

## Diffusion, Attachment and Attachment Cooling of Thermal Electrons in Oxygen and Oxygen Mixtures

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### Abstract

The Cavalleri electron density sampling technique has been used to measure the diffusion and attachment rate coefficients for thermal electrons in O<sub>2</sub>, and in O<sub>2</sub>-N<sub>2</sub> and O<sub>2</sub>-CO<sub>2</sub> mixtures. The observed pressure dependence of the three-body attachment rate coefficient  $\nu_a/N^2$  is shown to be caused by the selective removal of electrons from the distribution at the attachment resonance energy, and the magnitude of this effect (so-called 'attachment cooling') is shown to be a measure of the magnitude of the rotational excitation cross sections in O<sub>2</sub> and N<sub>2</sub>. Three-body rate coefficients for the formation of O<sub>2</sub><sup>-</sup> involving O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> as third bodies have been found to be 2.2, 0.11 and  $3.5 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  respectively. The value of the diffusion coefficient  $ND$  for thermal electrons in O<sub>2</sub> is found to be  $(37 \pm 3) \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ .

### 1. Introduction

Analyses of transport coefficients for electrons in atomic and molecular gases have been successfully used to obtain elastic and inelastic electron-atom/molecule cross sections at energies from thermal to a few electron volts (see e.g. Huxley and Crompton 1974). In molecular oxygen, however, it has been difficult to obtain reliable transport data upon which to base the analysis due to the rapid depletion of the electron population by the attachment process which has a very large rate coefficient at low energies. This loss of electrons also poses a problem in the analysis of the transport data. Most analyses treat the attachment (and ionization) process as an ordinary inelastic collision in which an electron loses energy in the collision but remains within the electron population (for a review see Tagashira 1981). However, Taniguchi *et al.* (1978), who analysed the case of attachment, showed that the actual removal of the electron from the population needs to be taken into account in order to calculate correctly the attachment rate coefficient from the relevant cross section data.

Hake and Phelps (1967) have shown that there are large differences between the momentum transfer cross section  $\sigma_m$  that is consistent with the d.c. swarm measurements and that which is consistent with the microwave conductivity data (van Lint *et al.* 1960; Fehsenfeld 1963; Mentzoni 1965) for energies below 0.5 eV. These large discrepancies highlight the need for more accurate transport data for low energy electrons in oxygen. To this end Reid and Crompton (1980) have recently measured electron drift velocities in oxygen down to  $E/N = 0.14 \text{ Td}$  (where  $E$  is the electric

field strength and  $N$  the gas number density;  $1 \text{ Td} \equiv 10^{-17} \text{ V cm}^2$ ). The present paper presents a series of measurements of the diffusion coefficient for thermal electrons in oxygen obtained using the Cavalleri (1969) electron sampling technique. As described in Section 2, this experimental technique allows a simultaneous determination of the diffusion coefficient  $ND$  and the three-body attachment rate coefficient  $v_a/N^2$ . In the course of this work we observed an unexpected pressure dependence of  $v_a/N^2$  (see Sections 3 and 4) which we attribute to the effect on the energy distribution function of the selective removal of electrons by attachment from within a relatively narrow energy range (Crompton *et al.* 1980). This effect ('attachment cooling'), which is discussed in Section 5, can in principle be used to obtain information about the cross sections for rotational excitation.

## 2. Experiment

The Cavalleri electron sampling method employed here has been described in detail by Cavalleri (1969) and Gibson *et al.* (1973). In this technique, electrons are created inside a gas-filled all-glass cell by a short ( $\sim 3 \mu\text{s}$ ) burst of soft X rays. Some time after the X-ray pulse, a large amplitude, highly damped r.f. voltage pulse having a duration of  $\sim 1 \mu\text{s}$  is applied to the sampling electrodes. The resulting r.f. field heats any free electrons inside the cell so that they excite the gas and the resulting light output as the excited species decay is measured by a photomultiplier. The amount of light is proportional to the number of free electrons present at the time of the r.f. sampling pulse, and by varying the delay time between the X-ray pulse and the sampling pulse, the decay time constant  $\tau$  for the electron population can be found. It is important to note that in this experiment the initial density of electron-ion pairs is so low ( $\lesssim 10^2 \text{ cm}^{-3}$ ) that the electrons diffuse freely. This is in contrast to most microwave cavity experiments where the density is  $\gtrsim 10^7 \text{ cm}^{-3}$  and the diffusion may be ambipolar.

