

## The Diffusion Coefficient for Thermal Electrons in Mercury Vapour at 470 K

R. Hegerberg and R. W. Crompton

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

### Abstract

The diffusion coefficient for thermal electrons in mercury vapour has been measured using the Cavalleri electron density sampling technique. The result indicates that the average momentum transfer cross section for electrons is  $\sim 27 \times 10^{-16} \text{ cm}^2$ , a result which favours previously derived cross sections from drift velocity data over recent theoretical calculations.

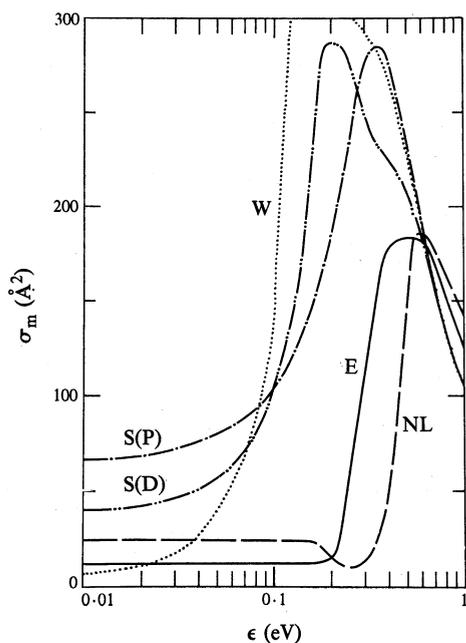
### Introduction

The scattering of low energy electrons by mercury atoms is of practical importance in mercury discharges (see e.g. Vriens *et al.* 1978, and references therein) and several attempts, both theoretical and experimental, have been made to determine scattering cross sections in this energy regime (see e.g. Elford 1980*a*, 1980*b*, and references therein). The most recent efforts to obtain the momentum transfer cross section  $\sigma_m$  are those of Nakamura and Lucas (1978) and Elford (1980*b*), who derived  $\sigma_m$  for energies between 0.1 and 5 eV from drift velocity data obtained in Hg vapour at elevated temperatures.

Walker (1975) performed an *ab initio* calculation of elastic scattering cross sections by solving the full Dirac equation, while Sin Fai Lam (1980) has recently calculated *ab initio* elastic scattering cross sections for the e-Hg system by applying a perturbation method to include relativistic effects. As can be seen from Fig. 1, while there is substantial agreement between theory and experiment at energies above the p-wave resonance, which occurs at about  $\varepsilon = 0.5 \text{ eV}$ , there is more than an order of magnitude difference between experimental and theoretical results below the resonance peak. There are, however, rather large uncertainties also in the cross sections derived from drift velocity measurements at energies below about 0.2 eV. This is because there is a large increase in the mean energy of the electrons when an external electric field is applied due to the small energy exchange in elastic collisions. The drift velocity therefore essentially depends on the cross section for energies above the onset of the resonance.

In an attempt to resolve the rather large discrepancy between theory and experiment, we have measured the diffusion coefficient for thermal electrons in mercury at a temperature of  $\approx 470 \text{ K}$ . The diffusion coefficient  $D$  is given by (see e.g. Huxley and Crompton 1974)

$$D = \frac{1}{3N} \left( \frac{2}{m} \right)^{\frac{1}{2}} \int_0^{\infty} \frac{\varepsilon f_M(\varepsilon)}{\sigma_m(\varepsilon)} d\varepsilon, \quad (1)$$



