

# THE DIFFUSION AND ATTACHMENT OF ELECTRONS IN WATER VAPOUR

By R. W. CROMPTON,\* J. A. REES,\*† and R. L. JORY\*‡

[Manuscript received July 1, 1965]

## Summary

The energy ratio and attachment coefficient for electrons in water vapour have been determined in the range  $20 < E/p < 60$  V cm<sup>-1</sup> torr<sup>-1</sup>. The results for the attachment coefficient are in general agreement with other recent determinations, but those for the energy ratio differ significantly from the results of Bailey and Duncanson. The use of these new data, in conjunction with values of the drift velocity determined by Pack, Voshall, and Phelps, is shown to remove the serious discrepancy which previously existed between the results of single-collision and swarm experiments.

## I. INTRODUCTION

When electrons having energies of the order of 5 eV pass through water vapour at a pressure of a few torr, an appreciable fraction of the electrons form negative ions by electron attachment. According to Laidler (1954), Craggs and McDowell (1955), and others, the dominant attachment process for energies up to about 10 eV is the following resonance capture process:



Laidler states that the water molecule is first raised to a repulsive  ${}^2A_1$  or  ${}^2A_2$  state of  $\text{H}_2\text{O}^-$  which at once dissociates into  $\text{H}^-({}^1S)$  and  $\text{OH}({}^2\pi)$ . The appearance potential is of the order of 5.5 eV, and the cross section is a maximum for electrons having energies of about 6.5 eV.

The curve showing the variation with electron energy of the rate of production of  $\text{H}^-$  ions from  $\text{H}_2\text{O}$  shows a second, smaller peak which has a maximum value at an energy of about 8.5 eV (Mann, Hustrulid, and Tate 1940; Buchel'nikova 1959). For electrons of energy greater than about 7.5 eV,  $\text{O}^-$  ions may also be produced, the reaction being



It is widely believed (see, for example, Cottin 1959) that the  $\text{H}^-$  ions formed as above are rapidly converted to negative hydroxyl ions by the following process:



At gas pressures of the order of 1 torr, Branscomb and Smith (1955) and Muschlitz and Bailey (1956) observed that the  $\text{OH}^-$  ions so formed were considerably more abundant than either  $\text{H}^-$  or  $\text{O}^-$  ions.

\* Ion Diffusion Unit, Australian National University, Canberra.

† Present address: Department of Electrical Engineering, University of Liverpool, England.

‡ Present address: Department of Chemistry, Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida, U.S.A.

The dependence of the cross sections for the various attachment processes on the energy of the incident electrons has been investigated in low-pressure beam-scattering experiments by Mann, Hustrulid, and Tate (1940), Buchel'nikova (1959), Schulz (1960), and others. In addition to these investigations, studies have been made of the behaviour of electrons in water vapour by Bailey and Duncanson (1930), Bradbury and Tatel (1934), Kuffel (1959), and Prasad and Craggs (1960), while Hurst, O'Kelly, and Bortner (1961) have carried out a series of experiments with argon-water-vapour mixtures. The experiments in this second group were carried out using swarms of electrons having energies distributed about some mean value  $\bar{\epsilon}$ . The method adopted by Kuffel was that used earlier by Bradbury and yielded values of the attachment coefficient  $\alpha_a/p$ , where  $\alpha_a$  is defined as the fraction of the population of an electron swarm that forms negative ions in drifting 1 cm in the direction of an applied electric field  $E$ , and  $p$  is the gas pressure. Kuffel's measurements were made for values of the parameter  $E/p$  lying between 1 and 28,  $E$  being measured in V/cm and  $p$  in torr. Bailey and Duncanson also measured values of the attachment coefficient, and in addition obtained values of the energy ratio  $k_1$  from which the Townsend energy factor can be derived. Prasad and Craggs studied the growth of electron current between plane-parallel electrodes for  $25 < E/p < 40$  and obtained values of the attachment and primary ionization coefficients. Using a parallel-plate ionization chamber, Hurst, O'Kelly, and Bortner measured pulse heights and drift velocities and analysed these data to obtain values of the attachment coefficient for argon containing small concentrations of water vapour. The measurements were made for a series of values of  $E/p$  and for varying concentrations of water vapour at each value. By extrapolating the data to zero concentration, they were able to obtain the cross section for electron attachment in water vapour averaged over the energy distribution appropriate to pure argon at each value of  $E/p$ . This method does not, however, enable the attachment coefficient for electrons in water vapour to be determined as a function of  $E/p$ .

