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J. Dutton, F. Llewellyn Jones, W. D. Rees and E. M. Williams

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IV. DRIFT AND DIFFUSION OF IONS IN HYDROGEN

By J. DUTTON, F. LLEWELLYN JONES, W. D. REES AND E. M. WILLIAMS

1. Introduction

In part II, the initial design of an apparatus to measure both the drift velocity W and the ratio of drift velocity to diffusion coefficient (W/D) for positive ions in gases was described. Measurements of W in argon and nitrogen using this apparatus were discussed in parts II and III, but it was shown that large leakage currents prevented the measurement of the ratio W/D. As a result of investigations of the leakage current, the apparatus was redesigned, and the purpose of the present part is to describe this new apparatus and to discuss the results obtained in hydrogen.

2. Description of apparatus

(a) *Electrode system*

A schematic diagram of the electrode system is shown in figure 11. The essential difference between this electrode system and the previous model lies in the design of collector electrodes P_1, P_2, P_3 of the diffusion section and in the general mounting of the electrode system inside its glass envelope.

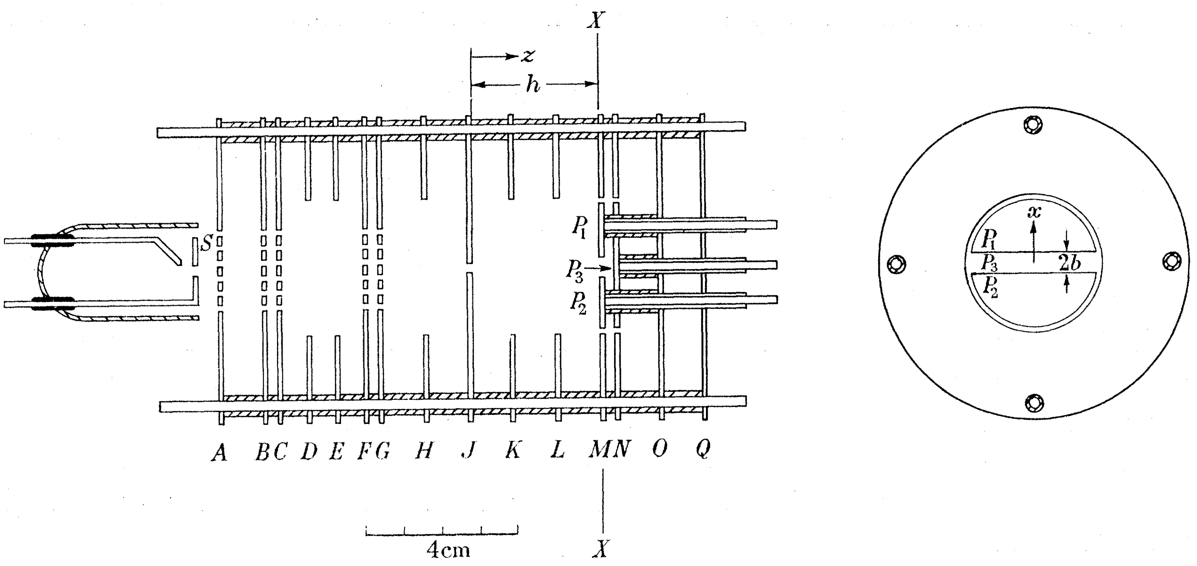

Figure 11. The electrode system. Right, section through *XX*.

With this apparatus the circular collecting electrode P_3 and the two D-shaped collecting electrodes P_1 and P_2 were supported by, and insulated from the earthed electrodes O and Q by means of quartz-sleeved copper rods welded on to the collecting electrodes and fitting through holes drilled in the earthed electrodes O and Q. In this manner, the leakage of charge from the quartz rods supporting the electrodes A to Q to the collecting electrodes was prevented. As in the previous design the electrode P_1 carried a metal foil, so that the gap between the collecting electrodes P_1 and P_2 could be masked off. The collecting electrodes were surrounded by the guard rings M and N from which they were insulated by a gap 0·1 cm wide. Precautions were also taken to stop any leakage of charge to the collecting electrode leads from the walls of the envelope, by means of earthed guard rings formed by inserting glass-metal seals in the glass side arms carrying the tungsten leads to the electrodes. The leads to the collecting electrodes were insulated from the guard rings by means of quartz sleeving.

In order to prevent the passage of ions through the gas outside the electrode structure, the diameter of all the electrodes except the collecting electrodes was such that they extended right up to the walls of the glass envelope. Connexions to these electrodes were made by means of spring loaded tungsten wires fitting into 0·05 cm diameter holes drilled 0·3 cm deep into the edge of the electrodes, and connected radially to tungsten-glass seals in the side arms of the envelope.

With a view to obtaining larger ion currents along the electrode system, the pattern of holes in electrode A was arranged in line with those in electrodes B, C, F and G, also, the three circular entrance holes to the diffusion chamber in the earlier design were replaced by three slits 0·05, 0·10 and 0·15 cm wide, 0·75 cm long and 0·25 cm apart in a spade-shaped electrode which could be moved in front of a fixed central slit in electrode J.

The demountable glow discharge ion source employed in the earlier design was replaced by a similar source permanently joined to the glass envelope; the construction of the whole electrode system was such that all parts could be degassed. All metal parts of the electrode system were cut from oxygen-free, high conductivity copper and plated with a layer of gold 0·00025 cm thick to prevent tarnishing and large contact potential differences.

