Momentum Transfer Cross Section for Electrons in Mercury Vapour Derived from Drift Velocity Measurements in Mercury Vapour-Gas Mixtures

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Abstract

The Bradbury–Nielsen time-of-flight method has been used to measure electron drift velocities at 573 K in pure mercury vapour, a mixture of $46 \cdot 80\%$ helium– $53 \cdot 20\%$ mercury vapour and a mixture of $9 \cdot 37\%$ nitrogen– $90 \cdot 63\%$ mercury vapour. The *E/N* and pressure ranges used were $0 \cdot 2$ to $1 \cdot 5$ Td and $5 \cdot 4$ to $15 \cdot 2$ kPa for pure mercury vapour, $0 \cdot 08$ to $3 \cdot 0$ Td and $5 \cdot 40$ to $26 \cdot 88$ kPa for the mixture containing helium and $0 \cdot 06$ to $5 \cdot 0$ Td and $3 \cdot 33$ to $16 \cdot 67$ kPa for the mixture containing nitrogen. It is shown that the use of mixtures significantly reduces the dependence of the measured in pure mercury vapour. An iterative procedure to derive the momentum transfer cross section for electrons in mercury vapour over the range $0 \cdot 04$ to 4 eV with an uncertainty between ± 5 and 10% is described. It is concluded that previously published momentum transfer cross sections for mercury vapour derived from drift velocity data are significantly in error, due to diffusion effects and the procedure used to correct for the influence of dimers. The present cross section is in good agreement with the semi-empirical calculations of Walker (personal communication).

1. Introduction

A knowledge of the momentum transfer cross section $\sigma_{\rm m}$ for electrons in mercury vapour is required for the detailed understanding of devices involving discharges or arcs in mercury vapour and also for testing *ab initio* calculations of elastic scattering of electrons by mercury atoms. There have been four derivations of $\sigma_{\rm m}$ from experimental data (McCutchen 1958; Rockwood 1973; Nakamura and Lucas 1978b; Elford 1980b) and all have been based either wholly or primarily on measurements of electron drift velocities in pure mercury vapour. McCutchen used an approximate formula to derive σ_m from his drift velocity v_{dr} data; Rockwood used McCutchen's v_{dr} data in conjunction with data for v_{dr} and D_T/μ (where D_T is the transverse diffusion coefficient and μ the electron mobility) obtained from studies of arcs, while Nakamura and Lucas and also Elford used their own data (Nakamura and Lucas 1978a; Elford 1980*a*). Although all the derived cross sections have a maximum at electron energies between 0.5 and 0.7 eV, their magnitudes at the maximum and at other energies differ significantly and, in fact, at certain energies below 0.5 eV some of the differences are more than an order of magnitude. Since a common method of analysis was used for all the derivations since 1973 it is clear that the large differences in $\sigma_{\rm m}$ reflect the large differences in the drift velocity values used.

In order to obtain accurate electron drift velocity values in mercury vapour it is necessary to deal with three major experimental difficulties caused by the very small mean fractional energy lost in elastic collisions $(2m/M \text{ is } \sim 5.5 \times 10^{-6} \text{ where } m \text{ and } M \text{ are the electronic and atomic mercury masses respectively}).$ These difficulties are as follows.

(a) Presence of Molecular Species

The presence of low concentrations of molecular species can cause a major change in the rate of energy lost by the electrons (via rotational and vibrational excitation) and hence a significant change in the drift velocity. These species can be either molecular impurities or clusters of mercury atoms. Although the concentrations of molecular impurities can be reduced to adequate levels by appropriate experimental procedures, mercury dimers are always present in mercury vapour at a concentration proportional to the vapour pressure.

In the work of both Nakamura and Lucas and Elford the measured drift velocities values were found to be a function of the mercury vapour pressure over a range of values of E/N (where E is the electric field strength and N the gas number density). For example, Elford found that the measured drift velocity at E/N = 0.1 Td $(1 \text{ Td} \equiv 10^{-17} \text{ V cm}^2)$ increased by as much as 20% when the vapour pressure was increased from 8.1 to 14.5 kPa at 573 K. Nakamura and Lucas and Elford attributed this dependence to the presence of mercury dimers and the change of concentration of the dimers with vapour pressure. In order to obtain drift velocity values corresponding to dimer-free mercury vapour they extrapolated the data at each E/N to zero pressure. However, for certain values of E/N the extrapolations are large and lead to large uncertainties in the extrapolated values.

(b) Relatively High Mean Energy of the Swarm at the Lowest E/N

The very small rate of energy transfer in elastic collisions results in the mean energy of the electron swarm being comparatively high even at the lowest values of E/N at which accurate measurements have been made. Consequently the drift velocity data are relatively insensitive to the cross section at energies below about 0.5 eV and there is therefore a much higher uncertainty in the derived cross section in this energy range.

(c) Large Values of D_L/μ

Corrections to the measured drift velocity for the effect of diffusion depend on the ratio D_L/μ (where D_L is the longitudinal diffusion coefficient) (Huxley and Crompton 1974). Due to the very small rate of energy transfer in elastic collisions D_L/μ is relatively large in mercury vapour compared with its value in other gases at the same value of E/N and thus significant corrections to the measured values of v_{dr} are required at the gas number densities normally used. No corrections for diffusion have been made in any of the published sets of drift velocity data. As Elford noted, this may be due to the fact that the pressure dependence caused by diffusion could not be distinguished from the much larger variation caused by the changing concentration of dimers. These three difficulties can be reduced by the use of mixtures of mercury vapour with a second gas whose identity and abundance is chosen to significantly increase the total rate of energy transfer in electron collisions. In such a mixture the proportion of the total rate of energy transfer due to mercury dimers and molecular impurities is reduced, thus reducing the magnitude of the dependence of the drift velocity on the mercury vapour pressure and lowering the sensitivity to molecular impurities. The addition of the second gas also lowers the electron mean energy and D_L/μ at a given value of E/N. In short, the use of gas mixtures enables the drift velocity to be corrected for diffusion, the derivation of the drift velocity corresponding to zero dimer concentration to be more accurately made and the derived momentum transfer cross section to be extended to lower energies than has been possible previously.

The choice of the second gas is limited to those for which sets of collision cross section data are considered to be reliable. In the present study two mixtures were used: $46 \cdot 80\%$ helium- $53 \cdot 20\%$ mercury vapour and $9 \cdot 37\%$ nitrogen- $90 \cdot 63\%$ mercury vapour. The cross section data assumed in calculations of drift velocities for these mixtures were those of Crompton *et al.* (1970) for helium and Haddad (1984) for nitrogen.

The two-term transport theory generally used to calculate drift velocities from cross section data (Huxley and Crompton 1974) has been shown in a number of cases to be inaccurate (see for example Segur *et al.* 1987) and more sophisticated theories have been developed. In the case of mercury vapour, however, Braglia *et al.* (1990) have demonstrated that the error incurred in calculations of drift velocities using two-term transport theory is less than 0.1% and a similar conclusion is expected to hold for the mixtures used in



Fig. 1*a.* Electrode structure of the drift tube: C is a cylindrical electrode containing the 241 Am foils, while G1 and G2 are Bradbury-Nielsen grids.



Fig. 1*b***.** The experimental system, showing the mercury vapour inlet system, the mounting of the electrode structure, the location of the heaters and the position of the manometer head.

this work. All calculations of drift velocities in this study were therefore made using two-term transport theory.

Details of the apparatus and experimental procedure are given in Section 2. A series of measurements designed to test the accuracy of the apparatus is described in Section 3 and the final measurements and derivation of σ_m for mercury are given in Section 4. The present σ_m is compared in Section 5 with a number of previously published cross sections obtained from experimental data, *ab initio* and semi-empirical calculations.

