbeck and Dr. G. H. Wannier very kindly reviewed and helpfully criticized the analysis and the manuscript.

[6] See, for example, Landolt-Bornstein, *Zahlenwerte und Funktionen* (Julius Springer, Berlin, 1950), Vol. 1, p. 358.

PHYSICAL REVIEW VOLUME 88, NUMBER 2 OCTOBER 15, 1952

Conductivity of Oxide Emitters*

RAY C. HUGHES AND PATRICK P. COPPOLA
Philips Laboratories, Inc., Irvington on Hudson, New York

(Received May 14, 1952)

Measurements of the conductivity of a BaSrCaO emitter over a range from room temperature to 1100°K indicate the existence, in well-activated cathodes, of a low temperature conduction mechanism having an activation energy of as little as 0.05 ev. Coincident with the temperature at which appreciable emission can be drawn, a high temperature conduction mechanism of 1 ev activation energy becomes evident. Application of a high pressure (25 atmospheres) of xenon to the cathode causes a marked decrease in conductivity in the high temperature range. These results are considered to confirm a hypothesis recently advanced by Loosjes and Vink that conduction in the high temperature region occurs predominantly through space currents in the pores of the oxide. The small activation energy of the low temperature conduction mechanism is considered to indicate the probability that this conduction occurs in a monolayer of barium on the surface of the oxide.

RECENT studies by Vink[1] and Loosjes and Vink[2] have led to the conclusion that the conduction through an oxide emitter, at operating temperature, occurs largely via space currents in an electron gas within the pore volume of the coating. In the present work, further evidence of conduction in this manner was sought.

The experimental approach has been to apply a relatively high pressure (25 atmospheres) of xenon gas to an activated emitter and to observe whether an apparent decrease in conductivity occurs. This method is based on the assumption that the electrons within the pores of the oxide will collide with the xenon molecules, and the average drift velocity under the influence of the applied field will be appreciably reduced.

The test cathode for measurement of resistance is of the design described by Loosjes and Vink, and is shown schematically in Fig. 1. A layer of oxide (BaSrCaO composition) of approximately 0.25-mm thickness is held between the flat ends of two 3-mm diameter nickel cathode sleeves of "*A*" nickel, the sleeves being spring loaded to hold the assembly under slight compression. Oxide coating on the cylindrical surfaces of the sleeve and a closely spaced anode permit measurements of emission to be made. The porosity of oxide in a processed tube was determined to be 70 percent by volume. The temperature of the sleeves is measured by thermocouples. Connections to the sleeves permit measurement of the resistance of the oxide by means of a dc bridge. The test assembly is enclosed in a metal envelope of rugged construction and is connected to the vacuum system and a gas purifying train via glass to metal seals, as shown in Fig. 2. Manipulation of gas and vacuum is provided by glass tip-off constrictions and glass percussion valves.

The xenon is treated for removal of oxidizing impurities by prolonged exposure to glowing zirconium wire and a fluffy deposit of barium obtained by evaporation from "Batalum" getters in a low pressure of the xenon. The xenon can be transferred quantitatively to the envelope of the test cathode by freezing out in a side arm on the envelope. Tipping off from the gas train

* Presented at the Twelfth Annual M.I.T. Conference on Physical Electronics, March, 1952.

[1] H. S. Vink, thesis, Leiden (1948) (unpublished).

[2] R. Loosjes and H. J. Vink, Philips Research Reports 4, 449 (1949).