If diffusion and attachment are the only loss processes present, the decay of the electron population  $n$  is given by the equation

$$\partial n/\partial t - D\nabla^2 n = -v_a n, \quad (1)$$

where  $v_a$  is the attachment collision frequency. The asymptotic form of  $n(t)$  is given by

$$n(t)/n(0) = \exp(-t/\tau),$$

where  $\tau^{-1} = DA^{-2} + v_a$  and  $A$  is the geometry-dependent diffusion length (see e.g. Huxley and Crompton 1974, p. 460). When attachment is a three-body process it is convenient to rewrite the equation for the time constant  $\tau$  in the form

$$N\tau^{-1} = (ND)A^{-2} + (v_a/N^2)N^3. \quad (2)$$

Then, if the three-body rate coefficient  $v_a/N^2$  is truly independent of  $N$ , a plot of  $N\tau^{-1}$  versus  $N^3$  derived from measurements of  $\tau$  versus  $N$  will be linear, and from such a plot values of both  $ND$  and  $v_a/N^2$  can be obtained.

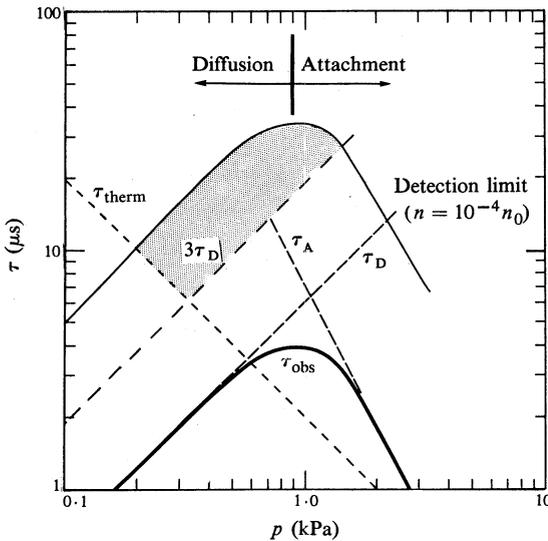
The choice of experimental parameters depends on the magnitudes of  $ND$  and  $v_a/N^2$  and the operational constraints of the experiment. Equation (2) can be written

$$\tau^{-1} = \tau_D^{-1} + \tau_A^{-1} \quad (3)$$

where, in terms of the number-density independent quantities  $ND$  and  $v_a/N^2$ ,

$$\tau_D^{-1} = (ND)A^{-2}/N, \quad \tau_A^{-1} = (v_a/N^2)N^2.$$

Thus, at low pressures, the observed time constant is dominated by the diffusion losses, while at high pressures the loss of electrons is predominantly by attachment. Fig. 1 shows the expected values of the observed time constant as a function of the gas pressure using published values of  $v_a/N^2$  (Shimamori and Hatano 1977) and  $ND$  (Nelson and Davis 1972) for oxygen. The left- and right-hand asymptotes of this curve give, respectively, the pressure dependences of  $\tau_D$  and  $\tau_A$ . As can be seen, for a pressure  $\gtrsim 1$  kPa the loss of electrons is dominated by attachment, while at lower pressures the loss is predominantly by diffusion to the walls.



**Fig. 1.** Time constant as a function of pressure in pure O<sub>2</sub>.

Fig. 1 also illustrates some of the operational constraints of this experiment. As described by Gibson *et al.* (1973), it is necessary that the high energy electrons created by the X-ray pulse are completely thermalized before the time constant measurements are made. The curve marked  $\tau_{\text{therm}}$  indicates a conservative estimate of the time needed for this thermalization.

It is also necessary to wait sufficiently long before a measurement is made so that the electron distribution inside the cell has settled down to the fundamental diffusion mode. The time needed for the higher order diffusion modes to decay to insignificant levels depends upon the initial spatial distribution of the electrons, and the line  $t = 3\tau_D$  indicates a 'worst case' estimate for this decay time based upon a  $\delta$ -function initial distribution.

The uppermost curve shows the limit of detectability in this experiment, assumed to be  $n(t) = 10^{-4}n(0)$ .

The region bounded by these three curves, shown shaded in Fig. 1, defines the working range for these experiments. At pressures  $\gtrsim 1.5$  kPa,  $\tau$  is dominated by  $\tau_A$ . Equation (2) is then not strictly valid, since higher order diffusion modes will contribute to  $\tau_D$ , but as  $p$  increases  $\tau \rightarrow \tau_A$ , and the error in  $\tau$  due to the decay of these modes becomes insignificant.

### 3. Measurements of Diffusion Coefficients

The measurements were carried out in both pure O<sub>2</sub> and in O<sub>2</sub>-N<sub>2</sub> mixtures. The results obtained will be discussed separately.

