

The Drift Velocity of Electrons in Mercury Vapour at 573 K

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Abstract

The drift velocity of electrons in mercury vapour at 573 K has been measured using the Bradbury–Nielsen time-of-flight method at vapour number densities ranging from 3.40×10^{17} to $1.83 \times 10^{18} \text{ cm}^{-3}$ and at E/N values from 0.1 to 3.0 Td. The measured drift velocities increase linearly with mercury vapour number density, the magnitude of the dependence being a function of E/N . This number density dependence has been attributed to the presence of mercury dimers and the drift velocity corresponding to dimer-free mercury vapour has been obtained by extrapolation. Sources of error are examined and the present results are compared with those of previous workers.

1. Introduction

There have been few measurements of the transport coefficients of electrons in metal vapours owing to the formidable technical problems that such measurements pose. However, the data are of considerable interest in the study of such phenomena as metal vapour discharges, the modelling of the behaviour of MHD generators and the investigation of excimer lasers. There appear to be only three previous sets of drift velocity data for metal vapours, namely those of McCutchen (1958) for mercury, Chanin and Steen (1964) for caesium, and Nakamura and Lucas (1978) who used a heat pipe oven technique to measure drift velocities in mercury, sodium and thallium.

The aim of the present work was to obtain drift velocity data for electrons in mercury with errors significantly lower than those of the previous measurements in this vapour. This lower error enables a momentum transfer cross section to be derived with less uncertainty and permits more reliable comparisons with available *ab initio* calculations (Walker 1975).

There are a number of errors involved in the measurement of drift velocities in mercury vapour which are usually negligible in measurements in other gases at room temperature or lower where the techniques for obtaining highly accurate data are now well established (see e.g. Huxley and Crompton 1974). The major problem in the case of mercury is the necessity for carrying out the measurements at high vapour pressures in order to avoid large errors due to diffusion effects. Such pressures entail the use of high temperatures and this leads to problems such as leakage currents across insulators, expansion effects on the electrodes and grids, and the difficulty of maintaining temperature uniformity and control. The pressure measurement system chosen must not only be capable of operating at high temperatures and have adequate precision but must also not cause contamination of the mercury vapour. Trace

quantities of impurities can have a drastic effect on the measured drift velocity, and the attainment of low outgassing rates at high temperatures therefore requires special attention. The solutions adopted in the present experiment to solve the problems outlined above are discussed in detail in Section 2.

In most drift velocity measurements the effect of dimers can be ignored. However, for heavy metal vapours where the energy lost by electrons in elastic collisions is so small, dimers can produce the same effect as that caused by gaseous diatomic impurities, i.e. a lowering of the mean electron energy. The first mention of the effect of dimers in mercury vapour on drift velocity measurements was made by Nakamura and Lucas (1978), who observed a dependence of drift velocity on gas number density in mercury and attributed the dependence to the presence of dimers. The effect of dimers on the accuracy of the present data is discussed in Section 4*b* below and their significance in earlier measurements is considered in Section 4*e*.

In previous experiments to measure drift velocities in mercury vapour no allowance was made for the effects of diffusion on the measurements. These effects have been discussed in detail by Huxley and Crompton (1974) and can constitute a significant error. Despite the choice of experimental parameters to minimize such errors (Section 2*a*) their magnitude needs to be considered carefully, and methods of estimating their influence are discussed in Section 4*c*.

2. Experimental Details

(a) *Choice of experimental parameters*

In order to obtain high accuracy in electron drift velocity measurements it is necessary to choose the drift length and operating conditions so as to avoid the necessity of making large corrections for diffusion effects. These corrections have the form $C(D_{\parallel}/\mu)/V$, where $D_{\parallel}$ is the longitudinal diffusion coefficient, C is a constant, V is the potential difference across the drift space and μ is the electron mobility defined as v_{dr}/E , with v_{dr} the drift velocity and E the electric field strength. (A more detailed discussion of diffusion corrections is given below in Section 4*c*). This correction may be rewritten as $C(D_{\parallel}/\mu)(E/N)^{-1}(Nd)^{-1}$, where N is the gas number density and d the drift length. Since $D_{\parallel}/\mu$ is a function of E/N only at a given gas temperature, the correction can be made small by making Nd large.

The drift length was limited both by constructional constraints and by the difficulty in maintaining a constant temperature over a long length. The distance chosen was 150 mm.

(b) *Effect of molecular impurities and vacuum requirements*

Since the mean fractional energy lost by electrons in elastic collisions with mercury atoms, namely $2m/M$, is only 5×10^{-6} , the electron transport coefficients are very sensitive to the presence of small quantities of impurities and particularly molecular species. Inelastic collisions with molecules involve a large exchange of energy compared with those involved in elastic scattering and they cause a significant reduction in the mean electron energy. The most common molecular gases expected to be present are hydrogen and carbon monoxide as a result of outgassing from the stainless steel of the envelope and tube components. To estimate the sensitivity of the electron drift velocity to the presence of the most abundant impurity, hydrogen, some approximate values of the drift velocity were calculated for various concentrations of hydrogen

in mercury vapour using the momentum transfer cross section derived by Rockwood (1973) for mercury and the cross sections derived by Gibson (1970) for hydrogen. It was found that the drift velocity changed by less than 0.2% due to hydrogen contamination over the E/N range 0.1–3 Td for hydrogen levels less than about 10 p.p.m. At the lowest vapour pressure used, 2.69 kPa, this corresponds to a total hydrogen influx of 0.2 Pa l. (since the drift tube volume is approximately 6.5 l.). If the mercury vapour is to be held in the drift tube for a period of 1 h with less than a 0.2% change in drift velocity due to hydrogen contamination, the hydrogen influx rate has to be kept below 5×10^{-5} Pa l. s⁻¹. To achieve such a low hydrogen influx rate at 573 K it was necessary to reduce substantially the quantity of gas in the stainless steel. The manifold was outgassed for 170 h at 250°C, 450 h at 300°C and 250 h at 450°C. The manifold with the electrode system installed was then heated for 700 h at 350°C. The residual gas was monitored during this processing by a quadrupole mass spectrometer and it was confirmed that hydrogen was by far the most abundant component, followed in abundance by carbon monoxide. The effect of outgassing on the experimental data was checked by taking data over 1 h. The results of these tests are described in Section 3.

(c) *Description of drift tube*

The Bradbury–Nielsen time-of-flight method for measuring drift velocities has been shown to be capable of high accuracy (Huxley and Crompton 1974) at both room and low temperatures, and this method was chosen for the present work. The construction of the drift tube used is shown in Fig. 1 and the pumping and pressure measurement system in Fig. 2. Ultra high vacuum valves V_2 and V_1 (Vacuum Generators Ltd, Type R25; see Figs 1 and 2) connected the drift tube to the vacuum system and mercury vapour source. The electrode structure was similar to that described by Elford (1972) and was constructed of stainless steel. The drift length, i.e. the distance between the planes of the electrical shutters, was 150.9 mm at 293 K and 151.3 mm at 573 K. The electrode structure was surrounded by a glass liner to postpone the onset of electrical breakdown. The electrons were produced in the source S (Fig. 1) by α -particle ionization using an americium 241 foil. The method of operation of the drift tube for obtaining accurate data has been described in detail by Elford (1972) and Huxley and Crompton (1974) and will not be discussed further here.