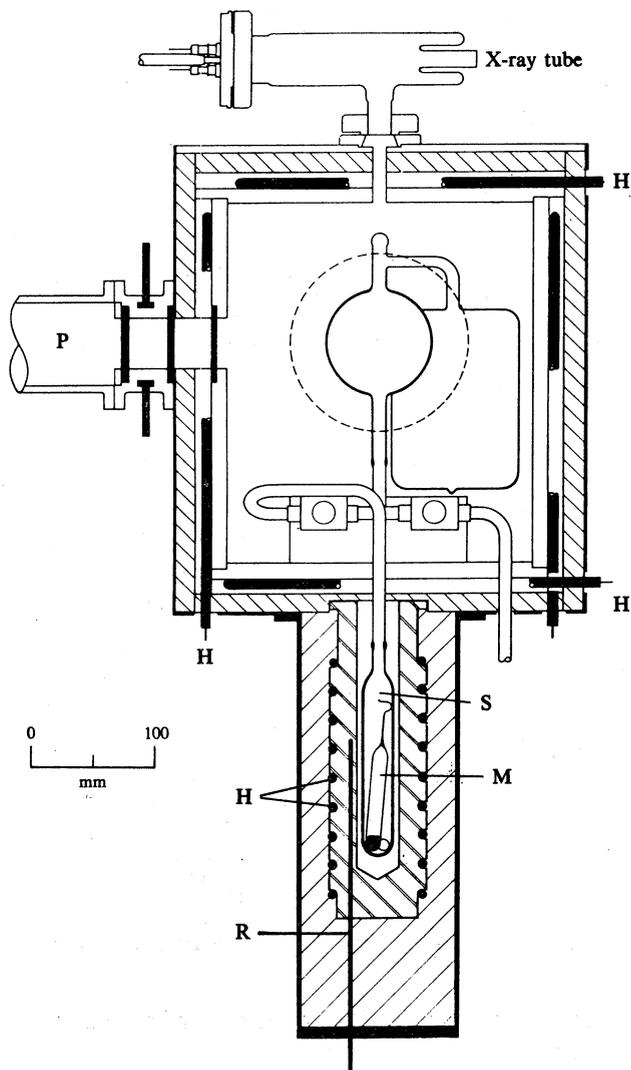
**Fig. 1.** Various momentum transfer cross sections  $\sigma_m$  derived theoretically and experimentally for electrons in mercury. Theory: S(P), S(D), Sin Fai Lam (1980); W, Walker (1975). Experiment: NL, Nakamura and Lucas (1978); E, Elford (1980b).

where  $N$  is the number density,  $m$  the electron mass and  $f_M$  the Maxwellian electron energy distribution. Since  $f_M(\epsilon)$  becomes negligible at  $\epsilon \gtrsim 5kT$ , which in our case corresponds to  $\approx 0.17$  eV, the value of  $D$  is primarily sensitive to the cross section  $\sigma_m$  below the resonance, and the results of this experiment should therefore discriminate between the various available estimates of  $\sigma_m$  in the energy range 0–0.2 eV. However, since the mean energy of the swarm cannot be varied appreciably due to the limits of the operating temperature of the experiment, we cannot expect to obtain an energy dependent cross section from these measurements.

### Experiment

The diffusion coefficient was measured by the method first devised by Cavalleri (1969) and modified by Gibson *et al.* (1973). In this experiment, electrons are first produced in the gas by a short ( $\sim 3 \mu\text{s}$ ) pulse of X-rays. Provided there are no stray electric fields, the number of electrons decays solely due to diffusion to the walls, and the asymptotic form of this decay is measured by applying an RF electric field of  $\sim 1 \mu\text{s}$  duration and observing the resulting light output, which is proportional to the remaining number of electrons.

The cell, made of Pyrex, was mounted inside an oven as shown in Fig. 2. The walls of the oven are made of two 12 mm thick aluminium plates clamped together with the heater element H located in a recessed groove in the inner plate. On the outside the thermal insulation is made of four layers of 3 mm thick asbestos sheet and aluminium foil sandwiched together. A watercooled feedthrough supplies the RF voltage to the sampling electrodes. The photomultiplier P views the cell through three Pyrex windows, two of which are mounted in a watercooled housing to reduce the infrared radiation impinging on the cathode of the photomultiplier.



**Fig. 2.** The cell and source: H, heater elements; S, source tube; M, mercury ampoule; P, photomultiplier housing; R, platinum resistance thermometer.

The vacuum system is shown in Fig. 3. The valves  $V_1$  and  $V_2$  are mounted inside the cell oven and can be operated from the outside. The ballast volume was added to the cell to reduce the effect of impurities outgassing from the inner walls of the cell. A break-seal glass ampoule M containing the mercury was placed in the source tube S (see Fig. 2). The mercury sample was triply distilled and further purified as described by Elford (1980a). The temperature of the source tube could be controlled independently of the cell temperature by means of a moveable oven (Fig. 3). The safety trap was kept at liquid-nitrogen temperature throughout the whole of the experiment in order to prevent any mercury accidentally escaping from the cell and contaminating the vacuum system. Prior to the experiments, the cell was outgassed at  $\sim 200^\circ\text{C}$  for two weeks.

