

Experimental Observations of the Diffusion Cooling of Electrons in Argon

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Abstract

The cooling by diffusion of electrons in argon and in argon-hydrogen mixtures has been studied by the Cavalleri density sampling technique. In the case of argon, the measured values of the reduced diffusion coefficient ND varied by more than a factor of two over the pressure range 2-8 kPa. When small quantities of hydrogen were added to the argon, the cooling effect was reduced due to the increased energy transfer between the electrons and gas molecules. For argon, the magnitude and pressure dependence of ND are in satisfactory agreement with the recent calculations by Leemon and Kumar (1975).

1. Introduction

When a group of electrons disperses in an unbounded volume containing gas at temperature T under conditions that ensure that the electron motion is uninfluenced by either external or space charge fields, the energy distribution function $\mathcal{F}^*(\varepsilon)$ for the whole group is the unperturbed Maxwellian distribution (Huxley and Crompton 1974). However, the energy distribution function at a given point $\mathcal{F}(r, \varepsilon, t)$ (the *local* energy distribution function) is a function of both position and time. The mean energy for the group is $\frac{3}{2}\kappa T$, while the diffusion coefficient D that may be used to determine the rate of dispersal of the electrons via the relation

$$d\langle r^2 \rangle / dt = 6D \quad (1)$$

is obtained from the usual relation

$$D = \frac{(2/m)^{1/2}}{3N} \int_0^\infty \frac{\varepsilon \mathcal{F}^*(\varepsilon) d\varepsilon}{q_m(\varepsilon)} = \frac{(2/m)^{1/2} \langle \varepsilon^{1/2} / q_m(\varepsilon) \rangle}{3N}, \quad (2)$$

where $\mathcal{F}^*(\varepsilon)$ is given by

$$\mathcal{F}^*(\varepsilon) = 2(\kappa T)^{-3/2} \pi^{-1/2} \exp(-\varepsilon/\kappa T) \quad (3)$$

and $q_m(\varepsilon)$ is the momentum transfer cross section.

Both the local energy distribution function and the distribution function for the group change when diffusion takes place in a volume bounded by completely absorbing walls. If it is assumed that the cross section has a simple power law dependence on energy, that is, $q_m(\varepsilon) = a\varepsilon^r$ then equation (2) indicates that, provided

we have $r < 0.5$, the diffusion rate of the class of electrons with energies in the interval ε to $\varepsilon + d\varepsilon$ increases with ε so that the more energetic electrons escape more rapidly to the walls and are removed from the volume. Therefore, initially, both \mathcal{F} and \mathcal{F}^* are time dependent. However, at times greater than the time constant of the fundamental diffusion mode it may be shown that both become independent of time and, moreover, that \mathcal{F} becomes independent of position and thus approaches \mathcal{F}^* (see e.g. equation (11) of Parker 1965). In this situation the mean energy of the electrons remaining in the cell is less than $\frac{3}{2}\kappa T$ but is constant with time. This phenomenon has been described as 'diffusion cooling' (Biondi 1954). Moreover, in the equation that describes the decay of the electron population at large times, namely (Leemon and Kumar 1975),

$$n = n_0 \exp(-D_{\text{eff}} A^{-2} t), \quad (4)$$

where n_0 is the initial population and A is a constant related to the geometry of the cell, the effective diffusion coefficient D_{eff} is no longer given by equation (2) but has a lower value.

When $r = 0.5$, there is no preferential loss of electrons, the energy distribution function remains the unperturbed Maxwellian, and we have $D_{\text{eff}} = D$ (Leemon and Kumar 1975). For $r > 0.5$, it is the low energy electrons that escape more rapidly to the walls resulting in 'diffusion heating'.

It is to be noted that, for $r < 0.5$ or $r > 0.5$, when there results an enhanced loss of either high or low energy electrons (i.e. either 'cooling' or 'heating'), then D_{eff} corresponding to the quasi steady-state (i.e. time-independent energy distribution function) must be less than D which is the average for all classes of electrons. This is consistent with equation (29b) of Leemon and Kumar (1975).

