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Ion Mobilities in Helium, Neon, and Argon*

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Measurements of the electron density as a function of time during the decay period of pulsed plasmas produced in helium, neon, and argon are reported. The values of the mobilities of positive ions in their parent gas, calculated from the rate of electron loss by ambipolar diffusion, are compared with those measured with the ion-transit-time methods. The values, consistent with data obtained with these two different measuring techniques, are $\mu_0(\mathrm{He}^+)=10.7$, $\mu_0(\mathrm{He}_2{}^+)=16.2$, $\mu_0(\mathrm{Ne}^+)=4.1$, $\mu_0(\mathrm{Ne}_2{}^+)=6.5$, $\mu_0(\mathrm{Ar}^+)=1.6$, and $\mu_0(\mathrm{Ar}_2{}^+)=1.9$ cm²/V sec. The dependence on gas pressure of the efficiency of the cataphoretic segregation of neon impurity atoms in helium is demonstrated and explained.

I. INTRODUCTION

DURING the last two decades various values for the mobility μ_0 of positive rare gas ions in their parent gas have been reported. These values were determined by means of the ion-transit-time method, in which the time needed by the ions to travel a given distance under influence of an externally applied electric field was measured.[1–5] Although good agreement existed between the measured values of the mobility of atomic rare gas ions and of molecular neon ions, the discrepancy between measured values referring to molecular helium and argon ions was considerably larger than could be explained from experimental uncertainties.

Another method, which gives information about the mobility values, is the measurement of the ambipolar diffusion coefficient D_a. This quantity determines the rate of change of the electron density in decaying plasmas when electron disappearance by electron-ion recombination and attachment to neutral gas particles can be neglected.

Comparing the values of the mobility of molecular helium ions as calculated from the measured ambipolar diffusion coefficient with that found with the ion-transit-time method, the discrepancy is very pronounced. For instance, the measurement of D_a as carried out by Brown and Biondi[6] leads to $\mu_0(\mathrm{He}_2{}^+)=12.5$ cm²/V sec[7] while Kerr[8] and Oskam[9] obtained from D_a a value $\mu_0(\mathrm{He}_2{}^+)=16.2$ cm²/V sec.[10] The value calculated from the measurement of D_a as a function of pressure by Phelps and Brown[11] is $\mu_0(\mathrm{He}_2{}^+)=19$ cm²/V sec.[12] The values measured until recently, with the ion-transit-time method are $\mu_0(\mathrm{He}_2{}^+)=19$, 20.3, and 20.9 cm²/V sec.[1,3,13]

Mulcahy and Lennon[14] determined the ambipolar diffusion coefficients of electrons during the afterglow period of plasmas produced in helium, neon, and argon. They concluded that their mobility values, with the exception of that for the $\mathrm{Ne}_2{}^+$ ions, were in agreement with those measured by Biondi and Chanin.[3] The validity and reliability of these conclusions are discussed in the next sections.

The present paper reports studies of the ambipolar diffusion process in helium, neon, and argon. The values of μ_0 calculated from the rate of change of the electron density as a consequence of this loss process are compared with those determined from the ion-transit-time techniques, including the value of $\mu_0(\mathrm{He}_2{}^+)$ as measured very recently.[15,16] Values obtained for the recombination coefficient of molecular helium, neon, argon, krypton, and xenon ions with electrons will be reported in a separate paper.

The microwave-cavity method used for measuring the electron density during the afterglow period is described only very briefly, since this method has been discussed in detail elsewhere.[6,9,17,18]

During the studies the necessity of removing neon

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

[2] R. N. Varney, Phys. Rev. **88**, 362 (1952).

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

[4] E. C. Beaty, Phys. Rev. **104**, 17 (1956).

[5] L. M. Chanin and M. A. Biondi, Phys. Rev. **106**, 473 (1957).

[6] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[7] Although these authors assumed that the mobility value measured was that of He^+ ions in helium, the pressure range studied (2 to 13 Torr) was such that the value reported has to be compared with the mobility value of $\mathrm{He}_2{}^+$ ions as found by other authors. The value $\mu=13.7$ cm²/V sec as given in Ref. 6 refered to a gas pressure of 760 Torr at 300°K. The values, μ_0, used in this paper refer to 760 Torr at 273°K.

[8] D. E. Kerr and C. S. Leffel, Bull. Am. Phys. Soc. **7**, 131 (1962).

[9] H. J. Oskam, Philips Res. Rept. **13**, 401 (1958).

[10] The values as given in Ref. 9 have to be corrected for a systematic error of 6% in the measurement of the gas pressure.

[11] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

[12] This value is calculated from Fig. 4 of Ref. 11 while assuming that the measurements were conducted at a gas temperature of 300°K. By extrapolating the measurements to zero pressure the authors arrive at $\mu_0(\mathrm{He}^+)=12.7$ cm²/V sec. Their conclusion that this value is in very good agreement with the measurements reported in Ref. 6 is not justified, since Biondi and Brown conducted their measurements in the pressure region where Phelps and Brown obtain $\mu_0(\mathrm{He}_2{}^+)=19$ cm²/V sec.

[13] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) **A134**, 125 (1931); and A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, Cambridge, England, 1938). These authors incorrectly identified the ion measured as the He^+ ion; this error in identification was first suggested by R. Meyerott, Phys. Rev. **70**, 671 (1946).

[14] M. J. Mulcahy and J. J. Lennon, Proc. Phys. Soc. (London) **80**, 626 (1962).

[15] P. Patterson and E. C. Beaty, Bull. Am. Phys. Soc. **7**, 635 (1962).

[16] H. J. Oskam and J. M. Madson, Bull. Am. Phys. Soc. **7**, 636 (1962).

[17] M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951).

[18] D. J. Rose and S. C. Brown, J. Appl. Phys. **23**, 1028 (1952).

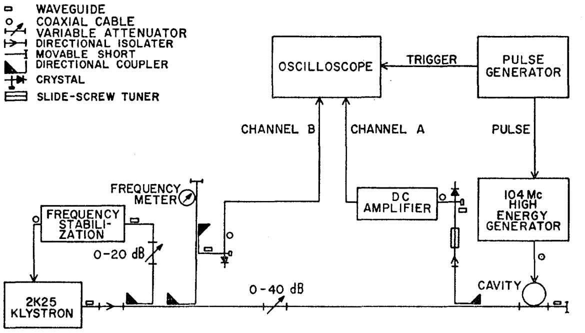

FIG. 1. Diagram of the measuring system.

impurities from commercially obtained helium became evident. This helium contained about $10^{-3}\%$ neon, which, according to studies reported by Oskam,[9] may strongly influence the properties of the afterglow. The method used to purify the helium was that of cataphoretic segregation. The dependence of the efficiency of this process on the gas pressure, as was first observed by Riesz and Dieke,[19] became evident during the studies. This pressure dependence is discussed in detail in Sec. VII.