2. Apparatus and Operating Procedures

The electron drift velocities were measured using the Bradbury-Nielsen time-of-flight method which has been discussed in detail by Elford (1972). Further information on experimental techniques to obtain high accuracy was given by England and Elford (1988). The drift tube and experimental procedure used in the present work were modified versions of those used by Elford (1980*a*). Since a number of these modifications are significant, a detailed description of the apparatus and the experimental procedure used in the present work will be given. The electrode system is shown schematically in Fig. 1*a* and the complete experimental system in Fig. 1*b*.



Fig. 2. Schematic diagram of the vacuum system. The regions enclosed by dashed lines are heated.

(a) Vacuum System and Pressure Measurement

The drift tube was operated at 573 K in order that large mercury vapour pressures could be used to reduce errors due to diffusion (the saturated vapour pressure at 573 K is 33 kPa). The choice of 573 K also enabled direct comparisons to be made with the earlier measurements of Elford.

The vacuum system is shown schematically in Fig. 2. Particular care was necessary to attain a low outgassing rate because the drift tube was required to

operate at a high temperature for extended periods and because even very low levels of molecular impurities can have a significant effect on the drift velocity, as has already been mentioned. Elford carried out an extensive outgassing of the manifold and electrode structure in order to lower the levels of hydrogen and carbon monoxide dissolved in the stainless steel. As a consequence the bakeout procedure required in the present work to obtain a sufficiently low outgassing rate was far less rigorous and holding the drift tube at 573 K for several days before measurements commenced was found to be adequate. No changes greater than the experimental scatter $<\pm 0.1\%$ were observed in the drift velocities measured in helium or pure mercury vapour over periods of more than 3 hours.

All pressure measurements made in previous studies of electron drift velocities in mercury vapour were made indirectly. In contrast, in the present work the pressures were measured directly using a capacitance manometer (MKS Baratron, type 315 BH head, range 0–133 kPa) with the head (manometer A in Fig. 2) mounted inside the main drift tube oven and held at 573 K using a separate heater. Hysteresis effects and zero shifts were found to be insignificant in measurements with this gauge. Buckman *et al.* (1984) investigated the conditions necessary for the operation of the manomater at high temperatures and demonstrated that the calibration can be maintained to within 0.25% for a period of three months.

As it was not possible to use manometer A at both 573 and 293 K (because of an inadequate range of zero adjustment), a second capacitance manometer (manometer B in Fig. 2) (MKS Baratron, type 315 BD head, range 0–13·3 kPa) was used for test measurements of the drift velocity of electrons in helium at 293 K. Since manometer B was more accurate than manometer A at low pressures, manometer B was also used to measure the pressure of nitrogen when preparing mercury vapour-nitrogen mixtures. The head of manometer B was maintained at 323 K. Both manometers were calibrated three times over the eight month period of the measurements using a dead-weight primary pressure standard (Gascoigne 1971). The shifts at any of the calibration points were less than $\pm 0.1\%$ for manometer B and $\pm 0.2\%$ for manometer A. The manometers were also checked against each other at frequent intervals using gas samples which were free from mercury vapour.

A liquid nitrogen trap (Fig. 2) was maintained cold throughout the period of measurements to prevent contamination of the pumping system by mercury vapour.

(b) Temperature Measurement and Control

The drift tube manifold and two enclosures, one surrounding the valves and the other the head of manometer A, constitute a cylindrical structure 15 cm in diameter and 1 m long. This cylinder was wrapped with a single heating tape and surrounded by four heating elements (two of which are shown in Fig. 1b). A copper shield was positioned between the heating elements and the cylinder to reduce the temperature gradient along the manifold and to prevent the formation of hot areas on the cylinder by direct radiation from the heaters. The four heater elements were of different lengths and individually controlled to enable the temperature difference between the top and bottom flanges of the manifold to be kept to less than ± 0.4 K.

The temperature of the drift tube was measured using calibrated platinum resistance thermometers (PRTs), which were held in small copper blocks attached to the top and bottom flanges of the drift tube manifold, in conjunction with a multi-sensor interface board (Sensoray Co.). The system was calibrated by comparing the temperatures indicated against those obtained using a resistance bridge (Leeds and Northrup, Model 8078) and a calibrated PRT (National Measurement Laboratory, CSIRO, Sydney).

The temperature of the drift tube was taken to be the average of the readings of the two PRTs. The temperature was maintained at 573 K to within ± 0.2 K by using the PRTs in conjunction with a personal computer, a proportional-integral-derivative algorithm and a programmable power supply to control the power supplied to the heater tape wound round the drift tube manifold and the two enclosures. After the temperature of the manifold had been raised to 573 K, a period in excess of 48 hours was allowed to elapse before drift velocity measurements commenced in order to ensure that thermal equilibrium between the manifold and the electrode structure had been attained.

The gas temperature, which must be known in order to calculate the gas number density N, is estimated to be in error by less than 0.2 K. This uncertainty is considerably lower than the ± 1.2 K reported by Elford (1980*a*) who used chromel-alumel thermocouples. The more accurately known temperature enabled higher accuracy to be achieved in the drift velocity measurements.

(c) Electron Source

Electrons were produced by α -particle ionisation, the α -particles being emitted by two nickel plated ²⁴¹Am foils mounted within the cylinder C (Fig. 1*a*). Only one such foil was incorporated in the source used by Elford. The additional ionisation available in the present source provided increased current and thus higher accuracy at low *E/N* values. The source has a triode-type electrode structure to provide enhanced ionisation at low gas densities (see Larsen and Elford 1986), although in the present work, where the gas densities were always relatively large, it was not possible to take advantage of this feature. Electrons were extracted from within the cylindrical grid and transported to the first shutter grid G1 by appropriate electric fields.

(d) Shutter Grids and Operation

The shutter grids which can operate over a wide temperature range without significant change in the wire tension were those used by Elford. The drift length, i.e. the distance between the planes of the two shutter grids, was 15.084 cm at 293 K and calculated to be 15.127 cm at 573 K.

The shutters were opened and closed in synchronism using rectangular pulses of variable amplitude and duration. The use of rectangular pulses, rather than the more conventional sine wave signals used by Elford, enabled the open time of the shutters to be varied independently of the signal amplitude to give higher currents and thus improved measurement accuracy. Tests using each of the two types of gating signal showed no variation of v_{dr} greater than the experimental scatter of $\pm 0.2\%$.

A typical arrival time spectrum is shown in Fig. 3.



Fig. 3. A typical arrival time spectrum obtained using pulsed gating of the shutters. The gas sample was approximately $9\% N_2-91\%$ Hg vapour at a pressure of $12 \cdot 7$ kPa, with $E/N = 1 \cdot 2$ Td and T = 573 K.

(e) Mercury Vapour Source

The mercury used in this work had been distilled under ultra high vacuum and stored in a break-seal glass ampoule (Elford 1980*a*). The ampoule was placed in the Pyrex source finger (Fig. 1*b*) and the finger pumped and outgassed before the ampoule was broken under vacuum. The finger was heated by an oven attached to the side of the drift tube oven to raise the vapour pressure to the required value. The finger temperature was maintained uniform by a thick-walled copper sleeve and the temperature monitored by a chromel–alumel thermocouple attached to the lower end of the finger.

(f) Adsorption/Absorption Effects

(i) *Mercury Vapour*. The pressure of all samples of mercury vapour let into the drift tube showed a significant decrease in time due to adsorption. A typical variation of pressure with time is shown in Fig. 4. In this case the pressure fell approximately 4% over the first two hours. Desorption also occurred for many days following the removal of mercury vapour from the drift tube.

The effect of the decrease in pressure on the drift velocity measurements was minimised by delaying the taking of data until the initial rapid drop in pressure had slowed and then taking data as quickly as possible. The failure of Elford to observe mercury vapour adsorption is attributed to three factors: shifts in the null point of his pressure measurement system; hysteresis effects in the Pyrex Bourdon spiral used as a null indicator; and the fact that he usually took measurements at a given pressure over periods of less than one hour.

