THE DIFFUSION OF ELECTRONS IN DRY, CARBON DIOXIDE FREE AIR

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Summary

Values of Townsend's energy factor k_1 for electrons in dry, carbon dioxide free air have been determined as a function of the parameter E/p for $0 \cdot 2 < E/p < 40$ at a temperature of 293°K. The results are first compared with those of other workers and are then utilized in a recomparison of the cross sections for electron attachment deduced from swarm and beam-type experiments.

I. Introduction

During recent years there has been considerable interest in the behaviour of electrons having mean energies of up to 5 eV in dry air e.g. Harrison and Geballe (1953*a*, 1953*b*), Craggs, Thorburn, and Tozer (1957), Buchel'nikova (1958), Prasad (1959), Kuffel (1959), Prasad and Craggs (1960), Dutton, Llewellyn Jones, and Palmer (1961), and Dutton, Harris, and Llewellyn Jones (1963*a*, 1963*b*). These investigations have been largely concerned either with measurements of ionization and attachment coefficients for electrons in dry air or, alternatively with measurements of the cross sections for ionization and attachment. In comparing the results of these various investigations, and also in attempting to correlate the behaviour of electrons in air with that in oxygen and nitrogen, it is of interest to have available reliable data for the variation with E/p (where E = electric field in V/cm and p = gas pressure in torr) of Townsend's energy factor k_1 for electrons in dry air which is free from carbon dioxide and other condensable impurities. At present the only data available for $E/p > 20$ are those of Townsend and Tizard (1913) while for $E/p < 20$ additional measurements have been made by Bailey (1925) and in this laboratory by Crompton, Huxley, and Sutton (1953) (referred to as C.H.S. in what follows). The present paper gives the results obtained in an investigation of the variation of k_1 with E/p over the range $0 \cdot 2 < E/p < 40$. The results are also presented in terms of the parameter D/μ, where D = coefficient of diffusion and $\mu = W/E$, W being the drift velocity of the electrons.

II. Experimental Procedure

The apparatus used in the present investigation has been fully described by Crompton and Jory (1962) and is shown schematically in Figure 1.

Electrons generated by the heated platinum filament F entered the diffusion chamber through the small hole at the centre of the cathode C and drifted under the influence of the applied uniform electric field to the receiving electrode A. The anode A comprised a central disk and surrounding annuli. From measurements of the ratios

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of the currents received by the sections of the anode, values of k_1 could be determined. In the present investigation, the ratio R of the current to the annulus A_2, to the sum of the currents received by the annuli A_2 and A_3 was measured, the central disk A_1 being earthed at all times. Experimental conditions were chosen so that any negative ions formed by electron attachment and passing through the source hole fell on A_1.

The air used in the investigation was obtained from outside the laboratory. The samples were stored over phosphorus pentoxide and before entering the diffusion apparatus passed through three liquid air traps, remaining in contact with the last trap during the course of the experiment. The results obtained did not indicate any variation in the composition of the gas samples used.

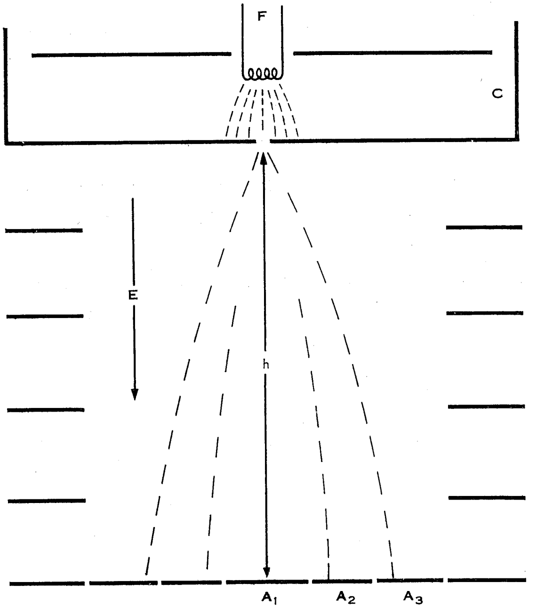

Fig. 1.—Schematic diagram of apparatus.

Measurements of the ratio R were made for values of h, the length of the diffusion chamber, between 2 and 10 cm and for gas pressures between $1\cdot5$ and 30 torr. Calculations were carried out to establish the influence on the analysis of the experimental data of the following phenomena:

(i) the formation in the diffusion chamber of negative ions formed by electron attachment,

(ii) ionization of the gas molecules in collisions with the electrons,

(iii) the spatial variation in the diffusion chamber of D/μ.

