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Diffusion coefficient for thermal electrons in neon at 295 K

T. Rhymes and R. W. Crompton
Electron and Ion Diffusion Unit, Research School of Physical Sciences, Australian National University, Canberra, Australia

G. Cavalleri
Centro Informazioni Studi Esperienze, Milano, Italy

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The diffusion coefficient for thermal electrons in neon has been measured by the direct sampling technique of Cavalleri. The result is compared with recent experimental determinations, which show a large scatter by comparison with similar data in other gases, and with values calculated using theoretically derived cross sections. There is satisfactory agreement with the value calculated using a cross section that has been derived from drift-velocity data through a direct application of modified effective-range theory. An analysis of the effects of Penning ionization on the measurement has been made from which the lifetime of the $^3P_2$ neon metastable has been estimated.

I. INTRODUCTION

Measurements of the diffusion coefficient of thermal electrons in neon at room temperature and below are important because of the information they provide regarding the behavior of the momentum-transfer cross section for electrons having energies less than 30 or 40 meV. The cross section at low energies is difficult to determine through drift-tube experiments alone because of the difficulty of achieving experimental conditions that enable good accuracy to be achieved when the mean energy of the electrons only slightly exceeds $\frac{3}{2}\kappa T$. The cross section in neon is known to decrease rapidly below 1 eV. At the lowest energies for which experimental data are available, its value is of the order of 5×10^{-15} mm^2.[1] This low value is to be compared with the cross sections for the other monatomic gases at similar energies (that is, 30–40 meV), which are 10–20 times as large.[2] As a consequence of this and the small average energy loss per collision (one-fifth that for helium), the mean energy of a swarm is three or four times the thermal value at the lowest values of E/N and the lowest temperature (77 K) for which reliable drift data are currently available. This is the reason why it has not been possible to place error limits on the cross section determined from drift experiments at energies less than 40 meV. One way of extending this range is by making measurements of the diffusion coefficients for thermal electrons at reduced temperatures.

The available data for the diffusion coefficient at thermal energies are conflicting. Nelson and Davis[3] list the results of five determinations of the coefficient prior to their own work, there being a factor of 2 between the largest and smallest values. The application of their own method to neon did not clarify the situation, since their results are scattered by ±30% about the mean value, in contrast to their measurements for other gases where the spread of the data is usually less than ±5%.

The experiments described here were undertaken in an attempt to resolve the unsatisfactory situation regarding the experimental data at room temperature. The application of the new result to the determination of the e-Ne scattering cross section at very low energies is discussed in a later paper.

For several reasons, the application of Cavalleri's technique[4] to neon is less straightforward than to helium. Section II describes the modifications that were made to the apparatus used by Gibson, Crompton, and Cavalleri[5] to improve the experimental accuracy of the basic method, while Sec. III describes its application to neon and the additional problems that were encountered. Although these problems restricted the range of the experimental parameters that could be used, it was possible to make measurements from which the diffusion coefficient can be determined in the pressure range between 10 and 15 kPa. The results of these measurements are given in Sec. IV. In Sec. V, the new result is compared with previously published results.

II. EXPERIMENTAL DETAILS

Apart from the calibration system described subsequently, the apparatus is the same as that described by Gibson *et al.*[5] The gas used was Matheson research grade neon. Measurements were made in a laboratory whose temperature was controlled to within ±2 K; the fluctuations in the cell temperature, which was monitored with a copper-constantan thermocouple, were less than ±1 K. Since the momentum-transfer cross section q_m is approximately proportional to the electron speed at low energies, the diffusion coefficient D is insensitive to small variations in the gas temperature, and errors from this source were negligible.[2]

The attenuators used by Gibson *et al.* to overcome possible nonlinearity in the detection system were found to exhibit sporadic changes in attenuation coefficient that were attributed to variations in the contact resistance of the switching relays. In the present experiments, the need for the attenuators was avoided by improving the linearity of the detection system.

Two calibrating systems were used to establish the linearity of the entire system beyond the photomultiplier, that is, the preamplifier, pulse-shaping amplifier, sample-and-hold circuit, and analog-to-digital converter. In the first system, an Ortec 448 Research Pulser was used to generate pulses having known relative amplitudes, and the corresponding numbers of counts from the ADC recorded in equal intervals of time were compared. The accuracy of this method of calibration was better than ±0.025% of full scale. The linearity of the detection system was found to be better than ±0.04% from 2 to 10 V. Below 2 V the nonlinearity increased, but this was outside the range of input signals which were accepted.