When gas samples were used with a mercury vapour partial pressure of more than 15.5 kPa, the decrease in pressure with time was interrupted by



Fig. 4. An example of the decrease in pressure of a pure mercury vapour sample due to adsorption (T = 573 K).

pulses. The effect was not observed with high pressure samples of helium and nitrogen and became more severe as the mercury vapour pressure was increased beyond $15 \cdot 5$ kPa. The cause of this effect, which set $15 \cdot 5$ kPa as the maximum useable partial pressure, is not known but may be related to the approach to the saturated vapour pressure of mercury at 573 K.

(ii) *Hydrogen*. It was initially planned to use H_2 -Hg vapour mixtures in this study since the electron collision cross sections for hydrogen are considered to be well established (England *et al.* 1988). However, in preliminary drift velocity measurements in pure hydrogen at 573 K, it was found that the measured pressure decreased more rapidly than had been observed with pure mercury vapour samples and, moreover, there was a significant rise in the reference pressure of manometer A. It is believed that these effects were caused by the relatively high rate of diffusion of hydrogen in stainless steel at 573 K (Redhead *et al.* 1968). Since the partial pressures of both components of a H_2 -Hg vapour mixture decrease with time due to absorption (in the case of hydrogen) and adsorption (in the case of mercury vapour), it is not possible to know the relative concentrations at any given time.

(iii) *Helium and Nitrogen*. Samples of helium and nitrogen held in the drift tube at 573 K at pressures up to 27 kPa showed no variation in pressure to within 0.1% over periods of many hours. Adsorption and absorption effects for these gases are therefore not significant.

(g) Choice of Mixture Concentrations

The concentrations of helium and nitrogen were chosen following calculations of transport coefficients using the σ_m for mercury of Elford (1980*b*) and the other relevant cross sections. The concentrations chosen were a compromise between the aims of obtaining a reasonable reduction in the mean electron

energy and the effect of dimers compared with pure mercury vapour, while ensuring that uncertainties in the calculated coefficients due to uncertainties in the helium or nitrogen momentum transfer cross sections remained small. Since the uncertainty in the helium σ_m is estimated to be only ±2% over a wide energy range, large concentrations of helium were considered acceptable. The uncertainty in the nitrogen cross sections, momentum transfer and inelastic, are much larger and it is therefore desirable to use a much smaller concentration of nitrogen. The mixtures chosen were 50% helium–50% mercury vapour and 10% nitrogen–90% mercury vapour. The actual mixture concentrations used differed slightly from these values due to the mixing procedure employed. Calculations showed that the mean electron energies for these mixtures were significantly lower than those for pure mercury vapour (e.g. ~30% lower at 0·1 Td for both mixtures).

(h) Preparation of Mixtures

Before the mercury ampoule was broken, the ratio of the volume of the source finger to that of the drift tube was measured as a function of the source finger temperature by volume sharing samples of helium. The change in the volume ratio introduced by breaking the ampoule was not significant.

The mixtures were prepared by first filling the drift tube (at 573 K) to the required pressure with the buffer gas (helium or nitrogen) and volume sharing with the mercury source finger (at room temperature). The source finger was then raised to a temperature for which the saturated vapour pressure was close to the partial pressure of mercury vapour required for the mixture. The source finger was held open to the drift tube for periods of more than 60 minutes to ensure that complete mixing occurred throughout the finger and drift tube volumes. It was found that the calculated mixture concentration was in error as a result of incomplete mixing if the temperature of the source finger, before it was isolated, differed by more than a few per cent from that required to produce the partial pressure of mercury vapour appropriate for the mixture.

The partial pressures of the two components of the mixture in the drift tube at the time the source finger was isolated was determined from the initial filling pressure of the drift tube with helium or nitrogen, the known volume ratio corresponding to the source finger temperature, and the measured total pressure.

During each experimental run, adsorption of mercury vapour (Section 2f(i)) caused the mixture concentration to vary, resulting in an increase in the measured v_{dr} of as much as 1%. In order to obtain the drift velocity corresponding to the arbitrarily chosen mixture concentration (46.80% helium-53.20% mercury vapour and 9.37% nitrogen-90.63% mercury vapour), the dependence of v_{dr} on the mixture concentration was found for each value of E/N by measuring v_{dr} at two different times during the experimental run (the mixture concentration was determined from the known helium or nitrogen partial pressure and the measured total pressure at a given time). Interpolations were then carried out assuming a linear variation of v_{dr} with concentration to obtain drift velocities for the chosen mixture concentration. The interpolation corrections were all less than 0.5%.

At the conclusion of an experimental run the isolation valve between the source finger and the drift tube was opened and the mercury vapour condensed over a period of several hours in the source finger, which had been allowed to cool to room temperature. The source finger and drift tube were then evacuated. To avoid the build up of impurities in the source, the source finger was pumped while at room temperature for about 20 minutes before the commencement of each experimental run. This preliminary pumping was also carried out on a number of occasions with the source finger at elevated temperatures to ensure that outgassing impurities were removed.

3. Test Measurements

(a) Helium

Before measurements were commenced in mercury vapour mixtures, the accuracy of the experimental apparatus and the measurement technique was checked by taking a set of measurements in helium over a range of pressures and values of E/N, and at two different temperatures, 293 and 573 K. After the removal of diffusion effects by extrapolation to infinite pressure, the values were found to agree, to within $\pm 0.2\%$, with the values of Crompton *et al.* (1967) for 293 K and those calculated for 573 K using the σ_m for helium of Crompton *et al.* (1970).



Fig. 5. Measured electron drift velocity as a function of pressure for pure mercury vapour at 573 K for 0.2, 1.0 and 1.5 Td: squares, present work; triangles, Elford (1980*a*).

E/N			Pressur	e (kPa)					
(Td)	5.397	8.005	10.80	14.68	20.67	26.88			
			V	ár			$v_{\rm dr}^{01}$	$v_{\rm dr}^0$	
0.08						3.278	2.886	2.753	
0.10						3.645	3.128	3.020	
0.12					3.779	3.911	3.328	3.225	
0.14					3.964	4.104	3.482	3.389	
0.17				4.030	4.166	4.308	3.653	3.579	
0.20			4.103	4.181	4.310	4.451	3.788	3.743	
0.25			4.302	4.369	4.483	4.611	3.983	3.960	
0.30		4.434	4.456	4.514	4.613	4.727	4.157	4.144	
0.35		4.574	4.588	4.637	4.721	4.822	4.300	4.300	
0.4		4.686	4.703	4.746	4.818	4.907	4.432	4 • 432	
0.5		4.907	4.910	4.941	4.996	5.068	4.691	4.691	
0.6	5.102	5.098	5.104	5.128	5.171	5.230	4.933	4.933	
0.7	5.296	5.299	5.297	5.316	5.350	5.398	5.164	5.164	
0.8	5.497	5.495	5.494	5.510	5.537		5.388	5.388	
1.0	5.937	5.926	5.921	5.930			5.841	5.841	
1.2	6.422	6.407	6.398	6.404			6.328	6.328	
1 · 4	6.987	6.962	6.947				6.885	6.885	
1.7	7.989	7.959	7.943				7.872	7.872	
2.0	9.265	9.219					9.116	9.116	
2.5	12.17						11.95	11.95	
3.0	16.14						15.82	15.82	

Table 1*a*. Values of $v_{dr}^{01} v_{dr}^{01} v_{dr}^{0}$ for electrons in a mixture of 46.80% He-53.20% Hg vapour at 573 K (in units of 10⁴ cm s⁻¹)

(b) Mercury Vapour

A series of measurements was carried out in pure mercury vapour (see Fig. 5) for comparison with the data of Elford (1980*a*). Although the present results are generally not for the same pressures as those of Elford, because of difficulties arising from the adsorption of mercury vapour, it can be seen that the present values show the same variation with pressure and agree with his values to within $\pm 2\%$. These differences are within the combined uncertainty limits.