The possibility of diffusion cooling appears to have been first recognized by Holstein (1946), although the case he treated theoretically was ambipolar rather than free diffusion.† Subsequently, Biondi (1954) reported the results of microwave experiments that could be interpreted satisfactorily only on the basis that the electron temperature was well below that of the gas. However, in these experiments in which the decay of electron density was measured in the after-glow of pulsed microwave discharges in neon and argon, it was ambipolar diffusion that was observed.

The first theoretical treatment of diffusion cooling in the absence of space charge was given by Parker (1965), who treated the problem of diffusion cooling for the case of infinite parallel plane geometry when only elastic scattering occurs. For the model situations of constant collision frequency and constant cross section, he obtained expressions for the electron distribution functions and for the time constants of decay for the various modes. In particular, his work enabled the decrease in the average electron energy to be calculated for these model cases, as well as the effective diffusion coefficient as already defined.

For some model gases Parker's (1965) analysis predicts large effects under conditions typically used in swarm experiments. Nevertheless, direct observations of the effect do not appear to have been reported previously, and thus the very low values of ND that were observed in the first of the series of experiments described in Section 2

† References to diffusion cooling are also to be found in the literature of neutron physics (see e.g. Beckurts and Wirtz 1964).

(below) were not initially attributed to the effects of diffusion cooling. However, the pressure dependence of the results in pure argon suggested an explanation based on this phenomenon. Further evidence was provided by the results of the subsequent experiments in argon-hydrogen mixtures that are also described in Section 2, and by the result of a calculation (described in Section 3), based on Parker's theory, in which constant collision frequency is used in modelling the experimental situation. Finally, Section 4 contains the results of a set of measurements that were made to investigate diffusion cooling in detail, thus enabling a comparison to be made with the recent work of Leemon and Kumar (1975) who extended Parker's analysis to allow for cylindrical geometry and for an arbitrary energy dependence of the cross section.

2. Experimental Details and Preliminary Results

(a) Diagnostic measurements

The measurements were made using the Cavalleri electron density sampling technique which has been described previously (Cavalleri 1969; Gibson *et al.* 1973 (hereafter referred to as GCC); Rhymes *et al.* 1975 (hereafter RCC)). This technique is subject to a number of systematic errors that are described in detail in these references. Some of the errors are characteristic of the apparatus itself, and thus require no further discussion. Others such as those described below depend on the gas under investigation and must therefore be investigated in detail in each case.

Primary and Secondary Space Charge

In the Cavalleri experiment, diffusion of the electrons is modified by the space charge produced by the positive ions generated in the initial ionization (primary space charge). The effect has been shown to be small under the conditions used in our experiments (RCC) and may be neglected in the present instance where maximum accuracy was not required. On the other hand, secondary space charge effects resulting from the more numerous ions generated during the sampling pulse were expected to be large in argon because, at the pressures used, the large atomic mass results in relatively large diffusion times (~ 0.01 – 1 s) for the ions. Tests had therefore to be made to ensure that sufficient time elapsed between each cycle of the experiment to permit the positive ions generated by the sampling pulse to diffuse to the walls.

The results of experiments in which the repetition rate was varied are shown in Fig. 1a from which it can be seen that, at a pressure of 5.3 kPa, repetition times \mathcal{R} in excess of 4 s were required to ensure that the results were free from error from this source. Simple scaling enabled the repetition rates at other pressures to be determined. It may be noted that, as expected, the repetition rates are lower than could be used in helium (GCC) and neon (RCC). The influence of secondary space charge places a restriction on the highest pressure that can be used, since the repetition rate must not be so low that the rate of charge replenishment to the walls is inadequate (GCC).

Penning Ionization of Impurities

The energy levels of the metastable states of argon (11.5 and 11.7 eV) are below the ionization potential of the most likely impurities, including water vapour. It was therefore not unexpected that the curves of measured diffusion time constant τ versus sampling time S , of which a typical example is shown in Fig. 1b, showed no evidence

of the upcurving for large values of S which was a feature of the measurements in neon (RCC). The relative magnitudes of the argon metastable levels and the ionization potential of hydrogen (15.4 eV) also enabled measurements to be made in argon-hydrogen mixtures without interference from this effect, since, as expected, the τ versus S curves for the mixtures showed no evidence of upcurving.