Two modifications were necessary to enable the tube to be operated in mercury vapour at 573 K, the first being the design of a new type of electrical shutter grid and the second the production of a low leakage current feedthrough. The electrical shutter described by Elford (1972) and used in a number of drift velocity measurements both at room and low temperatures (see e.g. Crompton *et al.* 1970; Robertson 1977) was found to fail at 573 K owing to the wires becoming slack and causing a short-circuit of the grid between adjacent wires. An alternative shutter design was developed to overcome this problem (Fig. 3). In this design, nichrome wires are threaded through holes drilled in two Macor (Corning Glass Works) machineable glass blocks which are spaced and held coplanar by nichrome pillars. The holes are positioned so that all wires are of the same length across the face of the shutter and this length is the same as that of the nichrome pillars, the ends of which are let into the Macor blocks. Straining nuts on each pillar are used to place the grid wires under the tension necessary to ensure that the wires are accurately coplanar and parallel.

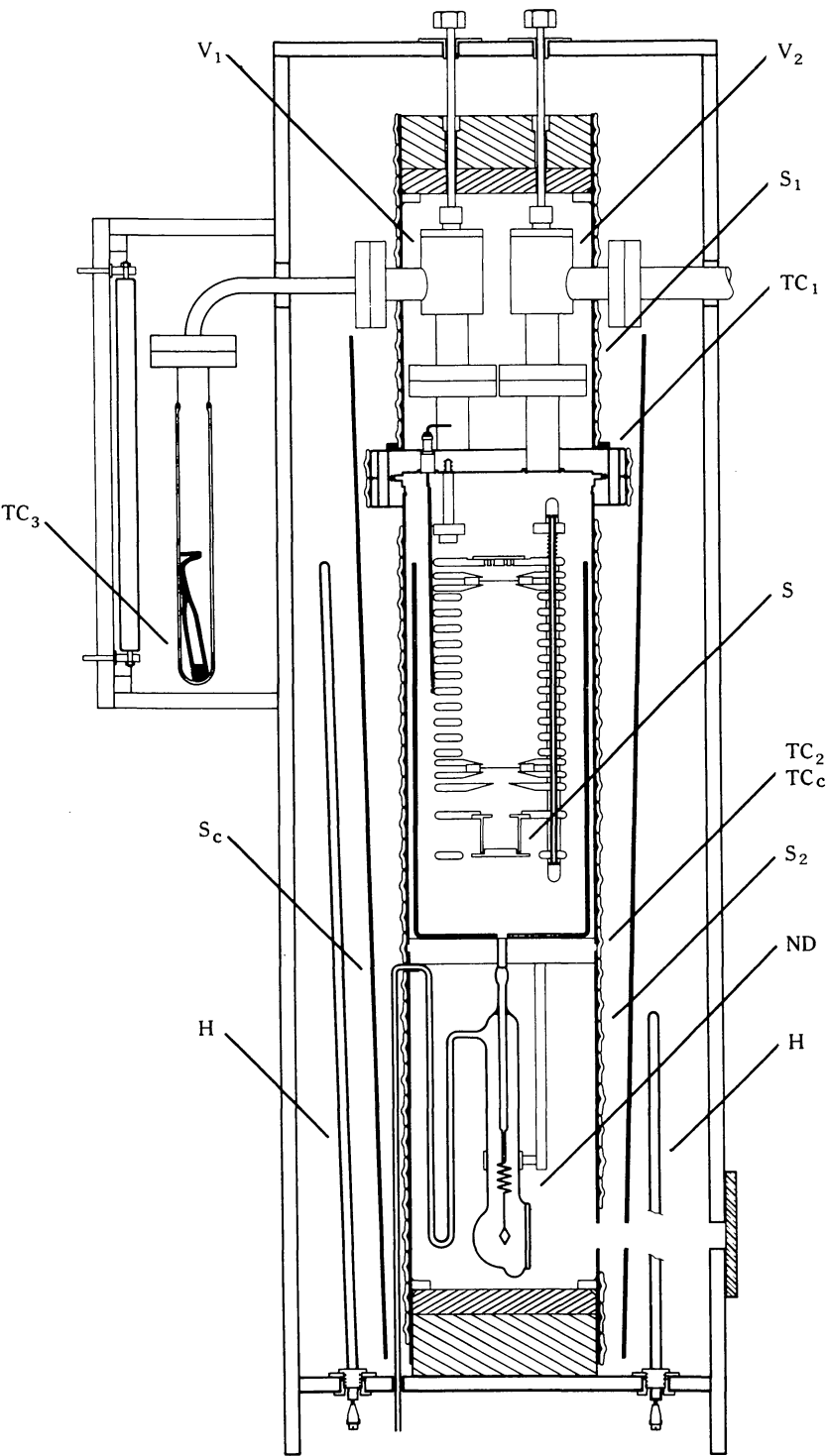


Fig. 1. Sectional drawing of the drift tube used to measure electron drift velocities in mercury vapour at 573 K: V_1, V_2 , UHV valves; S , α -particle ionization source; TC_1, TC_2 , chromel–alumel thermocouples used to determine the temperature of the drift tube; TC_c, TC_3 , chromel–alumel thermocouples used to control the temperatures of the drift tube and mercury vapour source tube respectively; S_c , copper screen; S_1, S_2 , cylindrical supports for heater tape; H , tubular heater element; ND , Pyrex glass spiral manometer used in the null detection system.

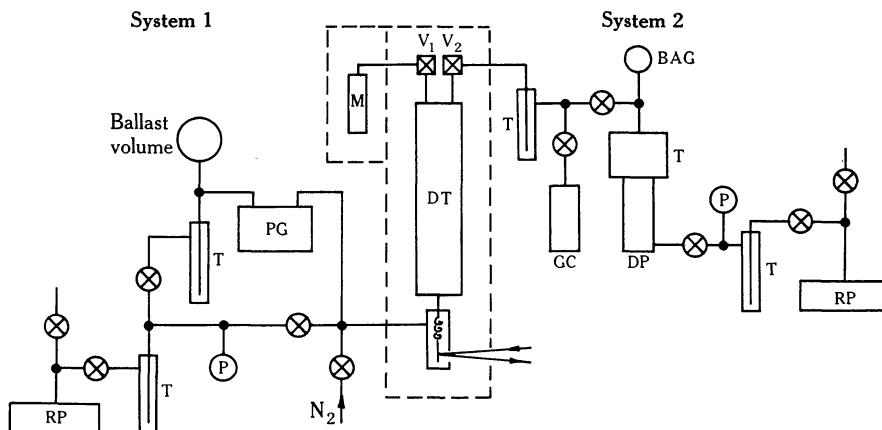


Fig. 2. Schematic diagram of the pressure measurement (system 1) and vacuum (system 2) arrangements: RP, rotary pump; T, liquid nitrogen trap; P, Pirani gauge; PG, quartz spiral pressure gauge; M, mercury vapour source tube; DT, drift tube; GC, gas cylinder; DP, diffusion pump; BAG, Bayard–Alpert ionization gauge. The regions enclosed by dashed lines are heated. The valves V_1 and V_2 are UHV valves operated at 300°C.