During the experiments, the cell oven was heated to a temperature  $T$  from an unregulated AC supply and the temperature monitored by three chromel–alumel thermocouples located on the inside of the top and bottom walls of the oven and on the earthed sampling electrode. The temperature  $T_1$  of the source oven, somewhat lower than  $T$ , was monitored (see Fig. 2) by a precision platinum resistance thermometer  $R$  (Leeds and Northrup 8078). The heater block of this oven (Fig. 2) has two heater elements wound around it. The power to one of them was adjusted to give a temperature some  $5^\circ$ – $10^\circ$  below the operating temperature, while power to the other was controlled by a proportional AC controller. In this way the temperature in the source could be controlled to within  $\pm 0.2^\circ$ .

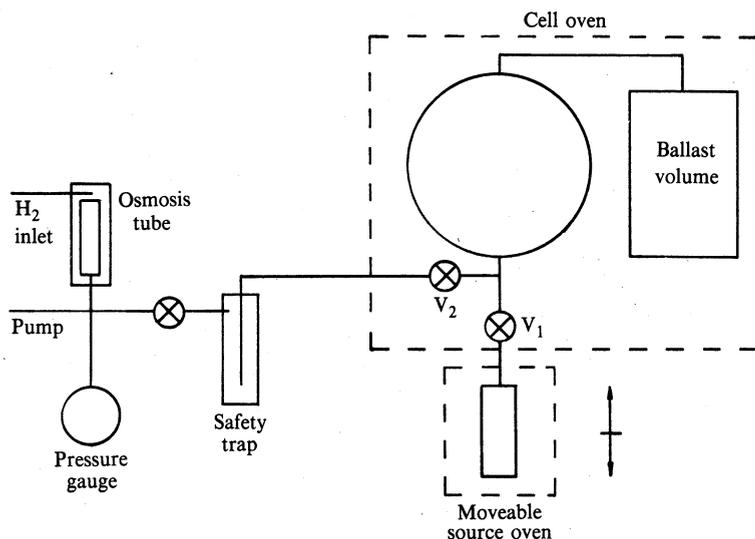


Fig. 3. Schematic diagram of the cell and associated vacuum system (see text).

The initial electrons created by the X-ray pulse may have energies of several keV. It is necessary that they and their progeny become completely thermalized before the electron population is sampled. Due to the lack of inelastic channels below  $\sim 4.8$  eV and the extremely small energy transfer in elastic collisions, the thermalization time would exceed the diffusion time constant for thermal electrons, even at the highest pressure used, if the experiment was conducted in pure mercury vapour. The measurements were therefore performed in a hydrogen–mercury mixture in order to achieve a rapid thermalization of the electron swarm. The diffusion coefficient in mercury was then obtained using Blanc's law:

$$1/(ND)_{\text{mix}} = f/(ND)_{\text{Hg}} + (1-f)/(ND)_{\text{H}_2},$$

where  $N$  is the total number density and the  $f$  the mole fraction of mercury. This relation is strictly valid only if the momentum transfer cross sections for the constituent gases have the same energy dependence, i.e.  $\sigma_m^i(\varepsilon) = a^i f(\varepsilon)$ , but model calculations show that for reasonably well behaved cross sections, the deviation from Blanc's law is small even when this condition is not fulfilled.

The mixtures were prepared in the following way:

(i) Before the mercury ampoule was broken, the source and cell were brought to operating temperatures and the system evacuated. The valve  $V_1$  (Fig. 3) was then closed, and the remainder of the system filled with  $H_2$  to a known pressure. Valve  $V_2$  was then closed and  $V_1$  opened. The pressure in the pipeline downstream was then reduced by an amount estimated to be the same as the reduction in the pressure of the cell and valve  $V_2$  opened again. The change in pressure was noted and the procedure repeated until there was no change in pressure when  $V_2$  was opened. In this way the ratio  $\alpha$  of the final pressure to the initial pressure was determined. (The variation of  $\alpha$  was negligible over the small range of source temperatures required because the source volume was only about 5% of the total volume.) With  $\alpha$  determined in this way, valve  $V_1$  was closed and the mercury ampoule broken.