4. Results

(a) Measured Drift Velocities

The measured drift velocities v'_{dr} of electrons in mixtures of 46.80% He-53.20% Hg vapour and 9.37% N₂-90.63% Hg vapour at 573 K are shown in Tables 1*a* and 1*b*. Drift velocities were measured in the helium-mercury vapour mixture at six pressures between 5 and 27 kPa and at values of *E/N* between 0.08 and 3.0 Td. Measurements in the nitrogen-mercury vapour mixture were made at six pressures between 3 and 17 kPa and values of *E/N* between 0.06 and 5.0 Td.

The lower limits to the pressure and the value of E/N were set by the lack of adequate current for accurate measurements. The upper pressure limit was set by the occurrence of the pressure pulses described in Section 2f(i), while the maximum E/N value was determined by the onset of electrical breakdown. The measurements were repeatable to within $\pm 0.3\%$.

E/N			Pressure	e (kPa)				
(Td)	3.334	5.333	7.334	10.00	12.67	16.67		_
			Vdr	'			$v_{\rm dr}^{01}$	$v_{\rm dr}^0$
0.06						2.294	2.183	2.034
0.07						2.550	2.368	2.206
0.08					2.710	2.769	2.515	2.342
0.10					3.036	3.127	2.739	2.543
0.12					3.272	3.393	2.878	2.679
0.14					3.441	3.585	2.954	2.777
0.17				3.464	3.601	3.767	3.015	2.888
0.20				3.547	3.677	3.862	3.060	2.954
0.25			3.480	3.608	3.739	3.927	3.108	3.040
0.30			3.512	3.633	3.755	3.935	3.150	3.112
0.35			3.538	3.647	3.760	3.924	3.199	3.177
0.4			3.569	3.664	3.766	3.914	3.261	3.238
0.5		3.583	3.636	3.712	3.795	3.916	3.379	3.366
0.6		3.679	3.720	3.781	3.850	3.948	3.505	3.495
0.7		3.785	3.818	3.869	3.926	4.008	3.635	3.629
0.8		3.898	3.927	3.967	4.017	4.086	3.766	3.763
1.0	4.143	4.149	4.167	4.195	4.235	4.286	4.034	4.042
1.2	4 • 422	4 • 422	4 • 434	4.455	4 • 487	4.525	4.326	4.332
$1 \cdot 4$	4.730	4-721	4.730	4.742	4.768	4.795	4.637	4.639
1.7	5.244	5-227	5.232	5.238	5.262	5.278	5.159	5.159
2.0	5.854	5.831	5.829	5.828			5.757	5.757
2.5	7.125	7.089	7.086				7.021	7.021
3.0	8.710	8.669					8.590	8.590
3 • 5	10.529	10.473					10.383	10.383
4.0	12.50						12.33	12.33
5.0	16.60						16.36	16.36

Table 1 <i>b</i> .	Values of v_{dr}^{01} , v_{dr}^{01} and v_{dr}^{0} for electrons in a mixture of $9 \cdot 37\%$ N ₂ -90 $\cdot 63\%$ Hg
	vapour at 573 K (in units of 10^4 cm s ⁻¹)

Some examples of the variation with pressure are shown in Fig. 6. Note that the magnitude of the variation of v'_{dr} with pressure for the mixtures is very much less than that observed in pure mercury vapour.

(b) First Order Corrections for Diffusion and Dimers

In the earlier work of Elford, the drift velocity at each value of E/N was extrapolated linearly to zero pressure to obtain drift velocity values corresponding to zero dimer concentration. Although, as can be seen from Fig. 5, such an extrapolation appears reasonable for measurements made in pure mercury vapour, Fig. 6 shows that the measured drift velocities for the mixtures are not linear functions of pressure, the values departing from linear relations at low pressures due to the combined effects of dimers and diffusion.

It has been well established (Elford 1972) that the effect of diffusion on the measured drift velocity can be represented by the relation

$$v'_{\rm dr} = v_{\rm dr}(1 + \alpha/p), \qquad (1)$$

where v_{dr} is the true drift velocity (i.e. the velocity of drift of the centroid of an isolated travelling pulse) and α is a positive constant for a given gas and value of *E/N*. As a first estimate of the pressure dependence of v_{dr} in the



Fig. 6. (*a*) Electron drift velocities measured in a 46.80% helium-53.20% mercury vapour mixture at 573 K and E/N = 0.2, 0.3, 0.4 and 0.6 Td. (*b*) Electron drift velocities measured in a 9.37% nitrogen-90.63% mercury vapour mixture at 573 K and E/N = 0.4, 0.6, 0.8 and 1.0 Td.

present measurements it was assumed that the presence of dimers gives rise to a linear dependence on pressure. Relation (1) may then be modified and written as

$$v_{\rm dr}' = v_{\rm dr}^{01} (1 + \alpha/p)(1 + \beta p), \qquad (2)$$

where β is a constant for a given gas and value of E/N and v_{dr}^{01} is a first estimate of the drift velocity at zero dimer concentration. Values of v_{dr}^{01} as a function of E/N were obtained by fitting the measurements for both mixtures using relation (2). The coefficients α and β were assumed to vary smoothly with E/N. At E/N values where measurements are available at only one or two pressures, the values of α and β used were obtained by extrapolation of plots of α and β versus E/N. All the values of v_{dr}^{01} for both mixtures were fitted to within 0.3% by this procedure. The values of v_{dr}^{01} obtained using relation (2) are shown in Tables 1*a* and 1*b*.

(c) First Estimates of σ_m for Mercury

When the cross sections of either Nakamura and Lucas (1978b) or Elford (1980b) were used to calculate drift velocities for the two mercury vapour mixtures the values were found to be in serious disagreement with the derived values of v_{dr}^{01} , the differences being as large as 50 to 100% at a number of E/N values.

In these calculations, and all those performed subsequently, it was necessary to use quadratic interpolation of the cross section because of its rapid variation in the vicinity of the resonance at about 0.5 eV. Although electronic excitation of mercury (threshold 4.7 eV) has a very small effect on the drift velocity for the mixtures at the *E/N* values used in this work, cross sections for electronic excitation derived from a number of sources were included in the calculations. The removal of these cross sections caused a change of less than 0.1% in the calculated drift velocities for both mixtures at all values of *E/N*, with the exception of the highest value of *E/N* at which measurements were made in the helium–mercury vapour mixture. The change at this value of *E/N* (3 Td) was approximately 1%.

A new momentum transfer cross section for mercury was obtained by fitting to the values of v_{dr}^{01} for the He–Hg vapour mixture. These data were used in preference to those for pure mercury vapour or the N₂–Hg vapour mixture as the dependence on pressure, and hence the uncertainty in v_{dr}^{01} , was least for this case. However, when this σ_m was used to calculate drift velocities for both pure mercury and the N₂–Hg vapour mixture, the differences from v_{dr}^{01} were found to be as large as 6% in the case of the N₂–Hg vapour mixture data and 35% in the case of Elford's (1980*a*) data for pure mercury vapour. For each data set the differences were largest at the lowest values of *E/N* where the corrections for the effect of dimers were largest.

These findings suggested that the assumption that the presence of dimers gives rise to a linear dependence of the drift velocity on pressure was incorrect. A model calculation was therefore carried out to investigate the validity of this assumption.

(d) Modelling the Influence of Dimers

The presence of dimers in pure mercury or the mixtures affects the electron drift velocity primarily through inelastic collisions [see for example the analogous situation for dilute mixtures of H_2 in Ne (England *et al.* 1988)].

