The Ratio of the Lateral Diffusion Coefficient to Mobility for Electrons in Argon at 294 K

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Abstract

The ratio of the lateral diffusion coefficient to mobility (D_T/μ) for electrons in argon has been measured at 294 K in the range $0.001 \le E/N$ (Td) ≤ 0.1 using pressures in the range 309-1171 kPa. The total error in the best-estimate values is estimated to be less than $\pm 2\%$ for $E/N \le 0.0035$ Td and less than $\pm 1.5\%$ for $E/N \ge 0.004$ Td. A discussion is given of the design of a Townsend-Huxley diffusion experiment in light of recent theoretical work on the influence of material boundaries on diffusing streams of charged particles and of the effects on the measurements of multiple scattering and dimer formation.

1. Introduction

The analysis of electron transport coefficient data is now a well-established technique for deriving the momentum transfer cross section $q_m(\varepsilon)$ for electron-atom collisions. This technique, generally regarded to be the most accurate available at energies less than about one electron volt, has been used to determine the helium (Crompton *et al.* 1970) and neon (Robertson 1972) cross sections. In the case of argon, however, there is considerable doubt about the magnitude of the cross section, particularly in the region of the Ramsauer minimum. The cross section derived by Frost and Phelps (1964) from an analysis of the mobility data of Pack *et al.* (1962) and the lateral diffusion data of Warren and Parker (1962) differs at energies near the minimum by as much as a factor of five from the cross section derived by Golden (1966) using atomic effective-range theory to analyse total cross section measurements at energies in the range 0.1-21.6 eV (Golden and Bandel 1966).

The use of the swarm approach is more difficult for argon than it is for helium and neon. First the minimum in the cross section presents problems of uniqueness in the analysis and this puts great emphasis on the accuracy of the experimental transport coefficient data. A second difficulty is that electron motion in argon is extremely sensitive to impurities in the gas sample. These considerations have stimulated a fresh attack on the argon problem, with particular emphasis on obtaining accurate experimental data. This paper reports data for the ratio of the lateral diffusion coefficient to mobility (D_T/μ) at 294 K over a range of E/N (*E* being the electric field strength and *N* the gas number density) from 0.001 to 0.1 Td. In the following companion paper (Milloy *et al.* 1977; present issue p. 61) these data, together with the data for the electron drift velocity reported in the previous paper (Robertson 1977; p. 39) are used to determine $q_m(\varepsilon)$ for electrons in argon in the energy range from 0 to 4 eV.

2. Theory and Experimental Design

The Townsend-Huxley method was used to measure the ratio $D_{\rm T}/\mu$. A description of the technique and of the factors which influence the design of an experiment based on the method is given by Huxley and Crompton (1974).

In the present application, a critical factor was the abnormally large values of the ratio $(D_T/\mu)/(E/N)$ which occur over the whole range of values of E/N covered by the measurements. For example, the highest value, which occurs at $E/N \sim 5 \times 10^{-3}$ Td, is about 40 times larger than the highest value in hydrogen at 293 K within the range of E/N investigated by Crompton *et al.* (1968). The high values result from the smallness of the momentum transfer cross section for electron energies near the Ramsauer–Townsend minimum and from the small fractional energy loss per collision due to the relatively large atomic mass of argon.

The fundamental problem caused by large values of the ratio $(D_T/\mu)/(E/N)$ relates to the validity of the analysis of the Townsend-Huxley experiment (Crompton 1972). In deriving values of $D_{\rm T}/\mu$ for a given set of experimental conditions from the measured current ratios, it has been customary to assume that the electron energy distribution function is spatially independent, an assumption which Parker (1963) showed to be invalid. The spatial dependence of the distribution function is due to electron density gradients which are inherent in any experiment to measure diffusion coefficients and which are enhanced by the influence of the cathode and anode boundaries. However, despite the demonstration of the significance of the spatial dependence, no one has succeeded in analysing the problem completely taking account of all the factors which cause it. Lowke (1971) suggested an analysis based on the validity everywhere within the apparatus of a continuity equation for the electron density n which allowed for anisotropic diffusion. A justification for this procedure was given by Huxley (1972) who based his analysis on the assumption that the spatial dependence of the electron number density can be expressed as a series expansion using the gradient operator as an expansion parameter. Subsequently Skullerud (1974) examined the validity of this approach and concluded that it could not be used to describe conditions near material boundaries. Skullerud's conclusion was based on an analysis of the initial development of a swarm released as a δ -function in space, and therefore possessing very large (initially infinite) density gradients at early times. An important conclusion from this analysis is that the effect of an absorbing boundary is restricted to a distance of the order of $2D_T/W$ from the boundary and that, within this distance, diffusion theory is inapplicable. A similar conclusion can be drawn from the recent work of Hall and Lowke (1975) who examined inter alia the variation of number density close to an absorbing boundary intercepting an electron stream which is uniform at an infinite distance from the boundary.