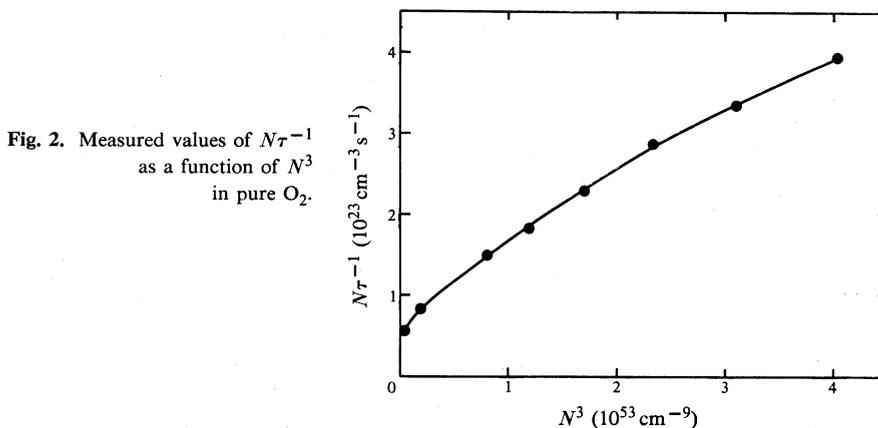


Fig. 2. Measured values of  $N\tau^{-1}$  as a function of  $N^3$  in pure O<sub>2</sub>.

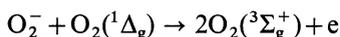
Table 1. Measured time constants and derived values of  $ND$  and  $v_a/N^2$  for oxygen

$p$ (kPa)	$\tau$ ( $\mu\text{s}$ )	$ND$ ( $10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ )	$v_a/N^2$ ( $10^{-30} \text{ cm}^6 \text{ s}^{-1}$ )
0.6	2.65		
		31.9	2.09
1.0	3.08	41.2	1.12
1.75	2.86	57.2	0.81
2.0	2.70	48.1	0.93
2.25	2.42	49.4	0.92
2.5	2.15	94.9	0.62
2.75	2.03	129	0.45
3.0	1.97		

#### (a) Results Obtained in Pure O<sub>2</sub>

The results obtained in pure O<sub>2</sub> are shown in Fig. 2 where  $N\tau^{-1}$  is plotted as a function of  $N^3$  (see equation 2). The values of  $ND$  and  $v_a/N^2$  computed from adjacent values of  $N$  are shown in Table 1. As can be seen, neither  $ND$  nor  $v_a/N^2$  appears to be independent of pressure. Several diagnostic tests such as those described by Rhymes *et al.* (1975) were performed in an attempt to determine whether this unexpected behaviour was due to an experimental artefact. The results of all these tests were negative. In addition, a series of measurements was performed in which the gas was flowed through the cell at a rate fast enough to replenish the gas sample between successive 'experiments', i.e. successive cycles each initiated by an X-ray pulse. This was done to see whether the possible presence of the long-lived oxygen

metastable states  $^1\Sigma_g^+$  and/or  $^1\Delta_g$ , which could have been produced by the sampling pulse, were the cause of the anomalously long time constants observed, especially at high pressures. These measurements proved that even if metastables were present they did not affect the results. This observation was unexpected because the states  $^1\Delta_g$  and  $^1\Sigma_g^+$ , which have radiative lifetimes of 45 min and 12 s respectively, are known to be abundant in oxygen discharges and to be very stable against de-excitation by collisions with glass walls (Zipf 1969). One would therefore expect that in the static gas experiments an equilibrium concentration of these states, possibly of the order of several per cent, would be rapidly built up in the cell. Since the detaching reaction



is very effective (Fehsenfeld *et al.* 1969), the presence of an appreciable population of metastables when coupled with this reaction would provide a source of electrons, increasing the observed time constant. That there is no evidence of this process occurring is thought to be due either to the production rate of metastables being very small, or to some quenching of the states. Eventually the nonlinearity in the  $N\tau^{-1}$  versus  $N^3$  curve was attributed to the 'attachment-cooling' effect, which will be discussed in Section 5.

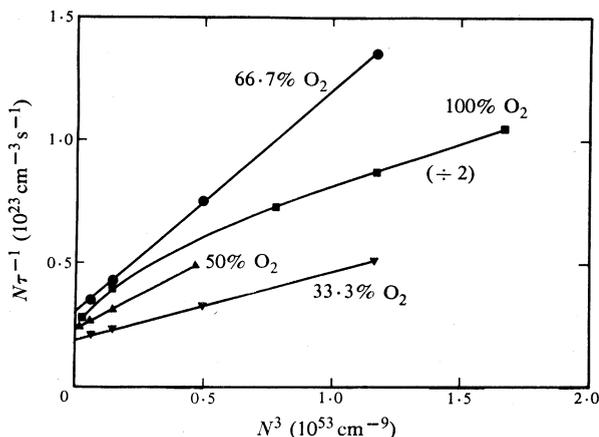


Fig. 3. Measured values of  $N\tau^{-1}$  as a function of  $N^3$  in  $O_2$ - $N_2$  mixtures.

Table 2. Values of  $(ND)_{mix}$  and  $(v_a/N^2)_{mix}$  for various oxygen-nitrogen mixtures

$p_{total}$ (kPa)	$(ND)_{mix}$ ( $10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ )			$(v_a/N^2)_{mix}$ ( $10^{-31} \text{ cm}^6 \text{ s}^{-1}$ )		
	$\frac{2}{3}^A$	$\frac{1}{2}^A$	$\frac{1}{3}^A$	$\frac{2}{3}^A$	$\frac{1}{2}^A$	$\frac{1}{3}^A$
2.29			12.5			2.71
2.0						
1.5	20.7		13.2	8.86		2.63
1.0	19.2	15.5	12.8	9.35	5.54	2.73
0.75	19.1	15.2	12.9	9.48	5.85	2.70
0.5	18.6	15.1		10.5	6.22	

<sup>A</sup> Fractional concentration of  $O_2$ .

