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Electron Diffusion in Finite Enclosures

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Abstract

Starting from the two-term approximation to the Boltzmann equation, a study is made of the time dependence of the density of electrons released inside a finite enclosure containing a neutral gas. The dominant behaviour can be represented by a diffusion equation containing an effective diffusion constant which depends upon pressure and dimensions of the enclosure. In the limit of large pressure and large enclosure the usual expression of the diffusion constant is obtained. The approach to this limit depends upon the electron–neutral interaction. The effect of various model and measured cross sections for some inert gases is discussed.

1. Introduction

In the experiment of Gibson *et al.* (1973) electrons are released into a cylindrical enclosure containing a neutral gas in thermal equilibrium. The electrons then diffuse and the total number in the enclosure is measured after various intervals. The data can be fitted to an exponential decay in time, and it is reasonable to assume that the electron number density can be described by an exponential form

$$n(\boldsymbol{r}, t) = R(\boldsymbol{r}) \exp(-D_{\text{eff}} \Lambda^{-2} t), \tag{1}$$

where the parameter Λ is related to the size and shape of the enclosure and D_{eff} is an effective diffusion coefficient. The number density then satisfies the diffusion equation

$$\partial_t n - D_{\text{eff}} \nabla^2 n = 0, \tag{2}$$

with

$$\nabla^2 R = -\Lambda^{-2} R. \tag{3}$$

One assumes that the number density vanishes at the boundary of the enclosure. For a cylinder of radius a and height h we take the lowest order solution of equation (3), namely

$$R(\boldsymbol{r}) = J_0(\xi_0 r/a) \sin(\pi z/h),$$

where ξ_0 is the first zero of the Bessel function J_0. Then

$$\Lambda^{-2} = (\xi_0/a)^2 + (\pi/h)^2$$

and Λ has the dimensions of length.

The usual treatments of diffusion starting from the Boltzmann equation are appropriate to an infinite enclosure in which the boundary conditions are not invoked

and the gradients are small. A diffusion equation of the form (2) is obtained, but instead of the effective diffusion coefficient D_{eff}, which appears in equation (2), the familiar diffusion coefficient D occurs. For the case of electrons, it is given by the well-known expression (e.g. Huxley and Crompton 1974)

$$ND = \tfrac{1}{3}\langle v/q_{\text{m}}\rangle, \tag{4}$$

where N is the number density of the neutrals, q_{m} is the momentum transfer cross section for electron–neutral collisions, v is the velocity, and the average is taken over the electron velocity distribution function.

The motivation for the present work comes from the observation by T. O. Rhymes and R. W. Crompton (personal communication) that the values of the effective diffusion coefficient obtained from the Cavalleri experiment (Gibson *et al.* 1973) for argon do not agree with the value of D calculated from equation (4), whereas in certain other cases (e.g. helium and neon) there is good agreement. They suggested that the reason for this may be related to the phenomenon of 'diffusion cooling' discussed earlier by Parker (1965), who was able to calculate the effective diffusion coefficient for constant collision frequency and constant cross section.

In this paper we develop a treatment applicable to all cross sections, which may be considered a generalization of Parker's (1965) approach. Starting from the Boltzmann equation in a finite enclosure we find that equation (2) is appropriate for the conditions of the Cavalleri experiment although corrections could be needed if greater accuracy were required. A method for calculating D_{eff} for the general case is given. It is shown that D_{eff} depends on the size and shape of the apparatus and other experimental conditions. In general D_{eff} is different from D but coincides with it in the limit of high pressures or large enclosures. The approach to the limit depends, among other things, on the electron–neutral cross section and explains the difference between the observations for argon and the other cases mentioned above.

