Electron Transport in Argon–Hydrogen Mixtures

G. N. Haddad and R. W. Crompton

Electron and Ion Diffusion Unit, Research School of Physical Sciences,
Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

Abstract

The transport coefficients v_{dr} and $D_\perp/\mu$ have been measured in mixtures of $0\cdot5\%$ and 4% hydrogen in argon. All measurements were made at 293 K. It is shown that for these mixtures the use of the solution of the Boltzmann equation based on the two-term Legendre expansion of the velocity distribution function introduces no significant error in the analysis of the transport data. All the experimental data have been predicted to within $\pm3\cdot5\%$ using previously published cross section data.

1. Introduction

This paper presents measurements of the drift velocity v_{dr} and the lateral diffusion coefficient to mobility ratio $D_\perp/\mu$ for electrons in mixtures of $0\cdot5\%$ and 4% hydrogen in argon. All measurements were made at 293 K.

Electron transport in mixtures of these two gases has been studied previously (Engelhardt and Phelps 1964), and discrepancies have been noted between the measured parameters and those calculated using available cross sections and a solution of the Boltzmann equation. For example, in a mixture of $1\cdot5\%$ hydrogen in argon there is a 20% discrepancy between the measured and calculated drift velocities at a value of E/N (the ratio of electric field strength to gas number density) of approximately $0\cdot2$ Td (1 Td $\equiv 10^{-17}$ V cm^2).

It was suspected that, for electron transport in hydrogen–argon mixtures, the solution of the Boltzmann equation based on retention of only the first two terms in the Legendre expansion of the velocity distribution function (the 'two-term' solution) might be inadequate, particularly in the energy region near the Ramsauer minimum in the argon momentum transfer cross section. In this region the ratio of the inelastic scattering cross section to the elastic cross section is a maximum, and it is a large value of this ratio which necessitates retention of more than two terms for an adequate solution. (See for example the investigation of electron transport in methane by Kleban and Davis 1977.)

This fact, coupled with the inconsistencies referred to above, suggested the need for further measurements on mixtures of these two gases and further calculations which avoided the 'two-term' approximation.

2. Cross Section Data

In order to calculate transport parameters over a nominated range of E/N, we need the scattering cross sections for all energetically possible processes in both gases. In addition, if we retain more than two terms in the Legendre expansion of the

velocity distribution function (i.e. we use a 'multiterm' solution), we need the angular distributions of the scattered electrons.

The momentum transfer cross section σ_m in pure argon has been determined previously (Milloy *et al.* 1977) by the analysis of measurements of $D_\perp/\mu$ as a function of E/N at 294 K and measurements of v_{dr} as a function of E/N at 90 and 293 K. These measurements were used to determine σ_m over the energy range 0–4 eV with an additional constraint imposed by the fact that the cross section had to conform to modified effective range theory (MERT) (O'Malley 1963) in the low energy region (<0.32 eV). The cross section was further verified here by using the program developed by O'Malley (O'Malley and Crompton 1980) which employs a search routine to determine the optimum set of MERT parameters to fit a given set of experimental data. A small modification to the program enabled a simultaneous fit to be made to the v_{dr} and $D_\perp/\mu$ data. Excellent agreement with the cross section of Milloy *et al.* was obtained up to an energy of 1.0 eV, illustrating the power of this technique in finding a cross section to fit experimental data using relatively few parameters, in this case four. The first inelastic threshold in argon is at 11.5 eV and, since this is well above the energy range of interest here, no attempt was made to include this process in the calculations.

