THE DRIFT VELOCITIES OF FREE AND ATTACHED ELECTRONS IN WATER VAPOUR

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Summary

The drift velocities of free and attached electrons in water vapour have been determined as functions of the parameter E/p at a temperature of 293°K. The results are compared with those of other workers and with theoretical predictions. Measurements of the drift velocity of free electrons in mixtures of hydrogen and water vapour are also presented.

I. Introduction

As part of an investigation into the behaviour of free and attached electrons in water vapour, the drift velocities of electrons in pure water vapour and in mixtures of water vapour and hydrogen have been determined. The drift velocity of the negative ions formed in collisions between electrons and molecules of water vapour has also been studied. The drift velocities in water vapour have been measured as functions of E/p (E = electric field in volt cm^{-1} and p = gas pressure in mmHg) at a temperature of 293°K. The results for free electrons are compared with those of other workers. From the drift velocity data for the negative ions, the mobility of the ions has been deduced and the value obtained compared with theoretical predictions. The experimental results for the drift velocity of electrons in mixtures of water vapour and hydrogen were obtained at $E/p = 2$ for mixtures in which the proportion of water vapour varied from 0 to 100%.

II. Experimental Method

The apparatus used in the present work has been described in detail elsewhere (Lowke 1963a) and is shown schematically in Figure 1. The method of measurement was that of Bradbury and Nielsen (1936), in which the drift velocities of the charged particles under the influence of a uniform electric field E are deduced from their times-of-flight between two electrical shutters (S_1 and S_2 of Fig. 1). The water vapour used for the measurements was obtained from distilled water which was de-ionized by passage through a mixed-bed resin and carefully outgassed to remove dissolved oxygen and other gases. The hydrogen used was commercial hydrogen purified by passage through a heated palladium thimble (Crompton and Elford 1962). The electrons were generated at the filament F (Fig. 1). By adjustment of the strength of the electric field in the region between the filament and the first shutter S_1, the number of electrons forming negative ions by attachment in this region could be varied. In this way, the composite beam of charged particles passing through the apparatus

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could be made either predominantly electronic or ionic in character. In the experiments carried out in pure water vapour, the variation of the current received by the collecting electrode C with the frequency of the alternating potential applied to the
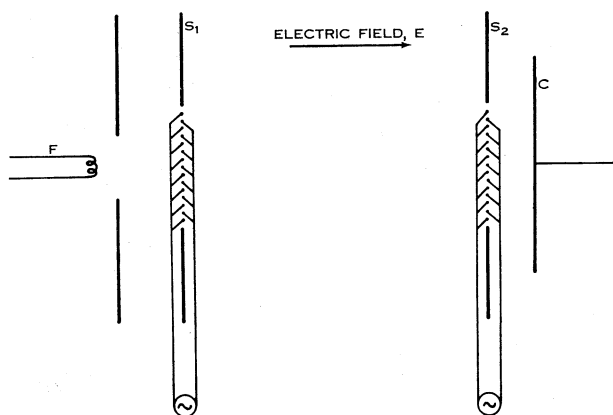

Fig. 1.—Schematic diagram of apparatus.

shutters S_1 and S_2 showed only two species of charged particles to be present. A typical current versus frequency curve is shown in Figure 2. The two species of particles had widely differing drift velocities; the particles of the faster species were
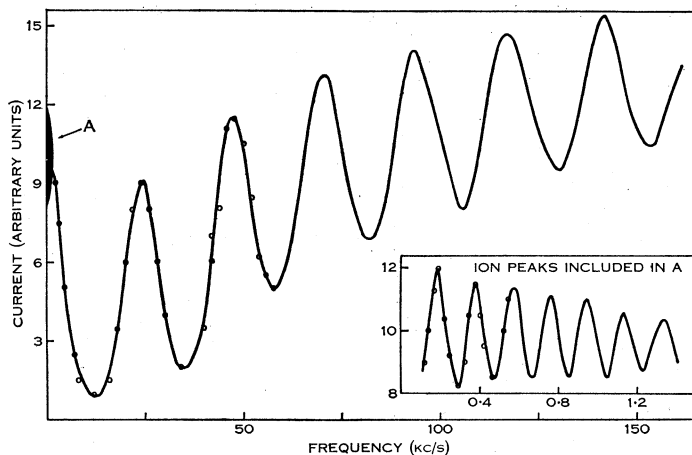

