Temperature Dependence of the Mobility of Positive Ions in Argon and Krypton*

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The mobilities of positive ions of argon and krypton in the parent gases have been measured at room temperature and at one lower temperature, 77.4°K in argon and 90°K in krypton. In each case the atomic ions were found to have a higher mobility at the lower temperature. For A^+ in A, the mobility, extrapolated to zero field, at 77.4°K was 1.36 times the value at 300°K. Extrapolation could not be carried out accurately in krypton, but evidence is found that the ratio of the mobility at 90°K to the value at 300°K is somewhat larger than 1.2. The change in temperature was found to have no effect on the mobilities of the molecular ions. Agreement of the room temperature results with those of other investigators is good except for a large disagreement with Biondi and Chanin on the molecular ions. The disagreement is particularly large for A_2^+ at low E/p_0 and suggests a difference in the ions measured in the two experiments.

RECENTLY several investigators have measured the mobilities of positive ions in the parent gas in a variety of gases at room temperature.[1] It has been fairly well established that mobilities depend on electric field strength and gas density only in their ratio, which is commonly represented by E/p_0 and is measured in units of volt/(cm×mm Hg). In this expression, p_0 is $p\times 273/T$, where p is gas pressure and T is the temperature. For ions whose drift velocities are small compared to thermal velocities, mobility is independent of E/p_0. The present investigation was conducted to determine the temperature dependence of mobilities of ions in argon and krypton.

EXPERIMENTAL PROCEDURES

The technique used is one which was developed by Hornbeck and used by him[2] and by Varney[3] to measure mobilities in several gases at room temperature. Present measurements were made under conditions similar to those reported by Hornbeck and Varney, and results at room temperature essentially duplicate theirs. For details of the method, electronic and vacuum techniques, and experimental procedures, reference should be made to their articles. The apparatus used here differs essentially only in that the design of the experimental tube, shown in Fig. 1, permitted the entire tube to be submerged in a refrigerating bath. The electrodes are two-inch disks of molybdenum and are separated by 1 cm. A flash of ultraviolet light from an external source travels down through the quartz window and reflects from the cathode into the Wood's light trap at the bottom of the tube. A current transient is caused by the photoelectrons and is measured by a special feedback amplifier and recorded on an oscilloscope. The amplifier was suspended close to the top of the tube, and an electrical shield enclosed both the amplifier and the Dewar. When low-temperature measurements were made, the Dewar was kept full of the refrigerant for several hours before data were taken. The gas used was Airco reagent grade and was admitted to the evacuated tube through an outgassed ceramic leak. The gas was reported by the manufacturer to contain a major impurity of nitrogen to the extent of less than 0.02 percent, all other impurities being much less. Drift velocity was determined by measuring the

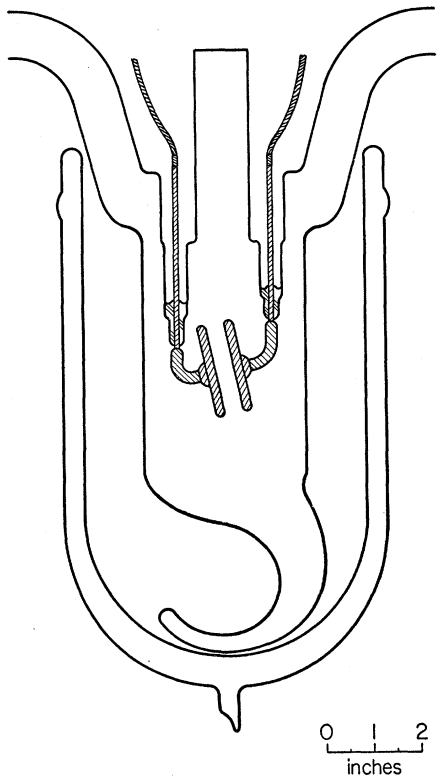

FIG. 1. The experimental tube. For low-temperature measurements the Dewar was kept full of refrigerant and covered with a Styrofoam block. The wires which were submerged in the refrigerant were insulated by a paraffin coating.