The second method employed a light-emitting diode (LED), placed within the light-tight box containing the diffusion cell and photomultiplier. By applying alternating pulses of approximately 100 and 200 nsec to the LED, light pulses differing in total output by approximately a factor of 2 were produced and could be used to replace those that resulted from the ionization and excitation produced by the density-sampling pulse acting on the residual electrons in the cell. The duration of each pulse is short compared to the time constant of the output circuit of the photomultiplier; the photomultiplier signal is thus proportional to the total light emitted by the LED. The linearity of the system was checked by varying the signal levels from the photomultiplier, either by varying its gain or by placing attenuators between it and the preamplifier. The system was also used to check the performance of a noise-subtraction system by which the signal produced by fluorescent light from the x-ray pulse is subtracted from the total signal recorded during a density-sampling pulse. The linearity figures obtained by this method confirmed those from the first, more precise, technique.

III. DIAGNOSTICS AND OPERATING CONDITIONS

The decay of electron number density in the cell can be affected by stray electric fields, space charge due to the x-ray ionization (primary space charge), space charge caused by the density-sampling pulse (secondary space charge), the effects of residual impurities in the gas sample, reflection of electrons at the boundaries, and diffusion cooling. In addition, it is essential to make measurements of the decay only after sufficient time has elapsed to ensure that the electrons are in thermal equilibrium and higher-order diffusion modes have decayed. Each of these effects restricts the range of operating parameters that may be used, so that it is necessary to examine the results for the influence of each of them in order either to adjust the experimental conditions to eliminate them, or to make appropriate corrections.

A. Thermalization and diffusion modes

The free electrons created by the x rays have energies as high as 10 keV. In order for the diffusion to be determined solely by the temperature and nature of the gas, these electrons and their progeny must lose energy until they are in thermal equilibrium with the gas. A theory whereby approximate thermalization times can be calculated from values of W (drift velocity) and D/μ (ratio of diffusion coefficient to mobility) is given in Appendix I, together with the resulting values for He and Ne.

The thermalization time is inversely proportional to pressure. Consequently, it is possible, in principle, to work at pressures that are sufficiently high to ensure that lack of thermalization does not affect the measurement. However, there is a limit to the maximum pressure that can be used because, as the pressure is increased, the voltage of the sampling pulse must be increased. Present equipment permits a maximum pressure, in neon, of about 20 kPa. The thermalization time at this pressure is of the order of 10 μsec. This value is about 50 times greater than for helium at the same pressure, the difference arising from the fact that the cross section at thermal energies and the average energy loss per collision for neon are about $\frac{1}{10}$ and $\frac{1}{5}$, respectively, of the corresponding values for helium.

Since, in analyzing the time dependence of the electron density, it is assumed that the amplitudes of higher diffusion modes are negligibly small, the presence of such modes may be a significant source of error if the electron-density sampling is performed too soon after the initial ionization. The first higher-order diffusion mode has a time constant $\frac{1}{9}$ that of the fundamental. Thus, by delaying the first measurement of relative density until the time elapsed after the initial ionization is equal to the time constant τ of the fundamental mode, the amplitudes of the higher modes will have decayed until they are less than 0.03% of the fundamental.[4]

The effects of lack of thermalization and higher diffusion modes can be separated by varying the pressure. The diffusion time constants are directly proportional to pressure, whereas the thermalization time is inversely proportional to it. Thus, if the diffusion time constant is determined at several pressures from measurements made at delay times that are always constant fractions of τ, any variation in the measured value must be attributed to lack of thermalization and not to higher diffusion modes. A pressure can therefore be chosen for which there is no measurable effect of lack of thermalization. Subsequently, delay times are selected in order to avoid the influence of higher diffusion modes.

B. Primary space charge

If either the x-ray energy or pulse duration is sufficiently large, space charge resulting from the positive ions produced during the initial ionization will measurably slow the decay of electron density. In order to isolate this effect from other effects such as those described in the next section, it is necessary to keep the *total* rate of charge production constant while the initial level of ionization is varied. This is achieved by adjusting the magnitude of the sampling pulse so that the light pulses are maintained at a constant level independent of the initial conditions.

The effect of varying the primary space charge by varying the x-ray pulse duration is shown in Fig. 1. There is a small, apparently linear, dependence of the time constant on the level of initial ionization which leads to a small (~0.3%) error at the lowest level used. It can be seen from the figure that negligible error is made in determining the true value by linear extrapolation to zero initial ionization.