(*b*) *Vacuum and current measuring systems*

The experimental tube was incorporated in an ultra-high vacuum system, but for the measurements described in this paper the spectroscopically pure hydrogen gas supplied by B.O.C. Ltd was admitted into the system after attaining a base pressure of about 5×10^{-6} mmHg with an outgassing rate which produced a pressure rise of the order 5×10^{-5} mmHg in 12 h.

The ion currents ranged from 10^{-8} to 10^{-14} A, those currents greater than 3×10^{-13} A were measured with a valve electrometer (Crompton & Sutton 1953), while smaller currents were measured using a vibrating reed electrometer constructed in the department to the design of Wood & Sutherland (1953). In principle, each instrument measured current by amplifying the potential difference developed by the current flowing through a high resistor to earth.

3. Operation of the apparatus

(*a*) *The drift section*

As in the previous apparatus (part II), the drift velocity section was found to be operating satisfactorily. Measurements of the drift velocity were made by pulsing electrodes B and G out of phase with sine waves from an advance signal generator. (As in previous work it was found that pulsing the electrodes B and G out of phase with square waves gave identical values). Although the ion current was accompanied by a current of photoelectric origin (attributed to photons from the glow discharge passing through the holes in electrodes A, B, C, F and G which were in line), this photoelectric current remained constant independent of the frequency of the pulses applied to electrodes B and G, and could be suppressed by applying an appropriate negative potential to the electrometer through the high resistance.

The drift velocity and mobility of ions issuing from a glow discharge source in hydrogen were studied for $4 < E/p_0 < 30\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ and for gas pressures $0{\cdot}5 < p_0 < 6{\cdot}0$ mmHg. In this range the graphs of current against frequency all indicated the presence of a single ion species with zero-field mobility $10{\cdot}8 \pm 0{\cdot}5\,\mathrm{cm^2\,s^{-1}\,V^{-1}}$. The results of mobility determination are shown plotted as a function of E/p_0 in figure 12. For $E/p_0 \lesssim 10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$, the mobility remained constant; for higher values of E/p_0, the mobility gradually increased.

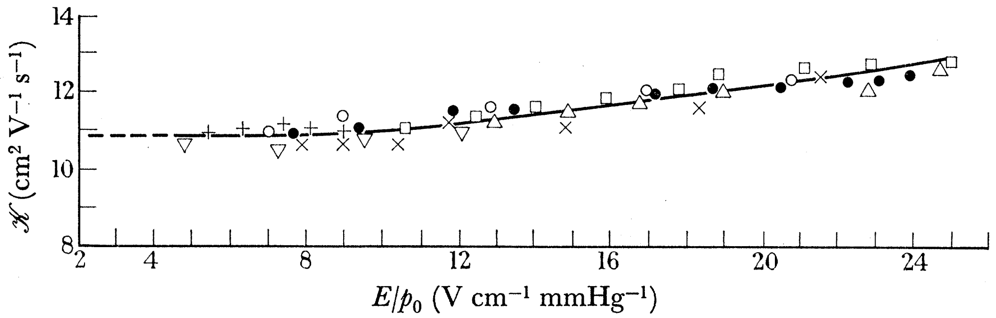

FIGURE 12. Observed variation of mobility with E/p_0 for hydrogen ions in hydrogen.

experimental points	p_0(mmHg)	experimental points	p_0(mmHg)
□	1·19	○	3·01
△	1·53	▽	4·40
●	2·44	+	5·84
×	2·88		

(*b*) *The diffusion section*

In view of the difficulties encountered with the previous design of the apparatus (part II) it was necessary to undertake preliminary experiments to find out whether the apparatus was now working satisfactorily. These experiments showed that the current received at the collecting electrodes was dependent on the frequency of the voltage pulses applied to electrodes B and G, and that by applying a reverse field in the drift region, it was possible to reduce the positive ion current collected at the collecting electrodes to zero. Furthermore, closing the entrance slit to the diffusion chamber cut off all current to the electrodes P_1 P_2 and P_3 and masking off the gap between the D-shaped electrodes P_1 and P_2 cut off all current to the electrode P_3. These tests showed that the new features introduced in the design of the present apparatus had eliminated the spurious current associated with the earlier apparatus, and that the ion currents now collected at the electrodes P_1, P_2 and P_3 were due to positive ions which entered the diffusion region through the slit in electrode J.

In order to determine the ratio W/D at a given value of the field E and gas pressure p_0 it is necessary to determine the ratio R of the ion current received at electrode P_3 to the total ion current received at electrodes P_1, P_2 and P_3. In order to maintain a uniform field along the whole length of the diffusion space J to N, it was necessary to maintain a field equal to the main field between the D-shaped electrodes and P_3. Even with the maximum field used (*ca.* 60 V cm^{-1}), the potential difference between the electrodes M and N was only 12 V, so that care had to be taken not to change the field configuration, by ensuring that the potential of the electrode at which the current was being measured did not rise even by 0·1 V above earth. For this reason, after suppressing the photoelectric component of the current (which remained stable to within $\pm 1 \times 10^{-15}$ A), the vibrating reed electrometer employed to measure the ion current was used as a null indicator, keeping the collecting electrode at earth potential by means of a measured potential applied to the reed through the high resistance. The requirement that the field between the D-shaped electrode and P_3 should equal the main field was met by the following procedure. When the current to electrode P_3 was being measured, P_1 and P_2 were connected to electrode M, and electrode N was earthed; when the current to electrode P_1 or P_2 was being measured, P_3 was connected to N, and M was earthed.