For molecular hydrogen, input from a number of experiments (Crompton *et al.* 1969; Gibson 1970; Crompton *et al.* 1970) and theory (Henry and Lane 1969; M. A. Morrison, personal communication) has been used to provide a complete set of cross sections which are consistent with the available swarm data. In summary, measurements of v_{dr} and $D_\perp/\mu$ in parahydrogen at 77 K were used to determine uniquely the $J = 0\rightarrow2$ rotational cross section from threshold to 0.3 eV, and a vibrational cross section and the momentum transfer cross section for energies less than 2 eV. Since the derived $J = 0\rightarrow2$ cross section and the theoretical calculations of Henry and Lane (1969) were in excellent agreement, the $J = 0\rightarrow2$ cross section was extrapolated to higher energies by using the theoretical curve. This procedure allowed the determination of the vibrational cross section. Measurements in normal hydrogen at 77 K were then used to determine uniquely the $J = 1\rightarrow3$ rotational cross section. Once again this was found to be in good agreement with the theoretical calculations (Henry and Lane 1969).

Since the current experiments are conducted at 293 K the $J = 2\rightarrow4$ and $3\rightarrow5$ cross sections are also required in the analysis. These were derived by using the scaling laws of M. A. Morrison (personal communication) and the previously determined $J = 0\rightarrow2$ cross section. A check on this procedure was made by comparing the ratio of the $J = 1\rightarrow3$ and $0\rightarrow2$ cross sections from Morrison's predictions with the values calculated using the previously derived cross sections. The satisfactory results of this comparison gave confidence in the results of applying this procedure to determine the cross sections for higher rotational states. It should be noted that it is not necessary to know these particular cross sections extremely accurately since, for example, a change of 10% in the $J = 2\rightarrow4$ cross section results in a change in either of the transport parameters of at most 0.5%.

The set of cross sections was completed by including the $v = 0\rightarrow2$ and $0\rightarrow3$ cross sections taken directly from the work of Ehrhardt *et al.* (1968). This complete set of cross sections is consistent with the measured transport parameters in pure hydrogen at 293 K (Crompton *et al.* 1968; Robertson 1971), predicting the parameters to within $\pm1.5\%$.

A multiterm solution of the Boltzmann equation requires angular distributions for the various processes. The angular distributions for elastic scattering are by far the most important because there are many more elastic than inelastic collisions. Since argon is by far the largest component of the mixtures (a minimum of 96% in the experiments and 90% in the calculations) we have attempted to represent the angular distributions for electrons scattered elastically by argon as accurately as possible. We have used the distributions calculated by D. Walker (personal communication) which have the advantage that they extend to very low energies (0·01 eV). These data are consistent with the experimental measurements of D. Andrick (personal communication) in the range of overlap. The angular distributions were interpolated within the range of the calculations (0·01–1·8 eV) and outside these limits were held equal to those at the upper or lower limit.

For elastic scattering in hydrogen we selected the one from the angular distributions of Linder and Schmidt (1971) which would maximize the difference between the two-term and multiterm solutions. We found that such a distribution is one which shows the most scattering in the backward direction, as expected on theoretical grounds (H. R. Skullerud, personal communication). Thus we chose the published distribution at an energy of 1 eV to represent the angular distribution for elastic scattering at all energies. The angular distribution at 4·5 eV for inelastic scattering involving the $v = 0 \rightarrow 1$ transition was chosen (again from Linder and Schmidt 1971) as being representative for all inelastic processes. This somewhat arbitrary choice was justified by the fact that the results are very insensitive to changes in the angular distribution for the relatively infrequent *inelastic* scattering events.

3. Calculations using Multiterm Solution

Using the assembly of data described in the previous section we have calculated transport parameters in argon–hydrogen mixtures with the concentration of hydrogen varying from 0·5% to 10%. The particular method used is described in detail by Lin *et al.* (1979). In principle we can retain as many terms in the spherical harmonic expansion of the velocity distribution function as we wish. In practice we limit the terms retained to the point where inclusion of further terms does not alter the results to within reasonable limits (say 0·1%). This, then, is the so-called 'converged' or multiterm result, and in practice one need retain only five or six terms in the expansion for most cases studied to date.

Over a wide range of values of E/N we found a difference of $<0·3\%$ between transport parameters calculated using either the two-term or multiterm solution. This difference is small compared with the uncertainties in the present measurements of the transport parameters.