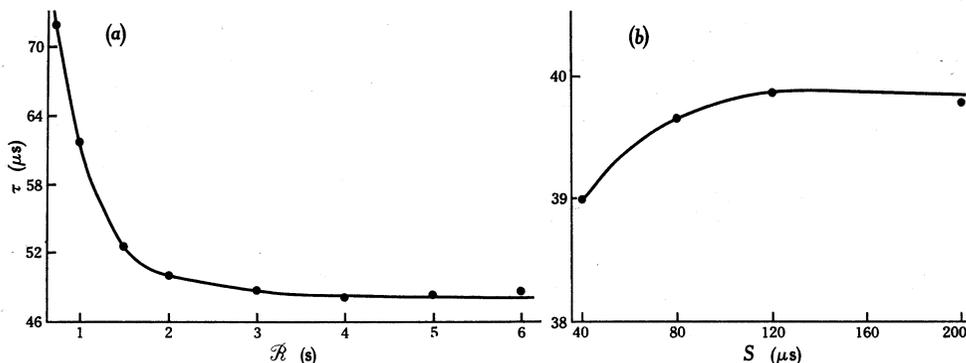


Fig. 1. Variation of the measured diffusion time constant τ with (a) the repetition time R and (b) the sampling time S . The mean statistical error on each point is $\pm 1\%$. The data shown were obtained at pressures of (a) 5.3 kPa and (b) 4.0 kPa.

Thermalization

Approximate calculations of thermalization times (RCC) for electrons in argon predict a time of the order of several hundred microseconds at a pressure of 4 kPa. This time, which was confirmed by a Monte Carlo simulation (personal communication from H. B. Milloy), is longer than might be expected in view of the relatively large cross section ($\sim 3 \text{ \AA}^2$) for electrons with energies in the vicinity of the most probable energy at room temperature. The large value arises from the presence of the Ramsauer-Townsend minimum through which the initial ionization electrons must pass before attaining thermal equilibrium. At this pressure, the thermalization time is much larger than the measured diffusion time constant τ and, furthermore, unlike the situation in neon, a pronounced dependence of ND on electron temperature T_e is expected. (If constant collision frequency is used to model the case of argon, equation (2) predicts that $ND \propto T_e$.) Consequently it is surprising that the results shown in Fig. 1b indicate a significant reduction in τ , corresponding to lack of thermalization, only for values of $S \lesssim 80 \mu\text{s}$.

The smaller value of thermalization time observed experimentally may be explained in terms of the diffusion cooling process (see e.g. von Dardel 1954). As an electron with energy higher than that of the Ramsauer-Townsend minimum reaches energies in the vicinity of the minimum, the rate of energy loss becomes very small, particularly if the cross section is as small as was suggested in 1972 by J. A. Rees (personal communication), and thus the time taken for the electrons to pass through this energy range would be expected to be a large fraction of the total thermalization time. However, the diffusion rate for electrons with these energies is large. Consequently, there is a high probability that these electrons will collide with the walls of the diffusion cell and be removed. Thus the thermalization time in the experimental

situation, in which the electrons that might contribute most to the thermalization time are preferentially removed, is lower than the calculated value since the calculation is based on electron motion in an unbounded medium.

(b) Preliminary results

The first measurements in pure argon were made at a pressure of 6.7 kPa and yielded a value of $ND \approx 20 \times 10^{20} \text{ mm}^{-1} \text{ s}^{-1}$, which was about 30% lower than the value calculated using the momentum transfer cross section derived by Robertson (1970) from his drift velocity measurements. Diagnostic measurements, as described in subsection (a) above, proved that the cause of the apparently anomalous result was not primary or secondary space charge (which were the most likely causes) nor Penning ionization of an impurity, the effects of which were neither expected nor observed. Lack of thermalization or the effect of the decay of higher diffusion modes would have raised the result.