There appears to be little information available on the ground electronic state of the mercury dimer Hg₂. Huber and Herzberg (1979) quoted the equilibrium separation as $3 \cdot 3$ Å, a separation of vibrational levels of $4 \cdot 5$ meV and a dissociation energy of between 65 and 91 meV. The rotational states of the dimer have an energy separation of the order of 10^{-6} eV and thus the energy loss from rotational excitation by collisions is unlikely to be important. The inelastic cross sections for dimers that are important in this present work are therefore those for vibrational excitation and dissociation, since energy losses in such collisions are much greater than those in elastic collisions with mercury monomers or those producing rotational excitation of dimers.

As no cross sections are available for these inelastic processes, their effects were modelled using a single inelastic cross section, $\sigma_{in}(\epsilon)$, to account for all energy losses in collisions with dimers. In performing the calculations $\sigma_{in}(\epsilon)$ was represented by an energy dependent cross section $\sigma_i(\epsilon)$ weighted by two factors, M_{dimers} and the pressure p. The factor M_{dimers} takes into account both the scaling of σ_i (assumed on an arbitrary scale of magnitude) and also the fractional abundance of dimers at unit pressure. Although the fractional abundance can be calculated for pure mercury, the equilibrium constants and hence the abundances are not known for the mercury vapour mixtures. The

pressure factor p accounts for the linear increase in the fractional abundance of the dimers with pressure. The shape, threshold energy of σ_i , and the value of M_{dimers} were varied to fit the experimental variation of v_{dr}^{\prime} with pressure for a range of values of E/N. Diffusion effects were included and assumed to be of the same magnitude as found earlier (Section 4b).



Fig. 7. Electron drift velocity v_{dr}^0 corrected for diffusion and dimers, as a function of *E/N* at 573 K for two mercury vapour–gas mixtures: curve a, 46.80% helium–53.20% mercury vapour; curve b, 9.37% nitrogen–90.63% mercury vapour.

The conclusion from the model calculations was that the pressure dependence introduced by the presence of dimers could not be assumed to be linear at all values of *E/N*. The departure from a linear dependence was greatest for pure mercury vapour and least for the He–Hg vapour mixture. The departure was also greatest for a given gas or gas mixture at low values of *E/N*. Diffusion causes the measured drift velocity to increase as the pressure decreases: a departure from linearity which is in the opposite sense from that due to dimers. It is therefore probable that, over the restricted range of pressures used by Elford for measurements in pure mercury vapour, the two effects largely cancelled leaving an apparent linear dependence. To avoid the errors introduced by the assumption of a linear dependence on pressure, an iterative procedure was developed to derive $\sigma_m(Hg)$ in the presence of the effects of dimers and diffusion.

5. Analysis to Obtain $\sigma_{\rm m}$ for Mercury Vapour

(a) Treatment of Dimer Effects

The use of a single inelastic cross section to account for the effects of dimers, as described above, was incorporated in an iterative procedure for determining $\sigma_m(Hg)$. In this procedure (described in detail in Appendix A), successively better approximations to the drift velocity in the absence of diffusion and the effects of dimers, v_{dr}^0 [and hence $\sigma_m(Hg)$], were obtained by deriving values of σ_i and M_{dimers} which fitted the pressure dependence for both mixures. The process was an iterative one because the fitting to obtain σ_i involved the assumption of a $\sigma_m(Hg)$. Incorporated in the iterations was a correction procedure for the effects of diffusion.



Fig. 8. Drift velocity as a function of pressure for a 46.80% helium–53.20% mercury vapour mixture at 573 K and E/N = 0.2, 0.3, 0.4 and 0.6 Td: squares, present experimental values; curves, calculated using the present σ_m (Hg) and σ_i . The deviations of the experimental points from the calculated values are due largely to diffusion effects.

The iterative procedure resulted in cross sections $\sigma_m(Hg)$ and σ_i which reproduce the variation of v'_{dr} with pressure at all E/N values for both mixtures generally to within the relative experimental uncertainty (see Appendix B1). The cross section $\sigma_m(Hg)$ predicts the v^0_{dr} values for both mixtures generally to within $\pm 1.6\%$. The values of v^0_{dr} are shown in Table 1 and Fig. 7. Examples of the calculated pressure dependence of v_{dr} due to dimers for the helium-mercury vapour mixture are shown for selected values of E/N in Fig. 8. The present $\sigma_{\rm m}({\rm Hg})$ is given in Table 2.

<i>е</i> (eV)	σ _m (Å ²)	<i>е</i> (eV)	σ _m (Å ²)	<i>е</i> (eV)	σ _m (Ų)
0.000	13.7	0.18	101.6	0.44	219.7
0.005	13.8	0.19	108.6	0.46	219.4
0.010	13.9	0.20	115.1	0.48	215.1
0.015	14.0	0.21	121.3	0.50	208.6
0.02	$14 \cdot 1$	0.22	127.3	0.55	190.4
0.03	14.5	0.23	133.0	0.60	173.8
0.04	14.9	0.24	138.5	0.65	161.0
0.05	15.5	0.26	149.0	0.70	151.3
0.06	17.0	0.28	159.0	0.75	143.4
0.07	20.0	0.30	168.3	0.8	136.5
0.08	25.1	0.32	177.3	0.9	123.5
0.09	31.9	0.34	186.2	1.0	113.2
0.10	39.4	0.36	195.0	1.2	95.5
0.12	54.9	0.38	203.8	1 • 4	82.0
0.13	62.9	0.39	207.7	1.6	70.0
0.14	71.0	0.40	211.0	1.8	60.5
0.15	78.9	0.41	213.9	2.0	53.0
0.16	86.5	0.42	216.6	2.5	37.5
0.17	94.2	0.43	218.7	3.0	27.0
				4.0	16.5

 Table 2. Present derived momentum transfer cross section for electrons in mercury vapour

Although experimental data for pure mercury vapour should provide the most sensitive test of the dimer model cross section they were not used in the analysis described above for two reasons. First, the assumption that one inelastic cross section can represent a large number of cross sections (for rotation, vibration and dissociation) becomes more inaccurate as the dimer inelastic cross sections become more important and may therefore be invalid for the pure mercury results. Secondly, diffusion effects are larger in pure mercury vapour and the diffusion coefficients are expected to show a large variation with changing dimer concentration (similar to the variation in v_{dr} measured by Elford). It is therefore possible that diffusion effects do not show the simple 1/p dependence expected in the absence of dimers and hence the treatment of diffusion effects is more prone to error than for the mixtures where diffusion effects are small.

Despite these misgivings about the use of the model dimer cross section to fit the pure mercury vapour results, all the v'_{dr} values of Elford (1980) could be fitted to within ±2% (with the exception of one datum point) using the present cross sections and without making corrections (expected to be less than 3%) for diffusion. The present cross sections are therefore clearly compatible with the data of Elford. The fits to the data at the two lowest values of E/N (where the effects of dimers are very large) are shown in Fig. 9. The dashed curves indicate the linear extrapolation to zero pressure used by Elford to remove the effects of dimers. The differences from the calculated values (shown by the full curves) demonstrate the error incurred by this procedure.



Fig. 9. Electron drift velocity as a function of pressure for pure mercury vapour at 573 K and the two lowest values of *E/N* used by Elford (1980*a*). Experimental points of Elford (1980*a*) are shown as squares for 0.1 Td and triangles for 0.2 Td. The full curves were calculated using the present $\sigma_m(\text{Hg})$ and σ_i . The dashed curves indicate the linear extrapolation to zero pressure used by Elford (1980*a*) to correct for the effect of dimers. Note the large differences between the linearly extrapolated values and those obtained by calculation.

