THE BEHAVIOUR OF FREE AND ATTACHED ELECTRONS IN OXYGEN

By J. A. REES*

[*Manuscript received September* 17, 1964]

Summary

The behaviour in oxygen of swarms of electrons having mean energies of up to 2 eV has been studied. Confirmation of the occurrence in oxygen of a three-body attachment process has been obtained, and the attachment coefficient has been measured for $0 \cdot 4 < E/p < 6$ V cm^{-1} torr^{-1}. Values of the Townsend energy factor k_1 have also been obtained over the same range of values of E/p. It was observed that at least three species of negative ions were formed either directly by the electron attachment processes or through secondary collisions between these primary ions and the gas molecules. The mobilities of the various ion species were determined over the range $0 < E/p \leqslant 20$. The ions were found to have zero-field mobilities of $3 \cdot 01 \pm 0 \cdot 04$, $2 \cdot 52 \pm 0 \cdot 04$, and $2 \cdot 39 \pm 0 \cdot 04$ cm^2 V^{-1} s^{-1}. The results obtained for the ion mobilities, the attachment coefficient, and the Townsend energy factor have been compared with those obtained in other investigations.

I. INTRODUCTION

The attachment of electrons to oxygen molecules to form negative ions has been the subject of many previous investigations. For summaries of the various methods employed and of the results obtained reference should be made to Loeb (1955, 1956), Branscomb (1957), Prasad and Craggs (1962), and McDaniel (1964). In addition to the investigations of the attachment processes, there have been a number of studies of the drift velocities of the resulting negative ions. The more recent of these studies are those of Doehring (1952), Burch and Geballe (1957*a*, 1957*b*), McDaniel and Crane (1957), Chanin, Phelps, and Biondi (1962) (to be referred to as C.P.B. (1962) in what follows), and Eiber (1963*a*, 1963*b*). In a third group of experiments measurements of the Townsend energy factor k_1 for electrons in oxygen have been made by Townsend and Bailey (1921), Brose (1925), Healey and Kirkpatrick (1939), and Huxley, Crompton, and Bagot (1959) (the latter paper will be referred to as H.C.B.).

The results obtained in the various swarm investigations for the variation with E/p (where E = electric field strength in volts/centimetre and p = gas pressure in torr) of the ratio of the attachment coefficient η to the gas pressure p show a considerable scatter at all values of E/p, but particularly for $E/p < 5$ and $E/p > 10$. For the intermediate range of E/p ($5 < E/p < 10$) the best agreement appears to be that between Doehring's results and those of H.C.B., with the latter results tending towards those of C.P.B. at $E/p \sim 10$. Prasad and Craggs (1961) have shown that for a Druyvesteyn distribution of velocities the data obtained in swarm-type experiments by H.C.B., C.P.B., Doehring, and Prasad and Craggs were in better agreement with the data from the beam experiments of Craggs, Thorburn, and Tozer (1957) and of Buchel'nikova (1959) than were the results of other swarm experiments.

* Ion Diffusion Unit, Australian National University, Canberra.

For $E/p < 5$ a large part of the discrepancy between the various determinations of η/p may be attributed to the fact that in the early investigations it was not recognized that for this range of E/p the dominant attachment process was a three-body process, that is, that η/p over this range of E/p was dependent on the gas pressure. The occurrence of the three-body attachment process was first shown by Chanin, Phelps, and Biondi (1959) and Hurst and Bortner (1959) and later confirmed by van Lint, Wikner, and Trueblood (1960) and by Schulz (1961). Evidence of the occurrence of the three-body process at higher values of E/p (≈ 35) at high gas pressures has been obtained by Dutton, Harris, and Llewellyn Jones (1963).

The determinations of the mobilities of the negative ions formed by attachment in oxygen have established that at least three species of ions may be formed, either by direct attachment or in secondary reactions between the ions initially formed and the gas molecules. However, the results of many of these investigations exhibit a considerable experimental scatter and it is difficult to decide with any real precision what the zero-field mobilities of the ions are. (Throughout this paper, the expression "zero-field mobility" will be taken to mean the mobility in $cm^2\ V^{-1}\ s^{-1}$ obtained by extrapolating to zero E/p and normalizing to a gas number density of $2\cdot 69\times 10^{19}$ molecules/cm^3. All other mobility values are to be understood to be normalized to the same gas number density.)

The present investigation may be divided into three sections. In the first of these the earlier work of H.C.B. was extended to cover the region of three-body attachment at low E/p, with the object of confirming the occurrence of the three-body process and of obtaining values of the parameter k_1 (or D/μ) for this region of E/p. In the second section, attachment coefficients for $E/p < 2$ and ion mobilities for $E/p < 8$ were determined by a modification of Doehring's method. In the final section, more accurate determinations of ion mobilities for $E/p < 20$ were obtained using the Bradbury and Nielsen method (Bradbury and Nielsen 1936).

The gas used throughout the investigation was Airco "Assayed Reagent Grade" oxygen containing 190 p.p.m. of nitrogen, 190 p.p.m. of argon, and 9 p.p.m. of carbon dioxide. The carbon dioxide was removed from the gas samples by the use of liquid-air traps. Although neither the diffusion apparatus nor the drift-velocity tube were bakable, their rates of rise of pressure when isolated from the pumps were such that the contamination, from this source, of the gas samples used was less than 20 p.p.m. in 24 hr.

II. Determination of η/p and k_1, for $E/p \leqslant 6$, by the Method of H.C.B.

The method adopted for this part of the investigation and the diffusion apparatus employed have been fully described previously (H.C.B. 1959; Crompton and Jory 1962). The source of electrons used in the present work was a heated platinum filament.

Measurements of R, the ratio of the current received by the inner annulus of the anode of the diffusion chamber to that received by the complete anode (excluding the central disk which was earthed at all times), were taken at gas pressures of between 4 and 20 torr for anode/cathode separations of 2, 5, and 10 cm, for values of E/p

between 0·4 and 6. From the measurements of R, values of k_1 and η/p were deduced, using the graphs prepared for the earlier investigation (H.C.B.).

(a) *Results*

The results obtained for $E/p \leqslant 1\cdot5$ showed the parameter η/p to be dependent on the gas pressure used, indicating that the operative attachment process was not a two-body collision process. The values deduced for η/p^2 are shown in Table 1, together with the values of k_1 obtained simultaneously. The values of k_1 are also shown in Figure 5.