II. MEASURING SYSTEM

The method for measuring the time dependence of the electron number density during the afterglow period was developed by Biondi and Brown[6,17,18] and consists of measuring the detuning of a microwave cavity, due to the presence of the electron gas inside the cavity, as a function of time after cessation of the discharge excitation. A diagram of the microwave system and associated equipment is shown in Fig. 1.

The magnitude of the constant microwave probing signal (frequency about 9000 Mc/sec) was kept very small (a few microwatts) in order not to influence the energy of the plasma electrons.[9]

The gas was contained in a quartz bottle inserted into the cavity and the plasma was produced by means of a pulsed high-frequency energy source. The frequency of the energy source used for gas excitation was 104 Mc/sec, its maximum power was 60 W, while the pulse length was about 10 μsec or longer. The use of this power generator as an excitation source for the pulsed discharge made it possible to completely isolate the relatively high excitation energy from the low-energy 9000-Mc/sec measuring system. The method of coupling the the 104-Mc/sec excitation energy to the gas contained in the cavities is shown in Fig. 2. In order to study the possible influence of the electron density distribution on the measurements, two different types of microwave cavities (TM_{010} and TE_{011} mode) were used.

The measurement of very small resonant frequency shifts were facilitated by stabilizing the frequency of the probing signal with Pound's stabilization circuit.[20] The temperature of the microwave measuring system was kept constant within 0.1° C.

The microwave system used made it possible to measure the electron density as a function of time during the afterglow period over a density range of about 5000 to 1, while keeping the linear relationship between the resonant frequency shift and the electron density.[21,22] The electron density range involved was from about 10^7 electrons/cm^3 to 5×10^{10} electrons/cm^3.

The quartz bottle containing the gas was permanently connected to an ultrahigh vacuum system and could be fired at 1000°C by using a separate furnace in conjunction with the ovens employed for baking the vacuum system at about 350°C. During the bake-out period the oil-diffusion pump and associated molecular sieve traps[23] were isolated from the system and a vac-ion pump was used. The ultimate pressure in the cold system was about 10^{-9} Torr with a rate of rise of about 5×10^{-10} Torr per minute. The gases used were obtained from the Air Reduction Company and the Linde Company and were further purified by means of the cataphoretic segregation method.[19] With the exception of studies conducted in helium at pressures smaller than about 15 Torr, the cataphoretic discharge was maintained during all the measurements. The small efficiency of the cataphoretic segregation of neon impurities in low-pressure helium discharges made it necessary to purify the helium at high pressures. A subsequent cataphoretic discharge at low pressures released neon

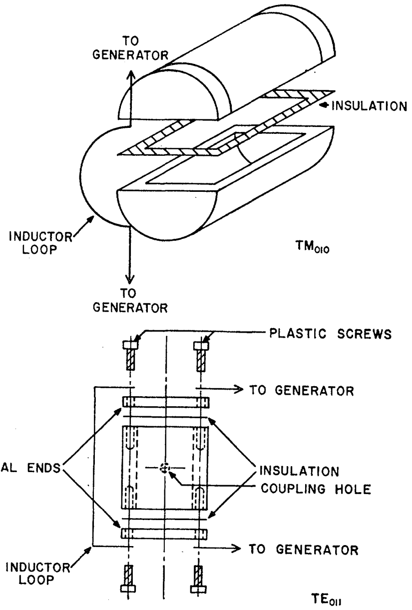

FIG. 2. Scheme for coupling the excitation energy to the gas inside the microwave cavities.

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[19] R. Riesz and G. H. Dieke, J. Appl. Phys. **25**, 196 (1954).

[20] R. V. Pound, Proc. IRE **35**, 1405 (1947).

[21] J. C. Slater, *Microwave Electronics* (D. Van Nostrand Company, Inc., New York, 1954).

[22] K. B. Persson, Phys. Rev. **106**, 191 (1957).

[23] M. A. Biondi, Rev. Sci. Instr. **30**, 831 (1959).

impurity atoms from the cathode region. These atoms were able, at these low pressures, to diffuse into the measuring tube and influence the measurements.

III. THE ELECTRON DENSITY DURING THE AFTERGLOW PERIOD

When the production of electrons by metastable atom–metastable atom interactions is neglected, the processes determining the disappearance of electrons and ions from a plasma produced in a rare gas are (a) ambipolar diffusion towards the walls followed by neutralization via the wall-recombination process and, (b) recombination with an opposite charged particle within the plasma volume.

It is assumed that the electron density and/or the gas pressure are small enough to ensure that the recombination process can be neglected compared to the diffusion process. Then, when taking into account the conversion of atomic ions into molecular ions by three-body collisions with two neutral atoms,[11] the rate of change of the ion densities during the afterglow period is given by[24]

$$dn_1(\mathbf{r},t)/dt = D_{a,1}\nabla^2 n_1(\mathbf{r},t) - \nu_{\text{con}} n_1(\mathbf{r},t), \tag{1a}$$

$$dn_2(\mathbf{r},t)/dt = D_{a,2}\nabla^2 n_2(\mathbf{r},t) + \nu_{\text{con}} n_1(\mathbf{r},t). \tag{1b}$$

Here D_a is the ambipolar diffusion coefficient, ν_{con} is the conversion frequency of atomic ions into molecular ions, and the indices 1 and 2 refer to atomic and molecular ions, respectively.

When the electron density $n_e(\mathbf{r},t)$ is equal to the sum of the positive ion densities (quasineutral plasma), the time dependence of the first mode of the electron density distribution is found to be[24]

$$n_e(t) = (1-A)n_1(0)e^{-t/\tau_1} + [n_2(0)+An_1(0)]e^{-t/\tau_2}, \tag{2}$$

where

$$A = \nu_{\text{con}}/(1/\tau_1 - 1/\tau_2), \tag{3}$$

and

$$1/\tau_1 = (D_{a,1}/\Lambda^2) + \nu_{\text{con}}, \tag{4a}$$

$$1/\tau_2 = D_{a,2}/\Lambda^2. \tag{4b}$$

Here Λ is the characteristic diffusion length of the plasma container.