(ii) At the start of each set of experiments with a given mixture, the cell and the source were first evacuated with the source at liquid-nitrogen temperature. Valve  $V_1$  was then closed and the cell filled to a pressure  $p_1$  with hydrogen which had been purified by passage through a silver-palladium alloy osmosis tube. Valve  $V_2$  was then closed and the liquid-nitrogen-cooled Dewar removed from the source. The source oven was then put in place and the source heated to the temperature  $T_1$ . The pressure  $p_2$  of mercury vapour was inferred from the vapour pressure tables. Valve  $V_1$  was then opened and a few hours allowed for the mixture to reach equilibrium. The mole fraction of mercury  $f$  is then given by

$$f = N_{\text{Hg}}/N_{\text{tot}} = 1/(1 + \alpha p_1/p_2). \quad (2)$$

The time constant  $\tau$  for the diffusion of the electrons to the walls is obtained by repeatedly sampling the electron population  $n$  within the cell at two different time delays  $t_1$  and  $t_2$  after the application of the ionizing X-ray pulse. Assuming that the decrease in  $n$  is due solely to the fundamental-order diffusion mode, we define the time constant  $\tau$  by

$$n(t_1)/n(t_2) = \exp(\Delta t/\tau),$$

giving

$$\tau = \Delta t/\ln\{n(t_1)/n(t_2)\}, \quad (3)$$

where  $\Delta t = t_2 - t_1$ .

The diffusion coefficient for electrons in the mercury-vapour mixture is then given by

$$D = A^2/\tau,$$

where  $A^2$  is a geometrical factor (the cell constant) related to the cell dimensions through

$$A^{-2} = (\pi/h)^2 + (2 \cdot 405/r)^2,$$

$h$  and  $r$  being the height and radius of the cell (Cavalleri 1969). In the following, we will be using the density-independent quantity  $ND$ , where  $N$  is the total number density of the gas in the cell.

### Diagnostic Tests

In order to establish that the results obtained in this type of experiment are free of experimental artefacts, there are several diagnostic tests that have to be performed.

Most of these are described in detail by Rhymes *et al.* (1975) and will not be considered further here. However, a new source of error is introduced by the operation of the glass cell at elevated temperatures. As described by Gibson *et al.* (1973), the absence of stray electric fields within the diffusion chamber relies upon the use of an all-glass cell. If an electric field is present inside the cell, this field modifies the motion of the electrons and ions in such a way that the final distribution of the charges on the surface cancels the potential differences and thereby the driving field. The self-compensating mechanism requires a continual replenishment of the charge that is lost by leakage through the glass walls; more specifically, the time between sampling pulses must be comparable to the decay time for charge on the cell walls. At room temperatures, the volume resistivity  $\rho$  of Pyrex is so large that the decay time constant for charge placed on the inner walls is several seconds, but at 210°C,  $\rho$  is reduced by several orders of magnitude and the decay time constant is estimated to be of the order of 10 ms. Thus the self-compensating mechanism might be expected to fail. It was therefore deemed necessary to test the cell at elevated temperatures using a gas in which the momentum transfer cross section is well known so that the results obtained could be compared with the values calculated using equation (1). For this purpose we used hydrogen both because  $\sigma_m$  is well known and also because it is used in the subsequent determination of  $D$  for thermal electrons in mercury.

Table 1. Values of  $ND$  for thermal electrons in  $H_2$

$T$ (K)	$ND$ ( $10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ )		Difference (%)
	Measured	Calculated <sup>A</sup>	
294	3.88	3.978	-2.5
408	4.48	4.459	+0.5
468	4.70	4.67	+0.6

<sup>A</sup> Calculated using the cross section of Crompton *et al.* (1969).

Table 1 shows the results obtained at three temperatures and, as can be seen, the agreement is to within  $\pm 2.5\%$  at all temperatures. The cell was also used to measure  $ND$  in  $CO_2$  (Hegerberg *et al.* 1980) and the same order of agreement was achieved with values of  $ND$  derived from mobility measurements. The fact that the correct results are obtained in hydrogen and  $CO_2$  indicates that the stray fields within the cell are negligible, possibly because the continuous operation at elevated temperatures for many weeks annealed any strain in the glass and thereby removed the most likely source of fields inside the cell.