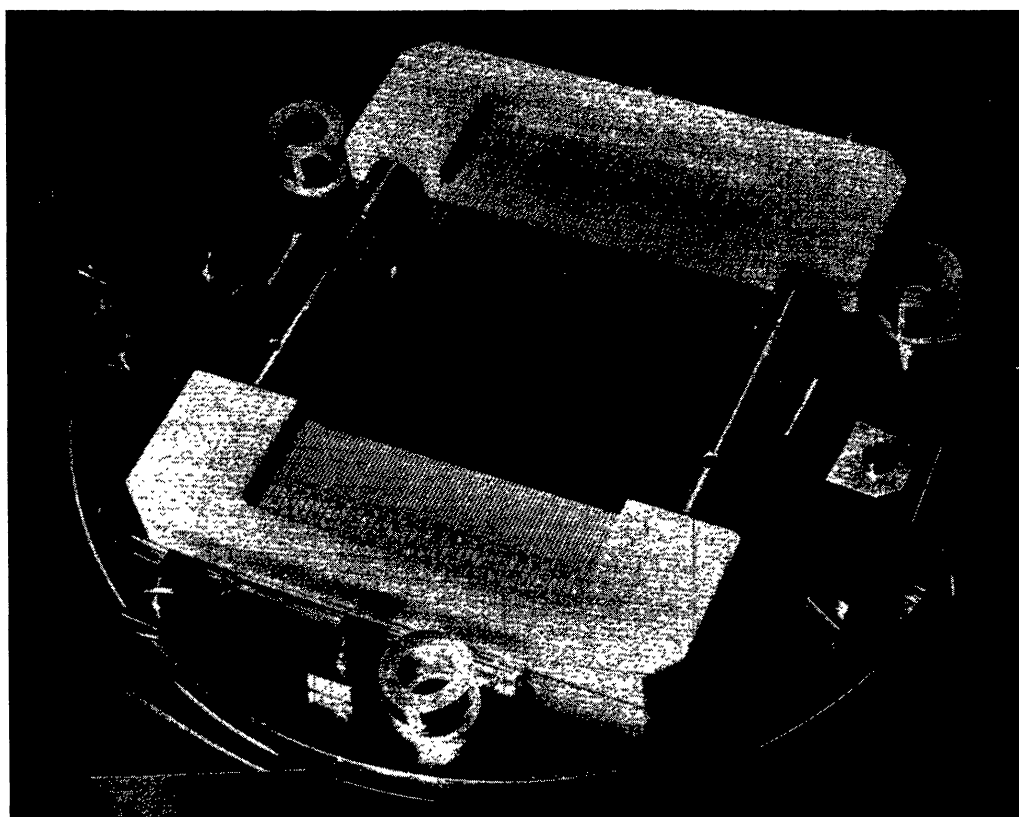


Fig. 3. View of one of the electrical shutters. Also shown are the three glass spacers used to hold the shutter support electrode in position.

Since the supporting pillars and all wires are of the same material and of the same length, there is no change in wire tension and hence wire position with change in temperature. This was confirmed by observing the behaviour of a grid in a muffle furnace.

The second modification was the construction of a feedthrough for the electrometer lead to avoid large leakage currents at 573 K arising from piezoelectric potentials and a low resistance to ground. The feedthrough consisted of a tubular Kovar-to-glass seal joined to a 20 mm length of quartz tubing which was in turn connected to a Kovar-to-glass seal. This feedthrough had a leakage current of less than 1×10^{-13} A at 573 K, which was acceptable for the present measurements.

(d) Measurement of mercury vapour pressure

The vapour pressure was measured using a null technique which is shown schematically as system 1 in Fig. 2. The mercury vapour pressure was balanced against the pressure of dry nitrogen gas, the null detector being a Pyrex spiral manometer. The null point was observed using an optical lever and a split photocell as the detector. The nitrogen pressure was measured with a quartz spiral pressure gauge (Texas Instruments Ltd) calibrated using a double dead-weight tester (Gascoigne 1972). The present method permits a range of pressures to be measured directly at a given temperature and has an inherent advantage over the method in which the saturated vapour pressure is used. If this latter method is employed to examine the density dependence of the drift velocity, the associated temperature change may cause a change in the drift velocity and make the interpretation of the observed density dependence more complicated.

Before experiments with mercury were commenced, a series of tests were made on the resolution and sensitivity of the null detector at 573 K using carbon dioxide. The smallest detectable pressure difference was found to be 6 Pa which represents an uncertainty of 0.2% at the lowest pressure of 2.69 kPa used in the present measurements. Hysteresis effects were negligible as long as the pressure differential was kept below 10 Pa.

As a final check on the accuracy of the null detector pressure measurement system, some drift velocity values were measured in CO₂ at 5.37 and 13.43 kPa using the system. These values were compared with those taken at the same E/N and pressure settings when the quartz spiral pressure gauge was connected directly to the drift tube. The values were found to be systematically 0.4% lower. This suggested that the pressure on the nitrogen side of the null detector was 0.4% lower than on the side containing carbon dioxide but the cause of this difference was not established.

A difficulty in operating the null detector was a movement in the null position with time at 573 K when pressures were applied to both sides of the null manometer. That the changed null point was not due to a genuine change in pressure in the drift tube was established by the fact that the observed drift velocities were stable to within $\pm 0.2\%$ over the period of this test (see Section 3). The rate at which the null point changed was approximately proportional to the pressure on both sides of the manometer. The effect produced an error due to the shift in the null point during the time taken for gas to be let into the tube. An estimate of the error incurred was obtained and has been included in the analysis of errors (Section 4d).

(e) *Measurement and control of temperature of drift tube*

The electrode structure was suspended from a Conflat flange and enclosed by a stainless steel manifold (Fig. 1). The Pyrex glass null detector (ND) was attached via a tubular Kovar-to-glass seal to the lower end of the manifold and the null detector was enclosed by a stainless steel cylinder (S_2) which was bolted to the upper Conflat flange of the manifold, thus producing a tubular structure approximately 90 cm long. Each end of this cylinder was closed off by copper plates and 50 mm of Miscolite (Lebah Products Pty Ltd, Sydney) insulation. The cylinder was surrounded by a 3 mm thick copper screen (S_c) which assisted in reducing temperature gradients and also in preventing the occurrence of local hot areas on the manifold caused by radiation from the heater elements. Four heating elements (H) were mounted from the base of the oven and individually controlled to maintain the temperature of the manifold approximately 15°C lower than the desired controlled value. The heaters were of two different lengths and the powers were adjusted to make the temperature gradient as small as possible. The final control was achieved using a heater tape wound over the surface of the manifold and also over the two cylindrical lengths attached to each end of the manifold. The power supplied to this heater tape was controlled from a proportional controller with the control temperature sensed by a chromel–alumel thermocouple attached to the bottom flange at TC_c . The walls of the oven were of 12 mm Miscolite sheet lined on the inside with aluminium, and all apertures were plugged with asbestos wool to reduce heat losses.

The temperature of the manifold was measured at the top and bottom flanges of the manifold with chromel–alumel thermocouples (TC_1 and TC_2 in Fig. 1) using an ice reference and a Leeds & Northrup K5 potentiometer. Tests on the thermocouple wire used were carried out by the Division of Applied Physics, CSIRO. The error in the temperature measurement is estimated to be less than 1.2°C. The temperature control system was able to maintain the temperature of the manifold at 300°C over a period of days with a variation of less than $\pm 0.2^\circ\text{C}$ and a temperature difference across the manifold which was usually less than 0.5°C. The largest difference observed for a particular experimental run was 1°C. Since the temperature used in the calculation of the mercury vapour number density was the mean of the temperatures measured at the manifold, this gradient introduces an uncertainty of only 0.5 K in 573 K or less than 0.1% error. After the manifold had been raised to its operating temperature, a period of at least 48 h was allowed to elapse before measurements were commenced, in order to ensure that thermal equilibrium between the manifold and electrode system had been achieved.

(f) *Mercury purity and vapour inlet system*

(i) *Purification and Ampoule Filling System*

The triply distilled mercury used in this work was supplied by Engelhard Industries Pty Ltd. In order to let the mercury vapour into the drift tube without introducing gaseous impurities it was necessary to place the mercury into break–seal glass ampoules. This was carried out using the purification and ampoule filling system described by Drullinger *et al.* (1975). A detailed description of the filling procedure used in this work is given in the Appendix.