2. Effective Diffusion Coefficient

We start with the two-term approximation to the Boltzmann equation which is known to be adequate for the motion of electrons in a neutral gas. In the usual notation (e.g. Parker 1965; Shkarofsky *et al.* 1966) we have the equation*

$$\frac{\partial_\varepsilon\{\varepsilon^{3/2}\nu(f^0 + kT\,\partial_\varepsilon f^0)\}}{\varepsilon^{3/2}} + \frac{M}{3m^2\nu}\nabla^2 f^0 = \frac{M}{2m\varepsilon}\partial_t f^0, \tag{5}$$

where the collision frequency ν is given by

$$\nu = Nvq_{\text{m}}. \tag{6}$$

Choosing a characteristic (constant) frequency ν_0, we introduce the dimensionless variables

$$x = \alpha r, \qquad \tau = \beta t, \qquad u = \varepsilon/kT, \qquad \xi = \nu/\nu_0, \tag{7}$$

* This equation, with the first term replaced by a different linear operator acting on f^0, also occurs in the theory of neutron thermalization, where similar methods of solution have been used (e.g. Purohit 1961). The effects of diffusion cooling and diffusion heating have also been studied in that connection (Beckurts and Wirtz 1964). We thank the referee for directing our attention to this comparison.

with

$$\alpha^2 = 3m^2v_0^2/MkT \qquad \text{and} \qquad \beta = 2mv_0/M. \tag{8}$$

Equation (5) now becomes

$$u^{-3/2}\,\xi\,\partial_u\{u^{3/2}\,\xi(f^0+\partial_u f^0)\}+\nabla_x^2 f^0 = \xi u^{-1}\,\partial_\tau f^0. \tag{9}$$

Setting $f^0(x,u,\tau) = R(x)\,F(u)\,T(\tau)$ and separating the variables, we get

$$\nabla_x^2 R(x) = -\kappa^2 R(x), \tag{10}$$

$$\partial_\tau T = -\kappa^2\theta T, \tag{11}$$

$$u^{-\frac{1}{2}}\,\xi\,\partial_u\{u^{3/2}\,\xi(F+\partial_u F)\}+\kappa^2(\theta\xi-u)F = 0. \tag{12}$$

As explained after equation (3) in the Introduction, we take the lowest order solution of (10) appropriate to the cylindrical enclosure, so that we have

$$\kappa^2 = (\alpha\Lambda)^{-2}, \qquad \Lambda^{-2} = (\xi_0/a)^2+(\pi/h)^2. \tag{13a, b}$$

With this value of κ^2, equation (12) can be solved to provide an eigenvalue θ which determines the time dependence of the solution of equation (11),

$$T(\tau) = \exp(-\kappa^2\theta\tau). \tag{14}$$

In general there will be several eigenvalues θ_m with eigenfunctions F_m, so that for the lowest space mode the solution of equation (9) has the form

$$f^0(x,u,\tau) = R(x)\sum_m F_m(u)\exp(-\kappa^2\theta_m\tau). \tag{15}$$

If the eigenvalues are well separated, the long-time decay mode is given by the least real positive eigenvalue. Negative or complex eigenvalues are to be excluded as being physically unacceptable. If the least positive real eigenvalue is denoted by θ, equation (1) is obtained from equation (15) by omitting the other eigenvalues and integrating over u, and we then have

$$D_{\text{eff}} = \theta\beta\alpha^{-2} \equiv \tfrac{2}{3}(kT/mv_0)\theta. \tag{16}$$

The problem is thus reduced to finding the lowest eigenvalue of equation (12). The corresponding eigenfunction is not required, its integral being absorbed in the normalization. If another eigenvalue appears close to the lowest one, the eigenfunctions would be required to determine the relative weights of the two modes, and one could expect deviations from the single exponential form for short times. For the cases considered below such analysis was not necessary.

A knowledge of the eigenfunction F_0 belonging to θ is needed if one is interested in the mean energy of the electrons and the effect of diffusion cooling (Parker 1965).