Although Hurst, O'Kelly, and Bortner were able to show that the data from their experiments with mixtures were consistent with the data from Buchel'nikova's beam experiment, the agreement between the results of other investigations in water vapour, particularly between the results of swarm and beam experiments, is in general poor (Prasad and Craggs 1960). The present investigation was undertaken in an attempt to remove some of the major discrepancies. In particular, measurements have been made of the variation with  $E/p$  of the energy ratio  $k_1$  and the attachment coefficient  $\alpha_a/p$ . The results obtained for  $20 < E/p < 60$  are given in the present paper.

## II. EXPERIMENTAL METHOD

The method adopted in the present investigation for the determination of  $k_1$  and  $\alpha_a/p$  was that proposed by Huxley (1959) (see also Hurst and Huxley 1960) and applied hitherto to measurements in oxygen (Huxley, Crompton, and Bagot 1959; Rees 1965). The apparatus used for the investigation has been fully described by Crompton and Jory (1962) and is shown schematically in Figure 1. The experimental method need only be outlined here and may be understood by referring to the figure.

Electrons from the heated platinum filament F passed through a small hole (1 mm diam.) in the cathode C and travelled under the influence of the applied

electric field  $E$  to the anode A, some of the electrons becoming attached to molecules of water vapour in their passage between the electrodes. The experimental parameters were adjusted so that any negative ions formed between the filament and cathode fell eventually on the centre disk  $A_1$  of the collecting electrode,  $A_1$  being connected to earth during the taking of all the measurements. For given values of the gas pressure and of the parameter  $E/p$ , the ratio  $R$  of the current received by the annular section  $A_2$  to the sum of currents received by the sections  $A_2$  and  $A_3$  of the collecting electrode was determined for two values of the length  $h$  of the diffusion chamber. The currents to the sections of the collecting electrode resulted, of course, from the incidence of free electrons and of negative ions formed by attachment in the diffusion chamber. From the pair of measurements of  $R$  taken at the two values of  $h$ ,

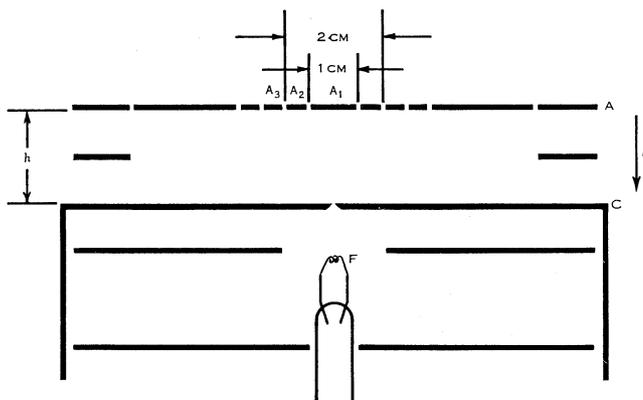


Fig. 1.—Schematic diagram of diffusion apparatus.

it was possible to determine the values of  $k_1$  and  $\alpha_a/p$  appropriate to the particular value of  $E/p$ . For all the values of  $E/p$  used, it was necessary to allow for the influence of ionization in the diffusion chamber, and for this purpose values of  $\alpha_1/p$  (the Townsend primary ionization coefficient) determined by Prasad and Craggs (1960) were adopted. The evaluation of  $k_1$  and  $\alpha_a/p$  was carried out with the aid of an IBM 1620 computer.

It was not possible to heat the diffusion apparatus to degas the electrodes and Pyrex envelope. However, with no liquid-air trap on the vacuum system, the background outgassing rate of the entire apparatus was  $1 \times 10^{-7}$  torr/min, and the system was evacuated to a pressure of the order of  $5 \times 10^{-5}$  torr before the gas samples were introduced. The water vapour was obtained from distilled water which had been further purified by passage through a mixed-bed resin. After being introduced to the vacuum system, the water was carefully treated by repeated pumping over the sample, both when liquid and when frozen, to remove any dissolved gases such as oxygen and carbon dioxide. When the whole of the vacuum system was connected to a liquid-air trap, the pressure in the system was gradually reduced to the background pressure of less than  $10^{-4}$  torr, showing that the level of impurity from non-condensable gases in the samples of water vapour was less than about 100 p.p.m. Since there is some controversy as to the level of impurity that can significantly affect

the attachment cross section in water vapour (Branscomb 1961; Pack, Vosshall, and Phelps 1962), the level of impurity present in these experiments should be borne in mind when assessing the reliability of the measurements of the attachment coefficient. On the other hand, the consistency of the results with change in pressure as shown in Figure 3 should also be noted, together with the agreement found with the data from single-scattering experiments as discussed in Section IV. It seems unlikely that the measured values of  $k_1$  will be sensitive to an impurity level of this magnitude, so that these values are considered reliable within the limits of experimental error discussed in Section III.