In the absence of a complete analytical description of the experiment it is necessary to choose the experimental conditions and design the apparatus to minimize the influence of the boundaries. Then, provided the thickness of the layer adjacent to the boundaries in which diffusion theory breaks down is a small fraction of the total length of the diffusion apparatus, it seems reasonable to analyse the results using Lowke's (1971) approach, which takes account of the influence of electron density gradients, on the assumption that the anomalous lateral diffusion in the boundary region will contribute only a second-order correction.

Since, as has already been stated, the thickness of the boundary region is of the order of $D_T/W = (D_T/\mu)/\{(E/N)N\}$, the thickness can be reduced by increasing N.





Fig. 1. Diffusion chamber: A, americium foil; B, gold annular shield; C, lead shield; D, Pyrex liner.

In order to work with boundary conditions comparable with those used, for example, in the hydrogen experiments quoted earlier, it would be necessary to use gas number densities as high as those equivalent to 40 atm (\sim 4 MPa) at ambient temperature. Although such large number densities would be desirable to reduce boundary effects to an insignificant level, they are technically difficult to achieve while meeting other equally important criteria such as the maintenance of adequate gas purity and the accurate measurement of pressure. Moreover, as N is increased, the advantage to be gained from a reduction in end effects must ultimately be offset by the increasing effects of dimer formation and multiple scattering phenomena (see Section 5).

A compromise was therefore made by designing the apparatus for use with pressures up to about 12 atm (~1.2 MPa). At this pressure the largest value of the factor $2D_T/W$ is 0.04 cm, and thus at worst the boundary regions account for only about 1% of the 10 cm length of the diffusion chamber. However, in order to test for the significance of systematic errors arising from a number of causes (see e.g. Huxley and Crompton 1974), measurements at each value of E/N were made over a range of pressures. The lowest pressure used was about 300 kPa (see Table 1). The largest value of $2D_T/W$ at any pressure was found to be 0.10 cm.

The final confirmation of the validity of the assumptions made in analysing the data is the lack of any large pressure dependence in the data recorded in Table 1 where, for the majority of values of E/N, the systematic trend in the data is less than 1% for a pressure variation of 2 to 1.

3. Experimental Details

(a) Apparatus and Gas Handling Techniques

The Townsend-Huxley diffusion chamber used in this work was the one described by Crompton et al. (1965) with the modified lower electrode as detailed by Crompton et al. (1968). The α -particle ionization source consisted of a ²⁴¹Am foil,* having an active area of 60×12.5 mm and a strength of 240 μ Ci cm⁻¹ (8.9×10^7 Bq cm⁻¹), formed into a cylinder and housed within a cylindrical container, as shown in Fig. 1. A 2 mm thick gold annulus was inserted in the source; this, together with the lead shield located behind the source electrode, reduced to an insignificant level volume ionization within the diffusion chamber produced by the γ radiation from the source. The source provided adequate current under all conditions because of the large gas number densities that were used; adjustment of the potential difference between the source and the adjacent electrode enabled the total current arriving at the anode to be kept within the range of about $1-7 \times 10^{-12}$ A. The glass vacuum envelope used in the earlier work was replaced by a stainless steel manifold capable of withstanding pressures of 1.5 MPa. The baseplate of the manifold, which is shown in Fig. 1, was fabricated from a 10 in. Conflat flange from which the apparatus was suspended by a supporting pillar. A Pyrex glass liner surrounding the diffusion chamber delayed the onset of electrical breakdown as the field strength was increased.