(b) Dimer Cross Section

The energy dependence of the dimer cross section σ_i used to fit the present v'_{dr} measurements is given in Table 3 and the values of M_{dimers} used for each mixture and for pure mercury vapour in Table 4. Since the population of dimers in pure mercury vapour can be calculated (Stogryn and Hirschfelder 1959), the value of M_{dimers} for pure mercury vapour can be used to obtain an absolute value for the cross section σ_i . The magnitude of this cross section at its maximum is calculated to be $8 \cdot 3 \text{ Å}^2$. Knowing the absolute cross section, it is then possible to estimate the fractional dimer populations in the mixtures; these are shown in Table 4.

The calculated fractional populations of dimers in the mercury vapour mixtures are less than the population in pure mercury at the same pressure. Since the second virial coefficient is related to the equilibrium concentration of dimers (Stogryn and Hirschfelder 1959), it can be concluded, as Elford

Energy (eV)	Cross section <i>o</i> (arb. units)		
0.04	0.0 (threshold)		
0.045	1.0		
0.09	1.0		
0.17	0.15		
0.40	0.10		
0.50	0.0		

Table 3	B. Cros	ss sec	tion	σ_{i}	as	а	function	o
		electro	on e	ne	rgy	,		

Table	4.	Dimer	norma	lisation	facto	r M _{din}	_{iers} and	calcu-
lated	frae	ctional	dimer	populat	ion fe	or the	mixture	es and
		pur	e mero	curv var	our a	t 573 J	ĸ	

Gas	$\frac{M_{\rm dimers}}{(\rm kPa^{-1}\times10^{-6})}$	Fractional population (ppm kPa ⁻¹)
Hg	180	21.8
N ₂ –Hg	136	16
He-Hg	53-9	6-6

(1980*a*) did for the case of pure mercury vapour, that no significant errors are incurred by using the ideal gas law to calculate the number density for the gas mixtures.

Two points concerning the dimer inelastic cross section should be noted. First, a unique cross section cannot be derived and, second, the cross section is an effective cross section representing the effect of inelastic collisions due to a number of excitation processes. In the present model it was found necessary to include in the calculations the effect of superelastic collisions, indicating that vibrational excitation of the dimers is the dominant electron energy loss process.

It must be emphasised that the corrections involved in using a dimer inelastic cross section and the iterative process described in Section 5*a* and Appendix A are relatively small. The technique introduces changes in v_{dr}^0 values from those obtained using linear extrapolation of less than 5% for the helium-mercury vapour mixture and less than 7% for the nitrogen-mercury vapour mixture. No changes were made to the v_{dr}^{01} values, obtained using relation (2), at values of *E/N* greater than 0.35 Td for the helium-mercury vapour mixture and greater than 1.0 Td for the nitrogen-mercury vapour mixture. Consequently, the only region of the derived cross section affected by nonlinearity in the pressure dependence of v_{dr}' due to dimers is that below 0.15 eV. On the other hand, this study indicates that the cross sections derived previously from measurements in pure mercury, where the effects of dimers are much larger, are subject to large errors at energies below 0.5 eV.

(c) Estimates of Uncertainties

The uncertainty in the derived σ_m is made up of contributions from the uncertainty in ν_{dr}^0 and the uncertainty in the cross sections for helium and nitrogen. The uncertainties in the final values for ν_{dr}^0 consist of contributions

from the uncertainty in the model dimer cross section, through its use in the extrapolation to zero pressure, and the systematic uncertainties in the measured values of v'_{dr} . Estimates of systematic uncertainties and those due to the dimer cross section are given in Appendix B. The total systematic uncertainty was determined by adding the separate uncertainties in quadrature. To obtain the total estimated uncertainty (shown for every second value of E/N in Table 5), the total systematic uncertainty was added arithmetically to the uncertainty in the extrapolation to zero pressure.

E/N	Heli	ium mixture		Nitrogen mixture			
(Td)	Systematic (%)	Dimer (%)	Total (%)	Systematic (%)	Dimer (%)	Total (%)	
0.06				1.42	2.48	3.9	
0.08	1.43	2.00	3 • 4	0.83	1.77	2.6	
0.12	0.69	0.90	1.6	0.52	1.11	1.6	
0.17	0.56	0.75	1.3	0.38	0.78	1.2	
0.25	0.47	0.66	$1 \cdot 1$	0.19	0.66	0.9	
0.35	0.49	0.67	1.2	0.17	0.60	0.8	
0.5	0.43	0.64	$1 \cdot 1$	0.20	0.57	0.8	
0.7	0.36	0.73	$1 \cdot 1$	0.19	0.55	0.7	
1.0	0.42	0.79	1.2	0.17	0.53	0.7	
$1 \cdot 4$	0.71	0.79	1.5	0.21	0.59	0.8	
2.0	1.22	1.10	2.3	0.34	0.96	1.3	
3.0	1.63	1.70	3.3	0.94	1.40	2.3	
4.0				1 · 45	2.00	3.5	

Table 5. Estimates of the total uncertainty in v The dimer columns give the estimated uncertainty in the extrapolation procedure

It is difficult to transform uncertainties in v_{dr}^0 into uncertainties in σ_m (Hg) determined from this analysis because v_{dr}^0 and σ_m (Hg) are related by an integral function. The only way to estimate uncertainties in σ_m is to make changes to $\sigma_{\rm m}$ and observe the resulting changes in calculated values of $v_{\rm dr}$. It was found that changes in σ_m of from 5 to 10% for energies between 0.04 and 4 eV were required to give a maximum change in v_{dr} of about 2% in both mixtures. Outside this energy range, larger changes could be made to $\sigma_{\rm m}$ without producing significant changes to the calculated values of v_{dr} . Uncertainties in the cross sections for helium and nitrogen will also contribute to the uncertainties in the mercury $\sigma_{\rm m}$ determined in the present work. The helium $\sigma_{\rm m}$ is estimated to be uncertain by $\pm 2\%$ over the energy range from 0.4 to 4 eV. However, since the mercury $\sigma_{\rm m}$ is much larger than the helium $\sigma_{\rm m}$ over this energy range, this uncertainty will be negligible compared with that from the uncertainties in the experimental v_{dr}^{\prime} values. The uncertainty in the nitrogen cross sections was not stated by Haddad (1984), but the fact that reasonable fits were obtained to the data for both helium and nitrogen mixtures suggests that the errors in the nitrogen cross sections do not contribute significantly to the overall uncertainty.

6. Comparisons with Previous Cross Sections

(a) Experimentally Determined Cross Sections

The present cross section is shown in Fig. 10 with the cross sections of Rockwood (1973), Nakamura and Lucas (1978b) and Elford (1980b). The

differences between these cross sections at energies between 0.5 and 1.5 eV are less than 30%, with the present one lying between the others. The present cross section is generally within $\pm 10\%$ of the one of Elford at energies between 0.5 and 4 eV, but is believed to be more accurate because corrections to account for diffusion effects were neglected by Elford. The cross sections of Rockwood and of Nakamura and Lucas are expected to be less accurate because of the neglect of the effects of diffusion on the measured drift velocities. In addition, the technique used by these authors to measure drift velocities is considered to be less accurate than the Bradbury–Nielsen method used in the present work.



Fig. 10. Momentum transfer cross section for mercury σ_m as a function of electron energy for the four experiments shown.

At lower energies, the present cross section differs greatly from those previously published, including that of Elford. This is due to errors in the previous drift velocity data used caused by either the neglect of the effects of dimers or incorrect extrapolation to remove such effects. These errors lead to high values of v_{dr} and, therefore, low values of the cross sections determined from them.

The cross sections of Rockwood, Nakamura and Lucas, and Elford were used to calculate values of v_{dr} for the present mercury vapour mixtures. The results obtained at a number of values of *E/N* were as much as 100% higher than the present v_{dr}^0 values.

(b) Theoretically Derived Cross Sections

Useful comparisons of the present cross section with those obtained theoretically are very limited. Studies by Scott *et al.* (1983), Bartschat and Burke (1986) and Haberland and Fritsche (1987) do not extend to sufficiently low energies, while in the work of Walker (1975), Sin Fai Lam and Baylis (1981) and McEachran and Stauffer (1987), polarisation of the atomic electron cloud is either over-estimated or neglected (Mitroy, personal communication).