TABLE I  
 VARIATION OF  $k_1$  AND  $\alpha_a/p$  WITH  $E/p$  IN WATER VAPOUR IN  
 THE RANGE  $20 < E/p < 60$  AT 293°K  
 Equivalent values of  $D/\mu$  appropriate to each value of  $k_1$  are  
 shown, and also the values of  $\alpha_i/p$  used in the computation of  
 the results for  $\alpha_a/p$

$E/p$	$k_1$	$D/\mu$	$\alpha_a/p$	$\alpha_i/p^*$
20	63·0	1·59	—	0·022
22·5	82·0	2·07	0·15	0·033
25·0	96·0	2·43	0·17	0·049
27·5	105·4	2·66	0·19	0·072
30·0	113	2·85	0·20	0·098
35·0	124	3·13	0·21 <sub>5</sub>	0·162
40·0	131	3·31	0·21 <sub>5</sub>	0·245
45·0	137	3·46	0·20 <sub>5</sub>	0·35
50·0	142	3·58	0·19	0·46
55·0	144	3·64	0·17	0·60
60·0	147	3·71	0·15	0·79

\* The values of  $\alpha_i/p$  in the range  $30 < E/p < 50$  are those of Prasad and Craggs (1960); the other values were obtained by extrapolation from this range.

### III. RESULTS

Measurements of the ratio of currents,  $R$ , were made with  $h = 2, 4,$  and  $5$  cm at pressures of  $1·17, 1·38,$  and  $2·13$  torr, and with  $h = 2, 4,$  and  $6$  cm at pressure  $1·23$  torr. The measurements were made over the range  $20 < E/p < 60$  and were taken at a temperature of  $20^\circ\text{C}$ . From the measured values of  $R$ , the values of  $k_1$  and  $\alpha_a/p$  were determined. These values are summarized in Table 1 together with values of  $D/\mu$  equivalent to each value of  $k_1$ ,  $D$  being the diffusion coefficient for the electrons and  $\mu$  the ratio of the drift velocity  $W$  to the electric field  $E$ . The table contains also the values of the ionization coefficient  $\alpha_i/p$  that were adopted in the calculation of  $\alpha_a/p$ . At the intermediate values of  $E/p$  the values of  $\alpha_i/p$  used are those given by Prasad and Craggs (1960), while for lower and higher values of  $E/p$  extrapolations of those workers' data have been used. It should be emphasized that the results given in Table 1 for  $k_1$  and  $\alpha_a/p$  could be readily recomputed if later determinations of  $\alpha_i/p$  differ markedly from the values shown in the table.

(a) Results for  $k_1$ 

The results obtained for  $k_1$ , which are shown in Figure 2, were subject to a maximum scatter of less than 3% and were independent of the gas pressure used. Further, the results were independent of the way in which the measured values of the ratios  $R$  were combined in the analysis; for example, the same values of  $k_1$  were obtained when the values of  $R$  determined at  $h = 2$  cm were combined with those determined at either  $h = 4$  or 6 cm. The main sources of error in the measurements were those arising from inaccuracies in the measurement of the relatively low gas pressures employed (measured to within  $\pm 1\%$ ) and from the heating of the gas in the diffusion chamber as a result of the high temperature at which it was necessary to operate the filament if adequate emission currents were to be obtained.