TABLE 1

VARIATION OF k_1 AND η/p^2 WITH E/p FOR $E/p \leqslant 1\cdot5$ AT 293°K

E/p (V cm^{-1} torr^{-1})	k_1	D/μ (eV)	$(\eta/p^2)\times10^4$ (cm^{-1} torr^{-2})						Mean η/p^2 $\times10^4$
			h = 5 cm			h = 10 cm			
			p = 10	15	20	10	15	$17\frac{1}{2}$ torr	
0·4	7·45	0·188	—	22	—	24	27	18	23
0·5	8·2	0·207	—	17	18	—	22	—	19
0·6	8·9	0·225	18	14	15	—	19	18	17
0·8	10·2	0·258	12	11	10	—	14	12	12
1·0	11·6	0·293	8	7	7·5	—	11	10	9·0
1·5	17·0	0·429	—	5·1	—	—	5·8	5·4	5·4

TABLE 2

VARIATION OF k_1 AND η/p WITH E/p FOR $E/p \geqslant 2$ AND $10 \leqslant p \leqslant 20$ AT T = 293°K

E/p (V cm^{-1} torr^{-1})	2·0	3·0	4·0	5·0	6·0
k_1	23·8	38·7	52·0	63·3	72·8
D/μ (eV)	0·601	0·977	1·31	1·60	1·84
η/p (cm^{-1} torr^{-1})			0·012	0·027	0·042

For values of E/p between 1·5 and 4 the values of η/p were too small to be accurately determined under the experimental conditions used. For this range of E/p, therefore, values of k_1 only are given (see Table 2). For $E/p \geqslant 4$ the values of η/p were found to be independent of the gas pressures used to within the limits of accuracy of the measurements. The results are included in Table 2.

(b) *Sources of Error*

The method of determining η and k_1 introduced by H.C.B. is based on the fact that the values of k_1 for electrons are in general considerably greater than those for negative ions under the same conditions. However, in the present work at the low values of E/p necessary for the investigation of the three-body attachment process the values of k_1 for the electrons were approaching those for the negative ions. The determinations of η were expected therefore to be subject to larger experimental errors than those normally encountered when using this method. The influence of the following sources of error was investigated.

(i) *Errors in the Measurement of* R.—Calculations showed that an error of $\frac{1}{2}\%$ in the measurement of R, the ratio of the currents to the sections of the anode, could lead to errors of up to 20% in η. The sensitivity of the results to small errors in R arose from the necessity of using experimental conditions which led to large values of R, these large values of R being relatively insensitive to η.

(ii) *Errors in the Values Found for* k_1.—The values of k_1 found in the experiment were largely determined by the values of R obtained for an anode/cathode separation of 2 cm. It was shown by calculation that an error of 1% in the value found for k_1 could lead to an error of approximately 5% in the value of η deduced from the measurements of R at $h = 5$ and 10 cm.

(iii) *Errors due to an Insufficiently Large Central Disk.*—Under the experimental conditions of the present investigation the stream of particles entering the diffusion chamber through the central hole in the cathode was a mixture of electrons and negative ions. Ideally, the experimental parameters are adjusted so that all the negative ions entering the diffusion chamber in this way are collected on the earthed central disk of the anode and so do not affect the measurements of R. However, at the low values of E/p of interest in the present work, it was difficult to do this while at the same time producing values of R which could be determined with the accuracy demanded by (i) above. Hence, for some combinations of p and h, "spillover" of negative ions off the earthed central disk on to the inner annulus of the anode occurred. The influence of such spillover on the values deduced for η was difficult to evaluate, but errors of 10% in η could well have been produced in this way. For example, for a stream consisting at the source hole of 90% electrons and 10% negative ions, the error due to spillover at $p = 10$, $h = 10$, and $E/p = 0 \cdot 5$ would be 10%. A stream composed of 90% electrons and 10% negative ions could be produced from a stream which was purely electronic in a distance of $0 \cdot 5$ cm at $p = 10$ and $E/p = 0 \cdot 5$.

By comparison with the errors discussed in Section II (*b*) (i)–(iii) above, errors arising from other sources (for example, those discussed by Crompton and Jory 1962) are not likely to have been significant. It can be seen that the combined errors in the measured values of η are likely to have been high, the individual values of η given in Table 1 probably being subject to errors of $\pm$10–20%. The self-consistency of the results is therefore within the experimental scatter. It should be noted that the probable errors for the values of k_1 given in Tables 1 and 2 are considerably lower than those for η, since the measured ratios R are far less sensitive to η than to k_1, particularly at low values of h and p. The tabulated values of k_1 are expected to be accurate to within $\pm 2\%$.

III. Determinations of η/p and of Ionic Mobilities using an Adaptation of Doehring's Method

As a result of the restricted range of gas pressures over which it was possible to use the method of H.C.B. for determining attachment coefficients and of the relatively large experimental errors involved in the measurements, the three-body nature of the attachment process at low E/p was not as adequately demonstrated in the experiment of Section II above as was desirable. Consequently, an attempt was made to obtain confirmation of the results of Section II in an entirely separate experiment. The experimental tube used was that later employed for determinations of the drift velocities of the negative ions formed in oxygen. The drift velocity tube was of the form used by Bradbury and Nielsen and is shown schematically in Figure 1.

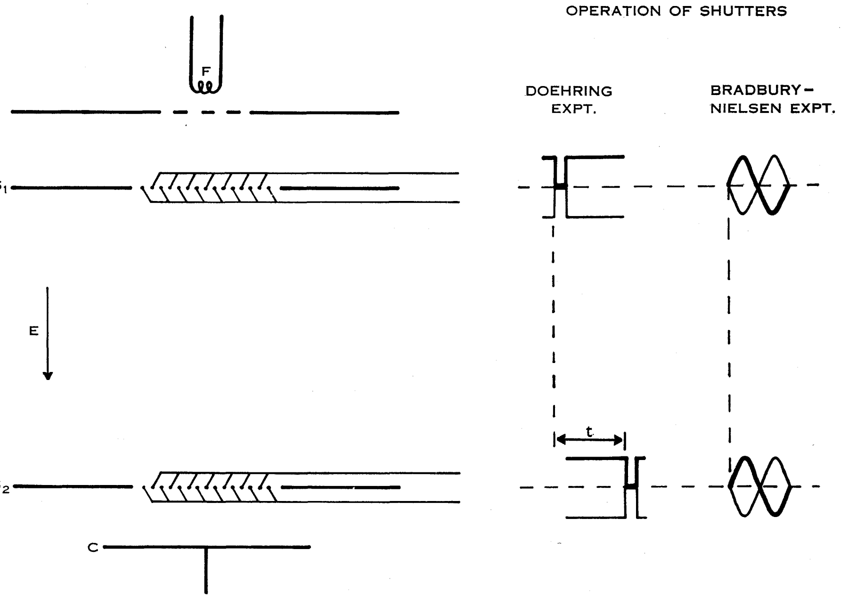

Fig. 1.—Schematic diagram of drift velocity tube and of the two methods used to operate its electrical shutters.