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[1] Leonard B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley and Los Angeles, 1955). A thorough and up-to-date review of the subject of ionic mobilities can be found in Chap. I.

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

[3] R. N. Varney, Phys. Rev. **88**, 362 (1952); **89**, 708 (1953).

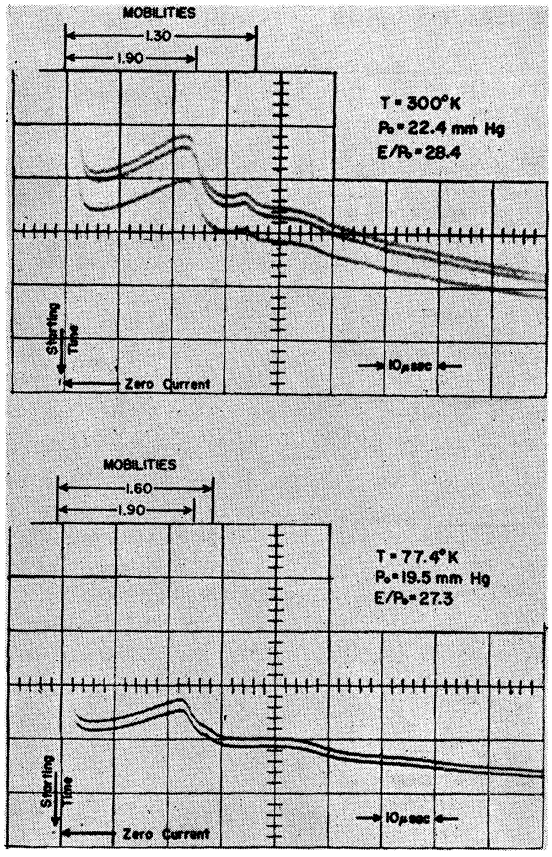

FIG. 2. Typical oscillograms from which data were taken. The upper set was taken at room temperature and the lower at 77.4°K, both are for argon. Each curve is the result of a single sweep, the several curves in each picture resulting from variations in the intensity of the light pulse. The time of flight, labeled with the corresponding mobilities, is indicated for each ion.

time of flight of the ions across the parallel plate diode. Oscilloscope photographs, shown in Fig. 2 are typical of the transients in the diode following the light pulse. An analysis of such transients, made by Hornbeck and by Varney,[2,4] shows that an ion which leaves the region of the anode at the beginning of the sweep, has its time of arrival at the cathode marked by a drop in the current. In each example shown, two ions are seen to be present, the slower one having been identified as the atomic ion and the faster one as the molecular ion. Since the shape of the wave form was very sensitive to the electric field, most consistent results could be obtained by limiting the electric field to values near the breakdown condition. Figure 3 is accordingly furnished to show the approximate values of pressures used to get each value of E/p_0 for the two gases used.

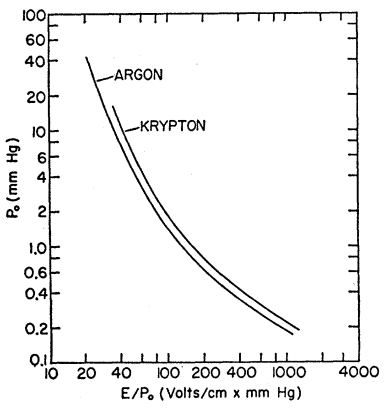

FIG. 3. Approximate values of p_0 that were used to get each value of E/p_0 for argon and krypton.

[4] R. N. Varney, Phys. Rev. 93, 1156 (1954).