The apparatus was used in conjunction with a conventional UHV system with the isolation and gas admittance valves arranged in such a way that parts of the system could safely withstand a pressure of 1.2 MPa. A technique was devised for purifying and storing the gas while ensuring that the remainder of the vacuum system, including

^{*} Type AMM3 from the Radiochemical Centre Ltd, Amersham, U.K.

the purifier, never exceeded a pressure of 100 kPa. Prior to the final set of measurements the system was baked at 120°C for 24 hr. The argon (Matheson Research Grade) was purified by passing through a quartz trap filled with titanium wire coils heated to about 800°C. This procedure had previously been shown to be extremely effective in removing trace quantities of diatomic impurities (Robertson 1977). The gas was continuously condensed in a stainless steel storage cylinder cooled to 77 K, thus maintaining the pressure in the purifier and associated vacuum system below the vapour pressure of argon at 77 K (~20 kPa). The gas was passed through the purifier at a rate of less than 500 kPa l hr⁻¹. When sufficient gas had been collected in the storage cylinder, the tap to the purifier was closed and the cylinder allowed to warm to 195 K. The gas pressure was then measured with a quartz spiral manometer, which had been previously calibrated with a double dead-weight primary pressure The gas temperature, which was measured with a standard (Gascoigne 1971). copper-constantan thermocouple attached to the collecting electrode, was stable to ± 0.5 K over the entire period of the investigation.

(b) Analysis of Results

The results were analysed on the assumption that the electron number density n within the diffusion apparatus obeys the equation

$$D_{\rm L}\frac{\partial^2 n}{\partial z^2} + D_{\rm T}\left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2}\right) = W\frac{\partial n}{\partial z},\tag{1}$$

where W is the electron drift speed and D_L is the diffusion coefficient in the direction parallel to the electric field E which is itself parallel to the z axis. The justification for this assumption was discussed in Section 2. The solution of equation (1) with the boundary conditions n = 0 over the source and receiving electrodes, except at the small hole in the cathode which acts as the point source of electrons, leads to the following equation for the fraction R of the total current received by the central circular disc of the anode of radius b:

$$R = 1 - \left(\frac{h}{d'} - \frac{1}{\lambda_{\rm L} h} + \frac{h}{\lambda_{\rm L} d'^2}\right) \left(\frac{h}{d'}\right) \exp\left(-\lambda_{\rm L}(d'-h)\right),\tag{2}$$

where h is the separation of the source and the receiving electrodes and

$$d'^2 = h^2 + b'^2, \qquad b' = (D_{\rm L}/D_{\rm T})^{\frac{1}{2}}b, \qquad \lambda_{\rm L} = W/2D_{\rm L}.$$

Provided b/h is small and $Wb/2D_T$ is not too large, equation (2) reduces to (Huxley and Crompton 1974)

$$R = 1 - \left[1 + \left(\frac{1}{2} - \frac{D_{\rm L}}{D_{\rm T}}\right) \left(\frac{b}{d}\right)^2\right] \frac{h}{d} \exp\left(-\lambda(d-h)\right),\tag{3}$$

where

 $d^2 = h^2 + b^2$ and $\lambda = W/2D_{\rm T}$.

In the present experiments, where h = 10 cm, b = 0.5 cm and $Wb/2D_T$ was always less than 17, the criteria for the validity of the approximations were well satisfied (Huxley and Crompton 1974), and equation (3) was therefore used to

calculate λ and hence $D_{\rm T}/\mu$ from the measured current ratios. Since $(b/d)^2$ is small, the second term in the square brackets is a small correction term which can be calculated with sufficient accuracy using computed values of the ratio $D_{\rm L}/D_{\rm T}$. The data plotted in Fig. 6 of Milloy *et al.* (1977) were used for evaluating this term.