The Bradbury-Nielsen shutters S_1 and S_2 consisted of a large number of coplanar wires of 0·003 in. diameter with 0·018 in. between centres, alternate wires being connected together to form two sets of wires. In the work on attachment described in this section the shutters were operated using square-wave pulses of variable duration, amplitude, and repetition frequency in place of the more usual sinusoidally varying voltages. The pulses applied to the two sets of wires of a single shutter were of opposite sign and were arranged so that for the duration of a pulse the shutter was "transparent" to electrons and ions while at all other times the electrons and ions were swept to one set of the shutter wires and collected there. The pulses used to operate the second shutter S_2 were applied at the same repetition rate f as those applied to S_1, but a variable delay-time was injected between the pulses applied to the two shutters. In this way S_2 could be "opened" to the electron and ion stream a time t after S_1 was opened, t being continuously variable from 0 to $\sim 1/f$.

The present adaptation of the Doehring method differs from the original form used by Doehring in that the halves of a single shutter are coplanar, whereas each of the shutters used by Doehring consisted of two electrodes separated a short distance

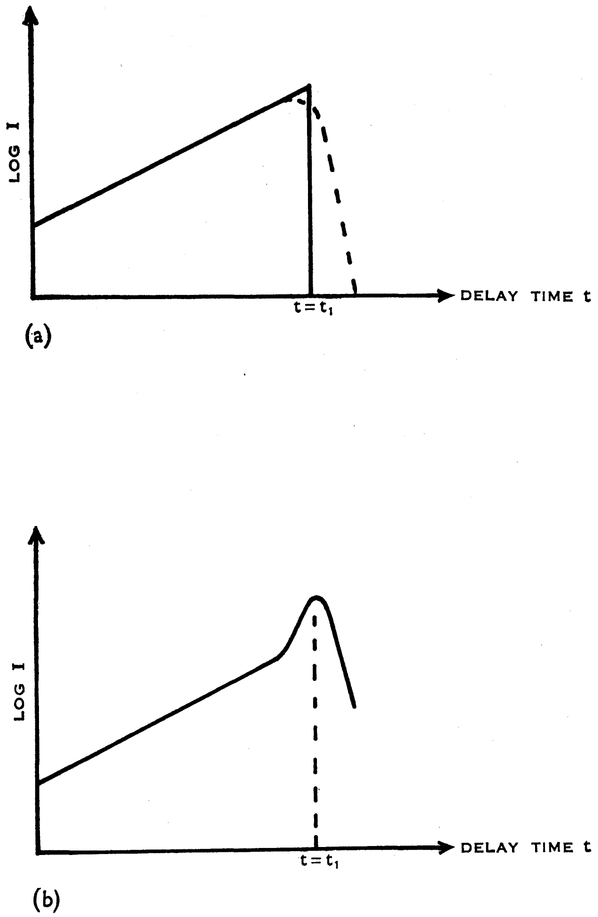

Fig. 2.—Idealized variation of ion current with delay time; (*a*) for apparatus used by C.P.B., (*b*) for apparatus used in present investigation.

from one another in the direction of the main electric field E. In the form used by C.P.B. the first shutter S_1 was dispensed with, the original electron pulses being provided by a pulsed source of ultraviolet radiation, and the second shutter S_2 was of the form used in the present work.

The dependence of the negative ion current received by the collecting electrode C (Fig. 1) on the delay time t is ideally of the form shown in Figure 2 (*a*) as a solid line, the current I being given by

$$I = I_0 \exp(\eta W_{\mathrm{i}})t, \tag{1}$$

and the time t_{i} at which the ion current falls to zero being given by

$$t_{\mathrm{i}} = d/W_{\mathrm{i}}, \tag{2}$$

where d is the distance between S_1 and S_2, and W_{i} is the drift velocity of the ions.

Obviously, the drift velocity of the ions can be determined from measurements of t_{i}, the values of η (and hence of η/p or η/p^2) then being determined from the slope of the ln I versus t curve. In general the ln I versus t curves obtained experimentally are affected by the diffusion of the ion pulses and by the finite pulse width employed. The major effect on the ln I versus t curves is to blur the cut-off at $t = t_{\mathrm{i}}$, the current following a curve of the form shown by the broken line of Figure 2 (*a*). The determination of t_{i} and hence of W_{i} and of η/p is made somewhat less precise as a result. It is worth noting that, while the ln I versus t curves obtained in the apparatus used by C.P.B. were of the form shown in Figure 2 (*a*), the curves obtained by Doehring and in the present work were of the form shown in Figure 2 (*b*). The additional current "spike" at $t = t_{\mathrm{i}}$ is caused by the transmission through both shutters of a pulse of negative ions which were formed in the space between the electron source and the first shutter. (Obviously, since there was no such region in the apparatus used by C.P.B., no spike could be produced in their ln I versus t traces.) The presence of the current spike can be an advantage, since it enables t_{i} to be determined with rather more precision than is possible if no spike occurs. However, if the number of negative ions formed before the first shutter is too high, the spike formed can make the determination of the slope of the ln I versus t curve very difficult. This did in fact occur in the present work for $E/p > 2$. In an electrode arrangement such as that of Doehring, the spike can be introduced or removed at will simply by altering the duration of the pulses applied to the first shutter. If these are sufficiently short, then the negative ions formed above the first shutter have insufficient time to pass from the first electrode of this shutter to its second electrode before the pulse is removed, and the current transmitted by the shutter is therefore purely electronic. With an apparatus such as the present one in which the two halves of the shutter are coplanar no such facility is available. Coplanar shutters do, however, possess the advantage of producing less distortion of the main electric field than do two-gauze shutters. The occurrence of a current spike at $t = t_{\mathrm{i}}$ is particularly useful in cases where more than one species of ion may be formed either by direct attachment or by a change of species of the ions originally produced. In such cases the resolving power of an apparatus having a short distance between the source of electrons and the first shutter can be considerably higher than that for an apparatus where no such region exists.