RESULTS

The results of the measurements are plotted in Figs. 4–7. Figures 4 and 5 show log-log plots of the drift velocities for the atomic ions of argon and krypton *vs* E/p_0, for two temperatures in each gas. For each ion the drift velocity is higher at the lower temperature, 77.4°K for A^+ and 90°K for Kr^+, than at the higher temperature, 300°K, even at drift velocities well above thermal velocities. However, at the highest values of E/p_0 [1000 volts/(cm×mm Hg)] the temperature effect vanishes, as it should whenever the drift velocities greatly exceed the thermal velocities. Root-mean-square thermal velocities are marked by the arrows on the left side of each graph. Since p_0 is strongly temperature dependent, a misjudgment of the temperature of the tube by as little as two or three degrees at the lower temperatures would cause a displacement of the velocity curves of Fig. 4 and Fig. 5. The coincidence of the curves at the high range eliminates the doubt as to the accuracy of the values of p_0. As the drift velocities fall toward thermal velocities a slope of one is approached, indicating that mobility is becoming independent of E/p_0. For argon, asymptotic lines of unit slope are drawn. In krypton it was not possible to approach thermal velocities for two reasons. The larger ionic mass causes thermal velocities to be lower than for argon, and the breakdown characteristics are

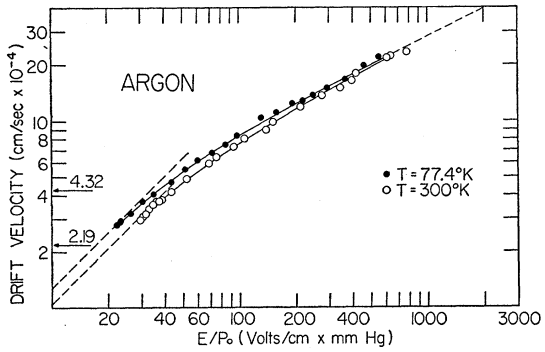

FIG. 4. Drift velocities of A^+ in A at 77.4°K and 300°K as a function of E/p_0. The arrows on the left indicate rms thermal velocities.

such that very much higher values of p_0 are required to get appreciably lower values of E/p_0.

Figures 6 and 7 show plots of mobility *vs* E/p_0 for both molecular and atomic ions at both high and low temperatures. For each atomic ion the mobility is higher at the lower temperature and at the lower E/p_0. The variation with temperature and with E/p_0 are not unrelated since each changes the average velocity of agitation of the ions. There is no appreciable temperature effect for the molecular ions of either gas, nor an E/p_0 dependence for Kr_2^+. The mobility of A_2^+ in A was found to depend on E/p_0 between 20 and 30 volts/(cm×mm Hg), the evidence being considerably stronger at 77.4°K than at 300°K.

The extrapolations to zero field are of particular interest. For A^+ ions in A, extrapolation can be most conveniently done by taking the asymptotic lines of Fig. 4, yielding 1.38 cm²/(volt×sec) at 300°K and 1.88 at 77.4°K. The ratio of these values, 1.36, is probably

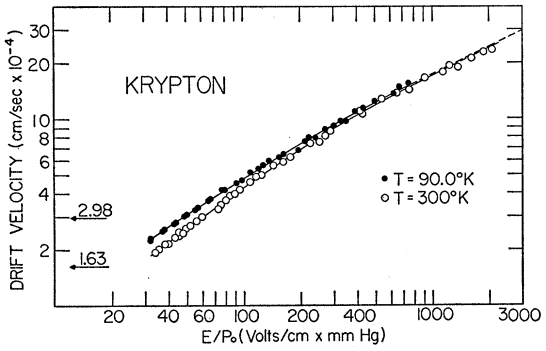

FIG. 5. Drift velocities of Kr^+ in Kr at 90°K and 300°K as a function of E/p_0. The arrows on the left indicate rms thermal velocities.

more accurate than either individually. No satisfactory method has been devised for extrapolating the krypton results, the velocity plot being too far from a slope of one to extrapolate. The ratio of the mobility at 90°K to the mobility at 300°K is approximately 1.20 for E/p_0 above 32 volts/(cm×mm Hg) and up to about 70. The ratio can be expected to increase at lower E/p_0 however, because the mobility becomes independent of E/p_0 for the two temperatures at different values of E/p_0.