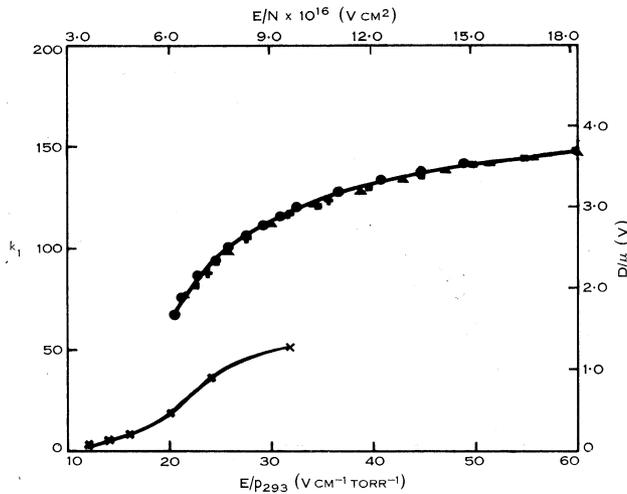


Fig. 2.—Experimental results for the energy ratio  $k_1$  in water vapour. ▲ 1.17 torr; ● 1.23 torr; ■ 1.38 torr; + 2.13 torr; × Bailey and Duncanson. (Note: Conversion factor between  $E/p_{293}$  and  $E/N$  is  $3.03 \times 10^{15}$ .)

The use of a receiving electrode of the configuration shown in Figure 1, in conjunction with a diffusion chamber of length 2 cm, enhances errors arising from the spatial dependence of the energy distribution as discussed by Parker (1963), but the magnitude of these errors is difficult to assess in specified instances in the absence of a complete theory. Nevertheless, it should be noted that the agreement between the results obtained by analysing the data obtained for different values of  $h$  is an indication that these errors are not serious.

In addition to the present results, Figure 2 includes the data obtained earlier by Bailey and Duncanson (1930), which we believe to be the only other data available. It is seen from Figure 2 that the present results lie well above the earlier data. One important consequence of this is discussed in Section IV.

(b) Results for  $\alpha_a/p$ 

The results obtained for  $\alpha_a/p$ , which are shown in Figure 3, are subject to an r.m.s. error of  $\pm 5\%$ . The major sources of this error were

- (i) errors in pressure measurement and fluctuations in gas pressure;
- (ii) errors in the measured values of the ratio  $R$ .

Both sources of error, in addition to influencing the accuracy of the values of  $\alpha_a/p$  directly, also influenced the results indirectly through errors introduced into the values of  $k_1$  used when calculating the values of  $\alpha_a/p$ . The errors introduced directly were less than  $\pm 5\%$ , while the error arising from an error of  $\pm 1\%$  in the value for  $k_1$  at a particular value of  $E/p$  was typically  $\pm 10\%$ .

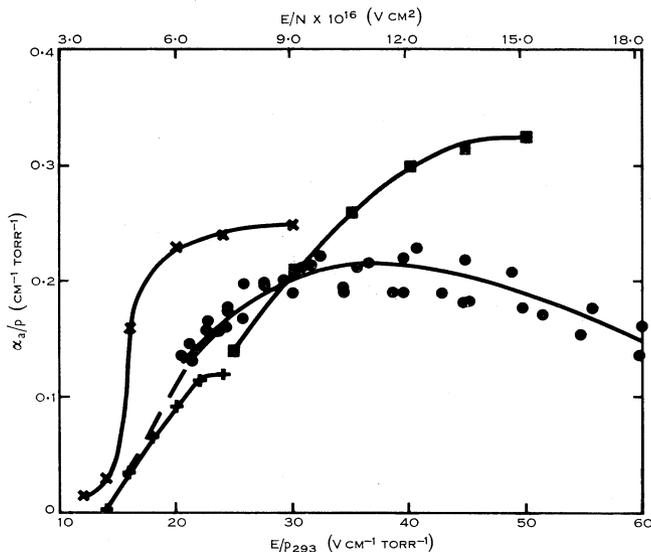


Fig. 3.—Experimental results for the attachment coefficient  $\alpha_a/p$  in water vapour. ● Present results; × Bailey and Duncanson (1930); + Kuffel (1959); --- Kuffel's data corrected for ionization; ■ Prasad and Craggs (1960). (Note: Conversion factor between  $E/p_{293}$  and  $E/N$  is  $3.03 \times 10^{15}$ .)