In the present investigation it was found that at least three species of ions were being produced, the relative numbers of the three species being dependent on the gas pressure and value of E/p used. Two typical current *v*. delay time curves are shown in Figure 3. The upper curve shows the presence of two species of ions. Up to Section V (*c*) (iv) we shall refer to the ions as belonging to species A, B, C, . . . , where ions of species A have a higher mobility than ions of species B and so on. The gas pressures employed were between 10 and 40 torr and the range of E/p studied was $0\cdot6 < E/p < 8$. The mobilities of the ions of species A and B were determined over this range of E/p and an estimate of the mobility of the ions of species C was made for $E/p \sim 0\cdot65$. As a result of the complication of the ln I versus t curves introduced by the presence of up to three species of ions, determinations of η/p had to be restricted to $E/p < 2\cdot0$. Two different sources of electrons were used in the measurements—an oxide-coated platinum filament and a tritium-impregnated titanium source of low energy β-particles.

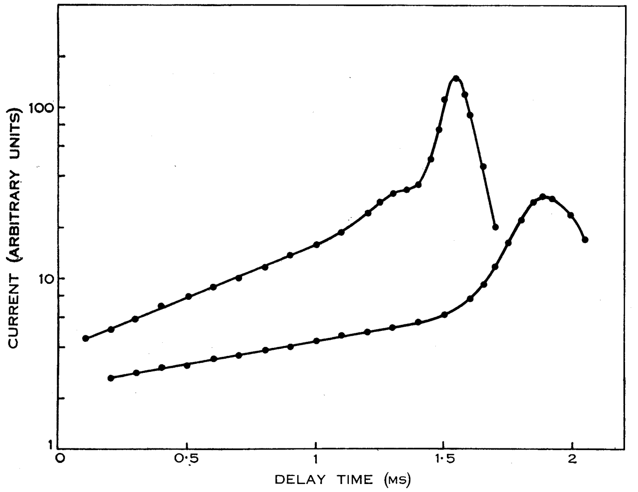

Fig. 3.—Typical current v. delay time curves obtained in Doehring type of experiment.

TABLE 3

VARIATION OF η/p^2 WITH E/p FOR $E/p \leqslant 1\cdot5$ AT 293°K

E/p (V cm^{-1} torr^{-1})	η/p^2 (cm^{-1} torr^{-2})			Mean η/p^2
	$p = 41\cdot3$	33·2	20 torr	
0·5	0·0019	0·0019	0·0020	0·0019
0·6	0·0016	0·0016	0·0016	0·0016
0·8	0·0012	0·0012	0·0012	0·0012
1·0	0·00090	0·00087	0·00090	0·00089
1·2	0·00069	0·00066	0·00070	0·00068
1·5	0·00051	0·00046	0·00053	0·00050

(a) *Results*

(i) η/p^2.—The values obtained for the variation of η/p^2 with E/p for $E/p \leqslant 1\cdot5$ are shown in Table 3. The drift velocities necessary for calculating values of η/p^2 from the measured slopes of the ln I versus t curves are believed to be those for the ions of species C (see Section V (c) (iv)). Consequently, since these drift velocities were not determined with precision until the experiments of Section IV were performed, the calculations of η/p^2 were delayed until the results described in Section IV (*a*) had been obtained. The values of η/p^2 shown in Table 3 were those obtained when the appropriate drift velocities for ions of type C were used. The tabulated values have been taken from lines of "best-fit" to the data taken at gas pressures of 41·3, 33·2, and 20 torr. The maximum scatter of the data about the lines of best-fit was $\pm 5\%$ at $p = 41\cdot 3$, $\pm 5\%$ at $p = 33\cdot 2$, and $\pm 15\%$ at $p = 20$.

(ii) *Ion Mobilities*.—As already stated, three species of negative ions were observed in the Doehring-type experiment. The zero-field mobilities (defined as in Section I) of the three species were as follows:

Species A	$\mu_0 = 3\cdot 05$	(maximum scatter $= \pm 0\cdot 06$)
Species B	$\mu_0 = 2\cdot 54$	(maximum scatter $= \pm 0\cdot 06$)
Species C	$\mu_0 \sim 2\cdot 35$.	

The mobility of the ions of type A was constant over the whole range of E/p studied ($1 < E/p \leqslant 4$) while that of the ions of type B was constant for $0\cdot 6 < E/p < 4$ and increased slowly for $4 < E/p < 8$ to a value of $2\cdot 66$ at $E/p = 8$. The observed mobilities of the three species were in agreement with the more reliable values obtained by the Bradbury-Nielsen method of Section IV and will be discussed together with the latter results in Section V (*c*).

IV. Determinations of Ion Mobilities by the Bradbury-Nielsen Method

The experimental tube used for the measurements of this section was that described in Section III and shown in Figure 1. However, the electrical shutters were now operated using sinusoidally varying voltages and the ion current reaching the collecting electrode C was observed as a function of the frequency of the alternating voltage. A current–frequency curve typical of those observed at high gas pressures is shown in Figure 4, two "orders" of the peak system being shown.

It can be seen that four species of ions were present for the particular conditions of E/p and p used in obtaining the data of Figure 4. The relative magnitudes of the four current maxima changed with changes in E/p and p and the variations could be used to assist in the identification of the various ion species. For reasons which are discussed below it is believed that the ions of the slowest species (peaks D of Fig. 4) were impurity ions emitted by the coated filament.

(*a*) *Results*

The results obtained for the variation with E/p of the mobilities of the four species of ions are shown in Figures 6(*a*), 6(*b*), and 6(*c*), together with data obtained by other workers. The mobilities of the four species of ions were observed to be independent of pressure over the whole range of pressures studied ($70 > p > 2\cdot 5$). The zero-field mobilities of the four species were found to be as follows:

Species A	$\mu_0 = 3\cdot 01$	Species C	$\mu_0 = 2\cdot 39$
Species B	$\mu_0 = 2\cdot 52$	Species D	$\mu_0 = 2\cdot 18$.

The experimental scatter of the results for each ion was $\pm 2\%$.