For the molecular ions there is no appreciable temperature effect for either argon or krypton. In krypton there is a suggestion of higher mobility at 90°K than at 300°K, but the effect is less than the range of scatter of the observations. Kr_2^+ was found to have a mobility of about 1.00 cm²/(volt×sec) and to show no significant variation of mobility with E/p_0. In argon, between E/p_0 of 20 and 30 volts/(cm×mm Hg) at 77.4°K, the mobility was found to rise with E/p_0. Above $E/p_0=32$, the mobility was found to be about 2.00 cm²/(volt×sec) for all values of E/p_0, and for

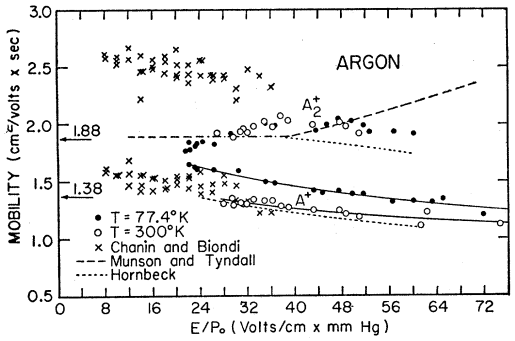

FIG. 6. Mobilities of atomic and molecular ions of argon at 77.4°K and at 300°K as a function of E/p_0. The arrows on the left indicate an extrapolation for the atomic ion, taken from Fig. 4.

both temperatures. There is good agreement between these results and those of Hornbeck for A_2^+ and Varney for Kr_2^+, the differences probably reflecting slightly different experimental procedures. Munson and Tyndall[5] also measured the mobility of A_2^+ in A at room temperature, although they characterized the ion as A^+. Agreement with their results is good for intermediate values of E/p_0 but is not so good for either high or low E/p_0. Biondi and Chanin[6] have made measurements of both Kr_2^+ and A_2^+ at 300°K and report mobilities appreciably higher than any of the other investigators, the disagreement being larger in the case of argon. At $E/p_0=20$ volts/(cm×mm Hg), their results in argon are 50% higher than present results.

DISCUSSION AND ANALYSIS

The substantial agreement on the mobilities of the atomic ions reported by the various observers indicates that the various techniques of measurement are not fundamentally in disagreement. There is fair agreement on the molecular ions except in the limited circumstance cited above. It is difficult to ascribe the lack of agreement to technical difficulties; in fact, the implication

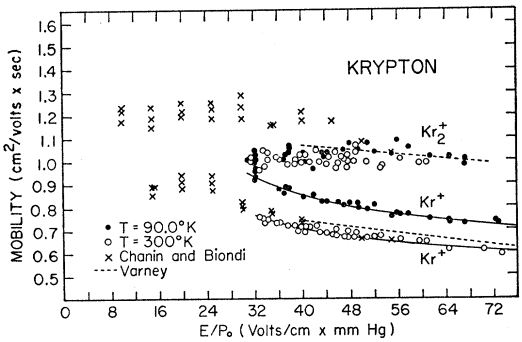

FIG. 7. Mobilities of atomic and molecular ions of krypton at 90°K and at 300°K as a function of E/p_0.

[5] R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) A177, 187 (1941).

[6] M. A. Biondi and L. M. Chanin, Phys. Rev. 94, 910 (1954).

is strong that a different type of ion must be observed by Biondi and Chanin than by the other workers at the lowest values of E/p_0. At this time, it is by no means clear what other ion than A_2^+ can be responsible for the results. A few comments are offered concerning the possibilities. There are three differences between the method used by Biondi and Chanin and that used here and by Hornbeck which might explain the different results. (a) Different methods of producing the ions were used, suggesting the possibility that different ions are formed in the two cases. (b) Lower pressures and lower fields were used by Biondi and Chanin for a given E/p_0, which could account for the different results if mobility is a function of density in some way other than through E/p_0. Compelling theoretical reasons indicate that mobility should be a function only of E/p_0 unless the ion is somehow changing its nature in flight. (c) If impurities are playing a part, they might be expected to be different for the various investigators. However, apparently the gases used here, by Hornbeck and Varney and by Biondi and Chanin, were all purchased from the same commercial source, and there is good reason to believe that in no case was the gas further contaminated to an appreciable extent by introduction into the experimental tube.