C. Secondary space charge and charge replenishment

Following the application of the sampling pulse, the number density of the electrons and ions in the cell is large by comparison with the number produced in the initial ionization. The electron density rapidly decays, but the residual positive space charge may influence the free diffusion of the electrons in the next measurement. Since it is not possible to apply a clearing field in these experiments (cf. Ref. 4), reduction of the positive-ion density to a negligible level takes place only by diffusion, and hence the effect of secondary space charge is altered by the repetition rate of the experiment. For sufficiently fast rates, the measured diffusion time constant is found to increase; in the limiting case, at very high repetition rates, the onset of ambipolar diffusion causes the electrons to diffuse at the same rate as the ions. It is therefore essential to choose repetition rates that are low enough to avoid significant secondary space charge effects. However, the rate cannot be reduced indefinitely for the following reason.

The presence of stray electric fields within the cell, even though weak, may cause rates of electron loss comparable with those resulting from free diffusion. In the present experiments, this problem is overcome by the self-compensating nature of the glass cell, whereby any stray field in the cell modifies the motion of the electrons and ions created by the sampling pulse in such a way that their final distribution tends to cancel the stray field.[5] This self-compensating mechanism requires a continual application of charge resulting from the sampling pulse in order to replace that lost by leakage through the glass walls. At slow repetition rates the replenishment of charge to the walls becomes inadequate, and the drift resulting from fields produced by uncompensated charges on the walls would be expected to cause an additional electron loss and hence a decrease in the measured time constant.

The behavior of the measured time constant τ as the repetition time $\mathcal{R}$ is varied is shown in Fig. 2. The very steep rise below $\mathcal{R} = 2.5$ sec is due to secondary space charge retarding the electron diffusion. The decrease in time constant at long repetition times is not so pronounced but is indicated by a drop in τ at $\mathcal{R} = 8$ sec. Very little data were taken in this region due to the very long times necessary to obtain reasonable accuracy. The plateau between 2.5 and 5 sec provides a suitable region in which to operate at this pressure without the danger of either drift fields or space charge affecting the result.

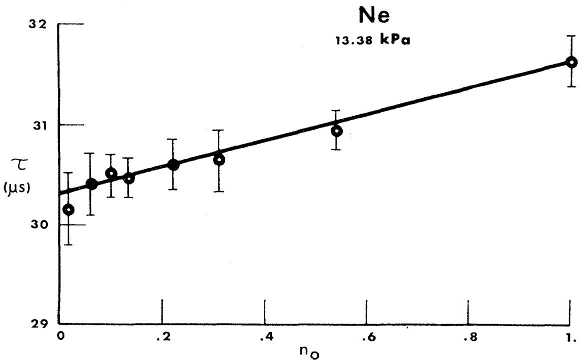

FIG. 1. Variation of the measured electron-diffusion time constant τ with relative initial electron number n_0.

D. Penning ionization of impurities

Molecular impurities in the cell may be ionized by metastable neon atoms which are created by the x-ray burst. Since a single exponential is assumed when analyzing the results, any additional electrons produced in this way will cause a change in the measured time constant τ as the time interval between the x-ray and sampling pulses (the sampling time) is varied, unless the time constant for decay of the metastables happens to coincide with the diffusion time constant τ_D.[4] The effect of impurities is considered to be negligible if there is no significant variation of τ as the time interval is increased from one to three or four time constants.

Figure 3 shows the results taken at 6.69, 10.04, and 13.38 kPa. The variation of τ with the sampling time is consistent, at least qualitatively, with there being electron production by Penning ionization, the time constant for the decay of the metastables being larger than τ_D even at the highest pressure. At the highest pressure, the effect of metastable ionization is seen to be negligible for sampling times less than about $4\tau_D$, while there is a plateau extending from $4\tau_D$ down to about $1.5\tau_D$ where the measured time constant is independent of the sampling time S, the values at times less than $1.5\tau_D$ being affected by lack of thermalization. As the pressure is reduced, the plateau is reduced from both ends; larger values of S are required before adequate thermalization is achieved, while the metastables begin to affect the measurements at smaller values of S.

Although the results recorded at the highest pressure indicate that there is an adequate range of values of S over which the diffusion coefficient can be measured without serious error from either effect, we have carried out an analysis to see whether the shapes of the curves taken at different pressures can be predicted theoretically in terms of Penning ionization of an impurity. This has been done primarily to determine what effect the presence of Penning ionization has on the accuracy of the value of τ_D obtained from the plateau in the 13.38-kPa curve.