The ions of type A were found to have a mobility which was constant for $E/p \lesssim 10$ and which then increased with increasing E/p. The mobilities for $E/p > 10$ are not shown in Figure 6(a) as the current–frequency curves obtained in this high E/p region for ions of type A were poorly resolved. For ions of type B the mobility was constant to within the experimental scatter for $E/p < 5$ and for higher values of E/p increased slowly with increasing E/p. The data obtained for ions of type C were obtained in two sets, one set of data being obtained at high p and low E/p and the other set being obtained at low p and high E/p. It was not found possible to extend the data for low p to values of E/p below $E/p = 12$, since at lower values of E/p ions of type C were not present in sufficient numbers for their current v. frequency curves to be examined. Attempts to extend the data for high p to higher values of E/p also failed,

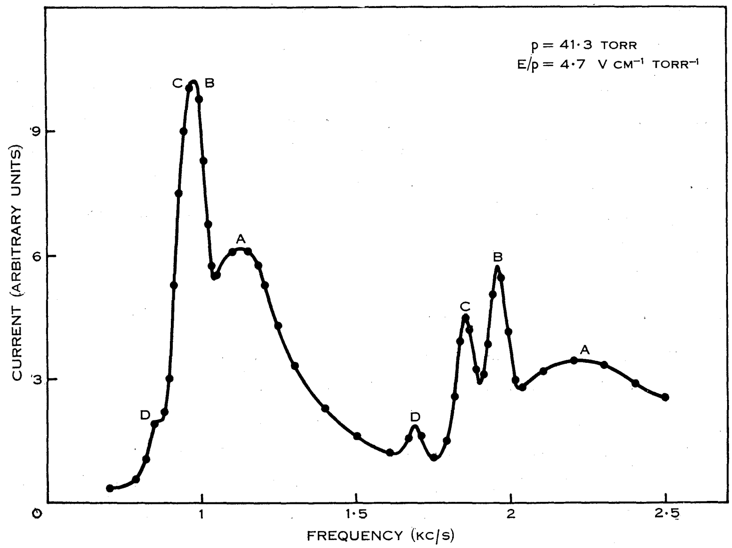

Fig. 4.—Typical current v. frequency curve obtained in Bradbury-Nielsen type of experiment.

the main reason being that electrical breakdown of the gas in the tube occurred. The reason for believing that the sets of data obtained at high and low pressures refer to the same species of ions is given in Section V (c) (iv). Ions of the fourth species (type D), which are thought to be impurity ions, had a mobility which was constant at $\mu_0 = 2 \cdot 18$ for $1 < E/p < 5$.

V. Discussion of Results

(a) *Results for* k_1

Figure 5 shows all the available data for the variation of k_1 with E/p for electrons in oxygen. It is seen that the present data are in excellent agreement at $E/p \geqslant 4$ with the data of H.C.B. At lower values of E/p the present results lie up to 8% below values obtained earlier in this laboratory by Crompton and Sutton. These earlier results have been quoted by Huxley and Crompton (1962) and by C.P.B. but were not published, as the effect of attachment on the measurements was not established.

The agreement between the present results and those of Townsend and Bailey, of Brose, and of Healey and Kirkpatrick is, with the exception of Brose's results for $E/p \leqslant 2$, not good. Brose's results for $E/p \leqslant 2$ are in satisfactory agreement with the present work.

(b) *Results for* η/p

It can be seen from a comparison of Tables 1 and 3 that the results obtained for η/p^2 for $E/p \leqslant 1 \cdot 5$ by the two entirely independent methods of Sections II and III are in good agreement. The results, particularly those described in Section III, confirm the observation by C.P.B. and others that the parameter η/p is pressure

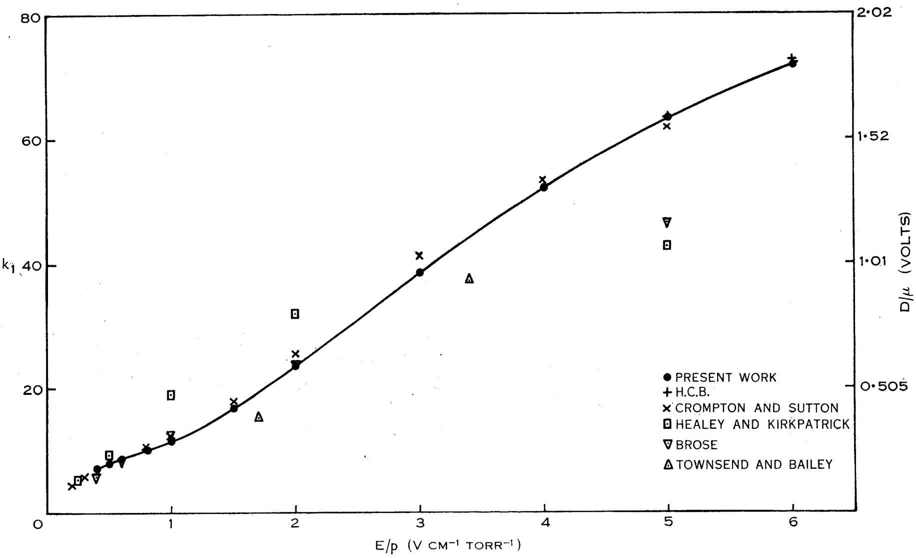

Fig. 5.—Variation of k_1 with E/p for $0 < E/p \leqslant 6$ at 293°K.

dependent for this range of E/p. For a given value of E/p in the range $0 \cdot 4 \leqslant E/p \leqslant 1 \cdot 5$, η/p^2 was found to be constant for gas pressures of between 10 and 40 torr. The agreement between the results of Tables 1 and 3 and those given by C.P.B. appears to be excellent, the results agreeing to within 5%. However, it can be seen from Figure 6(*b*) that for $E/p \leqslant 3$ the ions observed by C.P.B. had a mobility of $2 \cdot 7$ and hence this was the value used in their calculations of η/p^2. The corresponding mobility used in the present work was $2 \cdot 39$. It is probable that this discrepancy of 12% in the values adopted for μ_0 should be reflected in a 12% difference between the values of η/p^2 quoted by C.P.B. and those given in Tables 1 and 3 above.