The evaluation of the effects of (i) and (ii) above showed that, except for $E/p < 1\cdot5$, no significant errors would be introduced if the experimental data were analysed on the assumption that no attachment or ionization was taking place. These simplifying assumptions were therefore made in obtaining the results described in the following section. The maximum error introduced by ignoring the influence of electron attachment was found to be 1%, while that introduced by ignoring ionization was at most $\frac{1}{4}$%. It should be emphasized that if later determinations of ionization and attachment coefficients yield coefficients which are greatly in excess of currently accepted values, the necessary re-analysis of the present data could easily be undertaken.

The usual analysis of experimental data obtained using a Townsend-type diffusion apparatus, assumes that the electrons possess a distribution of energy which is independent of position. It has been shown by Parker (1963) that under certain conditions this assumption is not correct. The magnitude of the error introduced by ignoring the spatial distribution of energies depends markedly on the ratio b/h (where b is the radial distance at which the determination of D/μ is made and h is the length of the diffusion chamber). In the present apparatus, values of b/h between $0 \cdot 17$ and $0 \cdot 50$ were used, so that according to Parker's work the maximum errors to be expected in D/μ range between $\frac{1}{2}$% at $b/h = 0 \cdot 17$ and 5% at $b/h = 0 \cdot 50$. In fact, however, the values of D/μ obtained experimentally at the various values of b/h agreed to within the experimental error of ± 1%. The good agreement is perhaps attributable to the estimate of a 5% error for $b/h = 0 \cdot 50$ being a pessimistic one; the analysis carried out by Parker (1963) takes no account of the boundary conditions appropriate to the diffusion apparatus, and it may well be that when these are included in the analysis the expected errors in D/μ will be reduced. An alternative explanation of the good agreement might be thought to be the neglect in the analysis of the experimental data of the influence of electron attachment. However, calculations based on the attachment data of Prasad (1959) showed that errors of the type discussed by Parker could not have exceeded $1\frac{1}{2}$% if they were to be masked by attachment.

In addition to (i), (ii), and (iii) above, Crompton and Jory (1962) have discussed in detail other sources of error which need not be discussed further here.

It is concluded from the above that the values of k_1 given in Table 1 are accurate to better than $+2$%, -1%.

III. Results

For $1 \cdot 5 < E/p < 20$, the results obtained for k_1 as a function of E/p were in excellent agreement with those obtained earlier in this laboratory (with a different apparatus) by C.H.S. The results agreed to within the experimental error of the present investigation. The agreement with the earlier results of Townsend and Tizard and of Bailey was also reasonably good.

The results obtained in the present work for $20 < E/p < 40$ are summarized in Table 1 and are shown in Figure 2. They extend the range of the measurements of C.H.S. to cover the range of values of E/p of interest in ionization and attachment studies. The only other measurements for values of $E/p > 20$ of which we are aware, are those of Townsend and Tizard. These measurements fall up to 15% below the results given in Table 1. The effects of this discrepancy of 15% are discussed in the following section.

The good agreement obtained between the values of k_1 measured at high values of E/p (> 20) at various combinations of h and p confirmed that the neglect of the influence of attachment on the measurements of R was fully justified.

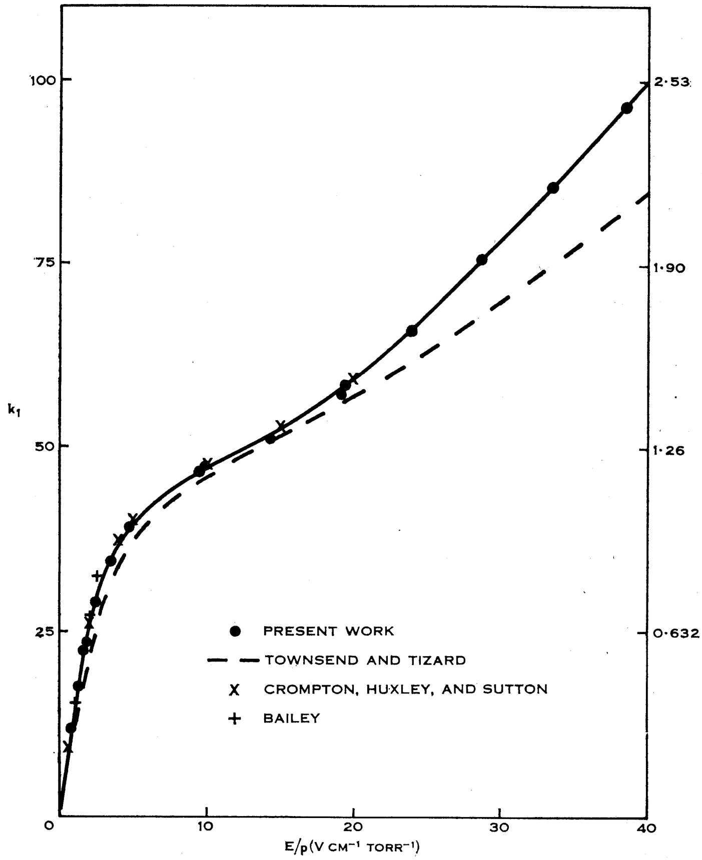

Fig. 2.—Variation of k_1 with E/p for electrons in dry air for $0 \cdot 2 < E/p < 40$ at 273°K.