Fig. 2.—Typical current versus frequency curve for water vapour. The curve shows two distinct systems of peaks, the peak system for the negative ions being superimposed on the first peak of the electronic system. Experimental points are shown for the first few peaks only.

taken to be free electrons while those of the slower species were negative ions. The results obtained for the drift velocities of the electrons and negative ions are discussed, separately, in the following section. This section also contains the results obtained using mixtures of water vapour and hydrogen.

III. Results

(a) Free Electrons in Water Vapour

The results obtained for the drift velocity W of free electrons as a function of E/p at 293°K are given in Figure 3 and in Table 1. It is considered that the values of W given in Table 1 are subject to an error of less than 2%. The values of E/p are expressed in units of volts cm^{-1} (mmHg)$^{-1}$ for an equivalent gas particle density at 293°K, i.e. $E/p = (E/N) \times 3 \cdot 30 \times 10^{16}$, where N is the gas particle density. The variation of W with E/p was determined for values of E/p between 0·35 and 15, for gas pressures ranging between 2 and 14·5 mmHg. The results indicated no dependence of W on gas pressure.
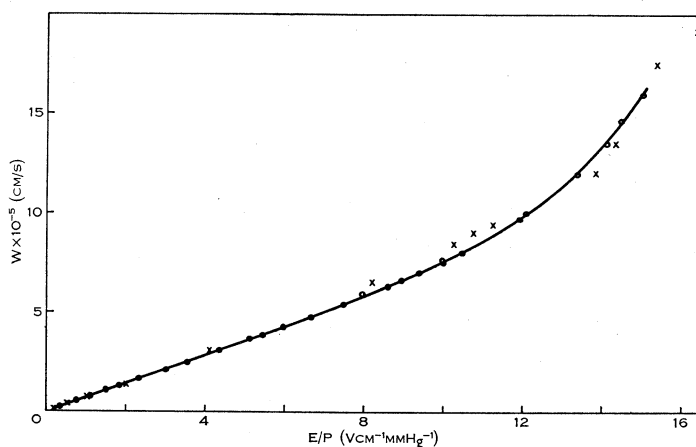

Fig. 3.—Drift velocity versus E/p for electrons in water vapour. The results of Pack, Voshall, and Phelps (1962) have been corrected to a gas particle density, $N = 3 \cdot 30 \times 10^{16}p$. ○ Present work, × Pack, Voshall, and Phelps.

Figure 3 also shows the results obtained recently by Pack, Voshall, and Phelps (1962) which, for values of E/p less than 20, disagree with the earlier results of Bailey and Duncanson (1930). It is seen from Figure 3 that, over the common range of E/p, the present results confirm the general dependence of W on E/p observed by Pack, Voshall, and Phelps. The discrepancies between the present results and theirs are at most 7%, which is just greater than the combined experimental errors of the two investigations. It has been stated by Pack, Voshall, and Phelps that they believe the presence of impurities in the water vapour used by earlier workers (e.g. Kuffel 1959; Bradbury and Tatel 1934) to be responsible for the discrepancies in the rates of electron attachment observed at values of E/p less than 10. It seems unlikely that the difference of up to 7% between the results of Pack, Voshall, and Phelps and those of the present investigation can be attributed to the presence of impurities in the water vapour used in the present work since, as already stated, the results exhibited no dependence of W on the gas pressure used.

It was not possible to extend the present measurements to values of E/p greater than 15, since at these higher values the number of free electrons in the stream of charged particles became greatly reduced. This observation is consistent with the variation of the attachment coefficient with E/p found by Kuffel (1959).