At the highest values of E/p used in the present work ($E/p = 4$, 5, and 6) the results obtained for η/p by H.C.B.'s diffusion method merged smoothly with the results obtained earlier by H.C.B., using the same apparatus. Further, the results (given in Table 2) are in good agreement with Doehring's, so that for $4 \leqslant E/p \leqslant 8$

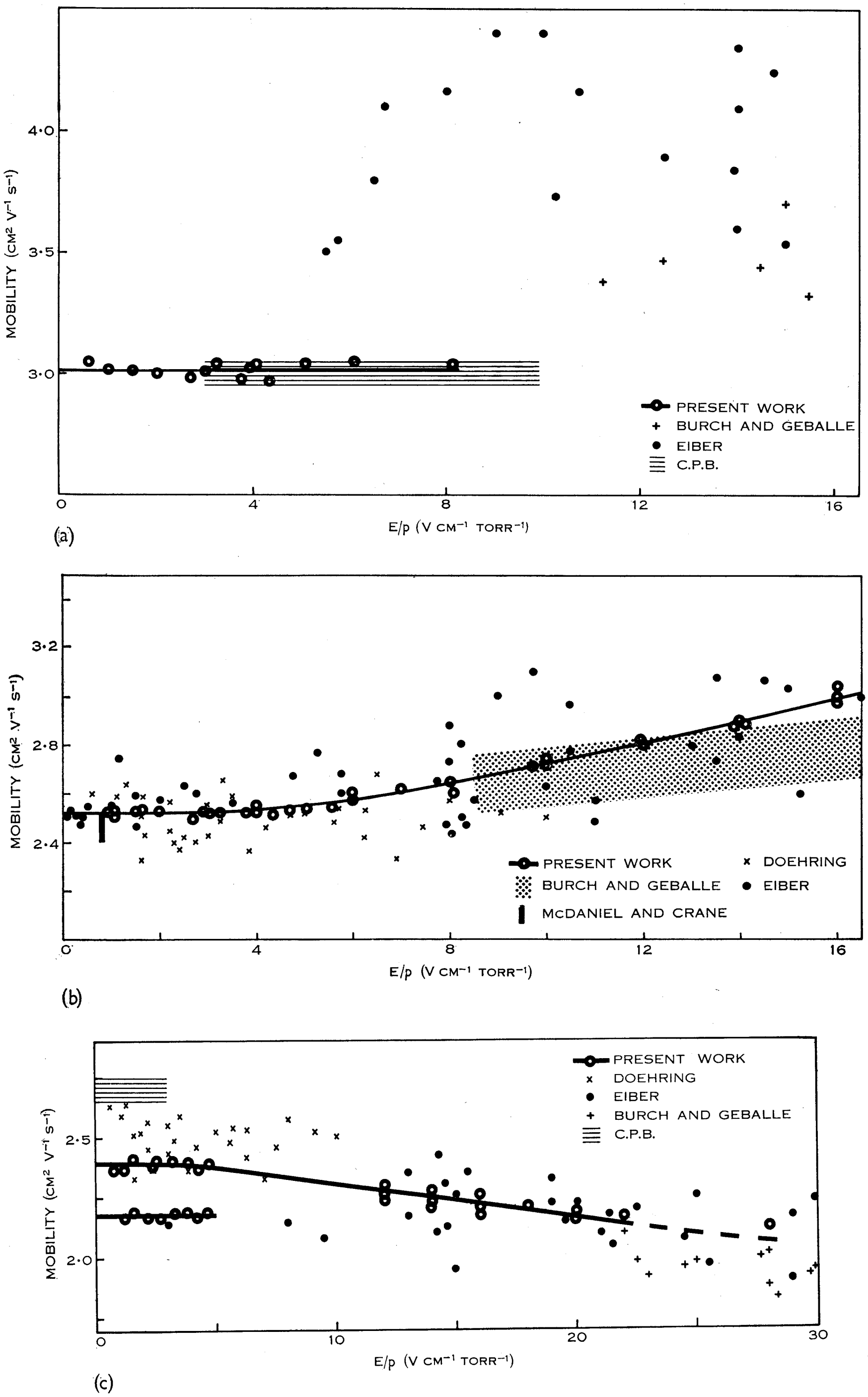

Fig. 6.—Variation of ion mobilities with E/p at 293°K. (*a*) Ions of species A; (*b*) ions of species B; (*c*) ions of species C and D.

the results of H.C.B., extended by the present work, agree with Doehring's to within 10% and differ by up to 45% from the results of C.P.B. and by even larger amounts from the results of Bradbury (1933), of Healey and Kirkpatrick (1939), and of Herreng (1952). It has been assumed in the present discussion that for $4 < E/p < 10$ the gas pressures used in the various swarm investigations have been such that the dominant attachment process has been the two-body dissociative attachment process:

$$e + O_2 \rightarrow (O_2^-) \text{ unstable} \rightarrow O + O^- + \text{Kinetic Energy.} \tag{3}$$

If the gas pressures used are very high then some contribution from the three-body process is to be expected and has in fact been observed in measurements carried out in air by Dutton, Harris, and Llewellyn Jones (1963).

(c) *Ion Mobility Results*

The results obtained for the dependence on E/p of the mobilities of the various species of negative ions observed in oxygen will first be discussed without any attempt being made to identify the species. In Section V (*c*) (iv) the available evidence concerning the identity of the ions will be briefly discussed.

(i) *Ions of Species A*.—It can be seen from Figure 6(*a*) that the present results for the ions of type A are in excellent agreement with those obtained by C.P.B. and extend their measurements down to $E/p = 0\cdot5$. The agreement with the data obtained by Eiber for what is presumed to be the same species of ion is poor, the present results and those of C.P.B. lying outside the large scatter of Eiber's data. It should be noted that the scatter of Eiber's data was attributed to changes in the nature of the ions as they passed through the apparatus and not to experimental errors. The latter were reported to be $\leqslant 7\%$. The results obtained by Burch and Geballe could be extrapolated to merge at low E/p with our data and those of C.P.B.

(ii) *Ions of Species B*.—Most of the available mobility data for oxygen have been obtained for ions of species B. The extrapolated zero-field mobility of $2\cdot52 \pm 0\cdot05$ obtained in the present work may be compared with values of $2\cdot46 \pm 0\cdot06$ (McDaniel and Crane 1957), $2\cdot50 \pm 0\cdot05$ (Eiber 1963*a*, 1963*b*, 1963*c*), $2\cdot48 \pm 0\cdot10$ (Doehring 1952), $2\cdot56 \pm 0\cdot12$ (Burch and Geballe 1957*a*, 1957*b*). It is seen that the general agreement is good. It should be noted that Doehring's value is $2\cdot48$ and not $2\cdot68$ as stated by C.P.B. and by McDaniel (1964). The value of $2\cdot68$ quoted by the latter authors was that obtained by Doehring before normalizing to a gas number density of $2\cdot69 \times 10^{19}$ mol/cm³. The reduced mobility of $2\cdot48$ is in agreement with the other values quoted above and does not, as claimed by C.P.B., agree with the value of $2\cdot7$ which they obtained for ions formed at low E/p.*

The variation of μ with E/p observed in the present work is similar to that observed by Burch and Geballe and by Eiber, although the actual values differ by up to 10%. In view of the experimental scatter of the results of the three investigations, this discrepancy is not significant.