(ii) *Vapour Inlet System*

The layout of the mercury vapour inlet system is shown in Fig. 1. The break-seal capsule was placed in the source tube, and the drift tube plus the source tube were evacuated. The drift tube was raised to the operating temperature (300°C) and the source tube was outgassed for 22 h at 250°C and 21 h at 290°C . Valve V_1 was then closed, the source tube allowed to cool to room temperature and the ampoule broken open using a steel ball. The temperature of the source tube was monitored using a chromel-alumel thermocouple (TC_3) attached to the source tube adjacent to the ampoule.

For safety reasons, the mercury was kept frozen at 77 K in the source tube between experimental runs. However, over a period of 24 h, gaseous impurities, presumably mainly water vapour, accumulated in the source tube and were subsequently released into the mercury vapour when the source tube was heated for the next experimental run, causing a significant initial increase in the measured electron drift velocities and a subsequent decrease with time due to adsorption of the impurity in the drift tube. This effect occurred despite the rigorous outgassing of the inlet system and it demonstrates the extreme sensitivity of the measurements to molecular impurities. The effect was eliminated by warming the mercury in the inlet tube to room temperature and pumping off the impurities before proceeding to heat the mercury using the inlet system oven. This procedure was found to give results which were reproducible and independent of time.

(g) *Operating procedure*

After evacuation of the drift tube to a base pressure of approximately 2×10^{-6} Pa, valve V_1 was closed and the mercury in the source tube was allowed to warm up to room temperature. Valve V_1 was then opened for about 5 min to pump off any condensable impurities. These impurities were trapped together with some mercury vapour in the liquid nitrogen trap situated between the drift tube and the pumping system. Valve V_1 was closed, the source oven installed and the source tube heated to a temperature which would result in a mercury saturated vapour pressure which was higher than the pressure required for the particular experimental run. When the desired source tube temperature was reached (after approximately 30 min), the drift tube was isolated from the pumping system by closing valve V_2 , the temperatures indicated by the thermocouples TC_1 and TC_2 were measured and the null detection system was checked for balance. The valve V_1 was then opened slowly to admit mercury vapour to the drift tube while at the same time dry nitrogen was admitted to the reference side of the null detector, care being taken to ensure that the pressure difference across the null detector was kept sufficiently small to avoid hysteresis effects. The time required to reach the required pressure was noted and the subsequent drift of the null detector with time was observed. This information was required to enable the uncertainty in the pressure measurement due to the null detector drift to be calculated.

Measurements of the drift velocity were then carried out. At the conclusion of the measurements, valve V_1 was opened and the mercury was frozen out in the source tube using liquid nitrogen. During this procedure it was necessary to pump out the nitrogen in the reference side of the null detector in order to avoid hysteresis effects as mentioned above. After some minutes when virtually all the mercury had

been removed, the zero of the null detector was observed in order to check on any significant shift that indicated a malfunction. Some 30 min later the drift tube plus inlet system were connected to the pumping system.

All pressures were measured in separate runs (i.e. no progressive increases in pressure were employed) in order to keep errors due to null detector drift as small as possible.

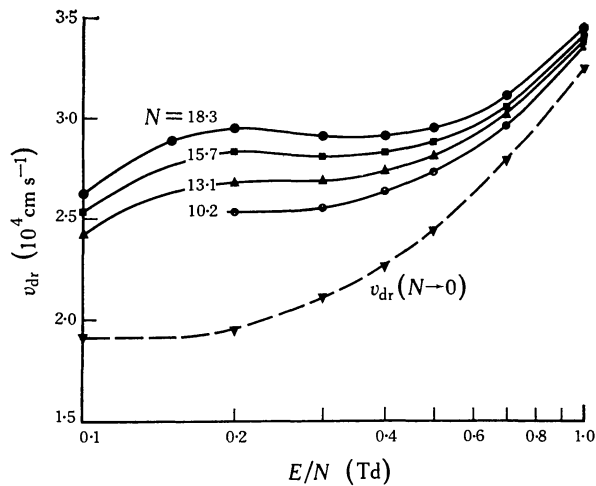


Fig. 4. Measured drift velocities of electrons in mercury vapour at 573 K as a function of E/N and the vapour number density N (specified on the curves in units of 10^{17} cm^{-3}).

Table 1. Drift velocity of electrons in mercury vapour at 573 K

E/N (Td)	p (kPa) = $N(10^{17} \text{ cm}^{-3}) =$		Drift velocity v_{dr} (10^4 cm s^{-1})					$v_{\text{dr}}(N \rightarrow 0)$ (10^4 cm s^{-1})	
			2.69	5.37	8.06	10.33	12.40		14.46
			3.40	6.79	10.20	13.07	15.69	18.26	
0.1						2.418	2.533	2.621	1.92
0.15								2.897	
0.2					2.503	2.677	2.828	2.961	1.94
0.3					2.558	2.691	2.816	2.918	2.11
0.4					2.636	2.740	2.836	2.922	2.265
0.5					2.742	2.816	2.895	2.968	2.45
0.7					2.969	3.020	3.066	3.121	2.785
1.0			3.331	3.360	3.382	3.414	3.462		3.27
1.5			4.123	4.135	4.148	4.166			4.10
2.0			5.221	5.276					5.11
2.5				7.086					7.09
3.0		9.568	9.555						9.57

3. Experimental Results

The measured drift velocities of electrons in mercury vapour are shown in Table 1 and Fig. 4 as a function of E/N and the vapour number density. The temperature was within 1.2 K of the nominal temperature of 573.2 K for all experimental runs. The vapour number density was calculated from the actual gas temperature and pressure. Measurements at two number densities (6.79 and $13.07 \times 10^{17} \text{ cm}^{-3}$) were

chosen to check on the reproducibility of the data. Of the nine points repeated the worst disagreement was 0.2%.

Tests were made for the effect of outgassing the impurities on the experimental data by taking a measurement at the end of each experimental run using the conditions for the initial measurement. No significant change in the data with time was observed. To demonstrate the degree of independence of the recorded drift velocity with time, the drift velocity was measured at intervals over a period of approximately 1 h at $E/N = 0.1$ Td, where the calculations showed that the sensitivity to the presence of H_2 impurities was greatest. There was no significant change in the measured drift velocity over this time to within the experimental scatter ($\pm 0.2\%$).