A very good approximation for $D_{a,1}$ and $D_{a,2}$ is found to be[24]

$$D_{a,1} = D_1(1+T_e/T_g), \tag{5a}$$

$$D_{a,2} = D_2(1+T_e/T_g), \tag{5b}$$

where D is the diffusion coefficient of the positive ion involved, T_e is the temperature of the plasma electrons (velocity distribution assumed to be Maxwellian), and T_g is the ion temperature (assumed to be equal to the gas temperature).

The conversion frequency ν_{con} relates to a collision process involving the ion and two neutral particles and, therefore, can be written as

$$\nu_{\text{con}} = Cp_0^2, \tag{6}$$

where C is a constant determined by the probability of the occurrence of the conversion process and p_0 is the gas pressure in Torr reduced to 0°C. By multiplying (4a) and (4b) by p_0 it may be shown that

$$\tau_1 \lesseqgtr \tau_2 \quad \text{for} \quad p_0^3 \gtreqless (D_{a,2}-D_{a,1})p_0/C\Lambda^2. \tag{7}$$

Since, due to the phenomenon of charge transfer between atomic ions and gas atoms, $D_2 > D_1$ and thus $D_{a,2} > D_{a,1}$, there exists a pressure range for which $\tau_1 > \tau_2$. This means that in this pressure range the first exponential of Eq. (2) dominates at late times during the afterglow period. For high pressures the second exponential determines the final disappearance of the electrons. The following two gas pressure regions can, therefore, be distinguished:

1. Low gas pressure region. The final slope of the logarithmic representation of $n_e(t)$ as a function of time is, neglecting higher diffusion modes, given by the expression (4a). The curve giving p_0/τ_1 as a function of p_0^3 should be a straight line, the slope of which is equal to the conversion coefficient C, while the intercept at p_0 equal to zero should give $D_{a,1}p_0/\Lambda^2$. At these low gas pressures the phenomenon of electron diffusion cooling must be considered.[25] The higher energy electrons can pass over the ambipolar diffusion barrier more easily than the low-energy electrons. Due to the poor thermal contact of the electrons with the gas at low pressures, the "temperature" of the electrons will decrease.[26] In the very low pressure region $T_e \ll T_g$, so that, according to (5a), the value of $D_{a,1}$ is equal to D_1. In the low-pressure region $D_{a,1}p_0$ is thus not independent of the pressure, but decreases with decreasing pressure. This cooling effect is most pronounced for electrons interacting with heavy gas particles, since the efficiency of energy exchange between electrons and atoms during a collision is about proportional to the ratio of electron mass to atom mass.

2. High gas pressure region. In the high gas pressure region the final slope of the logarithm of the electron density versus time is given by (4b), provided the influence of the electron-ion recombination process still can be neglected. Since in this pressure region $T_e = T_g$ during the afterglow period, the value of $p_0/\tau_2 = D_{a,2}p_0/\Lambda^2$ should be independent of the gas pressure p_0.

Substitution of (5b) with $T_e = T_g$ into the Einstein relation

$$\mu/D = e/kT, \tag{8}$$

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[24] H. J. Oskam, Philips Res. Rept. **13**, 335 (1958).

[25] M. A. Biondi, Phys. Rev. **93**, 1136 (1954).

[26] The concept of electron temperature loses its meaning in this pressure region, since the velocity distribution of the electrons will cease to be Maxwellian. Although the expression for D_a given by (5), which was derived by using Einstein's relation, is no longer valid, the result of the diffusion cooling effect will be a decrease in the value of the ambipolar diffusion coefficient.

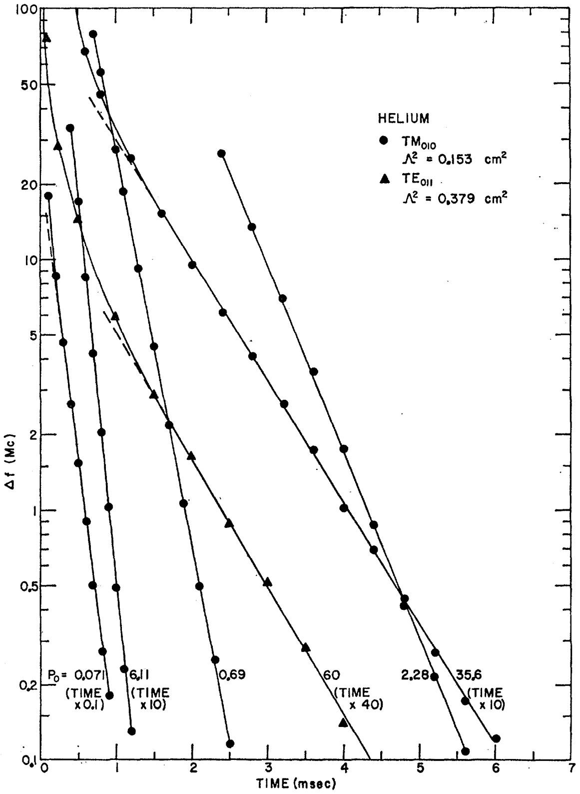

FIG. 3. Resonant frequency shift Δf as a function of time during the decay period of a plasma produced in helium.

which is valid for a Maxwellian velocity distribution, gives[9]

$$\mu_0 = (7.63/T_g) D_{a,2} p_0 \ \mathrm{cm^2/V\ sec}. \tag{9}$$

It is possible to associate with each time constant τ, measured at any pressure p_0, an effective ambipolar diffusion coefficient, which incorporates the conversion frequency ν_{con}, by defining

$$(D_a p_0)_{\mathrm{eff}} \equiv p_0 \Lambda^2/\tau. \tag{10}$$

From the $(D_a p_0)_{\mathrm{eff}}$ obtained in this manner an effective mobility μ_{eff} can be calculated via relation (9). From the above considerations it can be concluded that the effective mobility should exhibit the following behavior:

(a) At "high" gas pressures the value of μ_{eff} should be equal to the value of the mobility μ_0 of the positive molecular ions.

(b) At intermediate gas pressures, the value of μ_{eff} should decrease with decreasing pressure.

(c) At very low gas pressures the value of μ_{eff} should be larger than, or equal to, one half of the value of the mobility μ_0 of atomic ions. The value of one half times the mobility is approached when the diffusion cooling effect is so effective that $T_e \ll T_g$.

The analysis as outlined in this section is used in the next sections when comparing the value of the mobility of positive ions as calculated from the measured rate of electron loss by ambipolar diffusion with those determined by means of the ion-transit-time method at low electric field strength to pressure ratios.