## (b) Results Obtained in Gas Mixtures

In order to investigate the cause of the apparent pressure dependence of  $ND$  and  $v/N^2$  observed in pure  $O_2$ , some measurements were performed in  $O_2-N_2$  mixtures. The results obtained in mixtures having an oxygen concentration of  $\frac{1}{3}$ ,  $\frac{1}{2}$  and  $\frac{2}{3}$  are shown in Fig. 3. Also included for comparison are the results obtained in pure  $O_2$ . The values of  $ND$  and  $v_a/N^2$  for these mixtures are given in Table 2. As can be seen from Fig. 3, the nonlinearity of the  $N\tau^{-1}$  versus  $N^3$  curve observed in pure  $O_2$  is substantially removed in the mixture results. Table 2 shows that there is still some pressure dependence of both  $ND$  and  $v_a/N^2$  but that the effect is greatly reduced. As will be discussed later, this reduction can be explained by the reduction of the attachment cooling brought about by the addition of nitrogen.

When the momentum transfer cross sections for the constituent gases have the same energy dependences, that is, the ratio of the cross sections is the same at all energies, the diffusion coefficient for electrons in the mixture can be calculated from the diffusion coefficients for the constituents using Blanc's law

$$(ND_{\text{mix}})^{-1} = f(ND_{O_2})^{-1} + (1-f)(ND_{N_2})^{-1}, \quad (4)$$

where  $f$  is the fractional concentration of  $O_2$ . For some mixtures, for example water vapour and nitrogen, the disparity in the energy dependences of the cross sections can lead to relatively large errors in diffusion coefficients calculated in this way (Z. Petrović, personal communication), but in the present case the errors amounted to less than 2%.

Table 3. Measured diffusion coefficients in  $N_2$  ( $T = 296$  K)

$p$ (kPa)	$\tau$ ( $\mu\text{s}$ )	$(ND)_{N_2}$ ( $10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ )
3.0	49.98	9.62
2.0	33.32	9.63
1.5	25.09	9.60
1.0	16.79	9.58
0.75	12.68	9.54
		Av. 9.59

Table 4. Measured diffusion coefficients in  $O_2$  ( $T = 296$  K)

$f$	$(ND)_{\text{mix}}$ ( $10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ )	$(ND)_{O_2}$ ( $10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ )
$\frac{2}{3}$	18.64	35.3
$\frac{1}{2}$	15.04	34.8
$\frac{1}{3}$	12.85	40.0
		Av. 36.7

In order to recover the diffusion coefficient for electrons in  $O_2$  from equation (4) and the mixture data it is necessary to know the values of  $ND$  in pure  $N_2$ . The results of our measurements are summarized in Table 3. The average value for  $(ND)_{N_2}$  of  $9.59 \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$  agrees well with the value of  $9.50 \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$  calculated from the momentum transfer cross section given by Engelhardt *et al.* (1964) (see Huxley and Crompton 1974, p. 631) and the value of  $9.47 \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$  measured by Nelson and Davis (1969). Using the experimentally determined values of  $(ND)_{N_2}$  and  $(ND)_{\text{mix}}$  we obtained the values of  $(ND)_{O_2}$  given in Table 4.

#### 4. Measurements of Attachment Rate Coefficients

A series of measurements was made in  $O_2-N_2$  and  $O_2-CO_2$  mixtures to determine the attachment rate coefficients for thermal electrons in these mixtures, and to enable

the rate coefficient in pure  $O_2$  to be determined free from error introduced by attachment cooling. Before describing these results, we will include a short summary of the theory of the attachment process.

(a) *Attachment Process*

The attachment of low energy (i.e.  $\lesssim 1$  eV) electrons to oxygen to form the negative  $O_2^-$  ion proceeds via the well known three-body process first suggested by Bloch and Bradbury (1935) and modified by Chanin *et al.* (1962). In the Bloch–Bradbury (BB) process, a temporary negative ion in a vibrationally excited state is first formed which can subsequently either auto-detach or be stabilized by collision with a third body M:



where  $k$  is the rate coefficient for each reaction. This process has been investigated by many authors (see e.g. Shimamori and Hatano 1977 and references therein) and the reaction scheme depicted above found to be adequate to describe the process at the pressures used in the present experiment. [At higher pressures, temporary  $e.O_2.M$  complex formation will affect this reaction scheme (Shimamori and Hatano 1976; McMahon 1981, 1982; Shimamori and Hotta 1983).]