It is rather well established that in each experiment two ions were formed with each having a well resolved mobility, and that the slower of the ions is the atomic ion. If the other ion is not the molecular ion in one of the experiments, it seems that it must be a more complicated ion or cluster, perhaps one which changes its nature in flight. Clustering with impurities probably would not permit the mobility to be well resolved, since even at the highest pressure and lowest velocity encountered an ion would interact with only a small number of impurity (nitrogen) molecules.

From the theoretical work of Langevin[7] and Wannier,[8] one concludes that a lack of dependence of mobility on temperature and E/p_0 over a wide range of these variables, as found for the molecular ions, indicates that most of the scattering of the ions is caused by the long-range attractive forces resulting from an interaction of the electric charge on the ion with the dipole induced in the gas atom. If one assumes this conclusion to be true, mobilities at low E/p_0 can be calculated from knowledge of the dielectric constant of the gas and the masses of the ions and atoms. The results are: 2.09 for A_2^+ in A and 1.18 for Kr_2^+ in Kr. These values fall between those reported here and those reported by Biondi and Chanin. It is worthwhile to note that the theoretical values could be increased to Biondi and Chanin's value by assuming an appreciable hard-sphere cross section, or decreased to present results by assuming a larger ionic mass.

The temperature results for the atomic ions are in qualitative agreement with theoretical expectations based on an analysis of charge exchange effects. The mobilities of atomic and molecular ions at the lower temperature are approaching each other rapidly and show signs of crossing as E/p_0 drops. The crossover has been suggested as highly likely by Wannier and by Hornbeck in discussions of the subject. Holstein[9] has devised a general method for calculating the mobility of A^+ but the results at temperatures other than room temperature are not available at this time. A detailed comparison with theory is left for another paper.

ACKNOWLEDGMENTS

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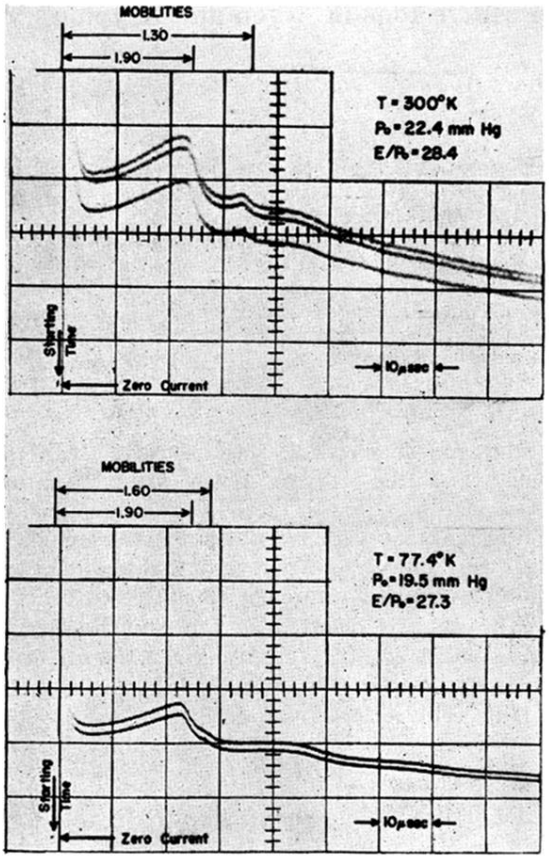
[7] P. Langevin, Ann. chim. et phys. **5**, 245 (1905).
[8] G. H. Wannier, Phys. Rev. **83**, 281 (1951); Phys. Rev. **87**, 795 (1952); Bell System Tech. J. **32**, 170 (1953).
[9] T. Holstein, J. Phys. Chem. **56**, 832 (1952).



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