IV. THE MOBILITY OF HELIUM IONS IN HELIUM

Typical curves representing the logarithm of the resonant frequency shift Δf (proportional to the number density of the plasma electrons) versus time during the afterglow period are shown in Fig. 3 for various pressures of helium. The time dependence of the electron density $n_e(t)$ was found to be exponential during the later part of the afterglow period for all gas pressures studied.[27]

The values of μ_{eff} as calculated from these curves as a function of gas pressure are shown in Figs. 4 and 5. At pressures above 3.5 Torr the value of μ_{eff} becomes independent of gas pressure for the measured pressure range of 3.5 to 34 Torr and is the same for both microwave cavities and equal to 16.2 cm^2/V sec,[28] which is identical to the value found by Kerr.[8]

Recently, independent measurements carried out by Patterson and Beaty[15] and Madson and Oskam,[16] employing the ion-transit-time method, resulted in values $\mu_0(\mathrm{He_2^+}) = 16.7$ and 16.5 cm^2/V sec. These authors observed that, when using commerically available helium, other types of ions were also present in the ion drift region. The extra ion observed by Madson and Oskam had a mobility value of about 24.5 cm^2/V sec, which, according to previous studies by Oskam,[9] indicates the presence of Ne$^+$ ions. These ions disappeared when the helium gas was further purified by means of the cataphoretic segregation process and only two types of ions having mobility values, at low values of E/p_0, of about 10.5 and 16.5 cm^2/V sec were observed. It was postulated that these ions are He$^+$ ions and He$_2^+$ ions, respectively. The excellent agreement between the values of $\mu_0(\mathrm{He_2^+})$ obtained by means of the two measuring methods indicates strongly that electron production via metastable atom–metastable atom collisions had a negligible influence on the measurements during the late afterglow period. The value $\mu_0(\mathrm{He_2^+}) = 20.3$ cm^2/V sec as reported by Biondi and Chanin[3] is about 20% higher than the more recent values and most probably refers to a different type of ion. The value $\mu_0(\mathrm{He_2^+}) = 12.5$ cm^2/V sec following from the value of $D_a p_0$ as measured by Biondi and

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[27] Mulcahy and Lennon (Ref. 14) mention that the ln n_e versus time curves measured in the pressure region of 0.8 to 22 Torr were all linear. Their conclusion is rather surprising since the curves measured by Kerr[8] and during the present studies showed that, during the early afterglow period, deviations from the exponential time dependence in general are observed.

[28] A recent measurement at a pressure of 60 Torr gave an identical result. In this pressure region precautions have to be taken in order that the change of the coupling of the probing signal to the microwave cavity during the afterglow period does not influence the determination of the time at which the frequency of the probing signal is equal to the resonant frequency of the cavity.

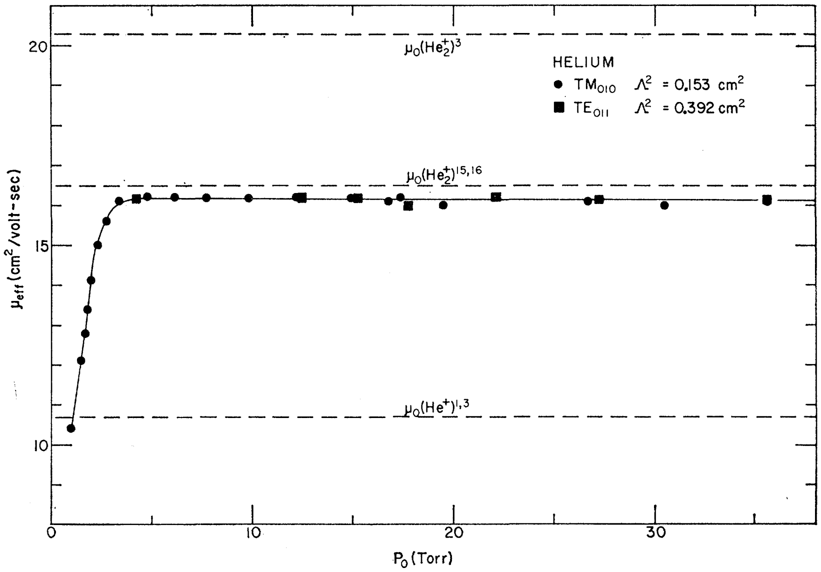

FIG. 4. Dependence of μ_{eff} on pressure p_0 in helium between 0.9 and 38 Torr. The value $\mu_{eff}=16.2$ cm^2/V sec measured at 60 Torr is not shown. The dashed lines indicate the mobility values as measured by means of ion-transit-time methods.

Brown[6] is in disagreement with both the ion-transit-time measurements and the more recent measurements of D_ap_0. The value $\mu_0(He_2^+)=20.3\pm0.6$ cm^2/V sec as calculated by Mulcahy and Lennon[14] from the measured value of D_ap_0 is questionable. These authors mention no further purification of the commerically obtained spectroscopically pure helium used. They claim that the measured value of D_ap_0 is constant in the pressure range of 3 to 22 Torr.[29] During both the present and previous studies a reliable value of D_ap_0 independent of pressure could not be obtained without further purification of commercially available helium. Only after a careful cleaning of the helium by means of the cataphoretic segregation process could a truly constant value of D_ap_0, associated with He_2^+ ions, be measured. The influence of very small concentrations of neon impurity atoms in helium on the determination D_ap_0 is discussed in detail in Sec. VII. The various mobility values measured with the ion-transit-time method are indicated in Fig. 4.

At gas pressures below 3.5 Torr the value of μ_{eff} decreases and shows, according to the expression (4a), the evidence of the conversion of He^+ ions into He_2^+ ions. The value of the conversion coefficient C, defined by (6), was calculated[30] to be 105 ± 10 sec^{-1} Torr^{-2}, which is about 60% larger than the value reported by Phelps and Brown.[11] The uncertainty in the value of C is mainly due to the possible influence of the diffusion cooling effect. Extrapolation of the straight part of the p_0/τ versus p_0^3 curve to zero pressure resulted in a value $\mu_0(He^+)=10.7$ cm^2/V sec, which is a very good agreement with both the value found by Kerr[8] and the ion-transit-time method measurements.[1,3,5] The dashed curve in Fig. 5 represents the calculated dependence of μ_{eff} on p_0 when using the measured values of C and $\mu_0(He^+)$ while neglecting the influence of diffusion cooling. The agreement of this curve with the experimental curve is very good for helium pressures between 1.2 and 2.0 Torr. The appearance of the diffusion cooling effect below 1.2 Torr is very clearly demonstrated.[31] At pressures above 2.0 Torr the influence of the He_2^+ ions on the disappearance of electrons becomes noticeable.