In the limit of very small κ, equation (12) is satisfied for any ξ if we have $F(u) = \exp(-u)$, so that from the definitions (6) and (7)

$$\theta = \int_0^\infty e^{-u}\xi^{-1}u^{3/2}\,du \Big/ \int_0^\infty e^{-u}u^{1/2}\,du$$

$$\equiv (\tfrac{1}{2}mv_0/kTN)\langle v/q_m\rangle .$$

Comparing equations (16) and (4),

$$ND_{\text{eff}}(\kappa^2 \to 0) = ND = \tfrac{1}{3}\langle v/q_m\rangle .$$

Thus D_{eff} tends to D in the limit of high pressures or large enclosures for any interaction.

In the subsequent development we need θ to higher orders in κ^2. For this purpose it is convenient to make the substitution $F(u) = e^{-u}G(u)$ in equation (12) and consider the eigenvalue equation in the form

$$uG'' + (\tfrac{3}{2} - u + u\xi'\xi^{-1})G' + \kappa^2(\theta\xi^{-1} - u\xi^{-2})G = 0, \tag{17}$$

where the primes denote differentiation with respect to u.

3. Model Cross Sections

A perturbation solution of equation (17) is best illustrated by considering momentum transfer cross sections of the form $q_m \propto \varepsilon^{\gamma-1}$, that is,

$$\nu = \nu_0 u^{\gamma-\frac{1}{2}}. \tag{18}$$

The special cases $\gamma = \frac{1}{2}$, 1 and $\frac{3}{2}$ correspond to the physically interesting cases of constant collision frequency, constant cross section and cross section proportional to velocity respectively. Equation (17) now becomes

$$uG'' + (\gamma + 1 - u)G' + \kappa^2(\theta u^{\frac{1}{2}-\gamma} - u^{2(1-\gamma)})G = 0. \tag{19}$$

The leading terms are those that occur in the equations for Laguerre polynomials (e.g. Erdélyi *et al.* 1953), which suggests an expansion in terms of these polynomials as

$$G(u) = \sum_{n=0} a_n L_n^\gamma(u). \tag{20}$$

Equation (19) is then converted to a matrix equation by using the orthogonality of these polynomials,

$$[\mathbf{J} + \kappa^2(\mathbf{C} - \theta\mathbf{B})]\mathbf{a} = 0, \tag{21}$$

where

$$\mathbf{J} \equiv J_{mn} = J_m\delta_{mn} = \{\Gamma(\gamma+m+n)/\Gamma(m)\}\delta_{mn}, \tag{22}$$

$$\mathbf{C} \equiv C_{mn} = \int_0^\infty du\, e^{-u}u^{2-\gamma}L_m^\gamma L_n^\gamma, \tag{23}$$

$$\mathbf{B} \equiv B_{mn} = \int_0^\infty \mathrm{d}u\, \mathrm{e}^{-u} u^{\frac{1}{2}} \mathrm{L}_m^\gamma \mathrm{L}_n^\gamma. \tag{24}$$

The integrals can be evaluated using the generating function for Laguerre polynomials.

Expanding $\mathbf{a}$ and θ in powers of κ^2 and equating coefficients of different powers, we obtain a hierarchy of equations which can be solved successively to obtain the solution to different orders:

$$\mathbf{a} = \mathbf{a}^0 + \kappa^2 \mathbf{a}^1 + \kappa^4 \mathbf{a}^2 + \ldots, \tag{25}$$

$$\theta = \theta_0 + \kappa^2 \theta_1 + \kappa^4 \theta_2 + \ldots; \tag{26}$$

$$\mathbf{J}\mathbf{a}^0 = 0, \tag{27a}$$

$$\mathbf{J}\mathbf{a}^1 + (\mathbf{C} - \theta_0 \mathbf{B})\mathbf{a}^0 = 0, \tag{27b}$$

$$\mathbf{J}\mathbf{a}^2 + (\mathbf{C} - \theta_0 \mathbf{B})\mathbf{a}^1 + \theta_1 \mathbf{B}\mathbf{a}^0 = 0. \tag{27c}$$