Adopting this procedure to measure the ion currents, the sum of the currents received by the electrodes P_1, P_2 and P_3 was found to be the same as the current received by P_1 and P_2 when the metal foil, attached to one of these D-shaped electrodes, masked off the gap between them. The current received at electrode P_3 was thus due to ions which traversed the gap between P_1 and P_2. Further tests with the diffusion section showed that for a given value of field, gas pressure and glow current, the ratio R was reproducible to within an absolute value of $\pm 0{\cdot}01$ and independent of the glow current at a given value of field and gas pressure.

With the same field maintained along the whole of the electrode structure, measurements of the ratio R were generally confined to electric fields $\gtrsim 20$ V cm^{-1} and gas pressure $\lesssim 3$ mmHg, because at lower fields and higher pressures the ion currents became too small to measure. However, by maintaining a higher field in the drift region (A to G) than in the region between electrodes G to N, it was possible to obtain sufficient ion current (with the species of ion of zero-field mobility 10·8 cm^2 V^{-1} s^{-1}) to enable measurements of R to be extended to fields as low as about 4 V cm^{-1} and to pressures up to 6 mmHg. In this way, ions selected by the time of drift analyser traversed the region GJ under the influence of a unidirectional electric field having the same value as that in the diffusion space JN. In order to assess the influence of the oscillating voltage applied to the electrode G on the ions passing through the slit in electrode J, measurements of the ratio R were also undertaken by pulsing electrodes B and F in phase with square waves from an E.T.C. pulse generator. Within the stated reproducibility of the measurements of R at a given value of field and pressure, no difference was observed in the values of R obtained in this manner and the values of R obtained when pulsing out of phase with sine waves. This indicated that the ions attained the energy distribution appropriate to the value of E/p_0 in the region JN before passing through the slit in electrode J.

4. DETERMINATION OF W/D FROM THE MEASURED RATIO OF CURRENTS

The differential equation relating particle density and the quantity W/D is (Townsend 1925)

$$\nabla^2 n = \frac{W}{D}\frac{\partial n}{\partial z}, \tag{1}$$

where the field is in the z direction.

It follows that if we neglect diffusion in the field direction, the expression for the ratio R of the current received at the collecting electrode P_3 to the total current received by electrodes P_1, P_2 and P_3 is (Townsend 1925)

$$R = \frac{2}{\sqrt{\pi}} \int_0^{b\sqrt{(W/4Dh)}} e^{-t^2}\, dt, \tag{2}$$

where h is the distance from J to M and $2b$ is the width of the gap between the collecting electrodes P_1 and P_2

Since the error integral

$$\frac{2}{\sqrt{\pi}} \int_0^{x} e^{-t^2}\, dt$$

has been tabulated by Jahnke & Emde (1933), equation (2) provides a convenient means of obtaining values of W/D from the experimental measurements of R.

A more accurate expression for R, containing an explicit expression for the longitudinal diffusion of ions, has been given by Professor P. M. Davidson of this Department and reads

$$R = \frac{2}{\sqrt{\pi}} \left[\int_0^{L} e^{-t^2}\, dt + \frac{5}{8} \frac{L e^{-L^2}}{\beta h} \right], \tag{3}$$

where

$$L = \left(\frac{\beta}{\psi} \sqrt{(h_1^2 + b^2)} - \beta h \right)^{\frac{1}{2}},$$

$$\beta = \frac{W}{2D_e}, \quad h_1 = \psi h, \quad \psi^2 = \frac{D_t}{D_e},$$

D_e being the longitudinal diffusion coefficient and D_t the lateral diffusion coefficient.

With the dimensions employed in the present diffusion apparatus ($h = 3{\cdot}20$ cm, $2b = 0{\cdot}326$ cm) and with $\psi^2 = \frac{1}{4}$ and 4, the values of R calculated from equation (3) for a large range of W/D_t are in close agreement with the values of R calculated for the same values of W/D using equation (2). The maximum difference in the values of R occurs at low values of W/D and for small ψ. For the lowest value of W/D determined in the present investigation (*ca.* 100 cm^{-1}) and with $\psi^2 = \frac{1}{4}$ this difference amounts to less than 1·3 %. This suggests that unless R can be measured with an error of $\lesssim \pm 0{\cdot}5$ %, then the Townsend equation (2) is adequate, especially in view of the fact that the entrance slit has a finite width.

If we consider an entrance slit of width $2a$, then neglecting the longitudinal diffusion of ions and assuming a uniform distribution of ions across the width of the entrance slit, the expression for R becomes

$$R = \frac{1}{2a} [(a+b)\, \mathrm{erf}\{\theta(a+b)\} - (b-a)\, \mathrm{erf}\{\theta(b-a)\}] + \frac{1}{2a\theta\sqrt{\pi}} [\exp\{-\theta^2 (b+a)^2\} - \exp\{-\theta^2 (b-a)^2\}], \tag{4}$$

where

$$\mathrm{erf}\, x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \quad \text{and} \quad \theta^2 = \frac{W}{4Dh}.$$

Computation of the error in R using these equations shows that the maximum error for a slit of width 0·15 cm is about 4 % while that for a slit of width 0·10 cm is about 1·2 %. Experimental observations with slits of these magnitudes, however, showed no detectable difference in the measured ratios within the error of measurement of about 1 %. This suggests that, as in the case of the diffusion of electrons (Crompton & Jory 1962), the assumption of a uniform distribution of ions across the slit leads to an overestimation of the error due to the finite width of the source.