E/N	$D_{\rm T}/\mu$ (volt) at pressure (kPa) of:							Best estimate
(Td)	309	485	672	840	1010	1107	1171	$D_{\rm T}/\mu$ (volt)
0.0010							0.0404	0.0404
0.0012						0.0467	0.0469	0.0468
0.0014						0.0553	0.0558	0.0556
0.0017				0.0712	0.0715	0.0713	0.0720	0.0715
0.0020				0.0894	0.0907	0.0902	0.0900	0.0901
0.0025			0.1225	0.1229	0.1239	0.1240	0.1239	0.1234
0.0030			0.1574	0.1583	0.1588	0.1587	0.1590	0.1584
0.0035			0.1920	0.1923	0.1933	0.1931	0.1937	0.1929
0.0040			0.2250	0.2256	0.2261	0.2263	0.2267	0.2259
0.0050			0.2859	0.2865	0.2862	0.2868	0.2870	0.2865
0.0060		0.3384	0.3382	0.3400	0.3404	0.3398	0:3403	0.3395
0.0080		0.4283	0.4295	0.4295	0.4314	0.4311	0.4323	0.4304
0.010		0.5012	0 · 5059	0.5074	0.5069	0 • 5069	0.5075	0.5060
0.012		0.5656	0.5701	0.5713	0.5719	0.5714	0.5726	0.5705
0.014		0.6265	0.6264	0.6283	0.6291	0.6295	0.6302	0.6283
0.017		0.6979	0.7017	0.7038	0.7036	0.7040	0.7049	0.7027
0.020	0.7613	0.7625	0.7650	0.7682	0.7689		0.7695	0.7659
0.025	0.8507	0.8545	0.8574	0.8593	0.8611		0.8617	0.8575
0.030	0.9293	0.9342	0.9371	0.9380	0.9387			0.9355
0.035	0.9962	1.003	1.006	1.005				1.003
0.040	1.054	1.060	1.064	1.064				1.061
0.020	1 · 159	1.162	1.167					1.163
0.060	$1 \cdot 245$	1 · 250						$1 \cdot 248$
0·080	1 · 391							1.391
0·100	1 · 508							1 · 508

Table 1. Experimental values of $D_{\rm T}/\mu$ for electrons in argon at 294 K

4. Results

The ratio $D_{\rm T}/\mu$ for electrons in argon was measured at 294 K over the range $0.001 \le E/N$ (Td) ≤ 0.1 using pressures in the range 309–1171 kPa. The results are listed in Table 1 and the best-estimate results (which in this case are arithmetic mean values) are plotted as a function of E/N in Fig. 2. To help understand the relationship between $D_{\rm T}/\mu$ and the form of the momentum transfer cross section, the mean electron energy $\tilde{\varepsilon}$, calculated using the cross section of Milloy *et al.* (1977), is also plotted in Fig. 2.

It was necessary to apply small corrections to the gas number density due to deviations from the ideal gas law. At the highest pressure used the correction was 0.8%. The upper pressure limit was set by the range of the pressure gauge. At pressures lower than about 500 kPa measurement errors increased rapidly with decreasing pressure due to there being an insufficient fraction of the total current on the central collector for accurate current ratio measurement. The potential difference between anode and cathode was always greater than 28 V in order to reduce possible errors from contact potential differences. There was no evidence that the results were affected by inelastic collisions between the electrons and molecular impurities introduced either with the incoming gas or by outgassing. The results were stable with time over a period of 1 week and there was no dependence of the results on the rate at which gas was passed through the purifier. The presence of small quantities of negative ions (probably oxygen) was detected in some of the experimental runs through a dependence of the results at low E/N on the current in the diffusion chamber. Even when the negative ion current is an extremely small fraction of the total current, space charge repulsion can significantly affect the divergence of the diffusing electron stream (Liley 1967). In the present work it was always possible to work in a current range where space charge errors were insignificant.



Fig. 2. Plots of the measured variation of D_T/μ as a function of E/N for electrons in argon at 294 K together with the corresponding E/N variation of the calculated mean electron energy $\bar{\epsilon}$.