4. Experimental Details

Both the drift velocity apparatus and the diffusion chamber used for the present measurements have been described in detail previously (Crompton *et al.* 1968; Milloy and Crompton 1977), so that no description need be given here.

The argon used was Matheson grade (99·9995% pure) which was further purified by condensing the gas over liquid nitrogen in a side arm of the system and then allowing the side arm to warm to 195 K. This provides a source of gas from which most of the likely condensible impurities have been removed. The hydrogen was

purified by admitting it to the system through a silver–palladium alloy osmosis tube (Crompton and Elford 1962). It is worth noting at this point that the sensitivity of these measurements to the presence of impurities in the gas sample is very much less than in the case of pure argon (Robertson 1977), since we are adding at least 5000 p.p.m. of a diatomic gas (in this case hydrogen) to the argon. Nevertheless, as a check on the purity of the argon, measurements of $D_\perp/\mu$ were made on a sample of the gas treated in the manner described above. The results were within 1% of the measurements of Milloy and Crompton (1977).
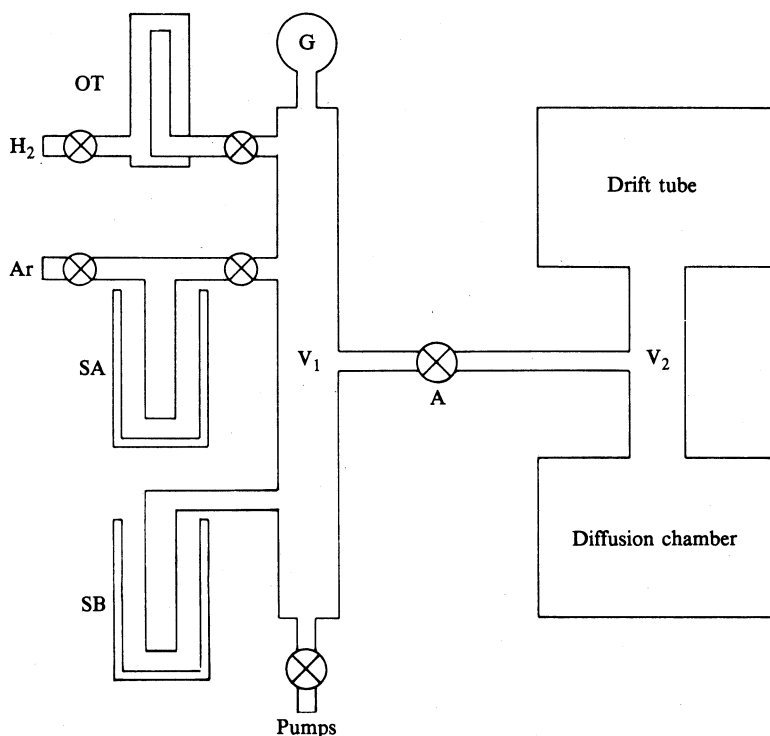

Fig. 1. Schematic diagram of the apparatus showing the system used to produce the argon–hydrogen mixtures. The legend is explained in the text.

Mixtures were made using a volume-sharing technique in order to obtain accurate ratios of the constituents of the mixture. The system is shown schematically in Fig. 1. The two volumes used in the volume sharing are labelled V_1 which is simply the gas handling section of the apparatus, and V_2 which comprises the drift velocity apparatus and the diffusion chamber connected together (for this series of experiments) via a length of 30 mm ID stainless steel tubing. This enables the same gas sample to be used for measurements of both v_{dr} and $D_\perp/\mu$. The volume ratio V_2/V_1 is of the order of 10:1. This ratio was measured accurately by having V_2 evacuated, filling V_1 to a known pressure, and then opening valve A and measuring the final pressure.

Mixtures were made using the following procedure. Argon was introduced into the side arm SA and condensed over liquid nitrogen. When sufficient argon had been accumulated the SA was allowed to warm to 195 K. The complete system $V_1 + V_2$ was then filled to a measured pressure of argon. Valve A was closed and V_1 evacuated.