At helium pressures below 0.3 Torr the value of μ_{eff} increases with decreasing gas pressure. This phenomenon was observed both for the TM$_{010}$ and the TE$_{011}$ mode cavities and was absent in plasmas produced in neon and argon. No explanation for the increase in μ_{eff}, at very low pressures, with decreasing pressure has as yet been found.

V. THE MOBILITY OF NEON IONS IN NEON

The values $\mu_0(Ne^+)=4.2$ cm^2/V sec and $\mu_0(Ne_2^+)=6.5$ cm^2/V sec have been measured by means of the ion-transit-time method.[1,3,5] Mulcahy and Lennon[14]

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[29] The conclusion of Mulcahy and Lennon that the measurement of D_ap_0 is limited to a maximum pressure of 22 Torr as a consequence of the value of the collision frequency for momentum transfer ν_m of the electrons with gas atoms is incorrect. As long as the linear relationship between the frequency shift Δf of the microwave cavity and the electron density is satisfied, the frequency ν_m has no influence on the slope of the $\ln\Delta f$ versus time curve.

[30] The value of C was calculated from the p_0/τ versus p_0^3 curve relating to $\Lambda^2=0.153$ cm^2. This curve was, within the experimental error, a straight line for p_0^3 values between 1.4 and 8 Torr^3. The value of the conversion coefficient has to be determined from the dependence of p_0/τ on p_0. The determination of C from the dependence of μ_{eff} on p_0 will lead to a wrong value, since the definition of μ_{eff} via (9) and (10) makes use of Einstein's relation, which is not valid for $(D_ap_0)_{eff}$.

[31] Mulcahy and Lennon (Ref. 14) did not observed the effect of the electron diffusion cooling in helium at low pressures. This is most probably due to the lower pressure limit of 0.8 Torr. The authors were apparently not aware of the influence of the value of Λ on the measured value of D_ap_0 in the low pressure transition region; this influence is predicted by formula (4a) and demonstrated in Fig. 5. Their extrapolation of the measurements to zero pressure, while using data obtained with different values of Λ^2 (0.16 and 0.77 cm^2) for the same curve, is not justified (Fig. 2 of Ref. 14).

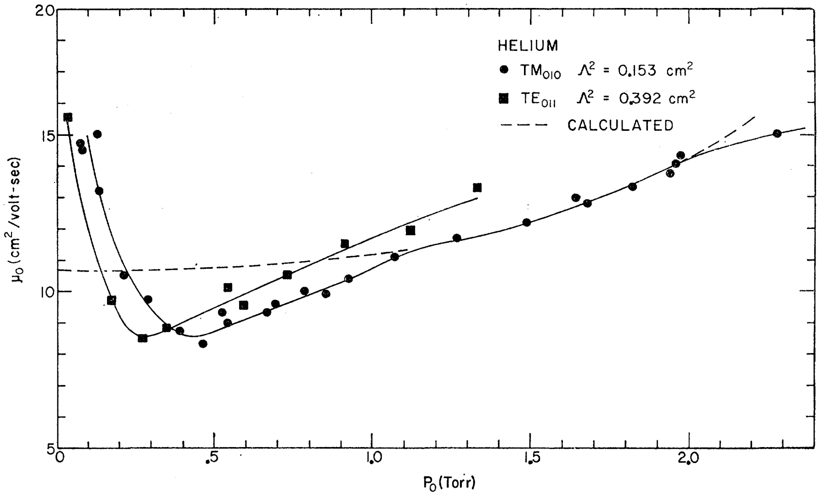

FIG. 5. Dependence of μ_{eff} on pressure p_0 in helium between 0.035 and 2.4 Torr. The dashed line indicates the calculated pressure dependence when neglecting the influence of diffusion cooling and assuming an infinite loss rate for the molecular ions. The experimentally determined values $\mu_0(He^+)=10.7$ cm²/V sec and $C=105$ sec^{-1} Torr^{-2} were used.

have reported the value $\mu_0(Ne_2^+)=7.5$ cm²/V sec calculated from the ambipolar diffusion coefficient. This value was obtained by rather extensive extrapolation of the data measured (Fig. 3 of Ref. 14). No Δf versus time curves were published, so that no comparison of the reliability of their calculated values of $D_a p_0$ with those obtained during the present studies is possible. The value $\mu_0(Ne^+)=2.6$ cm²/V sec as Biondi[32] calculated from $D_a p_0$ measurements in the pressure region 0.2 to 1.1 Torr apparently is influenced by the effect of electron diffusion cooling. Surprisingly, this author measures a constant value of $D_a p_0$ over this pressure range, while a decrease in $D_a p_0$ for decreasing gas pressures should have been observed. However, after remeasuring the value of $D_a p_0$ in the same pressure region under identical experimental conditions, Biondi[25] reports the observation of the phenomenon of electron diffusion cooling and from the data follows $\mu_0(Ne^+)=4.2$ cm²/V sec.

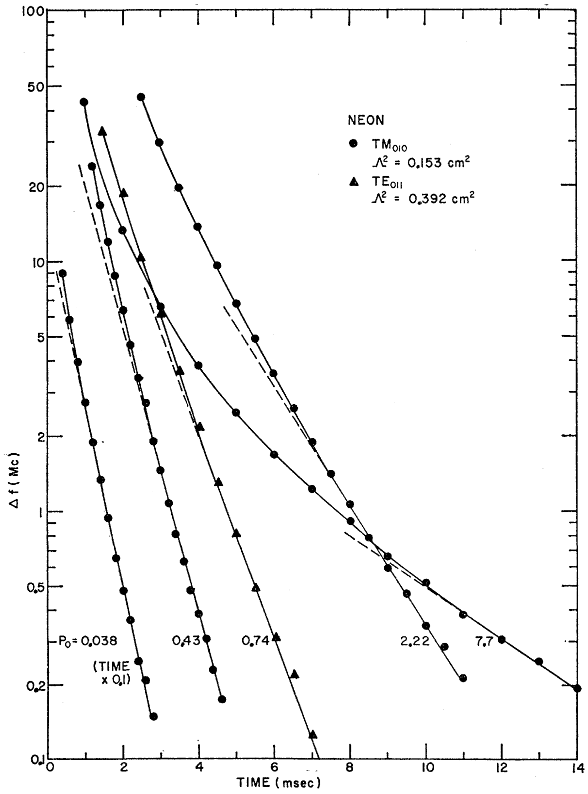

FIG. 6. Resonant frequency shift Δf as a function of time during the decay period of a plasma produced in neon.

Typical examples of curves representing the logarithm of the resonant frequency shift as a function of time during the afterglow period are shown in Fig. 6. It can be observed that, due to the large influence of the electron-ion recombination process on the disappearance of electrons from the plasma, the exponential dependence of the electron density on time is less pronounced than in the case of helium.