The most significant source of error arose from the measurement of the current ratios which ranged from about 0.12 (at E/N = 0.02 Td, p = 309 kPa) to about 0.41 (at 0.025 Td, 1171 kPa).* Under some conditions the uncertainty from this

* The current ratios that were measured can be obtained directly from the data in Table 1 by using equation (3). They can be calculated more easily, and to within a few per cent, by using the approximate formula

 $R = 1 - \exp\{-1.544 \times 10^{-2} (E/N) p/(D/\mu)\},\$

where E/N is in Td, p in kPa, and D/μ in volt.

source was 0.7% but a value of 0.4% is more typical. Many other possible sources of error such as those arising from the assumption and approximations used in deriving equation (3) (see Sections 2 and 3) and errors due to collective effects (see Section 5) appear to be small, as the systematic dependence on gas pressure (of the order of 1% over the pressure range of 2 or 3 to 1) is barely significant. The uncertainties in the pressure, field and temperature measurements were in each case <0.1%. Although the origin of the small pressure dependence cannot be isolated and therefore the error bounds on the data cannot be established with the same certainty as has been possible in other similar experiments (see e.g. Huxley and Crompton 1974), nevertheless it seems reasonable to assign to the best-estimate values listed in Table 1 error limits of $\pm 2\%$ for $E/N \le 0.0035$ Td and $\pm 1.5\%$ for $E/N \ge 0.004$ Td.

5. Discussion

The only other data available for D_T/μ in argon are the room temperature measurements of Townsend and Bailey (1922) and the 87 K data of Warren and Parker (1962). Neither set of data is plotted in Fig. 2 because there is no overlap between the present results and those of Townsend and Bailey and since a direct comparison with Warren and Parker's data is not possible over a significant part of the range of E/N because of the difference in gas temperature. Furthermore the experimental difficulties discussed in Section 2, which in Warren and Parker's experiments were exaggerated by the limitation of the maximum gas number density to a value somewhat less than the minimum density used in the present experiments, resulted in a relatively large scatter in their data thus limiting the value of a comparison between the two sets of data.

It is necessary to examine the results reported here for the possible consequences of the unusually large neutral densities that were used in the experiments.

(a) Collective Effects

Bartels (1973), using pressures in the range 20–97 atm ($2 \cdot 0$ –9 $\cdot 8$ MPa) observed a pressure dependence of electron drift velocities in argon at low E/N. The drift velocity was found to increase with increasing pressure, and at E/N values where the electrons were in thermal equilibrium with the gas atoms, the electron mobility at the highest pressure (97 atm) was observed to be a factor of 1.83 larger than at the lowest pressure. As E/N was increased the effect decreased and no pressure dependence was observed for E/N > 0.008 Td. The question therefore arises as to whether the $D_{\rm T}/\mu$ measurements in the present work are in error at low E/N due to the collective effects observed by Bartels. Two points need to be considered. First, as E/N decreases the ratio D_T/μ is controlled to an increasing extent by the gas temperature and to a decreasing extent by the microscopic details of the collisions. Thus one would expect the pressure dependence of D_T/μ at low E/N to be less than the pressure dependence of μ . Second, the pressure dependence of μ within the ranges of pressure and E/N used in the present work would be small. By extrapolating Bartels's data to lower pressures, it can be deduced that the pressure dependence of even the zero-field mobility would not be greater than 4% in the pressure range used here and could be as small as 1%; the pressure dependence of μ at the lowest E/N value used here would be even smaller. It follows that one would not expect multiple scattering effects to give rise to an observable pressure dependence in this work.

(b) Presence of Dimers

At first sight it is surprising that effects due to the presence of dimers were not observed through a dependence of D_T/μ on gas pressure. One might expect that inelastic collisions between electrons and dimers would reduce the mean electron energy and also D_T/μ in the same way as the addition of small quantities of diatomic impurities such as nitrogen and hydrogen (Robertson 1977). This would give rise to a pressure dependence, since the fraction of argon dimers in argon increases linearly with pressure in the pressure range used here, the fractional abundance of dimers being about 0.07% per 100 kPa at 300 K (Milne and Greene 1967). There are two possible reasons why the effects of dimers were not observed. First, the energy loss in an electron-dimer collision must be small. The dissociation energy of an argon dimer in the ground state is about 12 meV (Bruch and Magee 1970) but very few of the electrons would actually lose as much as 12 meV in a collision with a dimer since the dimers would normally be in excited vibrational and rotational states, for which the dissociation energy would be considerably less. Second, the magnitude of the relevant cross sections may be small.