An interesting feature of the behaviour of free electrons in water vapour is that, for $0 < E/p < 6$, the mean energy of the electrons is very nearly equal to that of the gas molecules (Pack, Voshall, and Phelps 1962). Confirmation of the thermal character of the electrons for $E/p < 6$ was obtained in the present work by examining the "resolution" of the peaks of the current versus frequency curves obtained (Lowke 1963b).

TABLE 1

DRIFT VELOCITY VERSUS E/p FOR ELECTRONS IN WATER VAPOUR

E/p	$W(\times 10^{-5})$ (cm/s)	E/p	$W(\times 10^{-5})$ (cm/s)
0·36	0·26	6·00	4·25
0·45	0·325	7·00	4·97
0·75	0·53	8·00	5·80
1·00	0·71	9·00	6·65
1·50	1·06	10·0	7·55
2·00	1·41	11·0	8·63
2·50	1·77	12·0	9·83
3·00	2·12	13·0	11·35
3·50	2·48	14·0	13·4
4·00	2·83	15·0	16·1
5·00	3·54		

(b) Negative Ions in Water Vapour

As already stated, an examination of the current versus frequency curves obtained in water vapour showed, in addition to the free electrons discussed above, the presence of a second species of negatively charged particles (see Fig. 2). From the work of other investigators (e.g. Craggs and McDowell 1955; Buckel'nikova 1958; Hurst, O'Kelly, and Bortner 1961) these particles are believed to have been formed as H^- ions through the reaction

$$H_2O + e \rightarrow H_2O^- \rightarrow H^- + OH, \tag{1}$$
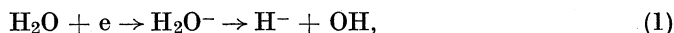
the appearance potential being $5 \cdot 7$ eV, and the cross section being a maximum for electrons of $6 \cdot 4$ eV energy. This identification was supported by our preliminary measurements of the mean energy and attachment coefficient of electrons in water vapour.

The variation with E/p of the drift velocity of the negative ions was examined for gas pressures between 1 and 14 mmHg at a temperature of 293°K. From the results, the mobility of the ions was calculated and was found to be constant over the

whole range of values of E/p used, i.e. for $1\cdot5 < E/p < 40$, and to be independent of the gas pressure. It should, perhaps, be stressed that the fact that the mobility of the ions could be determined at all values of E/p from $1\cdot5$ to 40 should not be taken as meaning that the ions were formed by attachment over the whole of this range. The number of ions present in the apparatus was controlled by the value of E/p in the region between the filament F and the shutter S_1 (see Fig. 1). This value was normally kept between 10 and 20. The value of the zero-field, reduced mobility of the ions (i.e. the value obtained by extrapolating the experimental results to $E/p = 0$ and normalizing to a gas particle density of $2\cdot69\times10^{19}$ cm^{-3}) was found to be

$$\omega_0 = 0\cdot67(4)\pm1\% \text{ cm}^2\text{V}^{-1}\text{s}^{-1}.$$

It is believed that there are no other experimental determinations of the mobility of negative ions in water vapour with which the present result could be compared. Theoretical predictions of the reduced mobility ω_0 are also difficult. If the mobility of the ions at low values of E/p is assumed to be controlled by the polarization of the gas molecules by the negative ions, an estimate of ω_0 may be made using the well-known expression

$$\omega_0 = 35\cdot9/(\alpha\mu)^{\frac{1}{2}}, \tag{2}$$

where α is the polarizability of the gas atoms, measured in atomic units, and μ is the reduced mass, $mM/(m+M)$, in proton mass units, m and M being the masses of the negative ions and gas molecules respectively.

The value of ω_0 obtained in this way for H$^-$ ions is $\omega_0 = 2\cdot6$, which is nearly four times the experimental value. It should be noted that this theoretical value of ω_0 has been obtained by neglecting the permanent dipole moment of the water vapour molecule. Taking this permanent moment into account will certainly decrease ω_0 below the value of $2\cdot6$ but the amount by which it would do so is at present uncertain.