During the diagnostic testing of the experiment using mercury-hydrogen mixtures two anomalous features were found:

(i) The value of  $(ND)_{Hg}$  showed a large dependence upon the partial pressure  $p_{Hg}$  of mercury, the value obtained at  $p_{Hg} = 2$  kPa being approximately twice as large as the value obtained at 0.4 kPa.

(ii) The value of  $\tau$  calculated from the measured population ratios and equation (3) showed a large dependence on the value of  $t$ , indicating that the decay of the electrons does not follow a single exponential law. Fig. 4 shows a typical decay of the electron number density  $n/n_0$  as a function of  $t$ . Similar decay curves were observed by Rhymes *et al.* (1975) for electrons in neon. Under these conditions, when an effective time constant  $\tau_{eff}$  is calculated from a population ratio using

equation (3), and  $\tau_{\text{eff}}$  rather than  $n/n_0$  is plotted as a function of  $t$ , the nonlinear decay curve of Fig. 4 results in a curve which exhibits increasing values of  $\tau_{\text{eff}}$  as  $t$  increases (see Fig. 6). Rhymes *et al.* showed that this ‘upcurving’ was caused by Penning ionization of impurities in the gas sample. This explanation is very unlikely to be correct in our case, since the mercury metastable atoms do not have sufficient energy to ionize any of the impurities likely to be present.

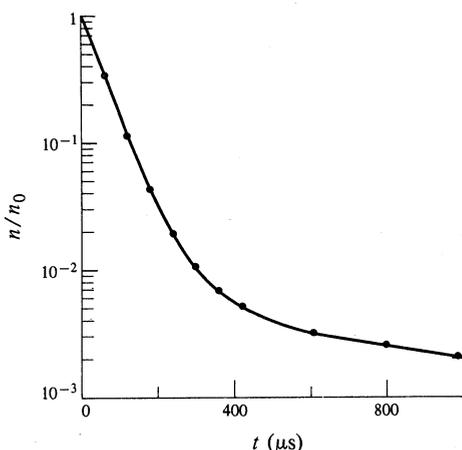


Fig. 4. Typical decay curve for the electron population  $n/n_0$  as a function of time  $t$  after the application of the X-ray pulse.

Several tests were performed in order to establish the cause(s) of these anomalous features. In the past, enhanced electron populations in mercury discharges have been reported (Vriens *et al.* 1978, and references therein) and have been ascribed to metastable–metastable collisions. Since the production of metastables in our experiment would be expected to be proportional to the duration  $t_\gamma$  of the X-ray pulse, the rate of production of electrons by this mechanism should be proportional to  $t_\gamma^2$ . A test for such a dependence was made by keeping the sampling-pulse voltage constant and measuring the relative amplitude of the photomultiplier output for two different values of the delay  $t_1$  as a function of  $t_\gamma$  (Fig. 5). In this experiment the diffusion time constant was  $\approx 100 \mu\text{s}$ . At  $t_1 = 100 \mu\text{s}$ , the main contribution to the signal stems from free electrons created in the X-ray pulse and the amplitude is a linear function of  $t_\gamma$ , as expected. (The curve does not extrapolate to zero amplitude at  $t_\gamma = 0$  due to the somewhat rounded shape of the pulse that drives the X-ray pulse.) At  $t_1 = 600 \mu\text{s}$  the population of freely diffusing electrons has been reduced by a factor of  $\approx \exp(600/100) \approx 400$ , and the signal is mainly caused by ‘spurious’ electrons, i.e. electrons not produced in the initial ionization. As we see, there is no evidence that these electrons are produced by collisions between metastables produced by the X-ray flash. That metastables produced by the sampling pulse do not affect the result is proved by the fact that the observed electron decay time constant is independent of the time between successive X-ray pulses (Rhymes *et al.* 1975).