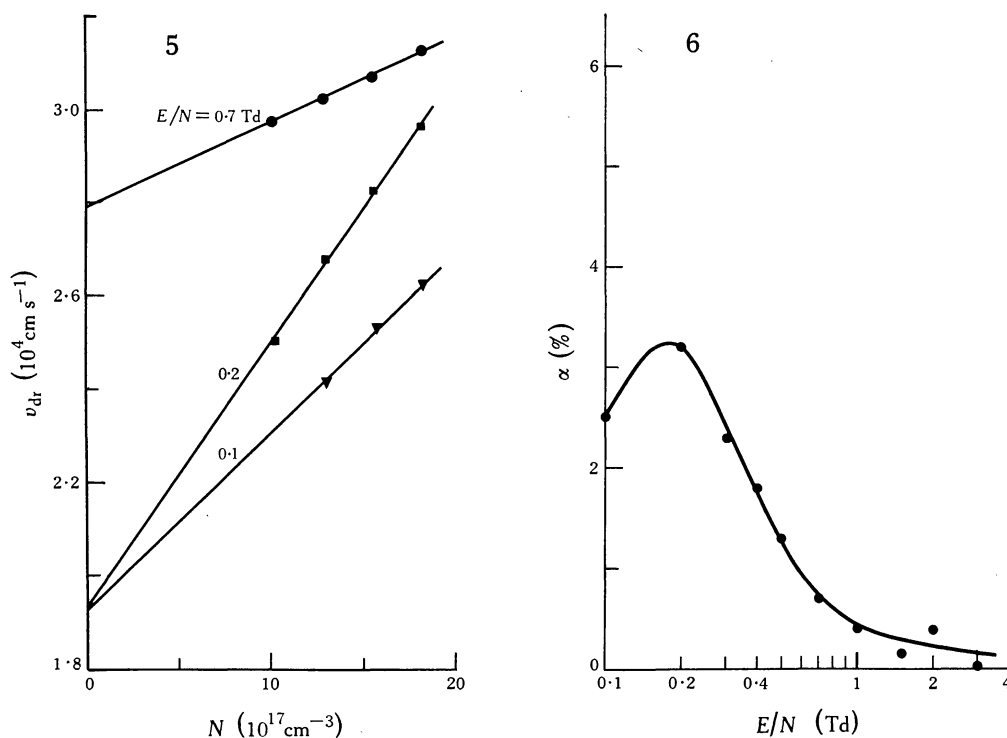


Fig. 5 (left). Variation of the measured drift velocity v_{dr} with vapour number density N for electrons in mercury vapour at 573 K, at the three indicated values of E/N .

Fig. 6 (right). Variation of the slope parameter α with E/N for electrons in mercury vapour at 573 K; α is defined by equation (1) in Section 3 of the text.

In order to obtain a check on the accuracy of the drift tube measurements at high temperatures, data were taken in helium at 553 K and pressures of 10.33 and 14.46 kPa. The pressures were measured using the null detector pressure measurement system. After correction for diffusion effects the value of the drift velocity was found to be $2.50 \times 10^5 \text{ cm s}^{-1}$ at $E/N = 0.3$ Td. This agrees to better than 1% with the value of $2.52 \times 10^5 \text{ cm s}^{-1}$ calculated using the momentum transfer cross section derived by Crompton *et al.* (1970) and Milloy and Crompton (1977).

If the data at a given value of E/N are plotted as a function of N it is found that v_{dr} increases linearly with N at all except the highest E/N values where the dependence on N disappears. Three typical plots are shown in Fig. 5. The scatter about the line

of best fit was in general $\pm 0.1\%$, the worst deviation being 0.3% . The slope of the lines obtained by plotting the measured drift velocities as a function of N is shown in Fig. 6 as a function of E/N . The slope is denoted by α and is expressed as the percentage change in the measured drift velocity per kilopascal change in pressure, that is,

$$\alpha = \{(\Delta v_{\text{dr}}/\Delta p)/v_{\text{dr}}(N \rightarrow 0)\} \times 100. \quad (1)$$

The upper limit to the E/N range at each gas number density was determined by the onset of electrical breakdown, while the lower limit was set by two factors: the first was insufficient current for accurate measurement and the second was the necessity for avoiding low potential differences across the drift length. Low potential differences may result in large diffusion effects and can only be avoided at low E/N values by using high vapour pressures. Thus progressively larger extrapolations to obtain $v_{\text{dr}}(N \rightarrow 0)$ have to be made as E/N decreases. The taking of data was terminated when the lowest pressure at a given E/N value was so large that a high uncertainty was incurred in obtaining the extrapolated value $v_{\text{dr}}(N \rightarrow 0)$.

4. Discussion

(a) *Effect of molecular species*

The two notable features of the present experimental measurements are the linear dependence of the measured drift velocity on the gas number density (Fig. 5) and the maximum in the measured drift velocity (at $E/N \sim 0.2$ Td) at high vapour number densities (Fig. 4). This second effect where the drift velocity decreases with increasing E/N has been called negative differential conductivity and is well known (see e.g. Long *et al.* 1976, and references therein). The effect occurs in gases or gas mixtures where the electron collisions are determined by a particular combination of elastic and inelastic processes. The essential features are firstly that the momentum transfer cross section σ_m has either a deep minimum or a small value near the threshold energy for an inelastic process for which the cross section rises to a relatively large value. Secondly, the momentum transfer cross section must increase rapidly at energies greater than that of the threshold for the inelastic process. Thus mixtures of argon, which has a deep Ramsauer minimum in σ_m , with gases such as N_2 and CO display the effect.

It is clear from the energy dependence of the momentum transfer cross sections for electrons in mercury vapour derived by Rockwood (1973) and Nakamura and Lucas (1978) that the conditions for the occurrence of negative differential conductivity would exist in the case of mercury if there was an inelastic scattering process present with a large cross section and a threshold energy less than about 0.5 eV. Since this energy is far below the threshold energy for the first electronic excitation of mercury (4.9 eV) it must be therefore associated with the presence of either molecular impurities or mercury dimers.

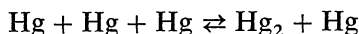
A molecular impurity can be introduced either in the mercury itself or from outgassing of the drift tube and vapour source. Because of the care taken in purifying the mercury, the first possibility is considered remote. The most probable outgassing impurity is hydrogen but it can be ruled out as a possibility on the following grounds. Firstly there is the experimental fact that the measured drift velocity was independent of the time the vapour was held in the drift tube or in the source tube before being let into the drift tube. Secondly, the quantity of hydrogen required

to produce negative differential conductivity has been calculated to be in excess of 500 p.p.m. An impurity level of this magnitude is inconsistent with the known outgassing characteristics of the drift tube and inlet system.

(b) *Van der Waals dimers*

The influence of van der Waals dimers on the transport properties of gases has long been recognized. However, there has been little evidence of their influence on electron transport coefficients in gases. Milloy and Crompton (1977) considered the influence of argon dimers on their measurements of $D_{\perp}/\mu$ for electrons in argon at 294 K and gas pressures ranging from 309 to 1171 kPa. They found no evidence for the presence of dimers although there should have been 0.07% of argon dimers per 100 kPa in their measurements. Recently Nakamura and Lucas (1978) have explained a number density dependence of electron drift velocities in mercury, sodium and thallium vapour in terms of dimer formation, and in the case of mercury they noted a small maximum in the drift velocity at $E/N = 0.3$ Td at a vapour pressure of 67 kPa.

Dimers are formed in the equilibrium reaction



via an intermediate metastable Hg_2 . The equilibrium constant $\kappa(T)$ for this reaction is

$$\kappa(T) = [\text{Hg}_2]/[\text{Hg}]^2,$$

where the square brackets indicate number density. Stogryn and Hirschfelder (1959) have derived an expression for $\kappa(T)$ assuming the interaction potential to have a Lennard-Jones (6-12) form. The Lennard-Jones potential parameters listed by Hirschfelder *et al.* (1954) for mercury have been used in the present work to calculate the relative abundance of mercury dimers as a function of temperature and number density. At a temperature of 573 K the abundance of dimers ranges from approximately 50 to 300 p.p.m. for the range of number densities used here.

The inelastic process responsible for the production of negative differential conductivity and the dependence on N at a given E/N would appear to be vibrational excitation. The energy lost by electrons in rotational excitation of the dimers is much smaller than that in vibrational excitation, and there are insufficient numbers of electrons at the low E/N values, where the N dependence is large, with energies sufficiently high (>4 eV) for dissociation or electronic excitation of the mercury dimer to be a significant energy loss process.

If the cross sections for vibrational excitation of Hg_2 were known it would be possible to include the effect of dimers when carrying out an analysis of the drift velocity data to obtain the momentum transfer cross section for mercury vapour. However, in the absence of such information it is necessary to extrapolate the data to zero number density at each E/N value in order to obtain drift velocities for mercury vapour containing only the monomer. It is these extrapolated values which are used in the Boltzmann equation analysis described in the following paper (Elford 1980, present issue pp. 251-9).