The effective three-body attachment rate coefficient in a mixture of  $O_2$  and a non-attaching gas M can be written

$$(v_a/N^2)_{\text{mix}} = (v_a/N^2)_{O_2} f \{f + (1-f)\gamma\}, \quad (6)$$

where  $\gamma = k_3^M/k_3^{O_2}$ , i.e. the relative stabilization efficiency of the third body M (see equation 5c). Therefore, in order to obtain  $(v_a/N^2)_{O_2}$  from the mixture measurements, we need to determine  $\gamma$  also. As shown by Shimamori and Hatano (1977), this can be obtained in the following way.

An effective two-body rate coefficient  $k_{\text{eff}}$  can be defined for the overall reaction



This rate coefficient is related to the observed *attachment* time constant  $\tau_A$  through  $\tau_A^{-1} = k_{\text{eff}}[O_2]$ . (Here, and in the following, square brackets indicate number densities.) Shimamori and Hatano have shown that, if the BB mechanism is valid,  $\tau_A$  is related to the rate coefficients in equations (5) in the following way:

$$\tau_A[O_2] = k_1^{-1} + \{k_3^{O_2}(r + \gamma)\}^{-1}[M]^{-1}, \quad (7)$$

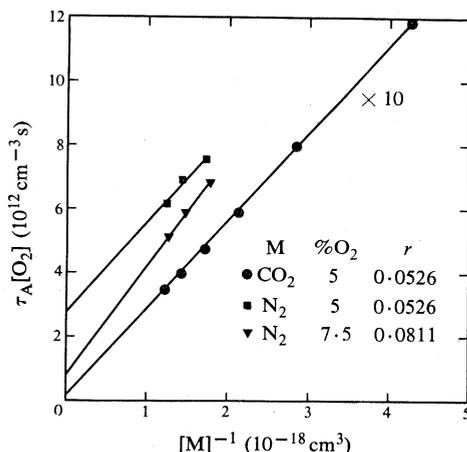
where  $r = [O_2]/[M]$ . Thus, a plot of  $\tau_A[O_2]$  versus  $[M]^{-1}$  for mixtures having a constant  $r$  should yield a straight line with slope  $\{k_3^{O_2}(r + \gamma)\}^{-1}$ , and from data obtained for two values of  $r$  both  $k_3^{O_2}$  and  $\gamma$  can be found.

(b) *Attachment in Mixtures*

In order to obtain a reasonable sensitivity to  $\gamma$  (see equation 7) and to avoid the pressure dependence of  $v_a/N^2$  associated with the attachment cooling effect (see

Section 5), the measurements were made in mixtures having low concentrations of  $O_2$ . Fig. 4 shows the results for  $\tau_A$  obtained for  $O_2-N_2$  and  $O_2-CO_2$  mixtures. The values of  $\tau_A$  were calculated from the measured values of  $\tau$  by using equation (3) and calculated values of  $\tau_D$ . Because, in general, the electron loss was dominated by attachment,  $\tau_D$  could be calculated with sufficient accuracy by using equation (4) in conjunction with known values of  $ND$ . From the slope of the two plots of  $\tau_A[O_2]$  versus  $[M]^{-1}$  for  $O_2-N_2$  mixtures corresponding to  $r = 0.0811$  and  $0.0526$  we find  $(v_a/N^2)_{O_2} = 2.24 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  and  $\gamma = 0.05$ . Using the value for  $(v_a/N^2)_{O_2}$  so obtained, we find from the curve for  $CO_2$  that  $\gamma = 1.57$ .

Fig. 4. Measured values of  $\tau_A[O_2]$  as a function of  $[M]^{-1}$ .



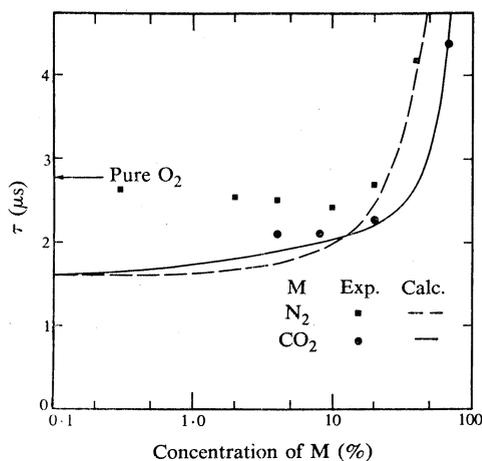
## 5. Attachment Cooling

The pressure dependence of  $v_a/N^2$  observed in pure  $O_2$  (see Section 3a) was investigated in a series of measurements in  $O_2-N_2$  and  $O_2-CO_2$  mixtures keeping the total pressure constant at 2.0 kPa and varying the concentration of the added gas. This investigation has been briefly reported before (Crompton *et al.* 1980), but a description will be included here for the sake of completeness.