In addition to the present results for  $\alpha_a/p$ , Figure 3 shows the data obtained by Bailey and Duncanson (1930), Kuffel (1959), and Prasad and Craggs (1960). The present results lie up to 40% below those of Bailey and Duncanson; their results are in any case considerably higher than those of the other investigations. The values given by Kuffel for  $\alpha_a/p$  are more accurately taken as being the values of  $(\alpha_a/p - \alpha_i/p)$ , and an attempt has been made in Figure 3 to adjust Kuffel's published data for  $\alpha_a/p$  to allow for the influence of ionization, an extrapolation of the data of Prasad and Craggs for  $\alpha_i/p$  being used in the correction. It is seen from Figure 3 that a smooth curve can be drawn through Kuffel's adjusted values and the present results. The results obtained by Prasad and Craggs for  $\alpha_a/p$  are in fair agreement with our results at low values of  $E/p$ , but there is considerable divergence between the two sets of data at higher values of  $E/p$ .

## IV. COMPARISON OF ATTACHMENT DATA FROM BEAM AND SWARM EXPERIMENTS

It is of interest to compare the results of single scattering experiments such as those of Buchel'nikova (1959) with those of swarm experiments. The most straightforward way of making such comparisons is to use the energy-dependent values of attachment cross section found from beam experiments to compute values of  $\alpha_a/p$  for a series of values of  $E/p$  (e.g. Emel us, Lunt, and Meek 1936; Asundi and Craggs 1964), the calculations depending on a known or postulated energy distribution within the swarm. Frequently, however, comparisons have been made (e.g. Craggs, Thorburn, and Tozer 1957; Bhalla and Craggs 1960; Prasad and Craggs 1960; Chanin, Phelps, and Biondi 1962; Rees 1964; Rees and Jory 1964) by comparing a "mean attachment cross section"  $\bar{\sigma}_a$ , derived from the swarm data, with values of the same quantity calculated by averaging the monoenergetic attachment cross section over the energy distribution of the swarm. This procedure is perhaps less satisfactory because of the difficulty in assigning a physical significance to  $\bar{\sigma}_a$  (see equation (6)).

Although in general the results of these comparisons for several gases (e.g. Prasad and Craggs 1961; Rees 1964; Rees and Jory 1964) have shown discrepancies no greater than might be expected as a result of imprecise knowledge of the appropriate energy distributions, the comparisons for water vapour (Prasad and Craggs 1960) were a notable exception. For this gas, values of  $\bar{\sigma}_a$  calculated from swarm experiments exceeded the corresponding values calculated from Buchel'nikova's data by a factor of 5 in some instances. The calculations described below suggest that the major part of this discrepancy can be attributed to the difference between the values of  $k_1$  as a function of  $E/p$  given by Bailey and Duncanson (1930) and those given in Table 1. The calculations of Prasad and Craggs were, of course, based on the data of Bailey and Duncanson, which were at that time the only data available. Because of several factors which will become apparent in the discussion, we have thought it advisable to repeat the earlier calculations with the new data to demonstrate the removal of the earlier discrepancies, in addition to adopting the alternative, somewhat more straightforward, method of comparison. The results of the alternative method of comparison are given in the Appendix. As will be shown, the result of any method of comparison cannot be regarded as highly significant at the present time because of the lack of some of the necessary data.

The method of calculating "mean attachment cross sections" from the two types of experiment has been described by Bhalla and Craggs (1960) and is briefly as follows. The collision frequency for attachment of electrons of energy  $\epsilon$  is given by  $\nu_{a\epsilon} = N\sigma_{a\epsilon}c_\epsilon$ , where  $N$  is the molecular number density and  $\sigma_{a\epsilon}$  is the attachment cross section for electrons of speed  $c$ ; the subscript  $\epsilon$  denoting that each value is appropriate to an energy  $\epsilon$ . If  $dn_\epsilon$  is the number of electrons per unit volume in the swarm with energy between  $\epsilon$  and  $\epsilon+d\epsilon$ , it follows from the definition of the attachment coefficient  $\alpha_a$  that

$$N \int \sigma_{a\epsilon} c_\epsilon dn_\epsilon = n_0 a_a W, \quad (4)$$

where  $n_0 (= \int dn_\epsilon)$  is the number density of electrons in the swarm.