The equations in each of the sets (27) are numbered by the Laguerre polynomial index $n = 0, 1, 2, \ldots$. In each of the equations corresponding to $n = 0$, the contribution from the $\mathbf{J}$ term vanishes and we obtain the contribution to the eigenvalues by equating the remaining terms to zero. Thus,

$$\mathbf{a}^0 \equiv a_n^0 = a_0^0 \delta_{n0}, \tag{28a}$$

$$\theta_0 = C_{00}/B_{00} \tag{28b}$$

and

$$\mathbf{a}^1 \equiv a_m^1 = a_0^0(\theta_0 B_{m0} - C_{m0})/J_m, \qquad m \neq 0, \tag{29a}$$

$$\theta_1 = -(C_{00}^2/B_{00}) \sum_{n=1}^{\infty} J_n^{-1}(B_{0n}/B_{00} - C_{0n}/C_{00})^2. \tag{29b}$$

Except for normalization the components a_0^0 and a_0^1 are arbitrary and do not affect the calculation of the eigenvalue. One can choose $a_0^1 = 0$ and fix a_0^0 alone by normalization. To the above order the eigenfunction is given by

$$G(u) = 1 + \kappa^2 C_{00} \sum_{n=1}^{\infty} J_n^{-1}(B_{0n}/B_{00} - C_{0n}/C_{00}) \mathrm{L}_n^\gamma(u) \tag{30}$$

and the average energy by

$$\langle \varepsilon \rangle = kT \int_0^\infty \mathrm{d}u\, \mathrm{e}^{-u} u^{3/2} G(u) \Big/ \int_0^\infty \mathrm{d}u\, \mathrm{e}^{-u} u^{1/2} G(u). \tag{31}$$

Parker (1965) uses a more involved perturbation procedure and shows that for the cases of constant collision frequency ($\gamma = \frac{1}{2}$) and constant cross section ($\gamma = 1$) diffusion cooling occurs, that is, the average energy is less than what would be expected in the limit $\kappa^2 \to 0$. From equations (29b), (22), (23) and (24) it is seen that the first-order correction to the eigenvalue is always negative, so that to this order the

effective diffusion constant D_{eff} will be less than the diffusion constant D. The two effects thus have a common physical origin.

We now quote the results for the special models:

Cross section proportional to speed ($\gamma = \frac{3}{2}$). This is a very special case where the matrices **B** and **C** are equal. The lowest eigenvalue $\theta = 1$ is independent of κ^2 so that $D_{\text{eff}} = D$ and there is no diffusion cooling. This may be considered the prototype of a cross section which moderately rises with energy (see discussion for neon in Section 5 below).

Constant collision frequency ($\gamma = \frac{1}{2}$). In this case $\nu = \nu_0$ and equation (17) can be solved exactly (Parker 1965) to give

$$\theta = \tfrac{3}{4}\kappa^{-2}\{(1+4\kappa^2)^{\frac{1}{2}}-1\}, \tag{32}$$

$$ND_{\text{eff}} = \tfrac{1}{2}ND\kappa^{-2}\{(1+4\kappa^2)^{\frac{1}{2}}-1\} \approx ND(1-\kappa^2). \tag{33a, b}$$

This is the prototype of a moderately decreasing cross section.

Constant cross section ($\gamma = 1$). Using the relevant equations above,

$$\theta = 2\pi^{-\frac{1}{2}}\left\{1-\kappa^2\sum_{n=1}^{\infty}\left(\frac{(2n-1)!!}{2n!!}\right)^2\frac{1}{n(n+1)}\right\}. \tag{34}$$

The value of the sum is 0·167 (the corresponding value quoted by Parker (1965) is 0·165). We have

$$ND_{\text{eff}} = ND(1-0\cdot167\kappa^2) \tag{35a}$$

$$= \tfrac{2}{3}(2kT/\pi m)^{\frac{1}{2}}q_{\text{m}}^{-1}(1-0\cdot167\,M/6m\Lambda^2N^2q_{\text{m}}^2). \tag{35b}$$