The process whereby the two metastable states $^3P_2$ and $^3P_0$ of neon are created and destroyed is complex when the neutral number density is within the range of the present experiments. Massey, Burhop, and Gilbody[6] have summarized the reaction rates for the competing processes as determined by Dixon and Grant[7] and Phelps.[8] On the basis of their work, we make the following simplifying assumptions: (a) the decay of the metastables responsible for the Penning ionization obeys an exponential law with essentially a single time constant; (b) even at the highest pressure, de-excitation of the metastables is predominantly via a two-body process involving collisions with neon atoms. The first assumption, whose validity will be tested finally by the adequacy of the fits to the

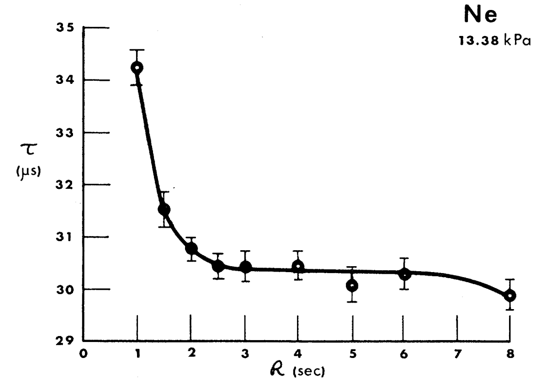

FIG. 2. Behavior of the measured electron-diffusion time constant τ when the repetition time $\mathcal{R}$ of the experiment is changed. The onset of the effect of drift fields is suggested by the value at $\mathcal{R} = 8$ sec and was confirmed in later experiments.

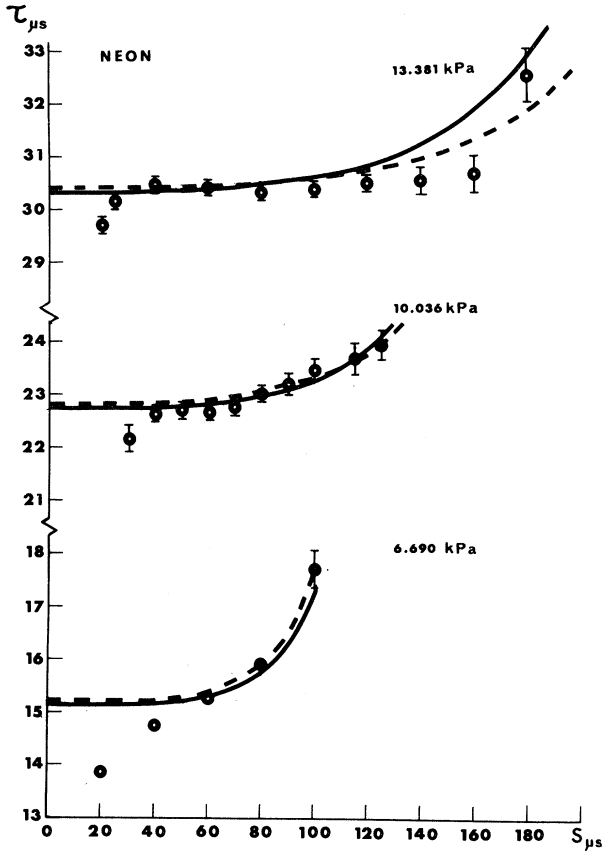

FIG. 3. Variation of the measured electron-diffusion time constant τ with differing sampling times S for three pressures.

experimental curves, would be applicable if the population of the $^3P_2$ state were to predominate in our experiment as in those of Phelps; in any case, the rate of loss of metastables tends to be dominated by the decay of the $^3P_2$ population, because a fraction of the shorter-lived $^3P_0$ metastables decays to $^3P_2$. The second assumption is reasonable in view of the magnitudes of the two- and three-body coefficients cited by Massey *et al.*; even if it is not strictly valid, it introduces no great error in the subsequent analysis because of the relatively restricted range of pressure used.

When the total electron population n in the cell is supplemented by the Penning ionization of an impurity, the equation describing n is [cf. Eq. (8) of Ref. 4]

$$\frac{dn}{dt} = -\frac{nD}{\Lambda^2} + \beta N_{\rm im} N_0^* \, e^{-t/\tau_m}, \tag{1}$$

where Λ^2 is the cell constant (see Sec. IV), $N_{\rm im}$ the number density of the impurity, N_0^* the initial metastable number, τ_m the time constant for the decay of the metastable population, and β the metastable deactivation rate through Penning ionization for unit number density of metastable atoms and impurity molecules. Equation (1) is derived on the assumption that the influence of higher-order diffusion modes can be neglected (i.e., the equation applies to times greater than the fundamental diffusion time constant) and that, as already stated, a single exponential adequately describes the decay of the metastable population.

The general expression for the time constant τ_m for the decay of the metastable population is given by

$$\tau_m^{-1} = D_m/\Lambda^2 + \gamma N + \delta N^2 + \beta N_{\rm im}. \tag{2}$$

With the low impurity levels expected in these experiments ($\lesssim 1$ ppm), and because of assumption (b) above, the fourth the third terms (corresponding to Penning and three-body de-excitation, respectively) are very much less than the two-body term γN. Similarly, since the time constant for diffusion of the metastables is of the same order as that for unexcited atoms (that is of the order of seconds at 10 kPa), D_m/Λ^2 is negligibly small. Thus

$$\tau_m^{-1} \approx \gamma N, \tag{3}$$

that is, τ_m is proportional to $1/N$.