The "mean attachment cross section"  $\bar{\sigma}_a$  can be defined through the equation (cf. Bhalla and Craggs 1960)

$$\bar{\sigma}_a = \frac{\alpha_a W}{N \bar{c}}. \quad (5)$$

Comparison of equations (4) and (5) shows that

$$n_0 \bar{\sigma}_a \bar{c} = \int \sigma_{a_e} c_e dn_e,$$

so that

$$\bar{\sigma}_a = \frac{\overline{\sigma_a c}}{\bar{c}}. \quad (6)$$

Equation (5) can be rewritten

$$\begin{aligned} \bar{\sigma}_a &= \frac{1}{N_0} \left( \frac{W}{\bar{c}} \right) \left( \frac{\alpha_a}{p} \right) \\ &= \frac{A}{\bar{c}^{\frac{1}{2}}} W \left( \frac{\alpha_a}{p} \right), \end{aligned} \quad (7)$$

where  $N_0$  is the gas molecular number density corresponding to unit pressure at some temperature, and  $A$  is a constant whose value depends in part on the form of the energy distribution in the swarm. Provided that  $k_1$ ,  $W$ ,  $\alpha_a/p$ , and the form of the energy distribution are known as functions of  $E/p$  from swarm experiments, values of  $\bar{c}$  can be calculated from the values of  $k_1$  (e.g. Huxley and Crompton 1962) and values of  $\bar{\sigma}_a$  then obtained by use of equation (7). A curve of  $\bar{\sigma}_a$  versus  $\bar{c}$  can then be plotted.\*

Equation (6) likewise enables  $\bar{\sigma}_a$  to be calculated for a series of values of  $\bar{c}$  from the data provided by single collision experiments, the integrations being carried out for the same form of energy distribution as was used for the evaluation of  $\bar{\sigma}_a$  from the swarm data.

In the absence of precise information on the form of the electron energy distribution in water vapour, comparisons have usually been made for typical energy distributions, for example the Maxwellian or Druyvesteyn distributions, although these may or may not resemble the true energy distribution in the gas (compare, for example, the energy distributions that have been reported for other molecular gases by Engelhardt and Phelps (1963), and by Engelhardt, Phelps, and Risk (1964)). Figure 4 shows such a comparison between Buchel'nikova's data and the data from our experiments where the data have been analysed on the basis of a Maxwellian distribution, using the values of  $k_1$  given in Table I and the values of Pack, Voshall, and Phelps for  $W$ . A difficulty exists in carrying out the calculations in that there are no values of the drift velocity in water vapour measured by a time-of-flight technique for  $E/p$  greater than 27. The computation of the values of  $\bar{\sigma}_a$  from the measured values of  $\alpha_a/p$  requires values of  $W$  for  $E/p$  as high as 40; those portions of the curves in

\* The values of  $\bar{\sigma}_a$  computed from data for  $\alpha_a/p$  for dry air and carbon dioxide by Rees (1964) and Rees and Jory (1964) are in error by 7%, the correct values being 7% higher than those quoted. This systematic error does not in any way affect the conclusions drawn from the comparisons of the values of  $\bar{\sigma}_a$  with corresponding values deduced from beam data for  $\bar{\sigma}_{a_e}$ , the latter values of  $\bar{\sigma}_a$  being correctly given.

Figure 4 represented by broken lines result from the use of values of  $W$  that have been extrapolated in the range  $27 < E/p < 40$ , so that less reliance should be placed upon these sections of the curves.

Also plotted in Figure 4 is the curve for  $\bar{\sigma}_a$  versus  $\bar{\epsilon}$  calculated by Prasad and Craggs (again for a Maxwellian distribution) from their measured values of  $\alpha_a/p$  and using values of  $k_1$  and  $W$  published by Bailey and Duncanson.\* The curve resulting