4. General Cross Sections: Numerical Method

The results from the model cross sections considered in the previous section are useful for a quick assessment of the trends to be expected. But the necessary treatment for real cross sections is very different. Usually q_{m} is given numerically for certain values of the energy. It also appears that the perturbation method will have to be extended to much higher orders. Thus we have to set up a method of finding eigenvalues whereby numerically given cross sections can be used and the effects of higher orders in κ^2 can be included.

For the present purpose we set in equation (17)

$$\xi = v/v_0 = Au^{\frac{1}{2}}q_{\text{m}}, \tag{36}$$

with a suitably chosen constant A, to obtain

$$uG'' + \{2-u+u(\ln q_{\text{m}})'\}G' + \kappa^2\{\theta u^{-\frac{1}{2}}(Aq_{\text{m}})^{-1}-(Aq_{\text{m}})^{-2}\}G = 0. \tag{37}$$

Since no polynomial system is specially singled out, we choose to expand in terms of $L_n^1(u)$. Equation (37) now takes the form

$$\sum_{n=0}^{\infty}\{-m(m+1)\delta_{mn}+nD_{mn}-(n+1)D_{m,n-1}+\kappa^2(\theta B_{mn}-C_{mn})\}a_n = 0, \tag{38}$$

with

$$D_{mn} = \int_0^\infty \mathrm{d}u\, \mathrm{e}^{-u} u (\ln q_\mathrm{m})' \mathrm{L}_m^1 \mathrm{L}_n^1, \tag{39a}$$

$$C_{mn} = \int_0^\infty \mathrm{d}u\, \mathrm{e}^{-u} u (A q_\mathrm{m})^{-2} \mathrm{L}_m^1 \mathrm{L}_n^1, \tag{39b}$$

$$B_{mn} = \int_0^\infty \mathrm{d}u\, \mathrm{e}^{-u} u^{\frac{1}{2}} (A q_\mathrm{m})^{-1} \mathrm{L}_m^1 \mathrm{L}_n^1. \tag{39c}$$

The integrals (39) were evaluated to construct a 20×20 matrix. A fixed integration interval from 0 to 1 eV was chosen for all elements with about 200 datum points. The points were distributed more densely in the low energy region where the greatest contribution to the integral is expected to arise. The trapezoidal rule was used. Since cross section data are not usually sufficiently refined (Crompton *et al.* 1970) for the regions where datum points need to be more densely distributed, values have to be interpolated to provide the necessary detail. It should be noted that the matrix elements with high values of m and n are likely to contain errors because of the truncation of the integration interval from $(0, \infty)$ to (0, 1 eV).

The matrices were truncated for successive dimensions from 2 to 20 and their eigenvalues were calculated. Consistent results for the least eigenvalue to within 3% were obtained in the intermediate range of dimensions. The smallest matrices, which are not sufficiently representative, and the largest, which accumulate errors of the type described above, produce values outside this range. Since the cross sections themselves are not quoted to better than 2% or 3% accuracy (Crompton *et al.* 1970; Robertson 1972), no attempt at further refinement of the numerical method was made.

In the constant cross section case, D_{mn} is zero and the integrals (39b) and (39c) can be evaluated exactly as linear combinations of integrals of the type

$$\int_0^\infty \mathrm{d}x\, x^\gamma \mathrm{e}^{-x}.$$

The numerical method was checked against this case, where the features described above can be studied in some detail. Here the matrices C_{mn} and B_{mn} are symmetrical and all eigenvalues are real. Still, the present problem is not one of finding eigenvalues of real symmetric matrices for which it is possible to say that successive truncations provide a monotonic decreasing sequence for the least eigenvalue (e.g. Bellman 1970). However, it was found that in practice, for this as well as for the general cross sections studied here, the least real eigenvalue had a simple variation with truncation which suggested that a limit was reached, and this was therefore taken to be the least real eigenvalue of the full matrix.