Hydrogen was then admitted to V_1 via the osmosis tube OT to a known pressure
Valve A was then opened and mixing began. All pressures were measured using a
quartz spiral manometer G which had previously been calibrated with a double
dead-weight primary pressure standard (Gascoigne 1971).

The particular configuration of the apparatus resulted in rather long times for
the gas mixture to become homogeneous. This is illustrated in Fig. 2 where measure-
ments of $D_\perp/\mu$ are shown as a function of time after mixing. In this particular case
the mixture (4% hydrogen in argon) took 800 h to reach equilibrium concentration
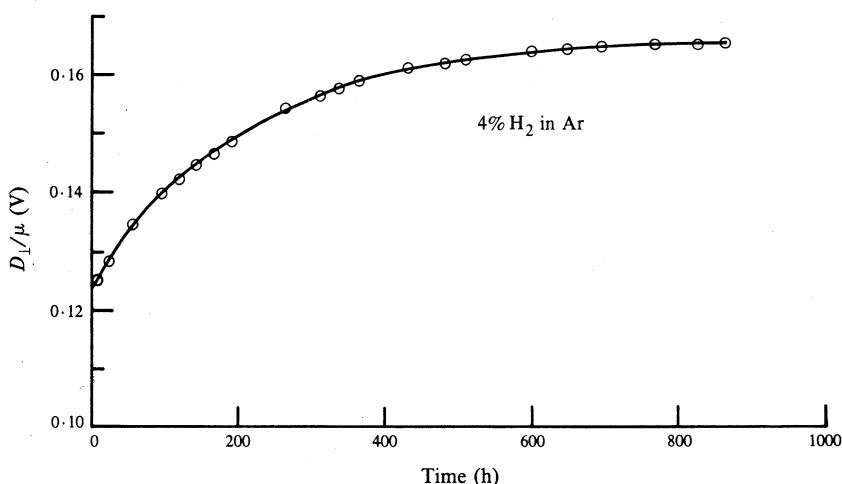throughout the apparatus.

Fig. 2. Measurements of $D_\perp/\mu$ in a nominal mixture of 4% H_2 in Ar at a pressure
of 100 kPa showing the time required for complete mixing.

The mixing process could be hastened somewhat (but still required some hundreds
of hours) by 'stirring' the gas in the apparatus. This was done by freezing out the
argon using liquid nitrogen on another side arm SB (Fig. 1) and then releasing it by
warming the side arm to room temperature, the procedure being repeated a number
of times. As a control, measurements of $D_\perp/\mu$ were made with a pure argon sample
which had been subjected to the procedure outlined above. There was no evidence
of the introduction of any impurity (for example, by the release of condensible
impurities from the walls of the apparatus) through the adoption of this procedure.

At times, samples of gas were held in the apparatus for up to 2000 h. Measure-
ments of the transport parameters as a function of time after completion of mixing
allows an upper limit to be placed on the uncertainty of the measurements due to
the introduction of impurities from the walls of the system into the sample (see
Section 6).

5. Results

The results of the measurements of v_{dr} and $D_\perp/\mu$ in 0·5% and 4% hydrogen in
argon mixtures are plotted as a function of E/N in Fig. 3 together with the previous
results in pure argon (Robertson 1977; Milloy and Crompton 1977).