For gas pressures lower than 9 Torr the contribution of the ambipolar diffusion mechanism to the volume loss of the charged particles becomes, at low plasma densities, large enough to make the time dependence of the electron density appear to be exponential. However, when the density ratio over which this exponential character is preserved is smaller than about 10, it can be expected that the electron-ion recombination process still may influence the slope of the $\ln\Delta f(t)$ versus time curve.

An estimate for the value of μ_{eff} is calculated from the slope of the asymptote to the $\ln\Delta f(t)$ versus time curve for late times during the afterglow period. It should be realized that this procedure may overestimate the value of μ_{eff}, as a consequence of the possible effect of electron disappearance by the volume recombination process.

The dependence of μ_{eff} on the gas pressure is shown in Fig. 7. The values of $\mu_0(Ne_2^+)$ and $\mu_0(Ne^+)$ as measured with the ion-transit-time method are also indicated.[1,3] As follows from this figure the value of μ_{eff} is equal to $\mu_0(Ne_2^+)$, within the accuracy of measure-

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[32] M. A. Biondi, Phys. Rev. 79, 733 (1950).

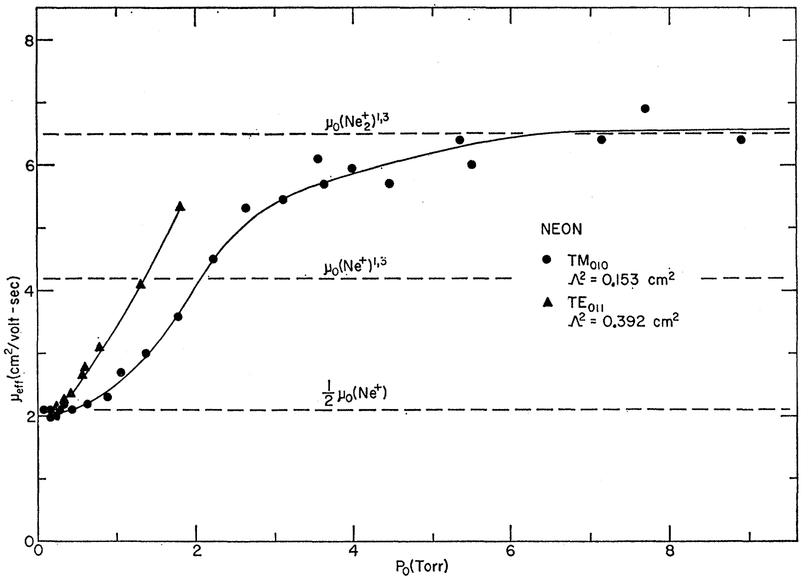

FIG. 7. Dependence of μ_{eff} on pressure p_0 in neon between 0.038 and 9 Torr. The dashed lines indicate the mobility values as measured by means of ion-transit-time methods.

ment, for pressures between 3.5 and 9 Torr. This means that apparently the determination of μ_{eff} via the asymptote method gives a rather good estimate of its value up to pressures of about 9 Torr, and that, moreover, the effect of ionization processes involving metastable atoms was negligible during the late afterglow period. For neon pressures below 3.5 Torr the value of μ_{eff} decreases for decreasing gas pressures and it becomes one half the value of $\mu_0(Ne^+)$ at very low pressures. This is consistent with the phenomenon of diffusion cooling, the large influence of which, on the measurements in the low pressure region, made it impossible to estimate a value of C referring to a conversion of Ne^+ ions into Ne_2^+ ions via three-body collisions with two neon atoms.

VI. THE MOBILITY OF ARGON IONS IN ARGON

Two values found in the literature for $\mu_0(Ar_2^+)$ are 1.90 and 2.65 cm^2/V sec. Both values were determined by means of the ion-transit-time method. Biondi and Chanin[3] observed two ions with mobility values of 1.6 and 2.65 cm^2/V sec, while Beaty[33] found three ions, the third having mobility value of 1.85 cm^2/V sec. The latter author assumed that $\mu_0 = 1.85$ corresponded to Ar_2^+, in contrast with Chanin and Biondi, who assumed that Ar_2^+ had a mobility value of 2.65 cm^2/V sec. Madson and Oskam[16] observed only two ions during their studies. They extracted the ions from a steady-state discharge, while the previous authors studied ions produced in pulsed discharges. The mobility values found were 1.6 and 1.85 cm^2/V sec and were assigned to Ar^+ ions and Ar_2^+ ions, respectively. The only value of $\mu_0(Ar_2^+)$ calculated from $D_a p_0$ was reported by Mulcahy and Lennon.[14] These authors arrive at the value $\mu_0(Ar_2^+) = 2.6$ cm^2/V sec from the observation that $D_a p_0$ increased with pressure and showed a tendency towards a constant value (Fig. 4 of Ref. 14). Unfortunately, Mulcahy and Lennon did not publish their measured Δf versus time curves, so that again no comparison with the present data is possible.

Typical examples of $\ln\Delta f(t)$ versus time curves showing the disappearance of electrons from a plasma produced in argon are shown in Fig. 8. It can be expected that the asymptotic approach method may more readily result in an overestimation of μ_{eff} in the case of argon than for neon. This is due to the fact that $\mu_0(Ar_2^+)$ in argon is smaller than $\mu_0(Ne_2^+)$ in neon, while the co-

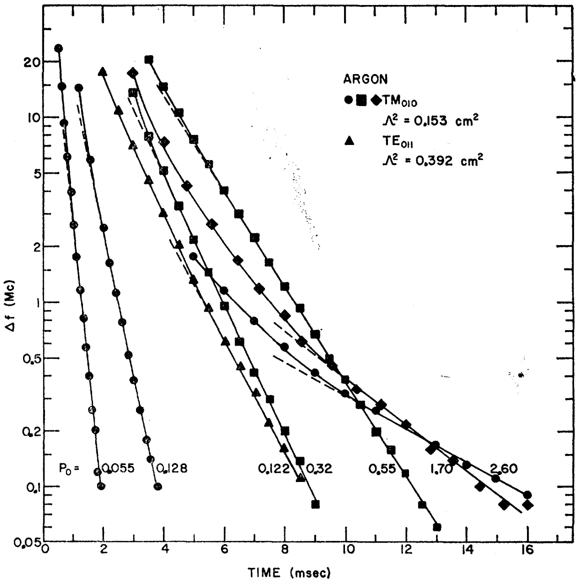

FIG. 8. Resonant frequency shift Δf as a function of time during the decay period of a plasma produced in argon.