5. Results and discussion

(a) *Measured values of current ratios*

The results of the measurement of the ratio R as a function of the electric field E for $2 < E < 50\,\mathrm{V\,cm^{-1}}$ and $0\cdot5 < p_0 < 6\,\mathrm{mmHg}$ are shown in figure 13. It is interesting to note that the only other published determination of the ratio W/D for gaseous positive ions is that of Llewellyn Jones (1935) for unselected argon ions in argon. The general nature of the R, E curves obtained in that work is similar to that shown in figure 13.

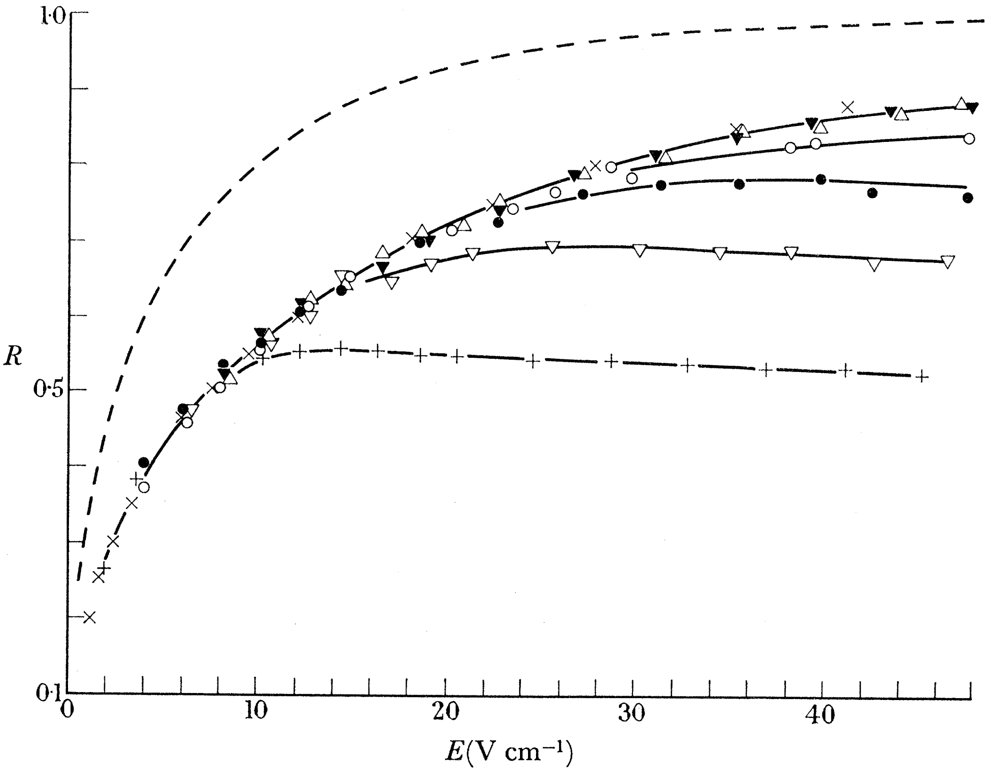

Figure 13. Variation of R with electric field for various gas pressures.

experimental points	p_0(mmHg)	experimental points	p_0(mmHg)
+	0·59	○	3·01
▽	1·19	▼	4·40
●	1·82	△	5·84

– – –, Theoretical curve calculated from equations (2) and (5). ×, Points of theoretical curve modified to take into account field distortion; calculated from equations (8) and (5).

For $E/p_0 \lesssim 10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ it is observed that the ratio R is a function of the electric field E only, independent of p_0. With increasing gas pressure, the range of E for which the ratio R is independent of p_0 correspondingly increases, and at $p_0 = 4\cdot40$ and $5\cdot84\,\mathrm{mmHg}$

the R, E curves are in agreement over the whole range of E investigated. Since values of R obtained for $E/p_0 \lesssim 10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ are independent of pressure and a function of the electric field only, it may be concluded that this range of E/p_0 corresponds to the range of E/p_0 for which the ions remain in thermal equilibrium with the gas molecules. It is interesting to note that for this range of E/p_0 the mobility remained constant. For higher values of E/p_0, it is observed that the values of R diverge from the R, E curve corresponding to thermal equilibrium, indicating an increase in lateral diffusion associated with an increase of the energy of the ions.

(*b*) *Experimental and theoretical ratios for thermal ions*

Under conditions of thermal equilibrium between ions and gas molecules, the values of R would be expected to be the same as those predicted by inserting in the equation (2), values of W/D given by the Einstein relation

$$\frac{W}{D} = \frac{eE}{kT}, \tag{5}$$

where e is the electronic charge, k Boltzmann's constant and T the absolute temperature. The theoretical curve of R, E so computed is shown in figure 13. It can be seen that at a given value of E a considerable difference exists between the computed and experimental values of R. A similar discrepancy was observed in the investigations of Llewellyn Jones (1935).