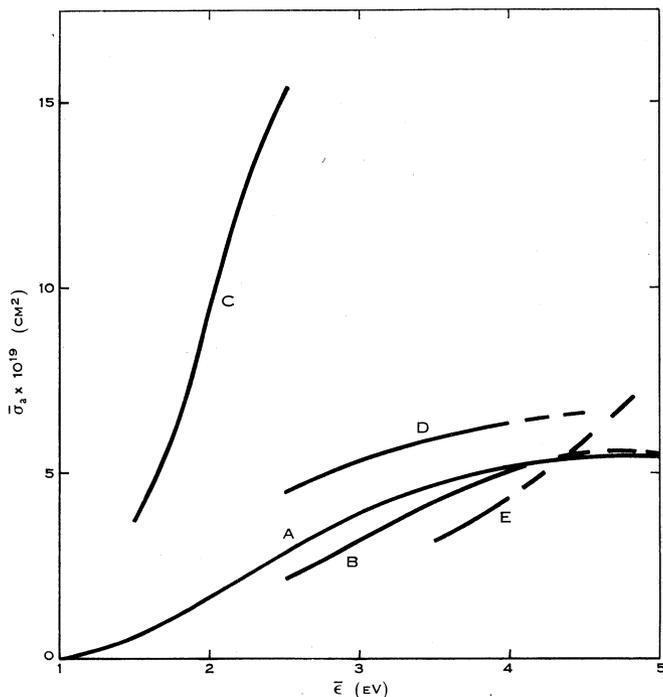


Fig. 4.—Comparison of the results of beam and swarm experiments for the “mean attachment cross section”  $\bar{\sigma}_a$  in water vapour (assuming a Maxwellian distribution). A, from Buchel'nikova's (1959) data; B, from the present data; C, Prasad and Craggs (1960); D, from the data of Bailey and Duncanson (1930) for  $\alpha_a/p$ , and the new data for  $k_1$  and  $W$ ; E, curve C recalculated using the new data for  $k_1$  and  $W$ .

from a recalculation of these data using the newer data for  $k_1$  and  $W$  is also shown. It can be seen that the use of the new auxiliary data results in very much closer agreement between the results of Buchel'nikova and those of Prasad and Craggs, the newer data for  $k_1$  being mainly responsible for this closer agreement, since the data for  $W$  of Bailey and Duncanson are not very different from the later results of Pack, Voshall, and Phelps for  $E/p$  greater than 20. Still better agreement exists, however, between the data of Buchel'nikova and those from our experiments, but the

\* The values of  $W$  given by Bailey and Duncanson were obtained using the magnetic deflection method. There exists, therefore, the possibility of large errors apart from experimental errors (see, for example, Jory 1965).

sensitivity of the comparisons to the form of energy distribution adopted (cf. Bhalla and Craggs 1960), together with the need to use extrapolated values of  $W$  for part of the curves, should be borne in mind when assessing the significance of the agreement. It is for these reasons that we do not feel justified in claiming more than the removal of a serious discrepancy between the results of single collision and swarm experiments.

## V. CONCLUSION

Although electrons having energies between 5 and 10 eV undergo considerable attachment to form negative ions when they pass through water vapour, the present investigation has shown that it is nevertheless possible, using the method suggested by Huxley, to determine values of the energy ratio  $k_1$  for the electrons. The values of  $k_1$  (or of the parameter  $D/\mu$ ) determined in this work for  $20 < E/p < 60$  are considerably different from those determined earlier by Bailey and Duncanson. In addition to the values of  $k_1$ , the present study yielded values of the attachment coefficient  $\alpha_a/p$  for electrons in water vapour which merge smoothly with those determined at lower  $E/p$  by Kuffel. From a comparison of the results of the single scattering data of Buchel'nikova with various sets of data for  $\alpha_a/p$  from swarm experiments, it is concluded that the values of  $k_1$  given in Table I are likely to be more reliable than those of Bailey and Duncanson.

## VI. ACKNOWLEDGMENT

The authors wish to express their thanks to their colleagues in the Ion Diffusion Unit for valuable discussions.