TABLE 1

RESULTS FOR THE VARIATION OF k_1 WITH E/p FOR $20 < E/p < 40$ AT A TEMPERATURE OF 293°K

E/p	20	25	30	35	40
k_1	59·5	68·3	78·0	88·8	100
D/μ	1·50	1·73	1·97	2·24	2·53

IV. Attachment and Ionization Cross Sections

Prasad (1959) and Prasad and Craggs (1960) have compared the cross sections for attachment and ionization in dry air deduced from what we may call "swarm-type" experiments, with those deduced from beam-scattering experiments. The method employed has been fully described by them and will not be given here.

Since the form of the distribution of electron velocities in air is not yet known, their calculations were carried out assuming the distribution to be alternatively a Maxwellian or Druyvesteyn distribution. The calculations involved the use as auxiliary data of values of Townsend's energy factor k_1 and of the drift velocity W of the electrons. The values used for k_1 and W were those of Townsend and Tizard. The comparison showed a Maxwellian distribution of velocities to give a reasonable degree of agreement between the results of the various experiments.

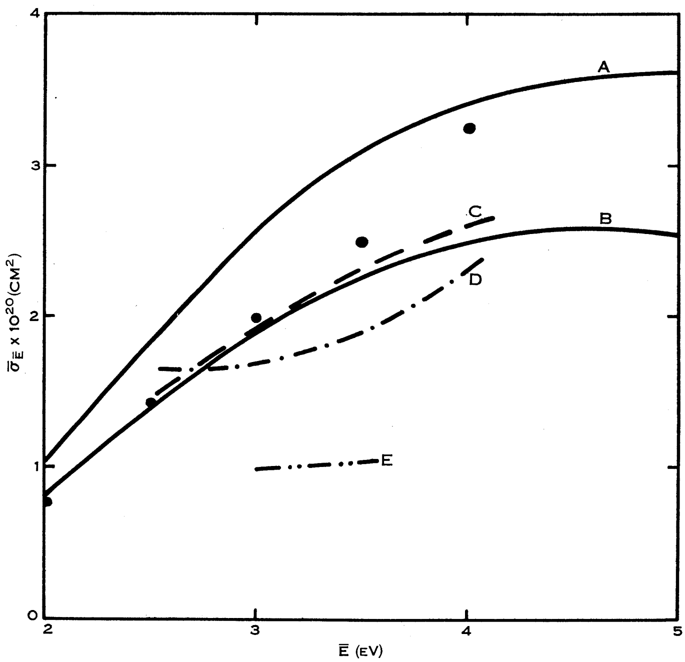

Fig. 3.—Variation of mean cross section, $\bar{\sigma}_{\bar{E}}$, for attachment with mean energy $\bar{E}$ for electrons in dry air. Maxwellian distribution of velocities assumed. Curve A, scattering data of Craggs, Thorburn, and Tozer (Prasad and Craggs 1960); curve B, scattering data of Buchel'nikova (Prasad and Craggs 1960); curve C, calculated from Prasad's data for η/p using values of k_1 given in Table 1 and Townsend and Tizard's values of W; curve D, as curve C, for Harrison and Geballe's values of η/p; curve E, as curve C, for Dutton, Harris, and Llewellyn Jones' values of η/p. Points ●: values calculated by Tozer (Prasad 1959).

In view of the differences between the values of k_1 given in Table 1, and those of Townsend and Tizard, we have repeated Prasad and Craggs' calculations using the data of Table 1. A Maxwellian velocity distribution again gave the better agreement and the recalculated attachment cross sections for this distribution are shown in Figure 3. Curves A and B of Figure 3 show the cross sections deduced from the beam-scattering experiments of Craggs, Thorburn, and Tozer (1957) (curve A) and of Buchel'nikova (1958) (curve B). These curves are to be compared with those deduced from the swarm-type experiments of Prasad (1959), Harrison and Geballe (1953*a*, 1953*b*), and of Dutton, Harris, and Llewellyn Jones (1963*a*).