It appears that the enhanced electron population at long times after the X-ray pulse is not due to a volume effect, and we have in fact gathered evidence that the effect is connected with surface reactions. It was found that running a discharge in the cell by increasing both the sampling voltage and repetition rate and subsequently repeating the experiment under identical conditions reduced the population of ‘spurious’ electrons. The effect of the discharge, which presumably changes the

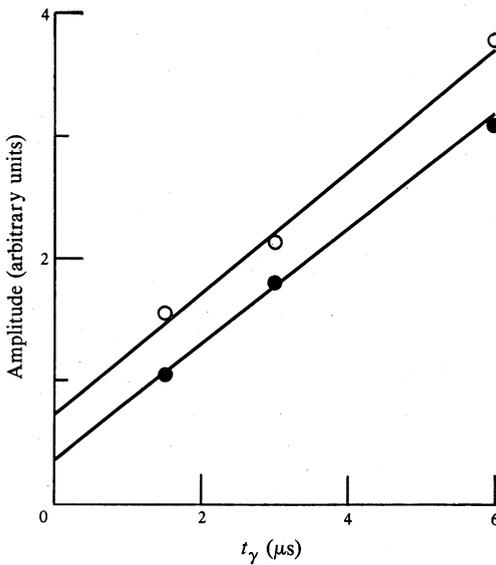


Fig. 5. Observed electron density as a function of the duration  $t_\gamma$  of the X-ray pulse for two different values of the delay  $t_1$ : 100  $\mu\text{s}$  (open circles) and 600  $\mu\text{s}$  (solid circles).

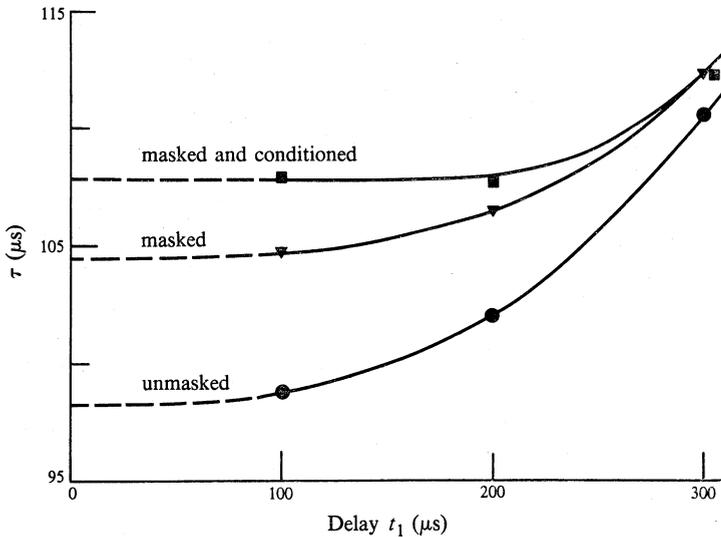


Fig. 6. Typical curve of the effective time constant  $\tau$  versus delay time  $t_1$  showing the effect of conditioning: circles—original measurements; triangles—measured restricting the view of the photomultiplier to the central region of the cell; squares—measured after applying the discharge (see text).

surface conditions of the inner walls of the cell, is semipermanent. Thus when the gas sample is changed after the discharge has been run and the experiment repeated, the decrease in the number of spurious electrons is still evident.

It was also observed that masking off the walls of the cell from the view of the photomultiplier changes the dependence of the effective time constant on the delay time  $t_1$ , primarily at times  $t_1 \lesssim (3-4)\tau_0$ , where  $\tau_0$  is the value of  $\tau$  extrapolated to  $t_1 = 0$ . This is also consistent with the hypothesis that the spurious electrons are

produced by a surface reaction, and the lack of any effect of the masking at large values of  $t_1$  can be due to the fact that surface-produced electrons have had enough time to diffuse back into the central region of the cell, thus contributing to the observed electron density. The effect on the observed time constant of applying these conditioning procedures is illustrated in Fig. 6.

Although these diagnostic tests strongly support our hypothesis that the spurious electrons are produced by a surface reaction, we have not been able to elucidate the mechanism by which this process occurs. However, the important question with respect to the present work is whether one is justified in giving preference to the values of  $ND$  obtained after conditioning. Apart from the fact that the conditioning substantially reduces the proportion of spurious electrons, the strongest evidence in favour of the results obtained after conditioning is that the conditioning substantially removes the anomalous pressure dependence of  $ND$  described previously.