5. Results and Discussion

The effective diffusion coefficient D_eff is related to the diffusion coefficient D through the parameter κ^2, defined by the formula (13a), but this relation can be quite complicated. Apart from the temperature, κ^2 depends upon the dimensions of the apparatus (i.e. Λ), the pressure P (or number density N) and the mass M of the neutrals. Also, for different cross sections the dependence of D_eff on κ^2 is different.

Table 1. Effective diffusion coefficients for constant collision frequency

The fixed parameters are $\nu/N = 10^{-14}\,\mathrm{m^3\,s^{-1}}$, $M = 6{\cdot}6\times10^{-25}$ kg and $T = 293$ K. The limiting value of ND_{eff} from equation (4) is $4{\cdot}44\times10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$

Method of calculation	$\Lambda^{-2} = 1{\cdot}50$	0·75	0·40	0·15	0·10	0·06	Values of ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$) at $P = 20$ torr ($10^4\,\mathrm{m^{-2}}$)
Exact eqn (33a)	3·45	3·83	4·07	4·29	4·34	4·38	
Perturbation (33b)	2·80	3·62	4·00	4·28	4·33	4·38	
Matrix method	3·4	3·8	4·0	4·2	4·3	4·3	

	$\Lambda^{-2} = 1{\cdot}50$	0·75	0·40	0·15	0·10	0·06	Values of ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$) at $P = 40$ torr ($10^4\,\mathrm{m^{-2}}$)
Exact eqn (33a)	4·09	4·25	4·34	4·40	4·41	4·42	
Perturbation (33b)	4·03	4·24	4·33	4·40	4·41	4·42	
Matrix method	4·0	4·2	4·3	4·4	4·4	4·4	

	$P = 60$	80	100	150	200	Values of ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$) at $\Lambda^{-2} = 1{\cdot}5\times10^4\,\mathrm{m^{-2}}$ (torr)
Exact eqn (33a)	4·27	4·34	4·38	4·41	4·42	
Perturbation (33b)	4·26	4·34	4·38	4·41	4·42	
Matrix method	4·2	4·3	4·3	4·4	4·4	

Table 2. Effective diffusion coefficients for constant cross section

The fixed parameters are $q_{\mathrm{m}} = 10^{-16}\,\mathrm{cm^2}$, $M = 6{\cdot}633\times10^{-26}$ kg and $T = 293$ K. There are no exact values for this case. The limiting value of ND_{eff} from equation (4) is $35{\cdot}45\times10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$

Method of calculation	$\Lambda^{-2} = 1{\cdot}50$	0·75	0·40	0·15	0·10	0·06	Values of ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$) at $P = 20$ torr ($10^4\,\mathrm{m^{-2}}$)
Perturbation (35a)	11·0	23·2	25·9	33·0	33·8	34·5	
Matrix method	23	27	30	33	34	34	

	$\Lambda^{-2} = 1{\cdot}50$	0·75	0·40	0·15	0·10	0·06	Values of ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$) at $P = 40$ torr ($10^4\,\mathrm{m^{-2}}$)
Perturbation (35a)	29·3	32·4	33·8	34·3	35·0	35·2	
Matrix method	30	32	34	35	35	35	

	$P = 60$	80	100	120	150	200	Values of ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$) at $\Lambda^{-2} = 1{\cdot}5\times10^4\,\mathrm{m^{-2}}$ (torr)
Perturbation (35a)	32·7	33·9	34·5	34·8	35·0	35·2	
Matrix method	33	34	34	35	35	35	

We present here the information on the variation of D_{eff} for particular choices of the parameters which are useful for understanding the phenomena in likely experimental situations.

The effectiveness of the numerical method, as well as the variation in D_{eff} with P and Λ, is best illustrated by the example of a constant collision frequency (Table 1).

