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Mobilities of Mercury Ions in Helium, Neon, and Argon

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The mobilities of mercury ions in helium, neon, and argon have been measured at 300°K. The values obtained are $\mu_0=19.6$ (He), 5.95 (Ne), and 1.84 (A) cm^2/volt-sec. These values are in agreement with extrapolations of the mobility *versus* mass-number curves obtained for alkali ions in the noble gases by Tyndall and collaborators. The experimental values for Hg$^+$ are compared with the Langevin theory in the polarization limit. Good agreement is obtained only for the case of argon.

I. INTRODUCTION

MEASUREMENTS of the mobilities of mercury ions in the noble gases provide an opportunity to study the motion of a simple heavy ion through simple gases under circumstances in which only interactions such as polarization attraction and short-range repulsion are expected to be of importance. In addition, the measured mobilities are of value for calculations of the positive column characteristics of mercury–noble gas discharge lamps. In the present paper we present the results of studies of the mobilities of mercury ions moving in helium, neon, and argon in small to moderate drift fields and compare our results with related measurements and available theories.

II. EXPERIMENTAL APPARATUS

A simplified block diagram of the mobility tube and the associated electronic equipment is given in Fig. 1. This apparatus has been described in detail previously[1]; therefore, only a brief résumé will be given here. A discharge lasting about 0.5 μsec is generated by application of a voltage pulse from the pulse amplifier to the discharge electrode at the left. Some of the ions formed in the discharge move through the grid and into the drift region where they are drawn to the collector as a result of the applied drift field. The motion of the ions in the drift space induces a current in the external circuit which develops a voltage across the resistor, *R*. Following amplification, the voltage wave form is applied to a synchroscope with calibrated time base. The transit time is determined form the break in the wave form when the ions reach the collector. The actual data are obtained by differential measurements using two different positions of the collector electrode. In this way injection effects through the grid are eliminated.

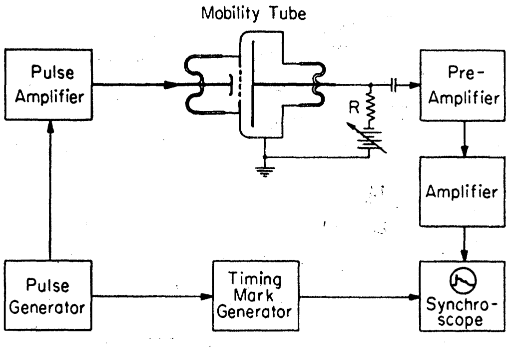

FIG. 1. Simplified diagram of the ionic mobility tube and associated equipment.

The gas-handling system used to introduce the mercury–noble gas fillings to the mobility tube is shown in simplified form in Fig. 2. The system is of the ultrahigh vacuum type[2] in that it is fabricated of components which can be baked at >450°C during processing. The system reached a pressure of ~10^{-9} mm Hg and a rate of rise of ~10^{-10} mm Hg/min when isolated from the pumps. The gas samples were Airco "Reagent" grade and the mercury was multiply distilled into the breakoff capsule. All-metal vacuum valves[2] served to isolate the system from the pumps and to admit gas to the mobility tube from the flask. The permanent gas pressure was read by means of the bakeable oil manometer[3] while the copper trap[4] prevented oil vapor from the manometer from contaminating the rest of the system. The liquid-nitrogen trap prevented mercury vapor from attacking the metal valves. The mercury vapor pressure in the mobility tube was somewhat less

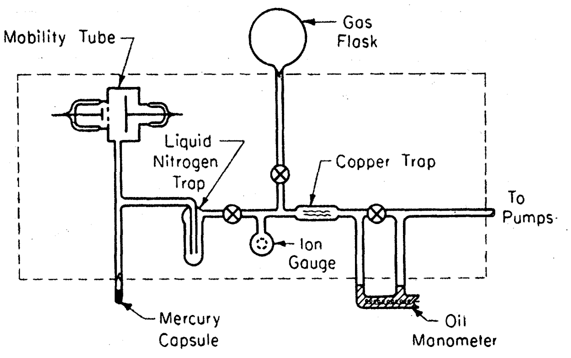

FIG. 2. Gas-handling system for the introduction of mercury-noble gas fillings to the mobility tube. The area inside the dotted line is baked out.

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

[2] D. Alpert, J. Appl. Phys. 24, 860 (1953).

[3] M. A. Biondi, Rev. Sci. Instr. 24, 989 (1953).

[4] D. Alpert, Rev. Sci. Instr. 24, 1004 (1953).