The solution of Eq. (1) is

$$n = A\, e^{-t/\tau_D} + \frac{\beta N_{\rm im} N_0^*}{1/\tau_D - 1/\tau_m}\, e^{-t/\tau_m}, \tag{4}$$

where A is a constant and $\tau_D = \Lambda^2/D$ is the time constant for diffusion of the electrons.

We now wish to use Eq. (4) to predict the experimental curves shown in Fig. 3. The experimental data presented in this figure were derived from measurements of the ratio $n(S)/n(S+\Delta t)$ of the electron populations recorded for the sampling times S and $S+\Delta t$. On the assumption that the decrease in population is due solely to diffusion, an effective time constant τ was calculated from the equation

$$n(S)/n(S+\Delta t) = e^{\Delta t/\tau},$$

that is,

$$\tau = \frac{\Delta t}{\ln[n(S)/n(S+\Delta t)]}\,.$$

From Eq. (4) it follows that τ can be calculated in terms of τ_D, τ_m, and a constant B (which is a function of gas pressure and composition) from the equation

$$\tau = \frac{\Delta t}{\ln[(e^{-S/\tau_D} + Be^{-S/\tau_m})/(e^{-(S+\Delta t)/\tau_D} + Be^{-(S+\Delta t)/\tau_m})]}\,, \tag{5a}$$

where

$$B = \frac{\beta N_{\rm im} N_0^*/n_0}{1/\tau_D - 1/\tau_m}\,. \tag{5b}$$

In what follows, it is assumed that N_0^*/n_0 is independent of the gas number density N.

The following two model cases are considered:

a. $N_{\rm im}$ proportional to N. This situation would occur if the getter used to maintain the purity of the gas sample[5] were fully effective in removing molecular impurities, but the gas samples contained as an impurity a low concentration of a heavier rare gas with an ionization potential lower than the metastable level in Ne (~16.5 eV). The most probable candidate is Ar, which an assay of a typical sample of the gas shows to be present at less than 1 ppm. In this event it follows that if measurements are made with a number density N_1 at which τ_D, τ_m, and B have the values τ_{D_1}, τ_{m_1}, and B_1, the corresponding values when the density is changed to $N_2 = RN_1$ will be

$$\tau_{D_2} = R\tau_{D_1}, \quad \tau_{m_2} = \tau_{m_1}/R$$

and

$$B_2 = R\frac{1/\tau_{D_1} - 1/\tau_{m_1}}{1/R\tau_{D_1} - R/\tau_{m_1}}\, B_1.$$

By scaling the parameters in this way and choosing values that lead to the best overall fit to the data recorded at the three pressures, we obtain the set of curves shown by the solid lines in Fig. 3.

b. $N_{\rm im}$ independent of N. The second possibility considered is that which corresponds to a molecular impurity held at a constant partial pressure within the cell by the action of the getter. Notwithstanding the fact that the cell was baked for a long period at 200°C, the possibility of Penning ionization arising from such an impurity (e.g., water vapor) cannot be ruled out, because of the extremely low levels required for the effect to be measurable. On this assumption,

$$B_2 = \frac{1/\tau_{D_1} - 1/\tau_{m_1}}{1/R\tau_{D_1} - R/\tau_{m_1}} B_1 ,$$

the scaling for τ_D and τ_m being as before. The dashed curves of Fig. 3 show the best fits to the data with this assumption. It can be seen that the fit is somewhat better than that obtained on the basis of the first assumption, although the correspondence between the calculated and measured curves for the highest pressure is not completely satisfactory.

The inclusion of a significant contribution from three-body de-excitation (for example, 20% of the total at the highest pressure) with a subsequent modification of the simple scaling law for τ_m [Eq. (3)] was found to produce only a slight modification to the curves, because of the relatively restricted pressure range.

Notwithstanding the oversimplification represented by the analysis, its success in predicting the τ-vs-S curves obtained at the three pressures suggests that the upcurving at late times is explicable in terms of a metastable ionizing process, probably of an impurity present with constant partial pressure. The value of τ_m obtained from this analysis (~180 μsec at 10 kPa) is of the right order when compared with Phelps's results for the de-excitation rate of $^3P_2$ atoms.