### (a) Experimental Observations

The results obtained in  $O_2-N_2$  and  $O_2-CO_2$  mixtures at a constant total pressure of 2 kPa are shown in Fig. 5. These are compared with the time constants calculated using our measured values of  $ND$  and  $v_a/N^2$ . As can be seen there are significant differences between measured and calculated values for  $N_2$  concentrations less than 40% and  $CO_2$  concentrations less than 20%; the differences rise to more than 50% for the lowest concentrations of  $N_2$ .

It is significant that the observed time constant initially *decreases* as nitrogen is added. Since the substitution of  $N_2$  for  $O_2$  reduces both the diffusion rate  $[(ND)_{N_2} < (ND)_{O_2}]$  and the stabilization rate coefficient  $[k_3^{O_2}/k_3^{N_2} = 20, \text{ see Section 4b}]$  this reduction of  $\tau$  by dilution with  $N_2$  must be caused by an *increase* in  $(v_a/N^2)_{O_2}$ . Now the three-body rate coefficient  $k = v_a/N^2$  is given by  $k_1 k_3/k_2$  (see equations 5). Therefore, provided the BB mechanism is applicable, a pressure dependence of  $k$  implies a pressure dependence of  $k_1$ . Such a dependence can be explained in the following way.



**Fig. 5.** Time constant in  $O_2$ -M mixtures as a function of concentration of M;  $p_{\text{tot}} = 2.0$  kPa,  $T = 294$  K.

The rate coefficient for the initial formation of the temporary negative ion (equation 5a) is given by

$$k_1 = (2/m)^{\frac{1}{2}} \int_0^{\infty} \varepsilon \sigma_A(\varepsilon) f(\varepsilon) d\varepsilon,$$

where  $\sigma_A$  is the cross section for reaction (5a). The cross section  $\sigma_A$  for the formation of  $O_2^-(v' = 4)$  has a resonance shape with the 'centre' at  $\varepsilon_A \sim 90$  meV and a width of  $\sim 30$  meV (Land and Raith 1974; Fiquet-Fayard 1975). Electrons are therefore selectively removed from the electron population at these energies, and if the energy exchange collision frequency  $\nu_e$  is insufficiently large, the distribution function  $f(\varepsilon)$  will become depleted in the vicinity of the resonance. In the present case  $\varepsilon_A$  is greater than  $kT$ . The selective removal of electrons therefore takes place from the high energy tail of the distribution leading to a lowering of the mean energy of the electron swarms and hence 'attachment cooling' in this instance. Since  $\nu_a \propto N^2$ , while  $\nu_e \propto N$ , depletion increases with increasing pressure; consequently  $k_1$  and hence  $k$  decreases, as observed (see Table 1). The increase in the attachment rate by dilution of the oxygen sample with nitrogen is due to the larger rotational excitation cross sections in  $N_2$  which increase  $\nu_e$  and reduce attachment cooling. For the same reason  $CO_2$  is even more effective in thermalizing the electrons as seen from Fig. 5.

#### (b) Calculations of Attachment Cooling Effect

Skullerud (1983; present issue p. 845) has developed a solution to the Boltzmann equation applicable to the present problem in which proper account has been taken of the loss of electrons. In most analyses up to the present, attachment (and ionization) have been treated as ordinary inelastic collisions (see e.g. Lawton and Phelps 1978). Recently, Taniguchi *et al.* (1978) have published an analysis of the attachment rate coefficient measurement of Grünberg (1969) in which the loss of electrons is properly taken into account, but their analysis applies only when superelastic collisions can be ignored, and hence not when  $E/N \rightarrow 0$ .

In the present case, where the energy distribution of the electrons is close to thermal, the main contribution to the energy exchange between the electrons and the gas molecules comes from rotational excitation and de-excitation collisions. The

amount of attachment cooling is therefore a function of the cross sections for these processes. In Skullerud's (1983) analysis direct rotational excitation and de-excitation are represented by the Gerjuoy and Stein (1955) formulae, and account is taken of excitation and de-excitation via negative ion resonances. Using the attachment cross section given by Fiquet-Fayard (1975) and normalized to give the observed attachment rate  $(v_a/N^2)_{O_2}$  ( $N \rightarrow 0$ ) Skullerud finds that he can obtain a good fit to the data for pure oxygen shown in Fig. 2 (see Fig. 2 of Skullerud 1983).

## 6. Discussion

### (a) Estimates of Accuracy

Reliable estimates of accuracy for the value of  $ND$  for oxygen and the effective three-body attachment rate coefficients for oxygen and the oxygen mixtures are difficult to make. The raw data from experiments of this kind are usually subject to an uncertainty of no more than  $\pm 2\%$  (Gibson *et al.* 1973). In the present experiments the uncertainty can be expected to be somewhat larger because of the additional difficulties associated with the measurement of very small time constants in many cases (see, for example, the data for pure  $O_2$  in Table 1). In addition, where the data are subject to appreciable attachment cooling, the measured time constants are sensitive to very small levels of contamination by water vapour (see Section 6c).