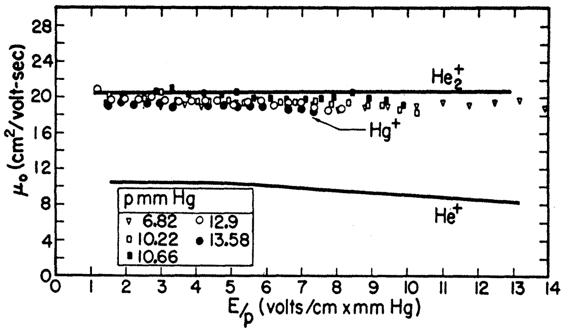

FIG. 3. Mobility as a function of E/p of mercury ions in helium at 300°K. The solid lines indicate the previously measured values for He^+ and He_2^+.

than the equilibrium value at 300°K as a result of the pumping action of the liquid-nitrogen trap. However, at all times, sufficient mercury vapor was present in the tube so that mercury ions were the predominant species. This point was checked by refrigerating a small part of the tube and observing the decrease in the mercury ion component of the current relative to the noble-gas ion component.

III. MEASUREMENTS

The measured mobilities of Hg^+ in helium, neon, and argon as a function of E/p, the drift field to pressure ratio, are shown in Figs. 3–5. Following previous convention, the mobility μ_0 is defined at a gas temperature of 300°K and a density of 2.69×10^{19} atoms/cc (equivalent to 760 mm Hg at 0°C). The measured points are shown for Hg^+ together with lines representing the average of the data obtained for the molecular and the atomic ion of the parent gas. In the case of helium, Fig. 3, the mobilities of He_2^+ and Hg^+ were found to be nearly identical over the measured E/p range. However, it was possible to see the Hg^+ ion current disappear and the He_2^+ ion appear as one part of the tube was cooled to reduce the Hg^+ vapor pressure. The pure helium data obtained in this way agreed with the previously obtained values.[1] At low E/p the ion energy is essentially thermal (300°K); extrapolation to $E/p=0$ yields a value of $\mu_0=19.6$ cm²/volt-sec for Hg^+ in helium.

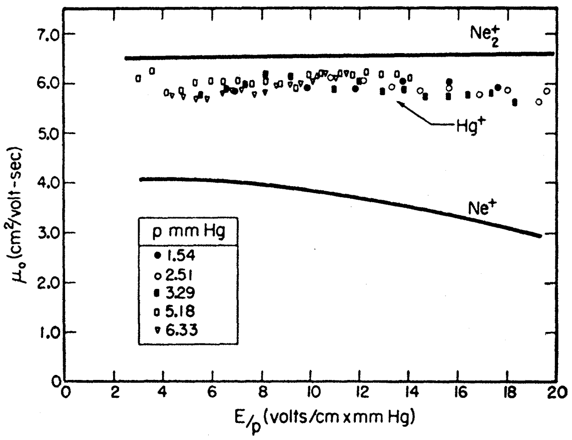

FIG. 4. Mobility *vs* E/p of mercury ions in neon at 300°K. The solid lines indicate the previously measured values for Ne^+ and Ne_2^+.

The data for Hg^+ in neon are shown in Fig. 4. It is again possible to distinguish clearly between the ions Ne_2^+ and Hg^+ by freezing out the mercury. The extrapolated thermal value for Hg^+ in neon is $\mu_0=5.95$ cm²/volt-sec.

The measured values in argon are shown in Fig. 5. In this case it is possible to observe all three ions, Hg^+, A_2^+, and A^+, simultaneously. As in neon and helium the molecular and atomic ion mobilities agree with our previous results. The thermal value for Hg^+ in argon is $\mu_0=1.84$ cm²/volt-sec.

IV. DISCUSSION

The present results for Hg^+ in helium may be compared with microwave measurements of the ambipolar diffusion coefficient of mercury ions in helium[5] by noting that under conditions of thermal equilibrium

$$D_a \simeq 2D_+, \tag{1}$$

where D_a and D_+ are the ambipolar and ionic diffusion coefficients, respectively, and that

$$D_+/\mu_+ = kT_+/e = kT/e, \tag{2}$$

where μ_+ is the ionic mobility, k is Boltzmann's constant, and e is the ionic charge; T_+ and T are the ion and gas temperatures, respectively, and are assumed equal under thermal equilibrium conditions. The measured value $D_a n = 2.6\times10^{19}$ (cm²/sec) (atoms/cc) at 290°K then yields the value $\mu_0=19.8$ cm²/volt-sec at 300°K. This value is in remarkably good agreement with the value $\mu_0=19.6$ obtained in the present experiment considering the fact that the experimental error in either experiment is several percent.