The observed drift velocity v'_{dr} is related to the true drift velocity v_{dr} through the relation (Huxley and Crompton 1974)

$$v'_{dr} = v_{dr}\left(1 + \frac{C D_{\parallel}/\mu}{V}\right),$$

where $D_{\parallel}$ is the longitudinal diffusion coefficient, V the potential difference between the shutter planes, and C a constant which depends in part on the mode of operation of the shutters, the ratio of the shutter open time to the transit time, and the relative sizes of the source and the collecting electrode.
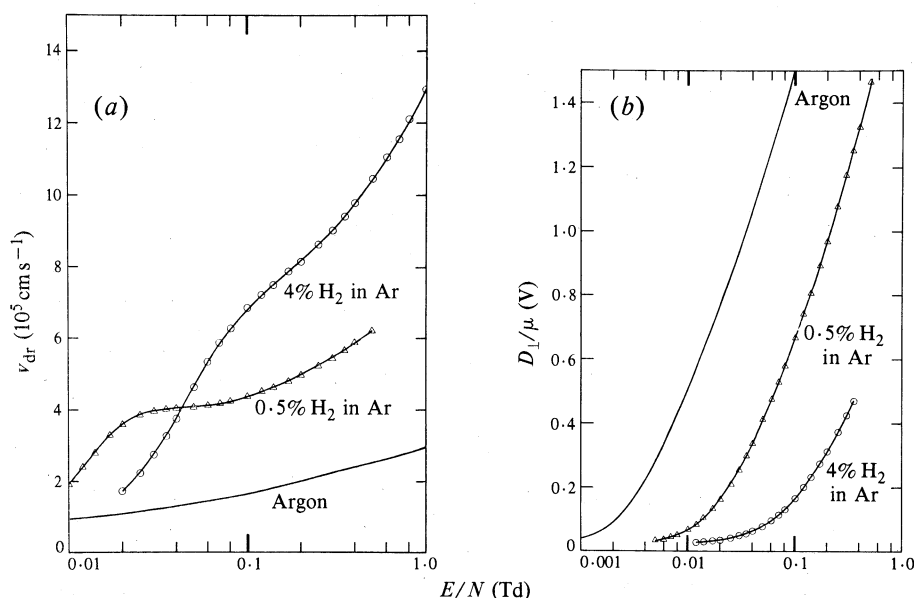

Fig. 3. Measurements of (a) drift velocity v_{dr} and (b) $D_{\perp}/\mu$ as functions of E/N for mixtures comprising 0.5% and 4% H_2 in Ar. The data for pure argon from the work of (a) Robertson (1977) and (b) Milloy and Crompton (1977) are shown for comparison.

The validity of a relationship of this form has been demonstrated many times (Elford 1971), at least to the extent required to make the corrections to v'_{dr} necessary to obtain v_{dr}, since these are usually less than 1%. Accordingly, drift velocities were measured as a function of pressure (for both mixtures) and values of v'_{dr} were plotted against N^{-1}. The resultant straight lines of best fit were then extrapolated to $N^{-1} = 0$. These extrapolated values are the data plotted in Fig. 3a. As in earlier work the largest correction applied to our raw data was of the order of 1%, and the constant C was found to have a value of the order of 1.2.

The values of $D_{\perp}/\mu$ are obtained from measurements of the current ratio in a Townsend–Huxley apparatus. The fraction R of the total current received by the central circular disc of the anode of radius b is given by

$$R = 1 - \{1 + (\tfrac{1}{2} - D_{\parallel}/D_{\perp})(b/d)^2\}(h/d)\exp\{-\lambda(d-h)\},$$

where $d^2 = h^2 + b^2$, $\lambda = W/2D_\perp$ and h is the separation of the source and receiving electrodes. Simplification of the formula to this expression (Huxley and Crompton 1974) requires both that b/h be small and that $Wb/2D_\perp \leqslant 100$. These conditions are well satisfied in the present experiment. Further simplification can be achieved by noting that $(\frac{1}{2} - D_\parallel/D_\perp)(b/d)^2$ is a small correction term. In the case of our analysis it was neglected since it was always less than $0 \cdot 2\%$. The formula then reduces to