* The value of $2\cdot7$ obtained by C.P.B. has been redetermined recently (Phelps, personal communication 1964). The redetermined value of $2\cdot42$ is likely to be that for ions of type C and is therefore to be compared with the present value of $2\cdot39$.

(iii) *Ions of Species C and D.*—The available data for ions having a mobility of less than $2\cdot5$ are rather limited and are shown in Figure 6. At high values of E/p (>10) the present results are in reasonable agreement with those of Eiber and show less scatter. The results of Burch and Geballe for $E/p > 20$ lie up to 10% below the present data. Doehring's data are shown in Figure 6(*c*) since there is some possibility that part of the data may refer to ions of type C.

The present data at low E/p for ions of type C considerably extend the range of E/p over which data for these ions are available. The zero-field mobility of the ions ($2\cdot39\pm0\cdot05$) is in excellent agreement with that of $2\cdot42$ reported for a temperature of 300°K by Phelps (personal communication, 1964).

As already stated, it is possible that the ions of species D were impurity ions coming from the coated filaments used. It was found that the magnitude of the current peaks obtained for ions of this species appeared to be largely independent of the gas pressures used and of the electric fields maintained between the filament and the shutter S_1. This behaviour seemed to indicate that the ions originated at the coated filament and that they were therefore likely to be impurity ions.

(iv) *Ion Identification.*—The need for positive identification of the ions observed in mobility studies has been recognized for many years. However, the identification of the ions under conditions similar to those existing in the mobility experiments poses formidable problems. Recently, Eiber (1963*b*, 1963*c*) has used an electrical shutter consisting of two coplanar sets of fine wires having very small gaps ($\leqslant 0\cdot00025$ in.) between adjacent wires to determine the ratio e/m (where m is the mass of the ions and e is their electric charge) for the positive and negative ions produced in oxygen under conditions similar to those used in his mobility tube. At a pressure of $1\cdot7$ torr he observed the presence of O^-, O_2^+, and O_3^- ions and obtained qualitative evidence of the presence of O_2^- ions. The observation of O^- and O_3^- ions is consistent with his earlier suggestion (Eiber 1963*a*) and that of Burch and Geballe that the three species of ions observed in their experiments were O^-, O_2^-, and O_3^-.

Burch and Geballe believed the O^- ions to be formed by dissociative attachment according to equation (3) above and the O_2^- and O_3^- ions to be formed from the O^- ions by secondary collisions. The most likely processes leading to the production of O_2^- and O_3^- ions were thought to be

$$O^-+2O_2 \rightarrow O_3^-+O_2 \tag{4}$$

and

$$O^-+O_2 \rightarrow O_2^-+O. \tag{5}$$

As emphasized by C.P.B., reaction (5) can only occur before the O^- ions lose the kinetic energy derived by them from the initial dissociative attachment collision. The parent O^- ions were taken by Burch and Geballe to be the fastest species of ions observed in their experiments and the O_2^- ions to be the slowest species. On the basis of Eiber's identification and the work of Burch and Geballe the ions of type A of the present paper would appear to be O^- ions, the ions of type B to be O_3^- ions, and the ions of type C to be O_2^- ions.

Confirmation of the identification of the ions of type A as O^- ions was obtained from a consideration of the form of the current *v.* frequency curves obtained for these ions in the Bradbury-Nielsen experiment. It can be seen from Figure 4 that the current *v.* frequency curve for the ions of type A is markedly different from that obtained for the other species. In particular, the decrease in current at frequencies above that giving maximum transmission is very slow. The observed variation of current with frequency can be readily explained as follows:

At the frequencies used to determine the mobilities of the negative ions the time in any cycle for which shutter S_1 transmits ions and electrons is long enough for the electrons in the pulse to set up a steady state distribution in the space between S_1 and S_2. For $E/p \gtrsim 3$ the electrons attach to form O^- ions, the distribution of ions set up being given by

$$n_x = A\mathrm{e}^{-\eta x}, \tag{6}$$

where n_x = number density of ions at a distance x from S_1, and A is a constant. The ions formed in this way drift towards S_2, under the influence of the applied electric field, with a drift velocity W, and the ion current received by the collecting electrode C (Fig. 1) is of course given as before by equation (1), where t, the time interval between the opening of S_1 and S_2, is now given by $t = 1/2f$, f being the frequency of the alternating potentials used to operate S_1 and S_2.

When the current *v.* frequency curves obtained for the ions of type A were plotted as $\ln I$ versus $1/f$ curves they were found to satisfy an equation of the form given by equation (1), and for $E/p = 4 \cdot 3$ and $4 \cdot 75$ the values of η/p calculated from the curves were in good agreement with the results of Section II above. Hence, the ions of type A are very probably O^- ions and, as assumed in Section V(c) (i) of the same species as the fastest ions observed by Eiber, by Burch and Geballe, and by C.P.B.

The behaviour of the ions of species B observed in the present work was so similar to that observed by Eiber for ions which he later identified as O_3^- ions that no further identification is necessary and the ions of species B are accordingly taken to be O_3^- ions. This identification agrees with that postulated by Burch and Geballe and is generally accepted.

There has as yet been no direct confirmation of Burch and Geballe's hypothesis that the slowest ions observed by them, which were assumed in Section V(c) (iii) above to be the same species as the ions of species C studied in the present work, were O_2^- ions. If this identification is correct then it is to be expected that O_2^- ions will be produced in oxygen by two entirely different mechanisms. At high E/p and low p, O_2^- ions will be formed, by a reaction such as that represented by equation (5), from the O^- ions produced by dissociative attachment, while, at low E/p and high p, O_2^- ions will be formed by a three-body attachment process such as:

$$e + O_2 \rightleftharpoons O_2^-; \qquad O_2^- + O_2 \rightarrow O_2^- + O_2 + \text{energy} \tag{7}$$

or

$$e + 2O_2 \rightarrow (O_4^-) \rightarrow O_2^- + O_2 + \text{energy}. \tag{8}$$

The behaviour of the ions of type C in the present work was consistent with this picture, one of the groups of ions observed at low E/p and high p having a mobility which agreed with that obtained by extrapolating the high E/p data for the ions of type C. Consequently there is some justification for taking these ions to be O_2^- ions, as postulated by Burch and Geballe. In addition, as already stated, Eiber obtained qualitative evidence of the presence in his mass-identification experiments of O_2^- ions. The ions were observed only for $E/p > 20$ and were presumably formed from O^- ions by a reaction such as that represented by equation (5).