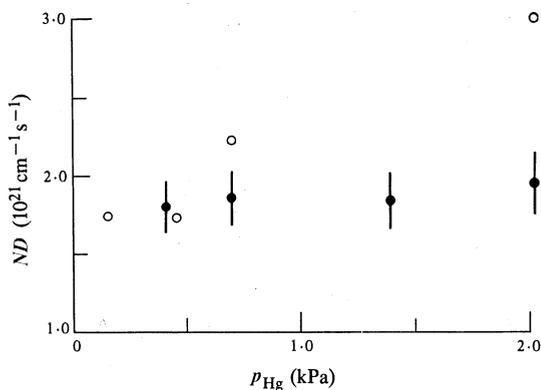


Fig. 7. Measured values of  $ND$  for thermal electrons in mercury as a function of the partial pressure of mercury both before (open circles) and after (solid circles) conditioning had been applied.

Table 2. Error estimates

Source of error	Percentage error
(1) Number density	$\pm 0.2\%$ from pressure measurement $\pm 0.8\%$ from temperature variation in source $\pm 0.3\%$ from temperature measurement
(2) Cell constant	$\pm 0.4\%$ from dimensional tolerances
(3) Time constant	$\pm 0.5\%$ (estimate) from possible nonlinearity and finite resolution of detection chain $\pm 2\%$ r.m.s. error
(4) Deviation from Blanc's law	$\pm 1\%$ (estimate)
(5) Calculation of $(ND)_{\text{Hg}}$	$\pm 0.3\%$ from $\pm 0.5\%$ error in $ND$ for hydrogen $\pm 5\%$ from extrapolation error
Total estimated error	$\pm 10\%$

## Results

Fig. 7 shows the results obtained after the conditioning was applied. All these results were obtained by an extrapolation of  $\tau_{\text{eff}}$  to  $t = 0$ , having ascertained that the conditioning produced a plateau in the  $\tau_{\text{eff}}$  versus  $t$  curve. For comparison, a few points are included to show the anomalous pressure dependence observed

initially. The values of  $ND$  were obtained from mixtures of mercury and hydrogen having a mole fraction of mercury ranging from 0.25 to 0.75. At a given partial pressure of mercury, the results from mixtures having different hydrogen pressures agreed to within the indicated error bars. The main sources of error are summarized in Table 2. Some sources of errors, while important in other transport measurements, can be neglected in this work. Radiation trapping, while taking place at the mercury number densities and cell geometry used (R. Zollweg, personal communication) will not contribute errors in the measured time constant. The time constant  $\tau$  is calculated from ratios of light intensities measured at times  $t_1$  and  $t_2$  on the assumption that the ratios correspond to the ratios of electron density. Since a constant fraction of the radiation is trapped no error is introduced.

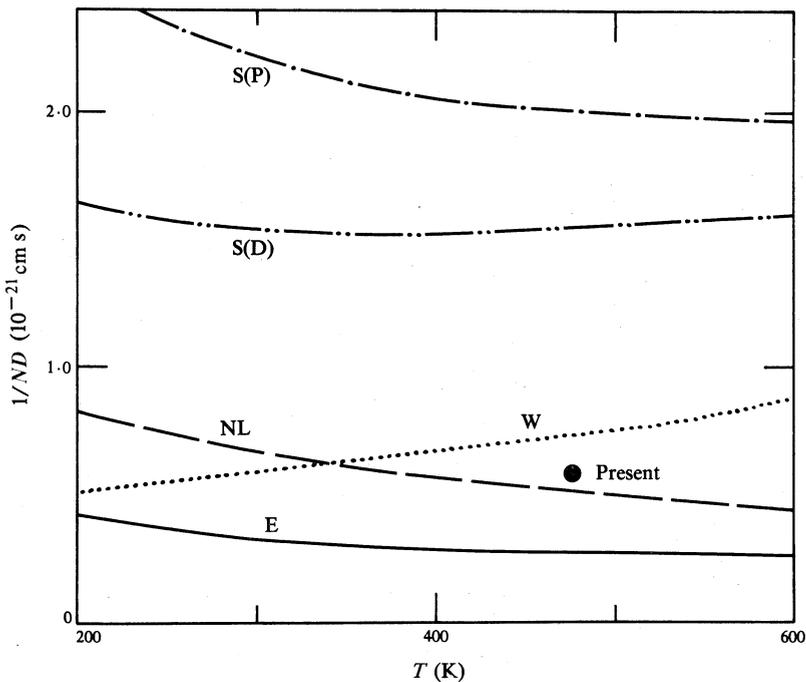


Fig. 8. Values of  $1/ND$  calculated from various theoretical and experimental cross sections (see Fig. 1) as a function of gas temperature, compared with the result of this work.