## VII. REFERENCES

- ASUNDI, R. K., and CRAGGS, J. D. (1964).—*In* "Atomic Collision Processes". (Ed. M. R. C. McDowell.) p. 549. (North-Holland: Amsterdam.)
- BAILEY, V. A., and DUNCANSON, W. E. (1930).—*Phil. Mag.* **10**: 145.
- BHALLA, M. S., and CRAGGS, J. D. (1960).—*Proc. Phys. Soc.* **76**: 369.
- BRADBURY, N. E., and TATEL, H. E. (1934).—*J. Chem. Phys.* **2**: 835.
- BRANSCOMB, L. M. (1961).—*Int. Conf. Ioniz. Phenom. Gases* **5**: 1.
- BRANSCOMB, L. M., and SMITH, S. J. (1955).—*Phys. Rev.* **98**: 1028.
- BUHEL'NIKOVA, N. S. (1959).—*Soviet Phys.—J.E.T.P.* **8**: 783.
- CHANIN, L. M., PHELPS, A. V., and BIONDI, M. A. (1962).—*Phys. Rev.* **128**: 219.
- COTTIN, M. (1959).—*J. Chim. Phys.* **56**: 1024.
- CRAGGS, J. D., and McDOWELL, C. A. (1955).—*Rep. Prog. Phys.* **18**: 374.
- CRAGGS, J. D., THORBURN, R., and TOZER, B. A. (1957).—*Proc. R. Soc. A* **240**: 473.
- CROMPTON, R. W., and JORY, R. L. (1962).—*Aust. J. Phys.* **15**: 451.
- EMELÉUS, K. G., LUNT, R. W., and MEEK, C. A. (1936).—*Proc. R. Soc. A* **156**: 394.
- ENGELHARDT, A. G., and PHELPS, A. V. (1963).—*Phys. Rev.* **131**: 2115.
- ENGELHARDT, A. G., PHELPS, A. V., and RISK, C. G. (1964).—*Phys. Rev.* **135**: A 1566.
- HURST, C. A., and HUXLEY, L. G. H. (1960).—*Aust. J. Phys.* **13**: 21.
- HURST, G. S., O'KELLY, L. B., and BORTNER, T. E. (1961).—*Phys. Rev.* **123**: 1715.
- HUXLEY, L. G. H. (1959).—*Aust. J. Phys.* **12**: 171.
- HUXLEY, L. G. H., and CROMPTON, R. W. (1962).—The motions of slow electrons in gases. *In* "Atomic and Molecular Processes". (Ed. D. R. Bates.) (Academic Press: New York.)
- HUXLEY, L. G. H., CROMPTON, R. W., and BAGOT, C. H. (1959).—*Aust. J. Phys.* **12**: 303.
- JORY, R. L. (1965).—*Aust. J. Phys.* **18**: 237.
- KUFFEL, E. (1959).—*Proc. Phys. Soc.* **74**: 297.

- LAIDLER, K. J. (1954).—*J. Chem. Phys.* **22**: 1740.  
 MANN, M. M., HUSTRULID, A., and TATE, J. T. (1940).—*Phys. Rev.* **58**: 340.  
 MUSCHLITZ, E. E., and BAILEY, T. L. (1956).—*J. Phys. Chem.* **60**: 681.  
 PACK, J. L., VOSHALL, R. E., and PHELPS, A. V. (1962).—*Phys. Rev.* **127**: 2084.  
 PARKER, J. H. (1963).—*Phys. Rev.* **132**: 2096.  
 PRASAD, A. N., and CRAGGS, J. D. (1960).—*Proc. Phys. Soc.* **76**: 223.  
 PRASAD, A. N., and CRAGGS, J. D. (1961).—*Proc. Phys. Soc.* **77**: 385.  
 REES, J. A. (1964).—*Aust. J. Phys.* **17**: 462.  
 REES, J. A. (1965).—*Aust. J. Phys.* **18**: 41.  
 REES, J. A., and JORY, R. L. (1964).—*Aust. J. Phys.* **17**: 307.  
 SCHULZ, G. J. (1960).—*J. Chem. Phys.* **33**: 1661.

## APPENDIX

Using the data of Table 1 for  $k_1$  and the values of Pack, Voshall, and Phelps for  $W$  as auxiliary data, values of  $\alpha_a/p$  have been calculated from Buchel'nikova's data for  $\sigma_{a\epsilon}$  by use of equation (4). The calculations were carried out for both Maxwellian and Druyvesteyn energy distributions. The resulting values of  $\alpha_a/p$  are compared in Table 2 with the data obtained in swarm experiments. The remarks made in Sections IV and V above in discussing the data of Figure 4 apply equally to the results of Table 2.

TABLE 2  
 COMPARISON OF EXPERIMENTAL VALUES OF  $\alpha_a/p$  WITH COMPUTED VALUES DERIVED FROM THE DATA OF BUCHEL'NIKOVA

$E/p_{293}$	$\alpha_a/p_{293}$				
	Bailey and Duncanson	Prasad and Craggs	Crompton, Rees, and Jory	Buchel'nikova (Maxwellian (Druyvesteyn Distribution) Distribution)	
22.5	0.236	—	0.15	0.18	0.10 <sub>5</sub>
25	0.24	0.14	0.17	0.195	0.16 <sub>5</sub>
27.5	0.24 <sub>5</sub>	0.17 <sub>5</sub>	0.19	0.20	0.20
30	0.25	0.21	0.20	0.20 <sub>5</sub>	0.22
35	0.25	0.26	0.21 <sub>5</sub>	0.21	0.24 <sub>5</sub>
40	—	0.30	0.21 <sub>5</sub>	0.22	0.26