The analysis also allows an estimate to be made of the influence of metastable ionization on the result for τ_D calculated from the value of τ measured under the most favorable experimental conditions, that is, with $S \sim 3\tau_D$ and $p = 13.38$ kPa. Assuming the validity of model b, which predicts somewhat greater upcurving for this sampling time than is observed experimentally, the error is about 0.5%.

E. Reflection at the cell walls

A further source of error may arise from the assumption of zero electron density at the walls. The breakdown of this assumption, as a consequence of significant electron reflection, can be investigated by measuring ND at various pressures since, as discussed in Ref. 5, significant reflection would lead to a pressure dependence of this product. In the present experiments, however, an investigation of the pressure dependence would not have been possible, because of the limited range of pressure over which ND could be accurately determined (see Sec. III A). Furthermore, the investigation was not necessary since the same glass cell was used as for the experiments in helium, in which no pressure dependence was observed over a sixfold change in pressure, the extended pressure range providing a more adequate test for evidence of electron reflection.

F. Diffusion cooling

The effect of diffusion cooling on measurements of this type has been investigated experimentally in argon by Crompton and Rhymes[9] and theoretically in helium, neon, and argon by Leemon and Kumar.[10] The experiments in argon demonstrated variations in the measured values of ND of more than a factor of 2 over the range of pressures used, whereas no measurable change had been observed in the earlier experiments in helium.[5] The experimental observations in these gases are in good agreement with theory. In the case of neon, theory predicts that the effect of diffusion cooling will be more evident than in helium, but not greatly so. At first sight this is surprising, since the effect depends, to first order, on the thermal coupling between the electrons and the gas. The coupling is much smaller for neon than helium, because both the cross section and average energy loss per collision in this energy range are considerably smaller. However, these factors are offset by the energy dependence on the cross section, the cross section increasing approximately as the electron speed. When the cross section is directly proportional to the speed, theory predicts the absence of diffusion cooling.[10] Taking the best current estimate for the cross section in the thermal region,[11] Leemon and Kumar predict that, for our cell dimensions, the asymptotic value of ND is reached at about 16 kPa, and that a reduction of about 1% can be expected in the value measured at 13.38 kPa. Unfortunately, the disappearance of the plateau in the τ-S curves at the two lower pressures makes it impossible to establish experimentally the magnitude of the effect in neon, but the agreement between theory and experiment in the case of argon, which is a more severe test of the theory, supports the theoretical predictions and suggests that a correction of about 1% should be made to the value obtained from the 13.38-kPa results.

IV. RESULTS

For the reasons discussed in Sec. III D, the measurements made at 13.38 kPa were capable of yielding the most accurate value of *ND*. The procedure for making the measurements at this pressure was as follows. Since the dependence of the measured time constant τ on the repetition time $\mathcal{R}$ and the sampling time S will be the same irrespective of the initial level of ionization, the majority of the diagnostic measurements were made using a level that was large enough to ensure good statistics but not so large as to cause large errors from primary space charge. Using an ionization level corresponding to 0.13 on the curve plotted in Fig. 1, the curves of τ vs $\mathcal{R}$ (Fig. 2) and τ vs S (Fig. 3) were first obtained and used to determine optimum ranges for $\mathcal{R}$ $(2.5 \leqslant \mathcal{R} \leqslant 5)$ and S $(1.5\tau_D \leqslant S \leqslant 3\tau_D)$. The data shown in Fig. 1 were subsequently taken using values within these ranges, and the curve extrapolated to zero initial density. The resulting value of τ_D is 30.32 μsec, with a standard deviation of ±0.06 μsec.

The diffusion coefficient is determined from the relation

$$D = \Lambda^2/\tau_D ,$$

with Λ^2 a geometrical factor (the cell constant) related to the cell dimensions through

$$\frac{1}{\Lambda^2} = \left(\frac{\pi}{h+2d}\right)^2 + \left(\frac{2.405}{r+d}\right)^2 , \qquad (6)$$

h and r being the height and radius of the cell, and d the extrapolation distance.[4] Uncertainty in the cell dimensions leads to an uncertainty of ±0.4% in Λ^2.[5] The values of d and hence Λ^{-2} appropriate to these measurements are given in Appendix II.

The pressure was measured to within ±0.1% using a quartz-spiral manometer. The temperature of the cell at the time of filling, which is required to calculate the gas number density, was measured to within ±0.5 K using a copper-constantan thermocouple.