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[33] E. C. Beaty, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1961), Vol. I, p. 183.

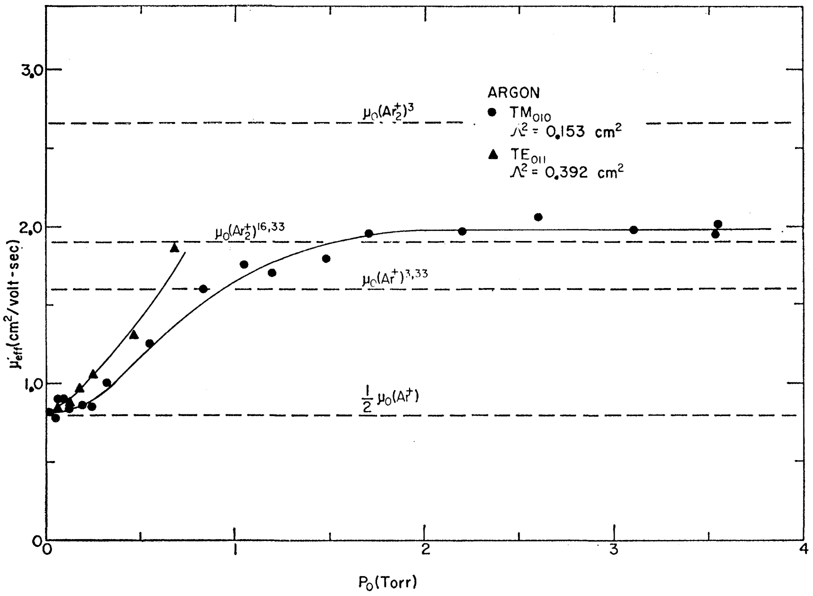

FIG. 9. Dependence of μ_{eff} on pressure p_0 in argon between 0.025 and 4 Torr. The dashed lines indicate the mobility values as measured by means of ion-transit-time methods.

efficient for electron-ion recombination for Ar_2^+ ions is larger than for Ne_2^+ ions.

The dependence of μ_{eff} on the argon pressure is shown in Fig. 9. For pressures between 1.7 and 4 Torr the value of μ_{eff} is, within the accuracy of measurement, constant and agrees with the value of $\mu_0(Ar_2^+) = 1.85$ cm^2/V sec as measured by means of the ion-transit-time method by Beaty[33] and Madson and Oskam.[16] The slightly larger value found for μ_{eff} is most probably a consequence of the asymptotic approximation method. The value of 2.65 cm^2/V sec, as measured by Chanin and Biondi,[3] can be considered to be in disagreement with the present results, since μ_{eff} is *at most larger than* $\mu_0(Ar_2^+)$. Their mobility value most probably refers to a different type of ion.

At low argon pressures the value of μ_{eff} reaches one-half the value of $\mu_0(Ar^+)$, as it should. The influence of diffusion cooling on the electron "temperature," made it impossible to determine the value of a coefficient related to the conversion of Ar^+ ions into Ar_2^+ ions via a three-body collision process.

VII. THE PRESSURE DEPENDENCE OF THE CATAPHORETIC SEGREGATION EFFICIENCY IN HELIUM

During the studies carried out in helium the pressure dependence of the efficiency of the cataphoretic segregation of neon impurity atoms in helium was found to be very pronounced. This phenomenon was first observed by Riesz and Dieke[19] and was studied in more detail by Schmeltekopf.[34]

The value of μ_{eff} as measured in helium, when cataphoretically cleaning the commercially obtained helium at the pressure involved, is shown in Fig. 10. At pressures above 12 Torr the value of μ_{eff} is constant and equal to 16.2 cm^2/V cm. At lower helium pressures, however, μ_{eff} increases with decreasing pressure, reaches a maximum at about 4.5 Torr and then decreases.

This phenomenon can easily be explained when taking into account the pressure dependence of the efficiency of removal of neon atoms from helium by cataphoretic segregation. For pressures above 12 Torr the neon atoms are effectively removed, so that the atoms present at the anode end of the cataphoretic cleaning tube are helium atoms exclusively. At helium pressures below 12 Torr the number of neon impurity atoms present in the measuring region increases with decreasing pressure, since the efficiency of the cataphoretic cleaning decreases according to the studies by Riesz and Dieke[19] and by Schmeltekopf.[34] By changing the purification technique at a fixed gas pressure, different values of μ_{eff} were obtained as indicated in Fig. 10.[35]

The He_2^+ ions, which determined the afterglow properties for pressures above 3 Torr, are converted into Ne^+ ions, according to the process

$$He_2^+ + Ne \rightarrow Ne^+ + 2\,He, \qquad (11)$$

which was postulated by Oskam[9] and has a large cross section (1.5×10^{-15} cm^2). The mobility of Ne^+ ions in helium, as estimated by Oskam, is $\mu_0(Ne^+) = 24.5$ cm^2/V sec and is larger than that of He_2^+ ions (in helium), so that the effective ambipolar diffusion coefficient increases with increasing number density of Ne^+ ions. Consequently, the value of μ_{eff}, as calculated from D_a, increases in the same manner.

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[34] A. L. Schmeltekopf, Doctoral dissertation, University of Texas, Austin, 1962 (unpublished).

[35] The constant value of $D_a p_0$ in helium reported by Mulcahy and Lennon (Ref. 14) for the pressure range of 3 to 22 Torr, while using commerically available helium, without the application of further purification techniques, is difficult to explain in view of both present and previous studies (Refs. 8 and 9).

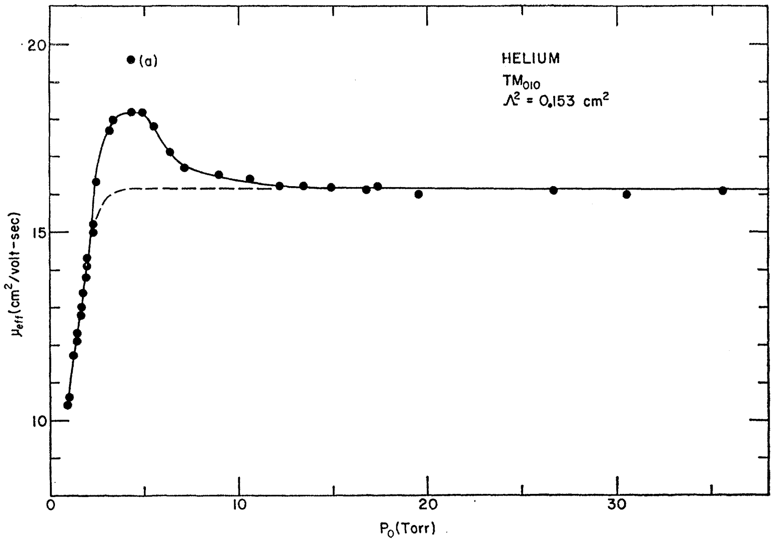

FIG. 10. Dependence of μ_{eff} on pressure p_0 in helium when cataphoretically cleaning helium at the pressure studied. The value (a) was obtained without further purification of the commercial helium. The dashed line refers to measurements during which the helium was purified at a pressure of about 40 Torr.