In employing the Einstein relation (5), the only assumption made is that the ionic distribution function is Maxwellian. Although this may not be strictly correct, it would be expected to be a good first approximation, because ions lose a large fraction of their acquired energy in collision with neutral gas molecules. The distribution function itself is also assumed to be unaffected by the presence of the density gradient, and consequently the ratio of drift velocity to diffusion coefficient is assumed to be independent of position. Parker (1963) has shown that with the dimensions employed in experiments on diffusion this assumption does not lead to any appreciable error. It thus does not seem that the theoretically computed values of R are likely to be greatly in error. It follows that the marked difference between the experimental and computed values of R is probably due to experimental factors.

Experimental factors, in addition to those already discussed, which could possibly influence the measurements are the interaction between ions and metal surfaces (resulting in the liberation of secondary (γ) electrons and/or perturbations in the uniformity of the electric field. If the value of the secondary coefficient γ were high, this would lead to the production of electron current from the collecting electrodes, which, in turn, would ionize the gas and give a substantial positive ion current to the collecting electrodes, with a distribution different from that of the original ions. This secondary ion current would, however, be markedly dependent on the pressure at a given value of E/p_0 because the primary ionization coefficient $\alpha = p_0 f(E/p_0)$ and, as a consequence, $D/\mathscr{K}$ would depend not only on E/p_0 but on p_0. Hence, by carrying out experiments over a range of pressures for a given value of E/p_0, it can be found whether this effect is of importance. Experiments in hydrogen showed that $D/\mathscr{K}$ was independent of pressure over the range investigated (see figure 14) and thus that secondary ionization due to ion impact could be neglected; this is in accordance with previous work on secondary ionization in hydrogen (Llewellyn Jones & Jones 1962).

In considering the possibility of field distortion, it seemed unlikely that distortion occurred in the main diffusion space where guard rings were employed to ensure uniformity; but it seemed possible that there might be slight distortion of the field in the region of the collecting electrodes P_1, P_2, and P_3 due to the finite thickness (0·06 cm) of the electrodes. Electrolytic tank experiments with a large scale model of the collecting electrodes showed that the field across the gap (0·326 cm) between P_1 and P_2 was slightly distorted near the edges of the electrodes. As a result, ions traversing the gap near the edges of the electrodes P_1 and P_2 were collected at these electrodes instead of travelling to the back collecting electrode P_3. If the observed discrepancy between the computed and experimental values of R at low values of E/p_0 were due to this cause, computation of R by replacing the half width of the gap b by b/c, where c is constant, should give a modified theoretical curve in agreement with the experimental curve R, E. Such a modified theoretical curve with $c = \sqrt{2 \cdot 8}$ is shown in figure 13, where it is seen that the computed curve is in agreement with the experimental R, E curve under conditions of thermal equilibrium for all values of the field. This suggests that the original discrepancy was in fact due to the slight non-uniformity of the field in the region of the collecting electrodes and could be corrected for by reducing the slit width from its actual value $2b$ to an effective value $2b/c$.

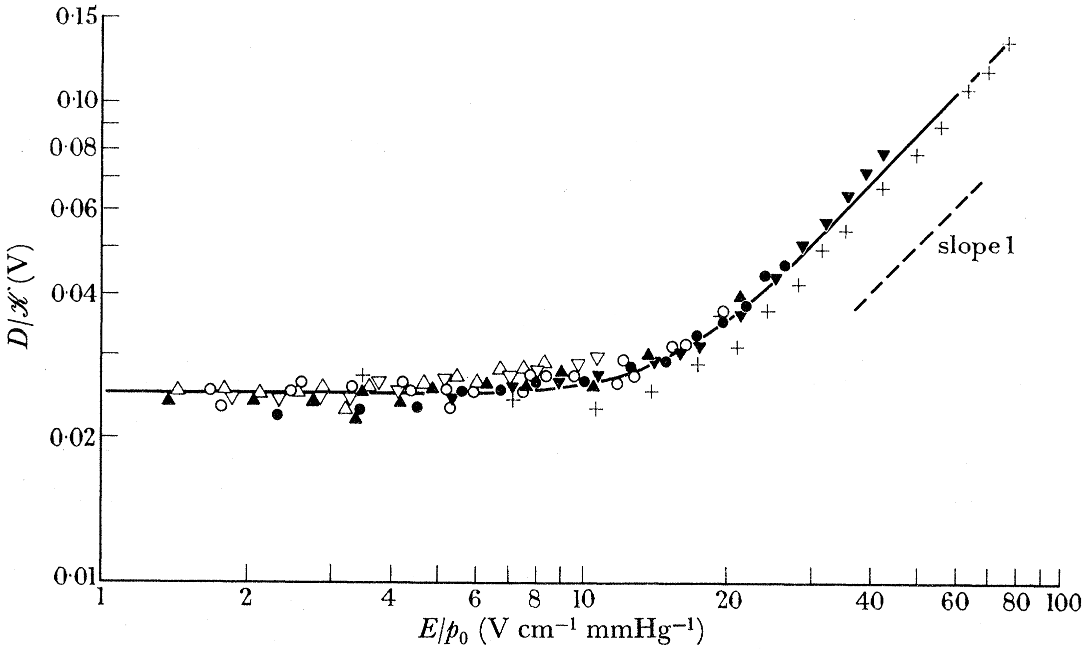

FIGURE 14. Variation of $D/\mathcal{K}$ with E/p_0. – – – –, Line of slope unity.

experimental points	p_0(mmHg)	experimental points	p_0(mmHg)
+	0·59	▲	3·01
▼	1·19	▽	4·40
●	1·82	△	5·84
○	2·44		

A normalizing correction to results recently obtained for the diffusion of electrons at very low values of E/p_0 has also been found to be necessary (Warren & Parker 1962) due to effects which were shown by Crompton & Elford (1963) to be caused by field non-uniformity.