(v) *Comparison with Theory.*—It is of interest to compare the zero-field mobilities of the various species of ions with the values predicted by theory. The values obtained from the polarization limit of Langevin's equation (Langevin 1905) are shown in Table 4 together with the available experimental data.

TABLE 4

COMPARISON OF THEORETICAL AND EXPERIMENTAL ZERO-FIELD MOBILITIES

Probable Ion Species	Langevin Equation	Experimental Zero-field Mobilities		
O^-	3·35	3·01 [a]	3·0 [b]	
O_2^-	2·73	2·39 [a]	2·7 [b]	2·42 [g]
O_3^-	2·49	2·52 [a]	2·48 [c]	
		2·50 [d]	2·56 [e]	2·46 [f]
O_4^-	2·37			

[a] Present work.
[b] C.P.B.
[c] Doehring.
[d] Eiber.
[e] Burch and Geballe.
[f] McDaniel and Crane.
[g] Phelps.

It is seen from Table 4 that there is some measure of agreement between theory and experiment, particularly for O_3^- ions. The agreement for O^- ions is not good, while the theoretical value of the reduced mobility of O_2^- ions is considerably higher than that observed experimentally. It should be remembered that the theoretical value given for O_2 in Table 4 takes no account of the occurrence of charge exchange between the ions and neutral gas molecules.

VI. CONCLUSIONS

The present investigation has confirmed the occurrence in oxygen of a three-body attachment process. The results obtained for the dependence of η/p^2 on E/p for $E/p < 2$ agree with those obtained by C.P.B. For $4 < E/p < 6$ the values of η/p obtained for the two-body, dissociative attachment process are in better agreement with those found by Doehring and by H.C.B. than with those found by C.P.B.

In addition to the results for the dependence of the attachment coefficients for the two processes on the parameter E/p, information concerning the mean energy of electrons in oxygen for $0 \cdot 4 < E/p < 6$ has been obtained which agrees at the higher E/p values with that of H.C.B. and extends their measurements to lower E/p values.

VII. Acknowledgments

The author wishes to thank Professor Sir Leonard Huxley, Dr. R. W. Crompton, and the other members of the Ion Diffusion Unit for their willing assistance during this investigation. The cooperation of Mr. G. R. Graf in setting up the electronic equipment used in Section III is gratefully acknowledged. The author is grateful to Dr. A. V. Phelps for supplying, in advance of publication, his revised value for the zero-field mobility of O_2^- ions.

VIII. References

Bradbury, N. E. (1933).—*Phys. Rev.* **44**: 883.

Bradbury, N. E., and Nielsen, R. A. (1936).—*Phys. Rev.* **49**: 388.

Branscomb, L. M. (1957).— *Advanc. Electronics Electron Phys.* **9**: 43.

Brose, H. L. (1925).—*Phil. Mag.* **50**: 536.

Buchel'nikova, N. A. (1959).—*Soviet Phys. J.E.T.P.* **8**: 783.

Burch, D. S., and Geballe, R. (1957*a*).—*Phys. Rev.* **106**: 183.

Burch, D. S., and Geballe, R. (1957*b*).—*Phys. Rev.* **106**: 188.

Chanin, L. M., Phelps, A. V., and Biondi, M. A. (1959).—*Phys. Rev. Letters* **2**: 344.

Chanin, L. M., Phelps, A. V., and Biondi, M. A. (1962).—*Phys. Rev.* **128**: 219.

Craggs, J. D., Thorburn, R., and Tozer, B. A. (1957).—*Proc. Roy. Soc.* A **240**: 473.

Crompton, R. W., and Jory, R. L. (1962).—*Aust. J. Phys.* **15**: 451.

Doehring, A. (1952).—*Z. Naturf.* **7*a***: 253.

Dutton, J., Harris, F. M., and Llewellyn Jones, F. (1963).—*Proc. Phys. Soc. Lond.* **82**: 581.

Eiber, H. (1963*a*).—*Z. angew. Phys.* **15**: 103.

Eiber, H. (1963*b*).—*Z. angew. Phys.* **15**: 461.

Eiber, H. (1963*c*).—Proc. 6th Int. Conf. on Ioniz. Phen. in Gases, Vol. 1, p. 305.

Healey, R. H., and Kirkpatrick, C. B. (1939).—*Quoted in* "The Behaviour of Slow Electrons in Gases." (Healey and Reed.) p. 94. (Amalgamated Wireless: Sydney.)

Herreng, P. (1952).—*Cah. Phys.* **33**: 7.

Hurst, G. S., and Bortner, T. E. (1959).—*Phys. Rev.* **114**: 116.

Huxley, L. G. H., and Crompton, R. W., (1962).—*In* "Atomic and Molecular Processes." (Ed. D. R. Bates.) p. 359. (Academic Press: New York.)

Huxley, L. G. H., Crompton, R. W., and Bagot, C. H. (1959).—*Aust. J. Phys.* **12**: 303.

Langevin, P. (1905).—*Annls. Chim. Phys.* **5**: 245.

van Lint, V. A. J., Wikner, E. G., and Trueblood, D. L. (1960).—*Bull. Am. Phys. Soc.* **5**: 122.

Loeb, L. B. (1955).—"Basic Processes of Gaseous Electronics." (Univ. California: Berkeley.)

Loeb, L. B. (1956).—"Handbuch der Physik." Vol. 21, p. 445. (Springer: Berlin.)

McDaniel, E. W. (1964).—"Collision Phenomena in Ionized Gases." (Wiley: New York.)

McDaniel, E. W., and Crane, H. R. (1957).—*Rev. Sci. Instrum.* **28**: 684.

Prasad, A. N., and Craggs, J. D. (1961).—*Proc. Phys. Soc. Lond.* **77**: 385.

Prasad, A. N., and Craggs, J. D. (1962).—"Atomic and Molecular Processes." (Ed. D. R. Bates.) p. 206. (Academic Press: New York.)

Schulz, G. F. (1961).—*Bull. Am. Phys. Soc.* **6**: 387.

Townsend, J. S., and Bailey, V. A. (1921).—*Phil. Mag.* **42**: 873.