Although the relative abundance of dimers is proportional to the vapour number density, it is not obvious that this should result in the measured drift velocities being

linearly dependent on the number density at a given value of E/N , and indeed a departure from linearity might be expected at very high dimer concentrations. However, there is no indication that such a departure occurs over the range of dimer abundances encountered in this work. It may be noted that calculations of drift velocities in mercury–hydrogen mixtures (no dimers assumed to be present) showed that for hydrogen abundances up to 0.5%, where negative differential conductivity was observed of the same order of magnitude as that found in the present measurements, the drift velocity was still a linear function of the mercury number density.

The variation of α with E/N (Fig. 6) can be explained qualitatively by considering the energy balance. If the temperatures and E/N values were sufficiently low (much lower in fact than those used in the present work) that the electron swarm had a mean energy much lower than the threshold for the inelastic process then there would be no dependence of the drift velocity on number density. At sufficiently high temperatures and E/N values, electronic excitation of the mercury atoms becomes the major energy transfer process and the energy lost by electrons in inelastic dimer collisions becomes negligible. Under these conditions there will again be no dependence on mercury vapour number density. This situation is reached in the present work by $E/N \approx 3$ Td. Between these two extreme cases a number density dependence would be expected whose magnitude depends on the cross sections for the scattering processes involved. As stated in Section 3, at low E/N values it is necessary to use relatively large vapour number densities to ensure that the potential difference across the drift length does not become so small that large diffusion effects are incurred (see Section 2a). When such large number densities are used very large extrapolations of the measured drift velocities to zero number density are required and this leads to enhanced error in the extrapolated value. In the present work the largest extrapolation made was 29% at $E/N = 0.2$ Td. However, it should be noted that α is less at 0.1 Td than at 0.2 Td (Fig. 6). If data could be obtained at $E/N < 0.1$ Td the extrapolation to zero pressure might therefore become a much less significant source of error in $v_{dr}(N \rightarrow 0)$ than at E/N values in the vicinity of 0.2 Td.

(c) *Correction for diffusion errors*

All measurements of electron drift velocities by time-of-flight methods are subject to errors caused by diffusion effects (see Huxley and Crompton 1974, Ch. 10). In the case of the Bradbury–Nielsen method, with electrical shutters operated by sine wave signals, the theoretical correction is $3(D_{||}/\mu)/V$ which can be rewritten as $3(D_{||}/\mu)(E/N)^{-1}(Nd)^{-1}$. This expression, however, does not adequately account for diffusion effects (Huxley and Crompton 1974, p. 344) and the most satisfactory correction procedure is to plot the observed drift velocity at a given E/N value as a function of N^{-1} and extrapolate the linear relation to $N^{-1} = 0$ (see e.g. Crompton and Elford 1973; Robertson 1977). In this way uncertainties in the factor 3 and the problem of obtaining $D_{||}/\mu$ data are avoided.

In the present work at E/N values less than about 1 Td, the measured drift velocity has a linear dependence on N , due to dimers, as well as an N^{-1} dependence due to diffusion effects. These latter effects become larger as N decreases, and at sufficiently small values of N their presence will result in the measured drift velocities lying above the straight line representing the expected linear variation of v_{dr} with N due to dimers.

However, as has been seen, there is no such deviation over the present range of N values, suggesting either that the diffusion correction is small or that the present experimental range of N values is not sufficiently large for the two different N dependences to be separated.

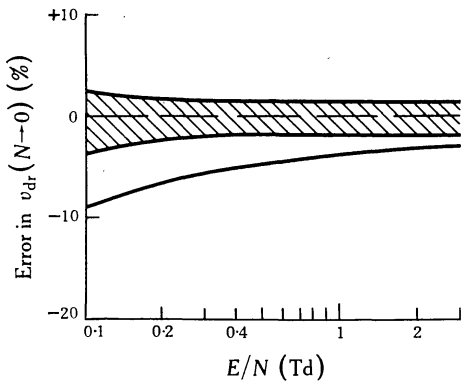


Fig. 7. Variation of the total estimated error in $v_{dr}(N \rightarrow 0)$ as a function of E/N . The region shown shaded is the error if diffusion effects are ignored.

Table 2. Example of analysis of errors
The calculated errors in v_{dr} here are for $E/N = 0.2$ Td

Classification of errors and their sources	Error (%) at p (kPa) of:			
	8.1	10.3	12.4	14.5
(i) Direct effect on v_{dr}				
(1) Peak frequency	± 0.1	± 0.1	± 0.1	± 0.1
(2) Drift length	± 0.1	± 0.1	± 0.1	± 0.1
(A) Resultant uncertainty in v_{dr}	± 0.2	± 0.2	± 0.2	± 0.2
(ii) Indirect effect on v_{dr} through E/N and N				
(1) Electric field strength E	± 0.1	± 0.1	± 0.1	± 0.1
(2) Calibration of thermocouples	± 0.2	± 0.2	± 0.2	± 0.2
(3) Temperature gradients	± 0.1	± 0.1	± 0.1	± 0.1
(4) Null detector resolution	± 0.1	± 0.1	± 0.1	$< \pm 0.1$
(5) Calibration of pressure gauge	± 0.1	± 0.1	± 0.1	± 0.1
(6) Zero drift of null detector	± 0.2	± 0.2	± 0.3	± 0.5
Uncertainty in E/N	± 0.8	± 0.8	± 0.9	± 1.0
(B) Resultant uncertainty in v_{dr}	± 0.6	± 0.6	± 0.6	± 0.5
Uncertainty in N	$< \pm 0.1$	$< \pm 0.1$	$< \pm 0.1$	$< \pm 0.1$
(C) Resultant uncertainty in v_{dr}	± 0.7	± 0.7	± 0.8	± 0.9
Uncertainty in v_{dr} from A, B, C above	± 0.5	± 0.5	± 0.5	± 0.4
(iii) Diffusion effects	± 0.2	± 0.2	± 0.2	± 0.2
	± 0.1	± 0.1	± 0.1	± 0.1
	± 0.4	± 0.4	± 0.4	± 0.4
	± 0.3	± 0.3	± 0.3	± 0.3
	-2.7	-2.1	-1.7	-1.5

In order to obtain some estimate of the magnitude of the diffusion effects the following procedure was adopted. The diffusion correction was assumed to be $C(D_{\perp}/\mu)/V$ where C is an arbitrary constant and $D_{\perp}$ the transverse diffusion coefficient. A momentum transfer cross section was fitted to the drift velocity values (without correction for diffusion effects) obtained by extrapolation to zero number

density (this fitting will be discussed in the following paper by Elford 1980) and $D_{\perp}/\mu$ values were predicted as a function of E/N . Once values of $D_{\perp}/\mu$ had been obtained, the next problem was to choose a value for C . To do this various values of C were chosen and the corrections for diffusion were applied to the data at given values of E/N . Values of C were rejected if after correction the drift velocities were no longer a linear function of N to within the experimental scatter. For example, at $E/N = 0.1$ Td a value of C ranging from 0 to 10 still gives an adequate linear fit to the diffusion-corrected data, whereas at $E/N = 1.0$ Td a value of C of 6 gives a non-linear plot. The best estimate of the value of C was considered to lie somewhere between 0 and 4 and a mean value of 2 was chosen and used in calculating the diffusion correction to the drift velocity data at all E/N values. The diffusion corrections calculated in this way were only used to obtain an estimate of the uncertainty due to this effect (see Section 4*d* below). No corrections were applied in obtaining the $v_{dr}(N \rightarrow 0)$ values listed in Table 1.