The E/N variation of the mean electron energy and D_T/μ shown in Fig. 2 can be explained in terms of the energy dependence of the momentum transfer cross section $q_m(\varepsilon)$. The rapid rise of D_T/μ and $\overline{\varepsilon}$ in the range up to about 0.003 Td reflects the steep decrease of $q_m(\varepsilon)$ with increasing energy up to 0.2 eV. For E/N > 0.008 Td the electron motion is largely controlled by collisions of electrons with energies on the high energy side of the Ramsauer minimum where the cross section increases rapidly, and consequently D_T/μ and $\overline{\varepsilon}$ increase less rapidly with increasing E/N. In the region 0.003 < E/N (Td) < 0.008, D_T/μ is very sensitive to the form of the cross section minimum and these values were crucial to the cross section derivation.

6. Conclusions

Despite the problems that result from the abnormally large values of ND_T in argon, it has been possible to measure the ratio D_T/μ with good accuracy using the conventional lateral diffusion method and neutral densities considerably larger than have been used previously for experiments of this kind. From the absence of any significant dependence of the results on the neutral density, it may be concluded that the choice of neutral densities was a reasonable one to avoid, on the one hand, errors arising from the use of equation (3) and, on the other, the observable consequences of dimer formation and the breakdown of the assumption of two-body electronneutral scattering. The application of these data to the problem of determining the electron-argon momentum transfer cross section in the energy range covering the Ramsauer-Townsend minimum is discussed in the following paper (Milloy *et al.* 1977).

Acknowledgments

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References

- Bartels, A. (1973). Phys. Lett. A 44, 403.
- Bruch, L. W., and McGee, I. J. (1970). J. Chem. Phys. 53, 4711.
- Crompton, R. W. (1972). Aust. J. Phys. 25, 409.
- Crompton, R. W., Elford, M. T., and Gascoigne, J. (1965). Aust. J. Phys. 18, 409.
- Crompton, R. W., Elford, M. T., and McIntosh, A. I. (1968). Aust. J. Phys. 21, 43.
- Crompton, R. W., Elford, M. T., and Robertson, A. G. (1970). Aust. J. Phys. 23, 667.
- Frost, L. S., and Phelps, A. V. (1964). Phys. Rev. 136, A1538.
- Gascoigne, J. (1971). Vacuum 21, 21.
- Golden, D. E. (1966). Phys. Rev. 151, 48.
- Golden, D. E., and Bandel, H. W. (1966). Phys. Rev. 149, 58.
- Hall, C. A., and Lowke, J. J. (1975). J. Comput. Phys. 19, 297.
- Huxley, L. G. H. (1972). Aust. J. Phys. 25, 43.
- Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley-Interscience: New York).
- Liley, B. S. (1967). Aust. J. Phys. 20, 527.
- Lowke, J. J. (1971). Proc. 10th Int. Conf. on Phenomena in Ionized Gases, Vol. 1, p. 5 (Donald Parsons: Oxford).
- Milloy, H. B., Crompton, R. W., Rees, J. A., and Robertson, A. G. (1977). Aust. J. Phys. 30, 61.
- Milne, T. A., and Greene, F. T. (1967). J. Chem. Phys. 47, 4095.
- Pack, J. L., Voshall, R. E., and Phelps, A. V. (1962). Phys. Rev. 127, 2084.

Parker, J. H. (1963). Phys. Rev. 132, 2096.

- Robertson, A. G. (1972). J. Phys. B 5, 648.
- Robertson, A. G. (1977). Aust. J. Phys. 30, 39.
- Skullerud, H. R. (1974). Aust. J. Phys. 27, 195.
- Townsend, J. S., and Bailey, V. A. (1922). Philos. Mag. 44, 1033.
- Warren, R. W., and Parker, J. H. (1962). Phys. Rev. 128, 2661.

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