The fact that the value of ND (actually ND_{eff}) was observed to increase as the pressure was increased suggested that the measurements were affected by diffusion cooling. This hypothesis was supported by an estimate of the magnitude of the effect made using Parker's (1965) theory, as described in the next section. Final confirmation was obtained from a set of experiments in which ND_{eff} was measured as a function of pressure in mixtures containing from $\frac{1}{4}$ % to 10% of hydrogen.

In the absence of diffusion cooling the value of ND would be expected to fall steadily as the hydrogen concentration is increased, going from the anticipated value of the order of 30×10^{20} for pure argon to $3.98 \times 10^{20} \text{ mm}^{-1} \text{ s}^{-1}$ for pure hydrogen, the lower value in hydrogen resulting from the larger average momentum transfer cross section for electrons with thermal energies. In addition to this behaviour, however, the very much larger average energy exchange between electrons and hydrogen molecules, due to the more favourable mass ratio and the presence of inelastic collisions, results in a closer coupling between the energy distributions of the electrons and gas molecules. This causes a reduction in the magnitude of the diffusion cooling effect which tends to raise ND_{eff} . Thus very small concentrations of hydrogen will raise the measured diffusion coefficient by suppressing diffusion cooling but, as the concentration is increased, the diffusion coefficient decreases due to the influence of the larger momentum transfer cross section for hydrogen.

In practice, the concentration of hydrogen necessary to suppress diffusion cooling completely, even at the maximum pressure used in our experiments, was such that the asymptotic (i.e. pressure-independent) value of ND was always significantly lower than the value in pure argon. Nevertheless, as the hydrogen concentration was increased, the pressure at which the asymptotic value was reached became progressively lower. This result was seen as providing conclusive evidence that the anomalous results in pure argon could be attributed to diffusion cooling.

The competing effects that result from the addition of hydrogen are illustrated in Fig. 2a, which shows the variation of ND_{eff} with the percentage of hydrogen in the mixture, the total pressure being held constant at 4.0 kPa. At this pressure, ~ 1 % of hydrogen leads to the result which is least affected on the one hand by diffusion cooling, and on the other by the reduction resulting from the larger cross section in hydrogen.

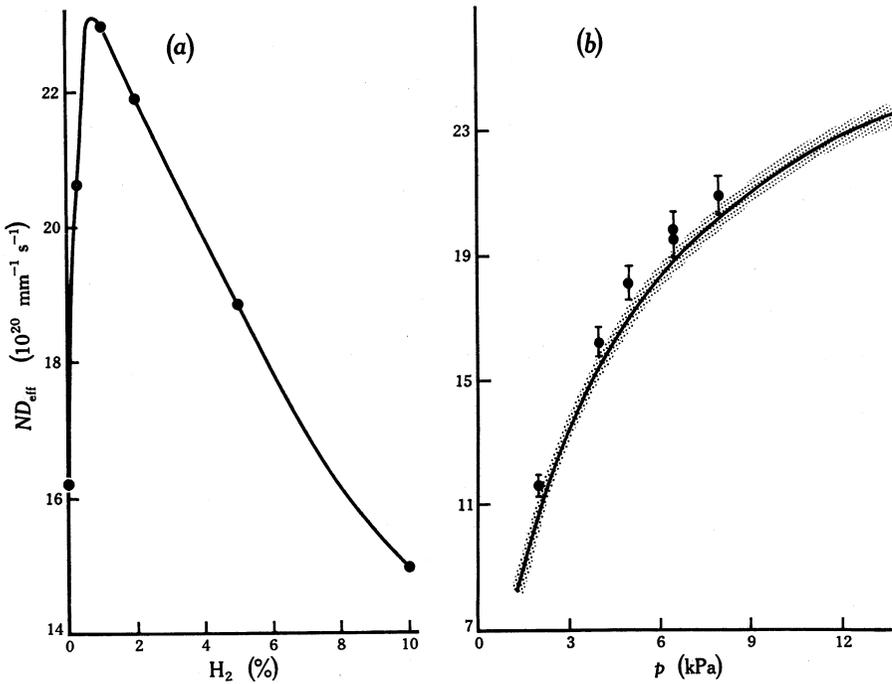


Fig. 2. Experimental results for the variation of ND_{eff} as a function of (a) the percentage of hydrogen in a hydrogen-argon mixture and (b) the pressure p in argon. In (b) the continuous curve corresponds to the theoretical results of Leemon and Kumar (1975); the shaded band indicates the uncertainty in the theoretical values while the error bars show the uncertainty in the experimental values.