When analysed using Townsend and Tizard's data for k_1 and W, Prasad's measured values of attachment coefficients gave cross sections which fell midway between curves A and B. If, however, Prasad's data are re-analysed using the values of k_1 given in Table 1, the resulting cross sections are those shown as curve C in Figure 3. It is seen that Prasad's results are now in excellent agreement with the scattering data of Buchel'nikova.

Curve D (Fig. 3) shows the cross sections recalculated from the swarm data of Harrison and Geballe. There is again reasonable agreement with the data of Buchel'nikova and of Prasad. The cross sections deduced from the measurements of Dutton, Harris, and Llewellyn Jones (curve E), however, lie well below those from the other investigations.

Figure 3 also shows the cross sections calculated by Tozer (Prasad 1959) for dissociative attachment assuming a Maxwellian distribution. For mean energies $\bar{E} \leqslant 3 \cdot 5$ eV the agreement with curves B and C is good.

The recalculated ionization cross sections are not shown in the present paper but again a Maxwellian distribution gave better agreement than did a Druyvesteyn distribution, the measure of agreement being similar to that found by Prasad and Craggs.

V. Three-body Electron Attachment

It is known from the work of Hurst and Bortner (1959) and of Chanin, Phelps, and Biondi (1962) that a 3-body attachment process occurs in oxygen and in mixtures of oxygen with nitrogen, helium, and other gases. Calculations showed that for the particular experimental conditions of the present investigation the influence of such an attachment process should become evident for values of $E/p < 1 \cdot 5$. This was in fact observed. When analysed under the simplifying assumption that the influence of attachment was negligible, the measured ratios R for $E/p < 1 \cdot 5$ gave values of k_1 which were dependent on the gas pressure and geometry used, and which fell considerably below the earlier C.H.S. values. The C.H.S. values were obtained in an apparatus with a short diffusion chamber ($h = 1$ and 2 cm) and at low gas pressures. Under these conditions, the neglect of the 3-body attachment process introduced no significant errors into the determination of k_1. Thus, the C.H.S. values can be used as standard values in a re-analysis of the present data for $E/p < 1 \cdot 5$. The data were re-analysed to give approximate values of η/p, the attachment coefficient. The values of η/p obtained in this way were dependent on the gas pressure and were not inconsistent with the coefficients measured at corresponding values of E/p in oxygen by Chanin, Phelps, and Biondi, provided due allowance was made for the 80% of nitrogen in air and for the relative efficiencies of oxygen and nitrogen molecules as stabilizing molecules in the 3-body attachment process (Hurst and Bortner 1959; Chanin, Phelps, and Biondi 1962).

In a recent paper Dutton, Harris, and Llewellyn Jones (1963*b*) deduced values of the 3-body attachment coefficient for air from their growth of current measurements at $E/p \approx 35$. They then compared these values with the value obtained by extrapolation of the low energy data of Chanin, Phelps, and Biondi and of Hurst and Bortner. The value obtained for η/p^2 by this extrapolation was $1 \cdot 0 \times 10^{-6}$, the calculation involving the use of an extrapolation of the C.H.S. data for k_1. If the values of k_1 given in Table 1 are used in the calculations in place of the extrapolation of the C.H.S. data, the value obtained for η/p^2 becomes $0\cdot84\times10^{-6}$. This reduction of 15% in η/p^2 does not affect the conclusions drawn by Dutton, Harris, and Llewellyn Jones from their calculations.

VI. Conclusions

Values of k_1 for electrons in dry air have been determined at a temperature of 293°K over a wide range of E/p $(0\cdot2 < E/p < 40)$. For values of $1\cdot5 < E/p < 20$ the results confirm the earlier results of Crompton, Huxley, and Sutton while for $E/p > 20$ the results differ by up to 15% from those of Townsend and Tizard which are the only other results available.

The values of k_1 obtained for $E/p > 20$ have been used in a re-evaluation of the comparison previously carried out by Prasad and Craggs of the cross sections for attachment deduced from scattering and swarm-type experiments. By so doing, the measure of agreement for a Maxwellian distribution of velocities was markedly improved. The calculations emphasize the need for using reliable auxiliary data for k_1 and W (particularly for k_1) in such comparisons.

For values of $E/p < 1\cdot5$ the present measurements exhibited the influence of the 3-body attachment process known to occur in oxygen. The present results when taken together with those of C.H.S. yielded approximate values of the attachment coefficient for the 3-body process which were not inconsistent with those deduced from the data for oxygen, and for mixtures of oxygen and nitrogen, of Chanin, Phelps, and Biondi and of Hurst and Bortner. Further experiments are planned in which this low energy region will be examined more closely.

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