Because of significant attachment cooling in oxygen even at the lowest pressures that are experimentally accessible,  $ND$  was determined from the mixture data recorded in Table 4. The rather large scatter in the values is not surprising when it is realized that a  $\pm 2\%$  uncertainty in the measurement of  $(ND)_{\text{mix}}$  leads to an uncertainty of  $\pm 6\%$  in  $(ND)_{O_2}$  for  $f = \frac{2}{3}$  and  $\pm 21\%$  for  $f = \frac{1}{3}$ , and that each value of  $(ND)_{\text{mix}}$  has to be estimated from the plots shown in Fig. 3. The values of  $(ND)_{O_2}$  in Table 4 have a spread of less than 15%, including the value for  $f = \frac{1}{3}$  where the application of Blanc's law amplifies considerably any error in the  $(ND)_{\text{mix}}$  value, so it seems not unreasonable to estimate the uncertainty as about  $\pm 10\%$ .

The principal source of error in extracting  $(v_a/N^2)_{O_2}$  from the mixture data shown in Fig. 4 results from the small range of  $[M]$  over which the measurements could be made and the consequent uncertainty in determining the slope of the plots of  $[O_2]\tau_a$  versus  $[M]^{-1}$ . While we have quoted the attachment rate to three figures we have done so only because our data is best fitted overall with this value. It is unlikely that our result is in error by more than 10% and it is probably correct to within 5%.

### (b) Diffusion Coefficient for Thermal Electrons in Oxygen

The only other direct measurement of the diffusion coefficient for thermal electrons in  $O_2$  is that of Nelson and Davis (1972) who used the drift-dwell-drift technique. In this method the electron swarm is introduced into the drift region where it drifts initially for some time under the influence of an electric field. The field is then turned off for some time during which the swarm diffuses freely in a field-free space. Subsequently it is extracted into the analyser region by a further application of the field. The diffusion coefficient can be determined from the arrival time spectrum of the electrons by an unfolding process.

Nelson and Davis obtained a value of  $Dp = 1.20 \times 10^6 \text{ cm}^2 \text{ s}^{-1} \text{ Torr}$  (1 Torr = 133 Pa) which, if the pressure refers to 300 K, corresponds to  $ND = 39 \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ . This value is in good agreement with our result for  $ND$  of  $37 \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$ .

Pack and Phelps (1966) estimated the thermal electron mobility  $\mu$  for electrons in  $O_2$  from measurements of the electron drift velocity in  $O_2$ - $CO_2$  mixtures. They quoted a value of  $\mu N = 4.1 \times 10^{23} \text{ V}^{-1} \text{ s}^{-1} \text{ cm}^{-1}$  at 300 K, which corresponds to  $ND = 10.8 \times 10^{21} \text{ cm}^{-1} \text{ s}^{-1}$  which is only one-third of the present value. We do not know the reason for this large discrepancy, but Pack and Phelps pointed out that their value corresponds to an average momentum transfer cross section  $\sigma_m$  of  $3.3 \text{ \AA}^2$  for energies below  $\approx 0.1 \text{ eV}$ , which is considerably larger than the value obtained from microwave experiments (Veatch *et al.* 1966 and references therein). Our results correspond to  $\sigma_m \approx 1 \text{ \AA}^2$ , in better agreement with the microwave results, and we feel that the more direct method we have used to obtain  $ND$  is the more likely to be correct.

Attachment cooling will, of course, change the value of  $ND$  from that corresponding to a thermal Maxwellian distribution but the change is smaller than the corresponding change in the effective value of  $v_a/N^2$ . For example, in pure  $O_2$  at 2.5 kPa Skullerud's (1983) results can be used to show that  $ND$  is increased by less than 10% compared with a reduction of about 60% in  $v_a/N^2$ . The effect on our value of  $ND$  obtained from the data for  $N_2$ - $O_2$  mixtures is negligible.

Table 5. Comparison of measured attachment rate coefficients

M	$(v_a/N^2)_M (10^{-30} \text{ cm}^6 \text{ s}^{-1})$		M	$(v_a/N^2)_M (10^{-30} \text{ cm}^6 \text{ s}^{-1})$	
	Other results	Present work		Other results	Present work
$O_2$	$2.3 \pm 0.2^A$	2.2	$N_2$	$0.085 \pm 0.003^E$	0.11
	2.1 <sup>B</sup>			0.06 <sup>P</sup>	
	2.0 <sup>C</sup>			0.11 <sup>F</sup>	
	2.8 <sup>D</sup>				
			$CO_2$	$\sim 3^{C,G}$	3.5

<sup>A</sup> Shimamori and Hatano (1977). <sup>B</sup> Truby (1972). <sup>C</sup> Pack and Phelps (1966). <sup>D</sup> Chanin *et al.* (1962).

<sup>E</sup> Shimamori and Hatano (1976). <sup>F</sup> Van Lint *et al.* (1960). <sup>G</sup> Warman *et al.* (1971).