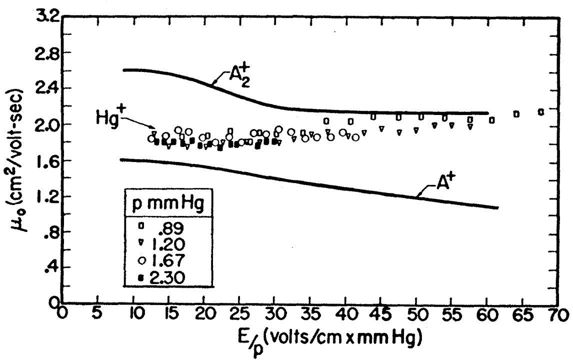

FIG. 5. Mobility *vs* E/p of mercury ions in argon at 300°K. The solid lines indicate the previously measured values for A^+ and A_2^+.

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[5] M. A. Biondi, Phys. Rev. 90, 730 (1953).

TABLE I. Comparison of measured mobility values, μ_0, and values calculated from the polarization theory for Hg^+ in various noble gases at 300°K. (The mobilities are given in cm^2/volt-sec at 300°K.)

Gas	Present experiment	Polarization theory	Difference
Helium	19.6	15.4	28%
Neon	5.95	5.13	16%
Argon	1.84	1.89	3%

The present results may also be compared with extrapolations of the mobility *versus* mass curves obtained by Tyndall's group[6] for alkali ions in the noble gases. The comparison for Hg^+ (mass number 201) with the alkali ions Li^+ through Cs^+ (mass numbers 7 through 133) is given in Fig. 6. In all cases good agreement is obtained, although the data for various ions in helium show a slightly greater scatter than is the case in neon and argon.

Also shown in Fig. 6 are the assumed values of Waymouth and Bitter[7] for neon and argon, based on modification of the microwave values for Hg^+ in helium "for the difference in mass and kinetic theory cross section." It will be seen that their estimated values are in very poor agreement with the measured values. As a result, in their analysis of the plasma of a fluorescent lamp, the calculations of the rate of loss of ions and electrons by ambipolar diffusion to the walls are seriously in error.

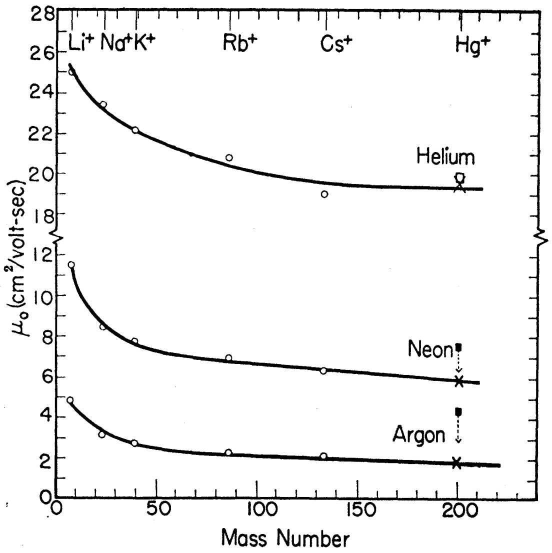

FIG. 6. The thermal (300°K) values of mobility as a function of the mass number of the ion for helium, neon, and argon. The o's indicate the measurements of Tyndall's group, ×'s indicate the present values, ☐ indicates the microwave result, and ■'s indicate the assumed values of Waymouth and Bitter.

A better estimate of the mobility of Hg^+ in the various noble gases can be obtained either by extrapolation of the Tyndall group data or by the use of Langevin's theory in the polarization limit.[8] Using the published dielectric constants[9] for helium, neon, and argon in the Langevin formula,

$$\mu=0.51[1+m_a/m_i]^{\frac{1}{2}}/[N(\epsilon-1)]^{\frac{1}{2}}, \tag{3}$$

where N is the gas density, ϵ the dielectric constant of the gas, and m_a and m_i are the masses of the gas atom and ion, respectively, we obtain the values listed in Table I. The agreement is poor for helium but improves in the heavier gases. Thus, one might expect a reliable estimate for the cases of Hg^+ in krypton and xenon through the use of the polarization theory. Such agreement between polarization estimates and measured values has been verified for the alkali ions.[6]

The authors wish to thank A. V. Phelps and L. S. Frost for interesting discussions of this work.

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[6] A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, London, 1938), Secs. 30 and 31.

[7] J. F. Waymouth and F. Bitter, J. Appl. Phys. 27, 122 (1956).

[8] P. Langevin, Ann. chim. et phys. 5, 245 (1905).

[9] Landolt-Börnstein Tables, *Atom- und Molekularphysik, 1 Teil, Atome und Ionen*, edited by A. Eucken (Springer-Verlag, Berlin, 1950).