The above method of estimating diffusion effects is open to serious objections: Use of the expression $C(D_{\perp}/\mu)/V$ assumes that $D_{\perp}$ rather than $D_{\parallel}$ is applicable, the value of C is assumed independent of E/N , and the values of $D_{\perp}/\mu$ are calculated for mercury in the absence of dimers and then applied to situations where dimers have a significant effect on the transport coefficients and hence on $D_{\perp}/\mu$. The most satisfactory method of removing diffusion effects is by measuring the pulse transit time at more than one drift length and calculating the drift velocity from differences. This was not done in the present work because of technical problems.

(d) Analysis of errors

The errors may be divided into three classes: (i) those which affect the drift velocity directly, (ii) those which affect the drift velocity indirectly through uncertainties in E/N and N , and (iii) those due to diffusion effects. The errors in these classes are as follows.

Class of error	Source of error	Estimated error (%)
(i) Direct	Peak frequency	± 0.2
	Frequency	—
	Drift length	± 0.1
(ii) Indirect	Determination of E	± 0.1
	Determination of N	
	(1) temperature:	
	calibration of thermocouples	± 0.1
	temperature gradients	± 0.1
	(2) pressure:	
(iii) Diffusion	reference pressure ^A	± 0.1
	zero drift of null detector	Pressure dependent
	resolution of null detector	Pressure dependent
	Diffusion effects	E/N and N dependent

^A Measured by quartz spiral gauge.

The procedure adopted to determine the final error in $v_{dr}(N \rightarrow 0)$ was as follows. Firstly the diffusion correction was applied to all the drift velocity values at a given E/N value. The errors in class (ii) were then summed to find the uncertainty in E/N

at each pressure. The resultant uncertainty in v_{dr} was found from the variation of v_{dr} with E/N for each of these pressures (Fig. 4). This uncertainty was then added to the sum of the errors of class (i) to obtain the total error in v_{dr} at each pressure for a given E/N . These error bars were placed on the diffusion-corrected drift velocity values and two linear extrapolations were performed, consistent with the maximum values of these error bars, to obtain the zero pressure values. The error in $v_{dr}(N \rightarrow 0)$ was then the difference between these extrapolated values and the extrapolated values given in Table 1. The percentage error in $v_{dr}(N \rightarrow 0)$ is shown in Fig. 7 as a function of E/N . An example of the calculation of the error in $v_{dr}(N \rightarrow 0)$ is shown in Table 2 for $E/N = 0.2$ Td. The area shown shaded in Fig. 7 is the uncertainty which results if no diffusion corrections are made. It is clear that it is the diffusion correction which is the single largest source of uncertainty and causes particularly large errors at low E/N values. At these low values the error in E/N has little effect on v_{dr} since the drift velocity changes very slowly with E/N but, because of the large dependence of v_{dr} on N , large extrapolation errors are incurred. At high E/N , small errors in E/N lead to significant errors in v_{dr} . However, the extrapolation error is now much smaller because at the higher E/N values the N dependence becomes very small.

(e) *Comparison with previous experimental drift velocities for electrons in mercury*

As noted in the Introduction, there have been two previous measurements of the electron drift velocity in mercury. The first was by McCutchen (1958) who used parallel plate electrodes spaced 1.9 cm apart situated inside a tubular manifold with an inside diameter of 3.2 cm. The electron transit time was measured using the oscillographic technique of Klema and Allen (1950). No temperatures are given for any experimental runs.

It is difficult to make a comparison with McCutchen's (1958) data because of the disagreement between his three sets of drift velocity data. His data for pressures of 50 and 140 kPa differ by about 25% systematically over the whole E/N range. The data chosen and included in Fig. 8 here for comparison with the present results are those shown for 50 kPa in his Fig. 4.* The difference between the two sets of data is large, being approximately a factor of 2 at $E/N = 0.3$ Td. It should be noted that the vapour pressures used by McCutchen were between three and five times the maximum pressures used in the present work. Extrapolation of the present data to the pressures used by McCutchen suggests that the large difference between the two sets of data is due to the much higher dimer abundances in McCutchen's mercury vapour samples.

McCutchen (1958) also carried out drift velocity measurements in carbon dioxide at high temperatures and his results may be compared with the data of Elford and Haddad (1980) taken at 573 K using the same drift tube as in the present work. Because the drift velocity in CO_2 changes very slowly with change in temperature, there is little error involved in assuming McCutchen's data are also valid for 573 K. The greatest difference between the two sets of data is 15% which is far smaller than the difference which exists between the two sets of drift velocity measurements in

* For $E/N > 4$ Td, these data disagree with the 50 kPa data shown in Fig. 3 of McCutchen's (1958) paper, the difference being 20% at 5 Td and 35% at 7.5 Td. The origin of this discrepancy is not known.

mercury, thus supporting the conclusion that the difference with mercury is due to dimers and is not an error in measurement.

The second set of measurements of the electron drift velocity in mercury was made by Nakamura and Lucas (1978) using a heat pipe oven. These authors also used the pulsed Townsend discharge technique, the drift length of their apparatus being 2 cm. Nitrogen was used as the buffer gas in the heat pipe oven. The vapour pressure was varied from 2 to 67 kPa by changing the temperature of the mercury from 468 to 608 K and the accuracy of the measurement system was checked by taking drift velocity measurements in nitrogen and comparing the values with those of Lowke (1962). Nakamura and Lucas found that their measured drift velocities were a function of the vapour pressure and they state that they corrected their drift velocity values for the effect of dimers by extrapolating to low vapour pressures.

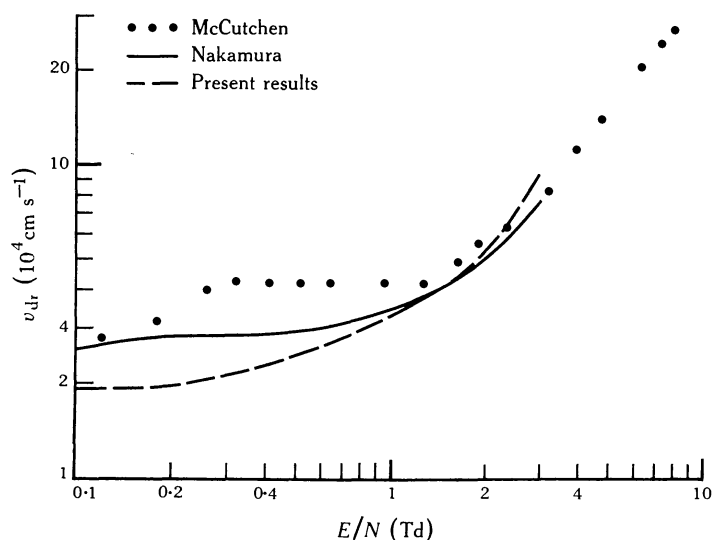


Fig. 8. Comparison of the present results ($v_{dr}(N \rightarrow 0)$) for the drift velocity of electrons in mercury vapour as a function of E/N with the data by McCutchen (1958; from his Fig. 4) and with a best fit curve to the data of Nakamura and Lucas (1978).

As it is difficult to recover the drift velocity data of Nakamura and Lucas (1978) from the figure in their paper, for the purpose of comparison with the present work their drift velocity values were computed using their derived momentum transfer cross section. These calculated values (Fig. 8) are up to about 50% larger than the present data at low E/N values and up to 30% lower than McCutchen's (1958) data at about $E/N = 0.4$ Td. Although Nakamura and Lucas attribute the pressure dependence of their results to the presence of dimers, their explanation of the effect in terms of a larger momentum transfer cross section for the dimer is incorrect. An increase in the effective momentum transfer cross section will cause a decrease in the drift velocity with increasing number density. This is opposite in sign to the number density variation observed by Nakamura and Lucas and in the present work.