In the drift velocity measurements of Elford (1980a) the presence of mercury dimers affected the observed drift velocity due to their effect on the electron energy distribution function. In this experiment such effects were absent, since the *thermal* electron energy distribution is unaffected. The dimers will therefore only affect the value of  $ND$  through their effect on the macroscopic momentum transfer cross section, i.e.  $N \sum_i x_i \sigma_i$  (where  $x_i$  is the mole fraction of species  $i$ ). Since the mole fraction of dimers is only of the order of  $10^{-4}$ , their effect is negligible.

### Discussion

Fig. 8 shows the temperature dependence of  $1/ND$  as determined from equation (1) using the various experimentally and theoretically determined momentum transfer

cross sections of Fig. 1. The reason for plotting  $1/ND$  rather than  $ND$  itself is that it is more nearly proportional to the cross section (see equation 1). As can be seen the *ab initio* calculations of Sin Fai Lam (1980) predict a value of  $ND$  that is only  $\approx \frac{1}{4}$  of the experimental value. While the  $ND$  values as calculated from the *ab initio* cross section of Walker (1975) are in better agreement with the present result, Elford (1980*a*) has shown that Walker's cross section is not compatible with the observed drift velocities (Elford 1980*b*). The agreement with the value calculated from the cross section of Nakamura and Lucas (1978) is within the combined error limits, while Elford's cross section gives an  $ND$  value about twice as large as observed. The problem of deriving a unique cross section from currently available drift velocity data is severe in the energy range that determines  $ND$  in our experiment (i.e. below  $\sim 0.15$  eV), and the difference between the Nakamura and Lucas and the Elford cross sections might not be significant in this energy range.

From Fig. 8 it can also be seen that due to the restricted range of temperature available in our experiment it is not possible to infer any information about the energy dependence of the cross section from our data.

The value of  $ND$  obtained corresponds to an average (in the sense of equation 1) cross section of  $27 \times 10^{-16}$  cm<sup>2</sup> with an estimated uncertainty of  $\pm 10\%$ . Despite its obvious limitations the present result is valuable in supplying a benchmark against which to test experimentally and theoretically derived cross sections and to decide between the relative merits of those presently available. It clearly favours the experimental cross sections, but nevertheless the present position cannot be regarded as satisfactory. Equally, the theoretical situation in the energy regime below the p-wave resonance requires resolution.

### Acknowledgments

The authors would like to thank M. T. Elford for many useful suggestions and discussions. We are also indebted to J. Gascoigne, K. B. Roberts and F. R. Johnson for the construction of the apparatus. One of us (R.H.) acknowledges the award of a Postdoctoral Fellowship from the Australian National University.

### References

- Cavalleri, G. (1969). *Phys. Rev.* **179**, 186.
- Crompton, R. W., Gibson, D. K., and McIntosh, A. I. (1969). *Aust. J. Phys.* **22**, 715.
- Elford, M. T. (1980*a*). *Aust. J. Phys.* **33**, 231.
- Elford, M. T. (1980*b*). *Aust. J. Phys.* **33**, 251.
- Gibson, D. K., Crompton, R. W., and Cavalleri, G. (1973). *J. Phys. B* **6**, 1118.
- Hegerberg, R., Elford, M. T., and Crompton, R. W. (1980). *Aust. J. Phys.* **33**, 985.
- Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley: New York).
- Nakamura, Y., and Lucas, J. (1978). *J. Phys. D* **11**, 337.
- Rhymes, T., Crompton, R. W., and Cavalleri, G. (1975). *Phys. Rev. A* **12**, 776.
- Sin Fai Lam, L. T. (1980). *Aust. J. Phys.* **33**, 261.
- Vriens, L., Keijsers, R. A. J., and Ligthart, F. A. S. (1978). *J. Appl. Phys.* **49**, 3807.
- Walker, D. W. (1975). *J. Phys. B* **8**, L161.