An alternative explanation of the large difference between the experimental value of ω_0 and that calculated for H$^-$ from equation (2) may be that the H$^-$ ions produced initially according to equation (1) form stable clusters through the addition of single H$_2$O molecules. If this is in fact the case, then the clustering must proceed rapidly and the clusters formed must be stable, since at no time during the investigation were there any indications of the presence of negative ions having a mobility greater than $0\cdot67$. Further, no increase in the mobility of the ions with E/p at high values of E/p was observed, as would have been the case if the clusters were being broken up by the increased electric field.*

(c) Experiments with Mixtures of Water Vapour and Hydrogen

The quantitative effect of slight traces of water vapour (20 p.p.m.) on the drift velocity of free electrons in other gases has been discussed by Lowke (1963a).

* Note added in Proof.—In a recent paper Eiber (1963) reports the observation in pure water vapour of negative ions having a mobility of $0\cdot68$ cm^{2}V^{-1}s^{-1}, the mobility being constant for $0\cdot8 < E/p < 50$. The agreement between this value of the mobility and that observed in the present work is well within the combined experimental errors of the two investigations. The present value of $\omega_0 = 0\cdot67(4)$ is in excellent agreement with that of $0\cdot671$ calculated by Eiber, from equation (2) above, for complex (H$_2$O)$_4$ ions in water vapour.

The earlier results were obtained for mixtures of water vapour and nitrogen. In the present work mixtures of water vapour and hydrogen were used, all measurements being taken at 293°K and for $E/p = 2$. The results are illustrated in Figure 4. The marked effect of traces of water vapour in pure hydrogen is seen from the fact that the addition of $0 \cdot 2\%$ of water vapour to pure hydrogen increased the drift velocity of electrons in the gas by about 3%. Variations in W of the same order of magnitude have been reported by Hurst, Stockdale, and O'Kelly (1963) when small amounts of water vapour were added to nitrogen and other gases.

The limiting value, $W = 1 \cdot 40 \times 10^5$ cm s^{-1}, obtained when the amount of water vapour in the water vapour/hydrogen mixture approached 100%, is consistent with the values given in Table 1 for the drift velocity of electrons in pure water vapour. Confirmation of the identification of the particles discussed in Section III(a) above as free electrons is thus afforded.
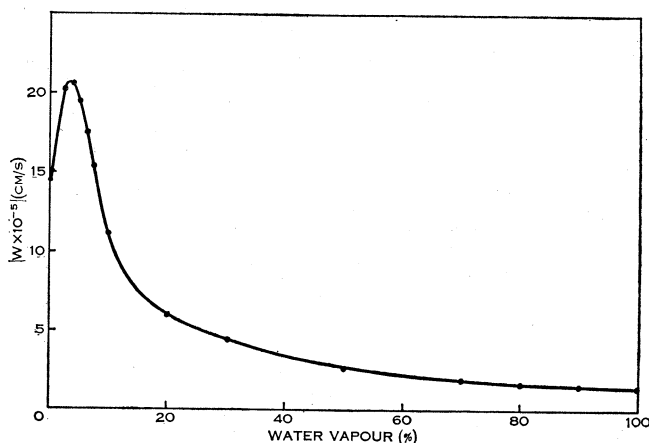

Fig. 4.—The drift velocity of electrons in mixtures of water vapour
and hydrogen at 293°K for $E/p = 2$.

IV. Conclusions

The variation with E/p of the drift velocity of free electrons in water vapour at 293°K observed in the present work confirms the observations of Pack, Voshall, and Phelps, both sets of data disagreeing with the results of Bailey and Duncanson by as much as a factor of 3 for $E/p < 20$. In addition, previously unavailable data for the mobility of negative ions in water vapour have been obtained. If these ions are in fact H$^-$ ions then their mobility differs by a factor of 4 from that calculated by ignoring the permanent dipole moment of the water molecule.

The results given for the drift velocity of electrons in mixtures of water vapour and hydrogen confirm earlier experimental results taken in mixtures of water vapour and nitrogen and illustrate the very marked effect of small traces of water vapour on drift velocity measurements in gases such as hydrogen and nitrogen.

V. ACKNOWLEDGMENTS

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