In this case exact values of ND_{eff} can be calculated from equation (33a). It is seen that the numerical method gives results in agreement with these values to within 2% over a wide range of parameters. On the other hand, the first-order perturbation formula (33b) shows as much as 20% deviation from the exact results for low pressures and small dimensions. The limiting value for high pressures and large volumes calculated directly from equation (4) provides another point of comparison.

In the constant cross section case, no exact results are known. The deviation between the results from the perturbation formula (35a) and the matrix method shows that in certain instances the former is inadequate. The approach to the limiting value calculated from equation (4) should be noted (see Table 2).

We now turn to the experimental cases. Cross sections are available for the cases of helium, neon and argon in the region of interest. The dimensions of the apparatus used by Gibson *et al.* (1973) were $a = 3{\cdot}772$ cm and $h = 2{\cdot}992$ cm, so that $\Lambda^{-2} = 1{\cdot}509 \times 10^4\ \text{m}^{-2}$. The temperature used was 293 K. In each case the variation of ND_{eff} with pressure has been studied to determine the conditions where it is appropriate to compare the experimentally determined value with the formula (4) and to provide relevant values for comparison where it is not.

Helium. The cross section given by Crompton *et al.* (1970) was used here. From 10 to 200 torr there was no significant variation in the calculated value of ND_{eff}, namely $6{\cdot}3 \times 10^{21}\ \text{cm}^{-1}\,\text{s}^{-1}$, which is also the value of ND. This confirms the estimates based on Parker's (1965) analysis (Gibson *et al.* 1973) that the diffusion cooling effect in this case would be small. The values of the diffusion coefficient observed experimentally are consistent with the value quoted above.

Neon. The cross section used in this case was that given by Robertson (1970, 1972), supplemented in the low energy region ($<0{\cdot}1$ eV) by the result calculated theoretically from the atomic effective range theory (T. F. O'Malley, personal communication). The limiting value attained at about 120 torr is discernibly different from the value at lower pressures, although the effect of diffusion cooling is quite small. The experimentally observed value at 100 torr is $72{\cdot}9 \times 10^{21}\ \text{cm}^{-1}\,\text{s}^{-1}$ (Rhymes and Crompton, personal communication). The calculated values at different pressures were:

P (torr)	50	60	80	100	120	150	200
ND_{eff} ($10^{21}\ \text{cm}^{-1}\,\text{s}^{-1}$)	66	69	71	71	72	72	72

Because of the larger mass and smaller cross section, neon–electron collisions are not as effective in transferring energy as helium–electron collisions. One may therefore expect that diffusion cooling will be more important in this case, and hence that there will be larger differences between ND_{eff}, at lower pressures, and ND. However, the inefficiency of energy transfer in this case is offset by the shape of the cross section versus energy curve. It is a rising cross section, roughly proportional to the speed, and we have seen in Section 3 that there is no diffusion cooling for the prototype of this cross section.

Argon. In this case the cross section exhibits a pronounced minimum at about $0{\cdot}2$ eV and varies strongly with energy. The calculated values, using the Robertson (1970, 1972) cross section, show a strong variation with pressure. The limiting value

calculated from the formula (4) is $29{\cdot}6\times10^{21}\ \mathrm{cm^{-1}\,s^{-1}}$ and is not attained even at 200 torr:

P (torr)	10	20	30	40	50	60	80	100	120	150	200
ND_{eff} ($10^{21}\,\mathrm{cm^{-1}\,s^{-1}}$)	9	13	16	18	19	20	22	23	24	26	27

The preliminary experiments at 20 torr which prompted this investigation are in good agreement with the calculated value. The strong effect observed in this case is the combined result of an extremely low cross section within the significant energy range and a large mass-ratio which makes the collisions very inefficient in energy transfer. In contrast to the neon case, the cross section is falling rapidly in the low energy region where the dominant processes take place.

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