$$R = 1 - (h/d)\exp\{-\lambda(d-h)\},$$

and this was used to compute the values of $D_\perp/\mu$ shown in Fig. 3b from the measured current ratios.
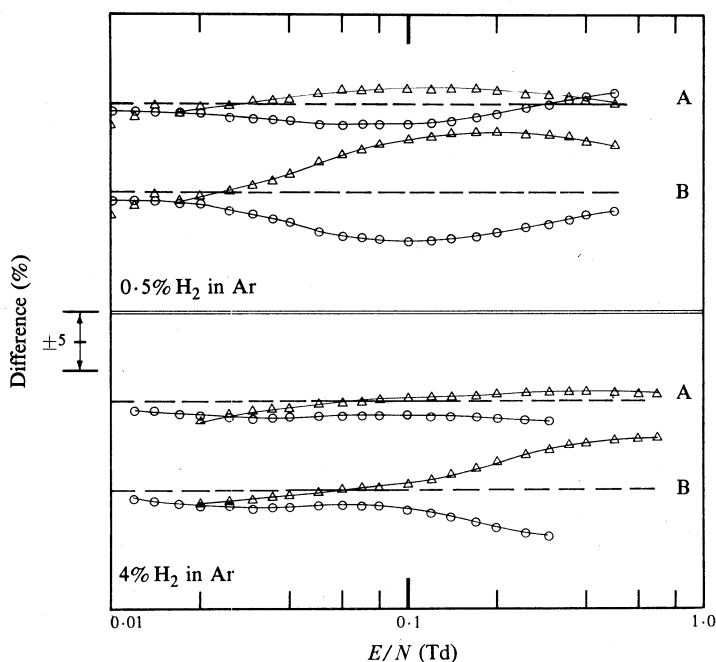

Fig. 4. Differences between calculated and measured transport parameters as a function of E/N for $0 \cdot 5\%$ and 4% H_2 in Ar. The triangles refer to v_{dr} while the circles refer to $D_\perp/\mu$. The series labelled A and B are explained in the text.

6. Errors

Error limits were assessed by adding the systematic and random errors. Since the total systematic error was obtained by adding the contributions arithmetically, the final assigned error may be regarded as the estimated maximum possible error. A detailed discussion of errors in these types of measurements has been given previously (Elford 1971). In addition to the usual error, we have contributions due to the error in the ratio of the component gases ($<0 \cdot 1\%$) and due to the introduction of impurities into the gas sample as discussed above. Errors from this latter source are estimated to be $\pm 0 \cdot 5\%$ in the values of v_{dr} and $\pm 1 \cdot 0\%$ in $D_\perp/\mu$.

Taking all sources of error into account the values of v_{dr} in the mixtures are estimated to be accurate to within $1 \cdot 5\%$ and the values of $D_\perp/\mu$ to within $2 \cdot 5\%$.

7. Discussion

Using the set of cross sections described above, we found the calculated values of v_{dr} and $D_\perp/\mu$ agreed with the measured values to within $2\cdot5\%$ and $3\cdot5\%$ respectively. The error curves which show the difference between the calculated and measured parameters as a function of E/N are the series labelled A in Fig. 4. While the largest differences are 1% outside the stated error limits on the measurements it must be noted that the previous determinations of the cross sections used in this analysis also have errors associated with them (Crompton et al. 1969; Gibson 1970; Crompton et al. 1970; Milloy et al. 1977), which may well account for some or all of the observed differences. The comparisons of calculated and measured values of v_{dr} and $D_\perp/\mu$ in pure argon at 90 K (see Fig. 3, Milloy et al. 1977) show the largest differences for values of $E/N < 2 \times 10^{-3}$ Td, and it is possible that these transport data are influenced by collective effects (O'Malley 1980). This possibility was discussed by Milloy et al. who pointed out that the spread of pressures used by them for the measurements in this range of E/N was too restricted to rule out such a possibility even though there was no evidence of a significant trend. These authors also noted that their cross section was compatible with the diffusion measurements of Rhymes and Crompton (1975) in argon–hydrogen mixtures at much lower pressures where such effects should be negligible. Nevertheless the possibility of errors from this source both in the transport data, and in the cross section derived from these data, cannot be dismissed at this time. For this reason we did not feel justified in attempting to improve the fit to the present data by adjusting either this cross section or the set of cross sections for hydrogen.