3. Theoretical Estimate of the Effective Diffusion Coefficient

In a group of electrons with a Maxwellian distribution of velocities at room temperature, the majority have energies less than 50 meV. Within this energy range, the electron momentum transfer collision frequency ν in argon is roughly constant (Frost and Phelps 1964), so that an estimate of the magnitude of diffusion cooling effects can be made using the work of Parker (1965).

In the case of constant collision frequency, the usual development of the Boltzmann equation leads to the following equation for the isotropic part of the electron distribution function $f_0(\mathbf{r}, \varepsilon, t)$, namely:

$$\varepsilon^{-3/2} \frac{\partial}{\partial \varepsilon} \left\{ \varepsilon^{3/2} \left(f_0 + \kappa T \frac{\partial f_0}{\partial \varepsilon} \right) \right\} + \frac{M}{3m^2 \nu^2} \nabla_r^2 f_0 = \frac{M}{2m\nu\varepsilon} \frac{\partial f_0}{\partial t}. \quad (5)$$

In this equation \mathbf{r} is the position vector, ε is the electron energy, and m and M are the electronic and atomic masses respectively.

The general solution of equation (5) corresponding to parallel plane geometry was shown by Parker (1965) to be

$$f_0(\mathbf{r}, \varepsilon, t) = \sum_{\beta=1}^{\infty} \sum_{l=0}^{\infty} A_{\beta l} \exp(-t/\tau_{\beta l}) F_{\beta l}(\varepsilon) \sin(\beta\pi x/h), \quad (6)$$

where h is the separation of the boundaries at which it is assumed that $f_0(0, \varepsilon, t) = f_0(h, \varepsilon, t) = 0$. The time constant $\tau_{\beta l}$ of a particular mode is given by

$$\tau_{\beta l} = (M/2mv)[l(1+4K^2)^{1/2} + \frac{3}{4}\{(1+4K^2)^{1/2} - 1\}]^{-1}, \quad (7)$$

where

$$K = (\beta\pi/mvh)(\frac{1}{3}M\kappa T)^{1/2}.$$

Thus the time constant decreases as β (or K) and l increase and, at long times, only the lowest mode need be considered.

When $l = 0$ and $K^2 \ll 1$, the time constant of the lowest order ($\beta = 1$) spatial mode is, from equation (7),

$$\tau_{10} \approx \left(\frac{h}{\pi}\right)^2 \frac{mv}{\kappa T} \left\{1 - \left(\frac{\pi}{mvh}\right)^2 \frac{1}{3}M\kappa T\right\}^{-1}, \quad (8)$$

and it can be shown (Parker 1965) that

$$F_{10} \approx k \exp\left[-\left\{1 + \left(\frac{\pi}{mvh}\right)^2 \frac{1}{3}M\kappa T\right\} \frac{\varepsilon}{\kappa T}\right], \quad (9)$$

where k is a constant. The effective diffusion coefficient D_{eff} is defined as (see equation 4)

$$D_{\text{eff}} = A^2 \tau_{10}^{-1}$$

where, for plane parallel geometry, $A^2 = (h/\pi)^2$. It follows that

$$D_{\text{eff}} = \frac{\kappa T}{mv} \left\{1 - \left(\frac{\pi}{mvh}\right)^2 \frac{1}{3}M\kappa T\right\} = \frac{\kappa T}{mv} (1 - \alpha), \quad (10)$$

where

$$\alpha = \left(\frac{\pi}{mvh}\right)^2 \frac{1}{3}M\kappa T.$$

As v or h approaches ∞ , $D_{\text{eff}} \rightarrow \kappa T/mv$, that is, $D_{\text{eff}} \rightarrow D$, where D is the diffusion coefficient for thermal electrons calculated from equation (2).