(*c*) *Values of $D/\mathscr{K}$ and ϵ*

It follows from the previous section, that in the present apparatus, the measured ratio R is related to the ratio W/D and the dimensions of the apparatus by the relation

$$R = \frac{2}{\sqrt{\pi}} \int_0^{t'} \mathrm{e}^{-t^2}\,\mathrm{d}t, \tag{8}$$

where

$$t' = \frac{b}{c}\sqrt{\left(\frac{W}{4Dh}\right)},$$

where

$$c = \sqrt{2{\cdot}8}.$$

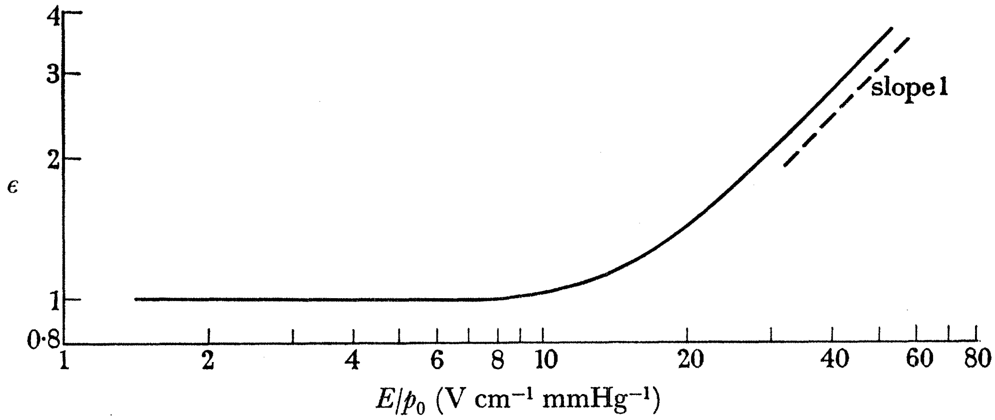

FIGURE 15. Variation of ϵ with E/p_0. ———, Curve computed from experimental data; ----, line of slope unity.

Values of the ratio of the diffusion coefficient to mobility $(D/\mathscr{K})$ derived from experimental measurements of R by the use of equation (8) are shown plotted as a function of the parameter E/p_0 in figure 14. It can be seen that the values of $D/\mathscr{K}$ obtained at various gas pressures are in general within $\pm 12\,\%$ of the solid line constructed to pass through a mean of the data. For $E/p_0 \lesssim 10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ the value of $D/\mathscr{K}$ remains constant at 0·025 V. With increasing E/p_0, the ratio $D/\mathscr{K}$ increases, and at the higher values of E/p_0, the ratio $D/\mathscr{K}$ becomes linearly dependent on E/p_0.

If we assume that the field is not great enough to produce a significant divergence from a Maxwellian energy distribution, then ϵ, the ratio of the mean energy of the ions to that of the gas molecules, may be written as

$$\epsilon = \frac{e}{kT}\frac{D}{\mathscr{K}}. \tag{9}$$

The values obtained for ϵ using the experimentally observed values of $D/\mathscr{K}$ in equation (9) are shown in figure 15. It is interesting to note that the ions remain in thermal equilibrium with the gas molecules at values of E/p_0 up to about $10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$, but that at higher values, the energy increases, becoming linearly dependent on E/p_0 at values greater than about $25\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$. The range of E/p_0 over which the ions remain in thermal equilibrium with the gas molecules, as obtained from these diffusion measurements, is the same as that over which the mobility obtained by independent means for the same ions in the same gas sample, remains constant (see figure 12). The implication is that the observed increase in mobility at values of $E/p_0 \gtrsim 10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ is attributable to an increase in the mean energy of the ions.

(*d*) *Values of* Dp_0 *and cross-sections*

By using the values of $D/\mathscr{K}$ given in figure 14 together with the values of $\mathscr{K}$ obtained for the same ions in the same gas sample (and given in figure 12), it is possible to obtain values of D. The values found in this way are given in figure 16 plotted as Dp_0, E/p_0. As is to be expected, whatever the ion-molecule interaction, Dp_0 is constant for low values of E/p_0. At higher values of E/p_0 ($\gtrsim 10\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$), Dp_0 increases as shown; it is not, however, possible to obtain information about the predominant forces of interaction in this region, because in this intermediate region of E/p_0 there is no adequate theory for the dependence of Dp_0 or of $\mathscr{K}$ on E/p_0 taking into account various forms of ion-molecule interactions.

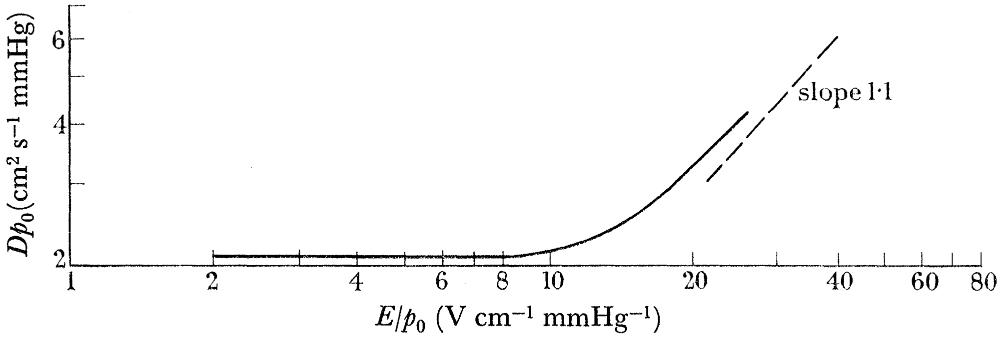

FIGURE 16. Variation of Dp_0 with E/p_0. ———, Curve computed from experimental data; – – – –, line of slope 1·1.