An analysis of the transport data in the mixtures can be used to re-examine the discrepancy between the $v = 0 \rightarrow 1$ vibrational cross section (in the threshold region) determined from swarm experiments and that determined by single collision methods. This discrepancy was treated in some detail by Crompton et al. (1970). The sets of curves labelled B in Fig. 4 are the result of using the $v = 0 \rightarrow 1$ vibrational cross section of Ehrhardt et al. (1968) in a calculation identical with the one above. It is clear that the inconsistency referred to in the work of Crompton et al. (1970) is reflected in the present data which support the cross section derived from swarm measurements in pure hydrogen.

8. Conclusions

Our conclusions with regard to the points which motivated this investigation are as follows. Firstly, for mixtures of hydrogen and argon up to concentrations of at least 10% hydrogen in argon, the use of the two-term solution of the Boltzmann equation introduces no significant error into the analysis of the transport data. Secondly, rather large discrepancies found previously between calculated and measured transport coefficients in hydrogen–argon mixtures appear to have been due to a combination of insufficiently accurate experimental results and the data and cross sections used in the analysis. Thirdly, the use of the cross section set described in Section 2 enables all the experimental data in the mixtures to be fitted to within $\pm3\cdot5\%$.

Thus, although small discrepancies remain between calculated and experimental transport data which are outside the experimental error, the success of the existing set of cross sections in predicting transport parameters for the mixtures lends con-

fidence in both the cross section set and the theory used to analyse the experimental data.

Acknowledgments

References

Crompton, R. W., and Elford, M. T. (1962). *J. Sci. Instrum.* **39**, 480.
Crompton, R. W., Elford, M. T., and McIntosh, A. I. (1968). *Aust. J. Phys.* **21**, 43.
Crompton, R. W., Gibson, D. K., and McIntosh, A. I. (1969). *Aust. J. Phys.* **22**, 715.
Crompton, R. W., Gibson, D. K., and Robertson, A. G. (1970). *Phys. Rev.* A **2**, 1386.
Ehrhardt, H., Langhans, L., Linder, F., and Taylor, H. S. (1968). *Phys. Rev.* **173**, 222.
Elford, M. T. (1971). *In* 'Case Studies in Atomic Physics' (Eds E. W. McDaniel and M. R. C. McDowell), Vol. 2, Ch. 2 (North-Holland: Amsterdam).
Engelhardt, A. G., and Phelps, A. V. (1964). *Phys. Rev.* **133**, 375.
Gascoigne, J. (1971). *Vacuum* **21**, 21.
Gibson, D. K. (1970). *Aust. J. Phys.* **23**, 683.
Henry, R. J. W., and Lane, N. F. (1969). *Phys. Rev.* **183**, 221.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley–Interscience: New York).
Kleban, P., and Davis, H. T. (1977). *Phys. Rev. Lett.* **39**, 456.
Lin, S. L., Robson, R. E., and Mason, L. (1979). *J. Chem. Phys.* **71**, 3483.
Linder, F., and Schmidt, H. (1971). *Z. Naturf.* a **26**, 1603.
Milloy, H. B., and Crompton, R. W. (1977). *Aust. J. Phys.* **30**, 51.
Milloy, H. B., Crompton, R. W., Rees, J. A., and Robertson, A. G. (1977). *Aust. J. Phys.* **30**, 61.
O'Malley, T. F. (1963). *Phys. Rev.* **130**, 1020.
O'Malley, T. F. (1980). *J. Phys.* B **13**, 1491.
O'Malley, T. F., and Crompton, R. W. (1980). *J. Phys.* B **13**, 3451.
Rhymes, T., and Crompton, R. W. (1975). *Aust. J. Phys.* **28**, 675.
Robertson, A. G. (1971). *Aust. J. Phys.* **24**, 445.
Robertson, A. G. (1977). *Aust. J. Phys.* **30**, 39.