We now use equation (10) to estimate the fractional difference α between D and D_{eff} in our experiment at 6.7 kPa. Using an experimentally determined value of ND in argon (Nelson and Davis 1969) the value of D at 6.7 kPa is found to be about $1.8 \times 10^6 \text{ mm}^2 \text{ s}^{-1}$. Hence from equation (2) it follows that $v \approx 2.5 \times 10^9 \text{ s}^{-1}$ on the assumption that the collision frequency is independent of electron energy. Thus with $h \approx 30 \text{ mm}$, where h is the height of our diffusion cell, and with $M = 40 \text{ a.m.u.}$, we have $\alpha \approx 20\%$. This is considerably less than the experimentally measured difference but is of the right order.

Finally it is of interest to estimate the reduction of the average energy due to diffusion cooling. Equation (9) represents a Maxwellian distribution of energies with a mean energy of

$$\varepsilon_{\text{av}} = \frac{3}{2}\kappa T \left\{1 - \left(\frac{\pi}{mvh}\right)^2 \frac{1}{3}M\kappa T\right\} = \frac{3}{2}\kappa T(1 - \alpha).$$

Thus diffusion cooling in this instance leads to a reduction in the electron temperature of the order of 20%.

4. Results and Discussion

Following the preliminary experiments described in Section 2, a more extensive set of measurements was made in pure argon to provide a comparison with the recent theoretical work of Leemon and Kumar (1975). Both theory and experiment indicated that the diffusion cooling effects were large. Consequently an adequate comparison with theory appeared possible without attempting to attain maximum experimental accuracy. Corrections for the effect of primary space charge were not attempted (see, for example, RCC), nor were the very long experimental runs made at the higher pressures that would be required to reduce the statistical fluctuations to the low level of the earlier experiments. The time required for these runs would have been excessive because of the low repetition rates that were necessary to avoid secondary space charge. Taking account of these factors, the measurements are estimated to have an uncertainty of about $\pm 3\%$. Fig. 2*b* shows the measured values of ND_{eff} in pure argon at 295 K for pressures between 2 and 8 kPa, together with the values calculated by Leemon and Kumar (1975) for a more extensive pressure range. (We are indebted to the authors for supplying us with their original data to construct this figure, thus enabling us to avoid rounding errors that would have arisen from the use of the published data which were given to two significant figures.) The calculations were made using a cross section based on the cross section derived by Robertson (1970) from drift velocity data, it being necessary to extrapolate the cross section to zero energy for this purpose. There is an uncertainty of $\pm 2\%$ in the calculated values of ND_{eff} due to possible computational errors. This uncertainty, which is represented by the shaded area in the figure, does not include the uncertainty arising from that in the cross section itself, which has yet to be finally determined (H. B. Milloy, personal communication).

Experimental limitations prevented the measurements being made over a more extended range of pressure. The upper limit was set by the requirement of excessively large repetition times to avoid secondary space charge, with the consequent onset of the influence of drift fields (see Section 2*a*). At pressures less than 2 kPa, where τ was less than 30 μs , measurement became difficult because of the need to use values of S such that $S/\tau > 4$ or 5, in order to avoid the effect of lack of thermalization.

The experimental results lie generally about 5% above the theoretical predictions. Of the possible sources of experimental error, only drift fields arising from inadequate charge replenishment at the walls could have raised the measured values of ND_{eff} , since lack of thermalization and the effect of higher-order diffusion modes were easily avoided. While at the highest pressures the values of \mathcal{R} were approaching those at which inadequate charge replenishment becomes significant, there was no evidence that the results were influenced by this effect, and in any case it could not have been responsible for the discrepancy between theory and experiment at the lower pressures where charge replenishment would have been more than adequate.

Over the range of pressure that was experimentally accessible, the value of ND_{eff} varies by almost a factor of two, so that the agreement between theory and experiment can be regarded as very satisfactory. At least part of the remaining discrepancy may be due to errors in the cross section used to calculate the theoretical values. The

good agreement in the case of argon, in which the energy dependence of the cross section is extreme, suggests that the theory can be confidently used to predict the magnitude of diffusion cooling effects in other gases, such as helium and neon, where the effects are smaller and the cross sections better known.

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