From the mobility data shown in figure 12 together with values of ϵ given in figure 15, it is also possible, using a procedure familiar in electron drift and diffusion studies (see Healey & Reed 1941), to estimate the kinetic theory cross-section of the ions. The kinetic theory equation for the mobility of ions in gases derived by Langevin (1903) may be written as

$$\mathscr{K} = \frac{0{\cdot}815}{m_i C_i}\,\frac{e}{NQ}\left(\frac{m_i+M}{M}\right)^{\frac{1}{2}}, \tag{11}$$

where m_i is the mass of the ion,

M is the mass of the gas molecule,

Q is the cross-section,

N is the number density of gas molecules,

and C_i is the r.m.s. velocity of the ions given by

$$\tfrac{1}{2}m_i C_i^2 = \tfrac{3}{2}\epsilon k T. \tag{12}$$

The absolute value of the cross-section Q depends on the mass of the ion species investigated, but the variation of Q with energy is independent of mass. As an example of this variation, Q is given as a function of C_i in figure 17 on the assumption that the ions have a mass of 3 atomic units. It can be seen that the cross-section decreases rapidly as U increases the slope on the log–log scale being $-1{\cdot}58$. Considering gas kinetic electron charge transfer and polarization ion-molecule interaction forces it is difficult to account for this rapid decrease of cross-section with energy, and a possible explanation is that the ions undergo dissociative reactions with the gas molecules as discussed in section (f) on ion identity.

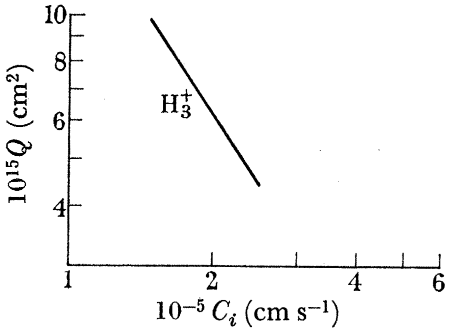

FIGURE 17. Variation of cross-section with ion velocity.

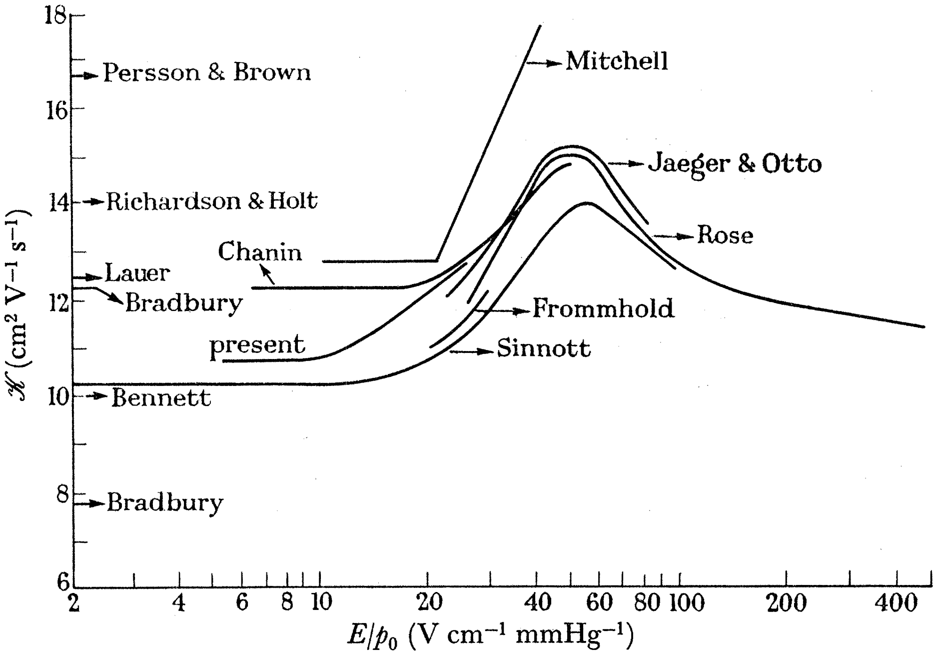

FIGURE 18. Available* data for the mobility of hydrogen ions in hydrogen.