In summary, the total uncertainty in the measurement of *ND* is the sum of errors incurred in measuring the following quantities: (a) number density—±0.1%, due to pressure measurement, ±0.2%, due to temperature measurement; (b) cell constant—±0.4%, due to dimensional tolerances; (c) time constant—±0.2%, (estimate) due to possible nonlinearity and the finite resolution of the detection chain, plus ±0.2% RMS error. In addition, as discussed in Secs. III D and III F, Penning ionization may have been responsible for the value being low by at most 0.5%, while diffusion cooling may have also lowered the value by a further 1%. With these estimates of the error, the result obtained at 295 K is *ND* $(10^{20}\ \mathrm{mm^{-1}\,sec^{-1}}) = 72.7^{+2.5}_{-1.0}\%$ (systematic) ±0.2% (RMS), which is consistent with the results taken at 6.69 and 10.0 kPa, as can be seen in Fig. 3.

V. DISCUSSION AND CONCLUSION

Table I shows the results of various measurements of *ND* in neon together with values of *ND* calculated from recently published theoretical calculations of the low-energy phase shifts for neon. Because the electrons are in equilibrium with the gas at temperature T, the formula for *ND* used in these calculations reduces to[5]

$$ND = \frac{2}{3}\left(\frac{2}{m\pi}\right)^{1/2} (\kappa T)^{-3/2} \int_0^\infty \frac{\epsilon}{q_m(\epsilon)}\, e^{-\epsilon/\kappa T}\, d\epsilon . \qquad (7)$$

The theoretical results of Thompson[13] and of Garbaty and LaBahn[14] include the scattering length and the phase shifts down to an energy of 0.136 eV. In order to estimate the momentum-transfer cross sections in the energy range required to evaluate the integral in Eq. (7), we have applied modified effective range theory[15] (MERT) to the data pub-

TABLE I. Measured and calculated values for *ND* in neon.

ND $(10^{20}\ \mathrm{mm^{-1}sec^{-1}})$	Source	Author
69.0 ± 2.4	measurement of diffusion of thermal electrons	Cavalleri *et al*.[a]
64.7	drift-dwell-drift experiment	Nelson and Davis[b]
$72.7^{+2.0}_{-0.9}$	present experiment	
95.0	calculated from theoretical cross section	Thompson[c]
57.8	calculated from theoretical cross section	Garbaty and LaBahn[d]

[a] Reference 12.
[b] Reference 3.
[c] Reference 13.
[d] Reference 14.

lished by these authors. The phase shifts at 0.136 and 0.544 eV were inserted into the MERT relations for $\sin(\eta_0 - \eta_1)$ and $\sin(\eta_1 - \eta_2)$ and the resulting equations solved to determine the parameters. The cross section could then be determined within the required range.

The agreement between the three most recent experimental determinations is disappointing. Nelson and Davis commented that their experiments had to be performed with somewhat lower than optimum pressures, and that this could have been the explanation for the relatively poor agreement obtained between the individual measurements made at 4 and 5.3 kPa. It is difficult to suggest possible reasons for the large scatter in their data, since there is no systematic trend of the data with variation in sample pressure, and the results taken at a single pressure (4 kPa) show wide variation. It is possible that the explanation lies in the fact that the energy relaxation times were significant compared with the drift and dwell times owing to the poor energy transfer and small cross section at low energies.

The present result and that of Cavalleri *et al.* disagree by about 5%, which is approximately equal to the sum of the error limits of the two results. The most likely source of residual error in the experiment of Cavalleri *et al.* is stray fields within the diffusion cell, since the inside surfaces were metallized. However, the presence of such fields would reduce the measured time constant and thus lead to values of D that are too large, whereas the value of Cavalleri *et al.* is lower than the present value. It is possible that their assumption that the maximum value of τ is the most probable value could have been responsible for their having incorrectly weighted their result towards a small value of D if an unknown source of systematic error had been present, but, since the effects of primary and secondary space charge were eliminated at the outset, there is no obvious reason why their assumption should be invalid.

The agreement between theory and experiment is even worse. The present result and that calculated using Thompson's cross section differ by a factor of about 1.3, the experimental result, which is lower than the theoretical one, suggesting that, for energies less than about 0.05 eV, Thompson's cross section is too low by about the same factor. Similarly, the theoretical cross section of Garbaty and LaBahn leads to a value of ND that differs from the experimental value by a factor of about 1.25, the experimental value in this case being the higher. Thus, in spite of the comparatively poor agreement between the recent experimental results, there seems to be overwhelming evidence that no *ab initio* calculation has so far yielded a scattering length that is within (10–15)% of the correct value.

Finally, an analysis of Robertson's[1] drift-velocity data provides additional evidence in favor of the present value of ND. As a first step, MERT was used to determine a cross section that yields satisfactory agreement with Robertson's drift-velocity data.[11,16] The MERT parameters found from this analysis were then used to calculate ND as already described. The resulting value of ND, 74.6×10^{20} mm^{-1} sec^{-1}, is 2.6% higher than the present value, suggesting that, although the measured value may be 1% or 2% low, the error limits placed on it are realistic.