Fig. 11. Momentum transfer cross section for mercury σ_m as a function of electron energy, where the full curve is the present work. The three remaining curves were calculated by Walker (1975 and personal communication) using: the calculated polarisation potential (Walker 1975); a polarisation potential with a cut-off parameter of $4 \cdot 2a_0$; and a polarisation potential with a cut-off parameter of $4 \cdot 2a_0$; and a polarisation potential with a cut-off parameter of $4 \cdot 2a_0$; and a polarisation potential with a cut-off parameter of $4 \cdot 8a_0$.

Walker stated that the result of over-estimating the effect of polarisation in his calculations is to cause the cross section to be too large and the resonance to occur at too low an energy. In order to adjust for the effect of polarisation Walker (personal communication) used an empirical polarisation potential $V_p(r)$ with an adjustable 'cut-off' parameter r_c :

$$V_{\rm p}(r) = -\frac{\alpha_0}{2r^4} [1 - \exp(-r/r_{\rm c})^6],$$

where α_0 is the static dipole polarisability and r the electron-atom separation. This potential has the correct form at very large values of r, while at small values of r the strength of the potential can be adjusted by changing the cut-off parameter. Decreasing r_c corresponds to an increase in the strength of the polarisation at small r and causes the calculated cross section to peak at a higher energy and to have a lower magnitude at the peak. The results of changing the cut-off parameter to fit the peak of the present cross section are shown in Fig. 11. Increasing the value of the parameter to a value of $4 \cdot 8a_0$ to reduce the strength of the polarisation potential gives agreement with the present σ_m to better than $\pm 10\%$, except below $0 \cdot 1$ eV. Although such differences are relatively small, calculations of drift velocities using the calculated cross section show that it is incompatible with the present experimental results (see Fig. 11).

Table 6.	Diffusion coefficient NDth for thermal electrons in mercury vapour at 470 K
	as calculated from various cross sections

The experimental value is $1.74\pm0.17\times10^{21}$ cm $^{-1}$ s $^{-1}$ (Hegerberg and Crompton 1980)					
Origin of $\sigma_{ m m}$	Calculated ND_{th} (×10 ²¹ cm ⁻¹ s ⁻¹)	Deviation from experimental value (%)			
Walker (1975)	1.36	-22			
Walker, $r_c = 4 \cdot 8a_0$	1.66	-4.6			
Walker, $r_c = 4 \cdot 2a_0$	1.52	-13			
Rockwood (1973)	1.87	7.5			
Nakamura & Lucas (1978 <i>b</i>)	1.96	13			
Elford (1980 <i>b</i>)	3-57	105			
Present	2.03	17			

(c) Diffusion Coefficient for Thermal Electrons at 470 K

It is of interest to test a number of electron-mercury cross sections to see if they are compatible with the diffusion coefficient for thermal electrons in mercury vapour at 470 K, which has been measured by Hegerberg and Crompton (1980). In a thermal electron energy distribution at a temperature of 470 K, the number of electrons with energies above about 5kT (0·17 eV) (where k is Boltzmann's constant) is negligible and consequently the diffusion coefficient for thermal electrons is sensitive to the cross section only at energies below 0·17 eV. Table 6 shows comparisons between the diffusion coefficient calculated from various cross sections with the experimental value of Hegerberg and Crompton.

The only cross sections which are clearly incompatible with the experimental value of ND_{th} are those of Walker (1975) and Elford (1980*b*). The reasons for errors in these cross sections have been discussed in Sections 5 and 6. The other calculations of ND_{th} differ from the experimental value by amounts less than the sum of the experimental uncertainty of $\pm 10\%$ and the uncertainty in the calculated value due to uncertainties in the cross sections. In particular, the present cross section at energies below 0.04 eV is very uncertain and errors in this region of the cross section will have a significant effect on the calculated value of ND_{th} . The difference of 17% between the value calculated from the present cross section and that from experiment is therefore considered acceptable.

6. Conclusions

The mercury momentum transfer cross section has been determined over the energy range 0.04 to 4 eV with an uncertainty estimated to be between ±5 and 10%. This cross section and an effective inelastic cross section for dimers predicts the drift velocities measured by us at six pressures in heliumand nitrogen-mercury vapour mixtures and those measured by Elford at six pressures in pure mercury vapour to within $\pm 2\%$ for all but a few values of *E/N*. The major advantage in using mixtures has been shown to be the reduction in the influence of mercury dimers, which was the cause of large uncertainties in previous analyses to obtain the momentum transfer cross section from drift velocity data for pure mercury vapour.

The value of the diffusion coefficient for thermal electrons at 470 K calculated from the present cross section is in acceptable agreement with the experimental value of Hegerberg and Crompton (1980) when the large uncertainties in the cross section below 0.04 eV are taken into account.

The theoretical cross sections for the present energy range of interest generally suffer from an over-estimation of the polarisation potential. A cross section obtained by Walker by varying the strength of the polarisation interaction is in good agreement with the present one over the energy range 0.1 to 4 eV.

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Appendix A: Iterative Procedure Used to Obtain σ_m (Hg) in the Presence of the Effects of Dimers and Diffusion

The iterative procedure used to obtain the momentum transfer cross section for mercury $\sigma_m(Hg)$, the drift velocity corrected for dimers and diffusion v_{dr}^0 , and the cross section σ_i may be followed by reference to a typical plot of the measured drift velocity v'_{dr} as a function of pressure at a fixed value of E/Nfor the N₂-Hg vapour mixture (see Fig. A1, curve A).



Fig. A1. Typical curves of drift velocity as a function of pressure for the N₂-Hg vapour mixture as generated by the iterative procedure. The experimental data are shown as triangles (i.e. the values denoted as v'_{dr}). The origins of the curves A, B, C and D are described in Appendix A.

Before commencing the iterative procedure it was necessary to obtain a first approximation to $\sigma_m(Hg)$. This was carried out by fitting to the set of v_{dr}^{01} values for the He–Hg vapour mixture, obtained using equation (2) and the procedure described in Sections 4*b* and 4*c*, which assumes a linear dependence of v_{dr} on pressure due to the effect of dimers.

The first step in the iterative procedure was to use the values of the coefficients β and ν_{dr}^{01} at the chosen value of *E/N* [obtained in the preliminary analysis of the experimental data for the N₂-Hg vapour mixture using relation (2)] to plot the straight line $\nu_{dr}^{01}(1 + \beta p)$ (see Fig. A1, line B). This line is an approximation to the pressure dependence of ν_{dr} caused solely by the effect of dimers, assuming they cause a linear dependence on pressure. The line B falls below curve A because the effects of diffusion have been removed.

Drift velocities at this value of E/N were then calculated as a function of pressure using the first approximation to $\sigma_m(Hg)$ (obtained by the procedure described above) and varying σ_i and M_{dimers} in order to obtain a curve (curve C)

which, at the three or more highest pressures used predicted the *variation* of the drift velocity with pressure. The slope of curve C is principally determined by σ_i , whereas both σ_i and $\sigma_m(Hg)$ determine the absolute values of the points on the curve. Note that it was not required that curve C fit the absolute magnitude of line B at high pressures since only a first estimate of $\sigma_m(Hg)$ was used in the calculation.