(e) *Mobilities*

The results of the present investigation are compared with the results of previous studies in figure 18. In the cases in which the mobilities were obtained over a range of values of E/p_0 (Mitchell 1938; Frommhold 1960; Rose 1960; Chanin 1961; Jaeger & Otto 1962; Sinnott 1964), the full lines indicate the range of E/p_0 covered, and represent smooth curves through the published data. Also shown are the values of mobility obtained by Bradbury 1932, by Bennet 1940 and by Lauer 1952 at low values of E/p_0 (the ranges of E/p_0 investigated were not specified). In Bradbury's measurements, the predominant ion observed

* See also Saporoschenko (1965 b)

had a mobility of 7·6 cm^2 V^{-1} s^{-1} but the existence of an ion with mobility 12·3 cm^2 V^{-1} s^{-1} was also reported. As the value of 7·6 refers to ions *ca.* 10^{-2} s old, these ions may not be hydrogen as has previously been pointed out (see Chanin 1961). In addition to previous results of direct measurements of the mobility, the values of zero-field mobility, deduced from microwave measurements of the ambipolar diffusion coefficient in hydrogen afterglows are also indicated (Persson & Brown 1955, Richardson & Holt 1951) in figure 18. It will be noted that these values lie considerably above the more directly determined values, and Rose (1960) has discussed possible sources of error in the microwave values. It is interesting to note, however, that in previous direct measurements of the drift velocity of hydrogen ions in hydrogen (purified using uranium hydride) undertaken at this laboratory (Rees 1959) an ion species with zero-field mobility 15·8 cm^2 V^{-1} s^{-1} close to the value of 16·5 cm^2 V^{-1} s^{-1} obtained by Persson & Brown was observed, in addition to the ion species of lower mobility observed in the present investigation.

The zero-field mobility value of 10·8 ± 0·5 cm^2 V^{-1} s^{-1} observed in the present work agrees within the experimental error with the recent data of Sinnott (10·2 ± 0·5) and is close to the value (10·0) obtained by Bennett. The differences at the higher values of E/p_0 in the values obtained by Sinnott and in the present investigation are discussed in § (*f*). The zero-field mobility obtained by Mitchell by Lauer and by Chanin are in close agreement with each other, but approximately 18 % higher than the results obtained in the present investigation. It thus appears that three different ion species, *A*, *B* and *C*, say, have been studied in the various investigations, these species having zero-field mobility values of about 16, 12·5 and 10·5 cm^2 V^{-1} s^{-1}, respectively.

(*f*) *Ion identity*

It has been known for some considerable time (Luhr 1933; Barnes *et al.* 1961) that H^+, H_2^+ and H_3^+ ions are formed in electron impact and glow discharge sources, and this was confirmed in mass spectrometric studies of the gas used in the present investigation. It is of interest to compare the experimental value of mobility with those computed for these ions. Calculations of the mobility of ions in hydrogen undertaken by Mason & Vanderslice (1959) give values of 18·3, 13·9 and 22·0 cm^2 V^{-1} s^{-1} for the mobility of H^+, H_2^+ and H_3^+, respectively. Varney (1960) suggested that the computed value for H_3^+ is too high because no account was taken of proton charge transfer*. Recent theoretical computation (Christoffersen & Hagstrom 1964) of the binding energy of H_3^+, however, shows that this energy is probably much larger than the value used by Varney in his considerations.

Direct comparison of the experimental and computed values of mobilities would seem to indicate that the species *A* (mobility ≃ 16 cm^2 V^{-1} s^{-1}) is H^+ and that the species *B* (mobility ≃ 12·5 cm^2 V^{-1} s^{-1}) is H_2^+. The identification of species *A* as H^+ seems to be generally accepted (McDaniel 1964). The identification of species *B* as H_2^+, on the other hand, was questioned by Chanin (1961), on the basis that mass analysis of initially mixed swarms of H^+, H_2^+ and H_3^+ ions after they have passed through a few centimetres of gas at a pressure ~ 10^{-1} mmHg showed (Luhr 1933; Barnes *et al.* 1961) that H_3^+ ions became the predominant species. Chanin consequently suggested that the ion species *B* is H_3^+, the mobility being reduced below the calculated value due to proton charge transfer.

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* See also Hasted (1965).

Recent mass spectrometric investigations (Dawson & Tickner 1962; Saporoschenko 1965*a*) have shown that a further ion species, H_5^+, must also be taken into consideration. In both of these investigations it was shown that H_5^+ ions were present in small amounts relative to H_3^+. The proportion of H_5^+ ions was shown by Saporoschenko to increase with increasing pressure in the range 10^{-5} to 0·5 mmHg and to decrease with increasing values of E/p_0 in the range 3 to 50 V cm^{-1} mmHg^{-1}. His results also indicated that the H_5^+ ions dissociated into H_3^+ ions in the mass spectrometer. In the light of this recent mass spectrometric evidence the results of the present investigation give further confirmation to the possibility, suggested by Sinnott (1964), that the ion species C is H_5^+, and that as the value of E/p_0 increases this species undergoes a dissociative reaction with the gas molecules to form H_3^+. Such a reaction would account for the increase of mobility with E/p_0 observed at the higher values of E/p_0 in both the present investigation and in the work of Sinnott. The increase does not occur at the same value of E/p_0 in each investigation, but this may well be due to the different experimental conditions, such as the slightly longer overall drift distance used in the present apparatus, which can be of importance if reactions are occurring between the ions and gas molecules.

The H_5^+ species would, on general grounds, be expected to have a low binding energy and this would account for its low intensity in mass spectrometric investigations. It would also be consistent with the results of the present investigation which shows that (i) the mobility begins to increase as soon as the mean energy of the ions (as obtained from measurements of diffusion) exceeds that of the gas molecules, and (ii) that the effective collisional cross-section of the ions decreases rapidly with increasing energy. It would clearly be of interest to measure the mobility of hydrogen ions in hydrogen in an apparatus incorporating a mass analyser, in order to establish directly the identity of the ion species on which measurements have been made; further work on this aspect of the problem is currently being undertaken in this laboratory.

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