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APPENDIX I

Consider an electron swarm that has not yet attained an equilibrium energy distribution appropriate to the electric field of strength E in which it moves. Suppose that the mean energy of the swarm is $\bar{\epsilon} \equiv \bar{\epsilon}(t)$, and that N is the number density of the gas. In what follows, it is also assumed that the functional form of the energy distribution is essentially invariant so that the energy distribution can be characterized by any of its moments. Then the mobility of the electrons can be defined as $\mu = \mu(\bar{\epsilon})$, since the mobility depends in this instance on the energy distribution and not on the electric field. The instantaneous drift speed W_E is then $W_E = \mu(\bar{\epsilon})E$, and since $\mu(\bar{\epsilon})$ is inversely proportional to N, $W_E = N\mu(\bar{\epsilon})E/N \equiv W_E(E/N, \bar{\epsilon})$.

The energy balance equation is

$$\frac{d\bar{\epsilon}}{dt} = eEW_E(E/N, \bar{\epsilon}) - NP(\bar{\epsilon}) = eE^2\mu(\bar{\epsilon}) - NP(\bar{\epsilon}), \tag{A1}$$

where $NP(\bar{\epsilon})$ is the mean rate of energy loss of electrons in collisions. If the energy distribution function is Maxwellian, then $\bar{\epsilon} = \frac{3}{2}eD/\mu$. In other cases, $\bar{\epsilon}$ is still $\sim D/\mu$.

Consider an electric field of strength X defined such that, at equilibrium, the mean energy of the swarm moving through a gas with number density N is $\bar{\epsilon}$. Then this swarm can be characterized by

TABLE II. Thermalization times for pressures used in the present experiment and a final energy of 50 meV.

p (kPA)	Neon	He
6	30 μsec	0.5 μsec
10	18 μsec	0.3 μsec
13	14 μsec	0.23 μsec

TABLE III. Values of Λ^{-2} corresponding to the three gas pressures used.

p (kPa)	d (mm)	Λ^{-2} (mm^{-2})
6.69	0.11	1.491×10^{-2}
10.036	0.07	1.497×10^{-2}
13.381	0.05	1.501×10^{-2}

X/N rather than $\bar\epsilon$, that is,

$$(D/\mu)(\bar\epsilon)\equiv(D/\mu)(X/N),\quad W_X(X/N,\bar\epsilon)\equiv W_X(X/N),$$

$$\mu(\bar\epsilon)\equiv\mu(X/N),\quad P(\bar\epsilon)\equiv P(X/N),\quad \text{etc.}$$

In this equilibrium situation, $d\bar\epsilon/dt=0$. It follows that

$$eXW_X(X/N)=eX^2\mu(X/N)=NP(X/N).$$

Thus, assuming that $\bar\epsilon\simeq\frac{3}{2}eD/\mu$, Eq. (A1) becomes

$$\frac{3}{2}e\frac{d}{dt}[(D/\mu)(X/N)]\simeq eE^2\mu(X/N)-eX^2\mu(X/N),$$

or

$$\frac{3}{2}\frac{d}{dt}[(D/\mu)(X/N)]\simeq\mu(X/N)(E^2-X^2).$$

Thus

$$Ndt=\frac{3d[(D/\mu)(X/N)]}{2N\mu(X/N)[(E/N)^2-(X/N)^2]}\ ;$$

consequently,

$$NT=\int_{(D/\mu)(E/N)}^{(D/\mu)(X/N)_{\max}}\frac{3d[(D/\mu)(X/N)]}{2W(X/N)[X/N-(E/N)^2/(X/N)]}\ ,$$

where T is the thermalization time or the time required for the electron swarm to come into equilibrium with the electric field E from some initial energy $(D/\mu)(X/N)_{\max}$. In practice, for NT to be finite, the lower limit must slightly exceed $(D/\mu)(E/N)$.

Using the equation for NT, thermalization times for electrons in neon and helium have been calculated using values of W and D/μ vs E/N from Huxley and Crompton.[2]

Table II shows the order of thermalization times for the pressures used in the present experiment and a final energy of 50 meV.

APPENDIX II

The extrapolation length d which appears in Eq. (6) is approximated by

$$d=0.71\lambda_m=(0.71/N)q_m,$$

where λ_m is the mean free path for momentum transfer. Using

$$q_m\approx4\times10^{-15}\ \text{mm}^2,$$

$$h=29.92\pm0.05\ \text{mm},$$

$$r=37.72\pm0.07\ \text{mm},$$

the values of Λ^{-2} listed in Table III are obtained corresponding to the three gas pressures used.

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