It should be noted that both McCutchen (1958) and Nakamura and Lucas (1978) used a drift distance of about 2 cm. This is nearly eight times smaller than the drift distance used in the present work. Since diffusion errors are inversely proportional

to the drift distance for the same E/N and N value, diffusion errors may be expected to be significant in these previous measurements at pressures comparable with those used here. Such diffusion effects will cause an increase in the measured drift velocity.

5. Conclusions

The drift velocity of electrons in mercury vapour at 573 K has been measured over a range of pressures and E/N values. The linear dependence of the measured drift velocity on mercury number density for E/N values between about 0.1 and 1 Td indicates that mercury dimers have a very serious effect on electron transport coefficients at this temperature and over this E/N range. The presence of dimers has two consequences. Firstly, in the absence of detailed knowledge of electron–mercury dimer cross sections, drift velocity data must be extrapolated to zero number density before analyses using the Boltzmann equation can be applied to obtain the momentum transfer cross section for electrons scattered by mercury atoms. Since the extrapolation required is often large, the measured drift velocities have to be obtained with high accuracy in order to avoid large errors in the extrapolated values.

The second consequence of the presence of dimers is that care should be taken when using drift velocity data in the study of electron transport in discharges or MHD models where mercury vapour is the gas or a component of the gas. Unless the temperature is very high and the pressures sufficiently low that the dimer abundance is negligible, the effect of dimers on the drift velocity must be taken into account. The concentration of the dimers and hence their effect will vary with temperature but to date the only information on the variation of the drift velocity is that for 573 K. It is therefore desirable that drift velocity measurements be extended to other temperatures. The temperature range accessible with the present apparatus is limited, however. The upper temperature limit is considered to be approximately 573 K, the temperature used in this study, while the lower limit is set by the necessity that the pressures be large enough to avoid large diffusion effects. Thus the temperature range for accurate and safe measurement is severely restricted.

Acknowledgments

I wish to acknowledge the very significant contributions made to this work by the following: Dr R. W. Crompton for initiating this project, Dr H. B. Milloy for preliminary design studies, Mr K. Roberts for the construction of the experimental tube and vacuum system, Mr J. Gascoigne for technical assistance, particularly with the null detector and mercury distillation system, and Mr F. Johnson for the construction of the shutter grids. I also wish to thank the Division of Applied Physics, CSIRO, for their thermocouple calibrations. I am grateful to Dr D. J. Evans for discussions on dimers and wish to acknowledge helpful criticism of this paper by Dr R. W. Crompton and other members of the Electron and Ion Diffusion Unit.

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Appendix. Mercury Purification and Ampoule Filling Procedure

The mercury purification and ampoule filling system is based on that of Drullinger *et al.* (1975) and is shown schematically in Fig. 9. The system was first extensively baked at 300°C or greater for 60 h, the base pressure achieved being 6×10^{-8} Pa when the system cooled to room temperature. The mercury was then placed in the reflux column by first pumping down the whole system and then cooling the isolating trap with liquid nitrogen. Valve A (Fig. 9a) was opened to admit helium and while helium continued to flow the inlet tube was cracked open at B (Fig. 9b) and mercury was poured in using a pipette. This arrangement ensured that the mercury was taken from below the mercury surface which is normally contaminated by impurities. The filling tube was resealed and the helium pumped out using the diffusion pump. This filling procedure was carried out to reduce the influx of impurities from the atmosphere to a minimum. The dry ice trap was lowered over the upper end of the reflux column and heating of the mercury commenced. The heater used was a copper cylinder wound with a nichrome heating coil. The temperature of the heater was monitored with a chromel–alumel thermocouple placed inside the heater cylinder, between the glass tube and the inside wall of the copper cylinder. The oven temperature was taken to 250°C in stages. The mercury vapour evaporated from the mercury, condensed on the walls of the reflux column and ran down the column to the heated reservoir. However, some mercury vapour diffused along the tube to which the ampoules were attached. A heater tape was wrapped around this tube

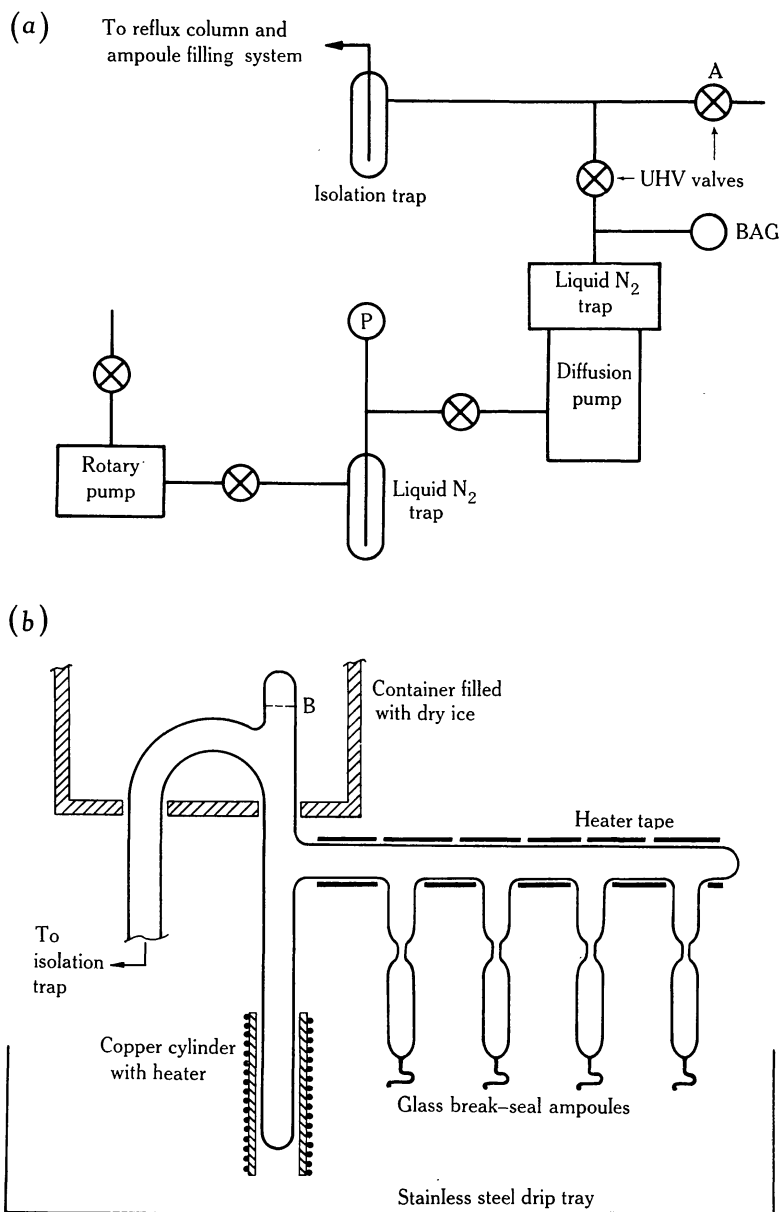


Fig. 9. Schematic diagrams (not to scale) of (a) the mercury purification and pumping arrangement for (b) the ampoule filling system. In (a), P is a Pirani gauge and BAG a Bayard-Alpert ionization gauge.

to prevent condensation of the mercury here rather than in the ampoules. As each ampoule was filled it was removed from the system. During the operation of the reflux column, including the time during the sealing off operation, the pressure indicated by the ionization gauge (BAG in Fig. 9a) was maintained below 6×10^{-7} Pa. Each ampoule contained approximately 2.5 g of mercury.

Manuscript received 23 July 1979, accepted 15 February 1980