Curve C was then scaled to coincide with line B at the highest pressures. This new scaled curve, curve D, is a new estimate of the *true* drift velocity in the presence of dimers. Assuming, as before, a hyperbolic dependence of the *measured* drift velocity on pressure, as represented by equation (1), a

<i>E/N</i> (Td)	Random	Relative	Uncertainty	Uncertainty
(14)	in v_{dr} (%)	uncertainty (%)	$\Delta v_{\rm dr} / \Delta p$ (%)	v _{dr} (%)
		Не–Нд vapou	r	
0.08	0.20	0.30*	0.51	2.00
0.12	0.15	0.15	0.30	0.90
0.17	0.14	0.15	0.29	0.75
0.25	0.13	0.15	0.28	0.66
0-35	0.15	0.15	0.30	0.67
0.5	0.16	0.15	0.31	0.64
0.7	0.18	0.15	0.33	0.73
1.0	0.21	0.15	0.36	0.79
$1 \cdot 4$	0.25	0.15	0.36	0.79
2.0	0.33	0.52	0.87	1.10*
3.0	0.45	1.00*	1.60	1.70*
		N ₂ –Hg vapou	r	
0.06	0.13	0.30*	0.46	2.48
0.08	0.12	0.24	0.38	1.77
0.12	0.10	0-20	0.30	$1 \cdot 11$
0.17	0.10	0.15	0.25	0.78
0.25	0.10	0.15	0.25	0.66
0.35	0.10	0.15	0.25	0.60
0.5	0.10	0.15	0.25	0.57
0.7	0.10	0.15	0.25	0.55
1.0	0.10	0.15	0.25	0.53
$1 \cdot 4$	0.10	0.15	0.25	0.59
2.0	0.14	0.18	0.32	0.96
3.0	0.19	0.51	0.77	1.4*
4.0	0.21	0.73*	1.07	2.0*

Table B1. Estimates of the contribution to the uncertainty in v_{dr}^0 due to uncertainties in the dimer model for the helium- and nitrogen-mercury vapour mixtures

* These values were estimated differently from the others because there was either only one pressure used or the model predicted that the dimer effects were insignificant at these values of E/N.

new value of the coefficient α can be found from the differences between the experimental values of the drift velocity v'_{dr} and the corresponding values of the drift velocity given by curve D. Using this value of α at the highest value of p, the value of v'_{dr} can be corrected for the effects of diffusion to determine the true value of the drift velocity at this pressure. Curve D is then translated to pass through this point giving curve E (not shown in Fig. A1). The differences between curves D and E were generally much smaller than 0.5%. The intercept of curve E with the ordinate axis gives the next approximation to v_{dr}^0 , that is v_{dr}^{02} .

The procedure used to obtain v_{dr}^{02} for the He-Hg vapour mixture was the same as that described above, although in this case, when the variation of the drift velocity with pressure due to dimers was calculated, the cross section σ_i used was that obtained by fitting to the N₂-Hg vapour mixture data. Only the factor M_{dimers} was varied to allow for the different dimer concentrations in the He-Hg vapour mixture. A second estimate of σ_m (Hg) was obtained by fitting to the v_{dr}^{02} data, with extra weight being placed on the He-Hg vapour mixture results.

Only two or three iterations were required to obtain converged results for v_{dr}^0 .

Appendix B: Estimates of the Uncertainty in Drift Velocities in Gas-Mercury Vapour Mixtures

(B1) Uncertainties Arising from Corrections for the Effects of Dimers

To estimate the uncertainties in the drift velocities arising from corrections to remove dimer effects it is necessary to determine the uncertainty in the cross section σ_i obtained by fitting to the change in the drift velocity with pressure $(\Delta v_{\rm dr}/\Delta p)$, for all values of E/N. The uncertainty in $\Delta v_{\rm dr}/\Delta p$ consists of two components. The first is the random measurement uncertainty arising from the random uncertainties in E and N, the mixture concentration and the determination of the frequency at which the current maxima occur. The second component is the uncertainty in the magnitude of the diffusion correction. Estimated values of these errors are shown in Table B1. The parameter M_{dimens} used to normalise σ_i for each mixture was varied at each value of *E/N* until the calculated values of $\Delta v_{\rm dr}/\Delta p$ were greater than those observed by an amount equal to twice the random uncertainty. This gave an estimate of how much the dimer model cross section could be in error while still giving results compatible with the experimental v_{dr} values. The new dimer cross sections were then used to calculate new v_{dr} -p curves at each value of E/N and these were used to obtain new drift velocities at zero pressure. The difference of the new values from the original corrected values (which are given in Table 1) gave an estimate of the uncertainty due to the extrapolation procedure (last column in Table B1).

(B2) Systematic Errors

Other sources of uncertainty in the corrected v_{dr} values are the systematic uncertainties in the parameters that determine the drift velocity (Table B2), and

Parameter	Estimated error
<i>E/N</i> (due to pressure, temperature, drift distance and voltage across the drift space)	±0 · 3%
Temperature T	±0 · 2%
Drift distance d	±0.05%
Mixture concentration (due to pressure and volume ratio)	±0-4%

Table B2. Systematic errors in the experimental parameters

vapour mixtures from systematic uncertainties						
<i>E/N</i> (Td)	ΔΕ/N (%)	ΔT (%)	∆d (%)	∆Concentration (%)	∆Diffusion (%)	
1 <u>44999999999999999999999999999999</u>			Не–На чарои	r		
0.08	0.20	0.03	0.05	0.20	1.40	
0.12	0.09	0.03	0.05	0.20	0.65	
0.17	0.06	0-02	0.05	0.21	0.51	
0.25	0.03	0.02	0.05	0.23	0.41	
0.35	0.05	0.01	0.05	0.25	0.42	
0.5	0.05	0.01	0.05	0.27	0.33	
0.7	0.08	0.01	0.05	0-28	0.20	
1.0	0.11	0.00	0.05	0.30	0.27	
1.4	0.18	0.00	0.05	0.32	0.61	
2.0	0.30	0.00	0.05	0.36	1.13	
3.0	0.53	0.00	0.05	0.37	1.50	
			N ₂ –Hg vapou	r		
0.06	0.23	0.04	0.05	0.03	1.40	
0.08	0.20	0.04	0.02	0.03	0.80	
0.12	0.12	0.03	0.05	0.02	0.50	
0.17	0.06	0.03	0.05	0.02	0.38	
0.25	0.02	0.02	0.05	0.03	0.18	
0.35	0.00	0.02	0.05	0.04	0.16	
0.5	0.02	0.01	0.05	0.05	0.19	
0.7	0.05	0.01	0.05	0.05	0.17	
1.0	0.08	0.01	0.05	0.06	0.13	
$1 \cdot 4$	0.14	0.00	0.05	0.06	0.14	
2.0	0.23	0.00	0.05	0.05	0.24	
3.0	0.35	0.00	0.05	0.03	0.87	
4.0	0.39	0.00	0.05	0.02	1.40	

Table B3.	Contributions to the uncertainty in v _{dr} for helium- and nitrogen-mercury
	vapour mixtures from systematic uncertainties

the uncertainty in the corrections for diffusion effects. Using the estimates of errors shown in Table B2, the contribution of each source of error to the uncertainty in v_{dr} was estimated by changing each parameter, in turn, and finding the change in the calculated values of v_{dr} . The uncertainties in the diffusion corrections were estimated to be half the diffusion correction at the highest pressure for each value of E/N where v_{dr} was measured at more than three pressures. Where two pressures were used the uncertainty was assumed to be equal to the diffusion correction, while at values of E/N where v_{dr} was measured at only one pressure the estimates were increased further. The results of these estimations are shown in Table B3.

The uncertainty in v_{dr} due to uncertainties in the value of E/N are small except at high values of E/N because v_{dr} generally varies slowly with E/N. The uncertainty due to the concentration is also surprisingly small, especially for the nitrogen mixture. This is partly because a *decrease* in v_{dr} caused by an increase in the mercury vapour concentration is offset by an *increase* in v_{dr} due to an increase in the dimer concentration.

The uncertainties listed in Table B3 and those due to the corrections for the effects of dimers (last column of Table B1) were added to give the total uncertainties listed in Table 5 (Section 5c).