### (c) Three-body Attachment Rate Coefficient for Thermal Electrons in Oxygen

The results obtained by us and by others for the three-body attachment rate coefficient  $(v_a/N^2)_M$  [where the subscript M denotes that stabilization occurs in a collision with a molecule M—see equation (5c)] are compared in Table 5. As can be seen, our results are in satisfactory agreement with those of Shimamori and Hatano (1977), Truby (1972) and Pack and Phelps (1966); the result of Chanin *et al.* (1962) appears to be somewhat too high.

As discussed previously, our results have been obtained using mixtures with concentrations of oxygen that are sufficiently low that the density dependence described in Section 3, now attributed to attachment cooling, is avoided. However many of our results, particularly those in pure oxygen at the higher pressures, are markedly affected by attachment cooling. Thus perhaps the most significant result of our work is the demonstration that very large errors in the determination of the attachment rate coefficient can result from this effect and, conversely, that the application of a three-body rate coefficient determined under conditions where the effect is negligible to a regime of much higher pressure can result in serious error.

Our results also have implications for the measurement and application of two-body attachment rate coefficients. In this case, unlike the situation for three-body

attachment, the energy exchange and attachment rates both scale linearly with  $N$ . Consequently, even though attachment cooling may be significant, the attachment rate coefficient determined at any pressure is applicable at any other pressure. However, the effect cannot be ignored in relating the attachment rate coefficient to the attachment cross section. The observation of a pressure independent two-body attachment rate coefficient does not guarantee the absence of attachment cooling. Thus the application of transport theory to relate the attachment cross section to experimental data for the attachment rate coefficient may not be valid unless the theory fully accounts for electron loss by attachment (Taniguchi *et al.* 1978; Skullerud 1983). In order to validly apply 'conventional' theory (see e.g. Huxley and Crompton 1974) in situations where the attachment collision frequency shows a strong energy dependence, it would be necessary to show that the energy exchange rate is large enough in comparison with the attachment loss rate to effectively eliminate attachment cooling.

#### (d) Attachment Cooling

The qualitative explanation for the unexpected density dependence of  $v_a/N^2$  in terms of attachment cooling, which was advanced in Section 4a, is supported by the excellent agreement between experiment and the theoretical results of Skullerud (1983). The fact that its effects were not seen in the experiments of Shimamori and Hatano (1977) suggests that the electron swarm was adequately thermalized, probably as a result of the much higher electron densities used by these authors (Koura 1983). An alternative explanation is that there was a small trace of water vapour in the oxygen used in their experiments, although the authors believe this is extremely unlikely (personal communication). During the course of preliminary investigations into the cause of the density dependence observed in our experiments we noted that when the measurements were made in an unbaked apparatus the measured time constants decreased with time. In terms of attachment cooling, a reasonable explanation of the time dependence of the results is that water vapour was being desorbed from the walls of the glass cell and, because of the very large elastic and inelastic cross sections associated with its permanent dipole moment, the water vapour was acting as a highly efficient thermalizing agent thus reducing attachment cooling. To test this hypothesis an oxygen sample at 3 kPa was doped with about 200 ppm of water vapour. In the 'pure' (undoped) sample the measured time constant was  $1.9 \mu\text{s}$ , and in the doped sample about  $1 \mu\text{s}$ . Increasing the concentration of the water vapour to 900 ppm decreased the time constant only marginally (to about  $0.9 \mu\text{s}$ ). The fact that the results tend towards an asymptotic limit as the water vapour concentration is increased suggests that it is attachment cooling that is being eliminated rather than an alternative enhancement of electron capture due to more efficient stabilization when an  $\text{H}_2\text{O}$  molecule acts as a third body. Attachment to water vapour molecules is unlikely to be the explanation if estimates of the upper bound for the attachment of thermal electrons to water vapour are correct (Pack *et al.* 1962; Z. Petrović, personal communication).

The extreme sensitivity of the measured time constants to the presence of water vapour suggests that the phenomenon of attachment cooling could be exploited to determine the energy exchange rate for thermal electrons and therefore some information about rotational and vibrational cross sections in water vapour about which relatively little is known.

## 7. Conclusions

The Cavalleri electron density sampling technique employed in this work has yielded information both on the diffusion coefficient and the attachment rate coefficient for thermal electrons in pure oxygen and in O<sub>2</sub>-N<sub>2</sub> and O<sub>2</sub>-CO<sub>2</sub> mixtures. While the distortion of the electron energy distribution function by attachment has been acknowledged as a possible source of error in measurements of  $v_a/N^2$  (Pack and Phelps 1966; Taniguchi *et al.* 1978), we believe this work provides the first direct experimental evidence for the effect. It also shows that the calculation of attachment rates in oxygen or oxygen mixtures based on a simple application of the appropriate three-body rate coefficient can be seriously in error. Finally, we believe that analyses of data similar to those presented in this paper could provide a useful check on the validity of energy exchange rates for very low energy electrons that have been derived by other means.

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