For decreasing helium pressures below 3 Torr, the properties of the He^+ ions increasingly determined the disappearance of electrons from the plasma. In this pressure region the disappearance of He^+ ions by ambipolar diffusion and by conversion into He_2^+ ions via the three-body collision process

$$He^+ + 2\,He \rightarrow He_2^+ + He \qquad (12)$$

is slower than the removal of He_2^+ ions by the combination of ambipolar diffusion losses and destruction via process (11). The value of the mobility of He^+ ions in helium is considerably smaller than that of the He_2^+ and Ne^+ ions; moreover, the He^+ ions can be expected to have a very small cross section for a destruction process of the type (11). The value of $D_a p_0$ will thus decrease with decreasing gas pressure as a consequence of the strong dependence on pressure of the conversion frequency associated with process (12).

From the above discussion follows that in the pressure region where the He_2^+ ions determine the disappearance of electrons via the ambipolar diffusion loss process, the presence of neon impurity ions can appreciably increase the rate of disappearance of electrons from the plasma. When the helium pressure is such that He^+ ions govern the disappearance of electrons, the influence of the presence of neon impurity atoms is relatively small. At pressures above 12 Torr the efficiency of the cataphoretic cleaning is large enough to ensure that the influence of neon atoms is negligible, so that μ_{eff} is equal to $\mu_0(He_2^+)$ in this region. The decreasing efficiency of the cataphoretic segregation of neon atoms in helium with decreasing pressure combined with the dependence on pressure of the destruction frequency of He^+ ions via process (12) explains the μ_{eff} versus p_0 curve as measured in commercially available helium when cleaning helium at each pressure involved. The effect of neon impurity atoms on the measurements was eliminated at all pressures by purifying the helium used at a pressure of about 40 Torr, at which pressure the efficiency of the cataphoretic cleaning effect was large. The μ_{eff} versus p_0 curve then obtained is shown in Fig. 4, and is indicated in Fig. 10 by the dashed line.

The detailed *explanation of the pressure dependence* of the segregation of very small concentrations of neon impurity atoms in helium has not been given previously. The theory of the segregation efficiency as presented by Druyvensteyn[36] predicts that the cataphoretic segregation efficiency, for a very small number of impurity atoms, should be independent of gas pressure. This author, however, neglects the pressure dependence of the production of impurity ions. The only effective process, aside from the small contribution of direct ionization of neon atoms, of producing Ne^+ ions in helium is via process (11), since a helium-neon mixture does not constitute a Penning mixture.[37] The production of He_2^+ ions in the positive column of the dc cataphoretic discharge is strongly pressure-dependent, since this type of ion is produced either via process (12) or by the Hornbeck-Molnar process[38]

$$He^* + He \rightarrow He_2^+ + e. \qquad (13)$$

Consequently, the efficiency of the production of Ne^+ ions via process (11) should increase with increasing gas pressure. It can, therefore, be expected that the efficiency of the removal of very small concentrations of neon impurity atoms from helium via the cataphoretic segregation effect increases also with increasing gas pressure.[39,40]

It should be realized that the efficiency of the segrega-

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[36] M. J. Druyvensteyn, Physica 2, 255 (1935).

[37] F. M. Penning, Physica 1, 1028 (1934).

[38] J. A. Hornbeck and J. P. Molnar, Phys. Rev. 84, 625 (1951).

[39] H. J. Oskam, J. Appl. Phys. 34, 711 (1963).

[40] The dependence on pressure of the rate of ionization of impurity atoms in a dc discharge also explains why, for example, the efficiency of the segregation of argon impurity atoms in neon shows only a very small dependence on pressure (Ref. 39).

tion mechanism is determined by the number of He_2^+ ions present during an active discharge, while the value of μ_{eff} refers to the type of ion which is dominant during the late part of the afterglow period. The production of He^+ ions ceases immediately after termination of the discharge pulse and these ions are converted into He_2^+ ions via process (12). At helium pressures larger than 3 Torr the relevant conversion frequency is large enough to ensure that, for the container used, the properties of the late afterglow are determined by He_2^+ ions, although their number density during the active discharge may be relatively small. The discharge tube used for purifying the gases was 55 cm long and had a diameter of 1 cm. For discharge currents between 50 and 100 mA the helium pressure had to be increased to a value larger than 12 Torr in order to ensure that a sufficient number of He_2^+ ions, which are required for an efficient segregation of neon atoms, was produced during the active discharge. This explains why the value of $\mu_0(He_2^+)$ could be measured at pressures considerably lower than the pressure for which the efficiency of cataphoretic segregation of neon atoms in helium is sufficiently large.

VIII. SUMMARY

The values of the mobility μ_0 of ions in their parent gas as measured by means of the ion-transit-time methods were compared with those calculated from the rate of electron loss by the ambipolar diffusion process as measured during the afterglow period of plasmas produced in helium, neon, and argon. The values which were found to be consistent with data obtained by means of these two quite different measuring techniques are: $\mu_0(He^+)=10.7$, $\mu_0(He_2^+)=16.2-16.7$, $\mu_0(Ne^+)=4.1$, $\mu_0(Ne_2^+)=6.5$, $\mu_0(Ar^+)=1.6$, and $\mu_0(Ar_2^+)=1.9$ cm²/V sec. The definite identities of the types of ions involved have not been established as yet and studies in this direction are being carried out.

The value of the conversion coefficient C relating to the probability of production of He_2^+ ions via three-body collisions of He^+ ions with two neutral helium atoms was estimated to be 105 ± 10 sec^{-1} $Torr^{-2}$. Analogous values relating to the production of Ne_2^+ ions and Ar_2^+ ions could not be determined due to the large influence of the electron diffusion cooling process in neon and argon at low gas pressures.

The pressure dependence of the efficiency of the cataphoretic segregation of neon atoms in helium was demostrated. This dependency could be explained by taking into account the pressure dependence of the rate of production of Ne^+ ions in helium containing very small concentrations of neon impurity atoms.

ACKNOWLEDGMENTS

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