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Critical Review

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I. CRITICAL REVIEW

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1. Introduction

A full understanding of electrical discharges and plasma requires knowledge of the motion of electrons and ions in gases in electric fields. For electrons, a large amount of published information (see, for example, Townsend 1915, 1925; Thomson & Thomson 1928; 1933; Healey & Reed 1941; Allis 1956; Bates 1962; Hasted 1964; McDaniel 1964) exists concerning collisional properties such as the mean free path, mean energy, diffusion coefficient and mobility. For ions, on the other hand, basic data on the various collisional properties other than mobilities is much more scanty. Positive ions, however, play an important role in the mechanism of electrical discharges not only in the initial breakdown of the gas but also in the development of the current and in the maintenance of the discharge (Llewellyn Jones 1953, 1957). The various collisional processes involving ions such as the liberation of secondary electrons from the cathode, space charge formation, ambipolar diffusion, recombination and charge exchange have been discussed by Mott & Massey (1949) and by Massey & Burhop (1952).

Although positive ion mobilities have been studied by many investigators (see Bates 1962) there are considerably fewer results available about the other collisional properties, especially in weak electric fields. This is due to the formidable difficulties encountered in both the theoretical and experimental studies especially in the case of slow ions. Theoretical calculations relating to the collisional properties of positive ions require a knowledge of the forces of interaction exerted between ion and molecule. When the period of interaction is comparatively long, as in the case of slow positive ions colliding with gas molecules, these forces of interaction are often unknown. This is particularly so for positive ions travelling through their parent gas where the phenomenon of charge exchange occurs. Hence, in these circumstances, accurate experimental data concerning such slow collisions are of particular value.

The purpose of the present investigation is first to make a critical survey of present knowledge, both theoretical and experimental, of the motions of slow positive ions in gases, and then to discuss the results of an experimental investigation of the mobility of various ions in nitrogen and argon and of mobility and diffusion of ions in hydrogen. This investigation forms part of a general study of the mobilities, diffusion and energies of ions in their parent gases which is being undertaken in the Department of Physics, University College of Swansea.

2. Previous theoretical studies of mobilities

(a) *Forces of interaction and energy distribution*

On the classical view the scattering of electrons by atoms is spherically symmetrical and, moreover, only a small fraction of the electron energy (m_e/M where m_e is the electron mass and M the atomic mass) is lost at each elastic collision. Hence, when an electric field is present the electron acquires energy in the form of random motion so that the velocity distribution function is almost spherically symmetrical in velocity space. For ions, on the other hand, only scattering in the forward direction takes place and in the presence of an electrical field the velocity distribution is not spherically symmetrical. This is one of the main difficulties in developing a satisfactory theory of ionic mobilities since for ions very little concerning the velocity distribution is known. It is to be expected, however, that when the electric field is small the distribution will not differ appreciably from Maxwellian, because the ions lose a large fraction of the energy acquired from the field in collisions with neutral gas atoms. In order to specify the distribution exactly, the forces of interaction between ions and molecules must be accurately known. The forces include those of gas kinetic repulsion, polarization attraction and charge exchange.

Gas kinetic repulsion forces are short range forces which result from repulsion between the powerful electric fields surrounding the ion and the atom. These forces are usually accounted for by a model in which the ions and atoms are hard elastic spheres whose closest distance of approach is fixed by the sum of the radii of the colliding particles. This model gives a collision cross-section which is independent of the velocity of approach of the colliding particles, that is a constant mean free path.

Polarization attraction forces arise from the displacement of the electron clouds of neutral molecules, relative to their nuclei, in the high electric field surrounding an ion. The force between the ion and this induced dipole is approximately inversely proportional to the fifth power of separation at large separations. As a consequence of the polarization attraction the mean free path of the ion is reduced (Thomson 1924) and collisions between ions and molecules become more head-on. Moreover, although the collision cross-section needs careful definition in this case, Wannier (1952) has shown that the cross-section should be inversely proportional to the velocity of approach and should thus give a constant mean free time between collisions.

Charge exchange forces arise because there is a probability, depending on the energy difference ΔE and the relative velocity U of the particles, that an ion X^+ will, in collision with a neutral gas atom Y, capture an electron. This process represented by

$$X^+ + Y = X + Y^+ \pm \Delta E$$

is a quantum mechanical phenomenon. It leads to the production of fast neutral gas atoms (Horton & Millest 1946) and a reduction in the drift velocity of the ions. The process has a maximum probability (Massey & Burhop 1952) for a particular relative velocity when ΔE is zero, a condition satisfied, for example, by atomic ions moving in the parent monatomic gas. For both positive and negative ΔE, the cross-sections for the reaction at fixed relative velocities rapidly fall off as ΔE increases. For zero ΔE the cross-section slowly decreases with increasing U. Since in the case of exact resonance the variation of cross-section with relative velocity is small, attempts have been made to insert an appropriate hard sphere cross-section into the Langevin formula (equation (4)) to predict ion mobilities in the rare gases (Hornbeck 1951*b*; Wannier 1951, 1952, 1954).

Although the general nature of the forces of interaction between ions and gas molecules is known, little progress has been made towards the solution of the problem of determining the energy distribution function of ions in an electric field. The reason for this is that, under many conditions, the detailed contribution of the various forces to the total interaction cannot be completely specified. For this reason most theoretical treatments of mobility assume that the ions are in thermal equilibrium with the gas (the zero-field approximation) and possess a Maxwellian distribution of velocities. These treatments are expected to be good approximations at low values of E/p_0 (E is the field in V cm^{-1} and $p_0 = 273p/T$ where p is the gas pressure (mmHg) at a temperature of T°K) when the energy gained by an ion in a free path is negligible compared with its thermal energy. It is, however, possible in certain circumstances to compute ionic mobilities without a full knowledge of the velocity distribution, and the most notable contribution in this direction is due to Wannier (1952, 1953) whose work is described later.

These theoretical studies of ionic mobility may be conveniently considered in two groups: (i) those applicable at low values of E/p_0, and (ii) those applicable at high values of E/p_0.

(*b*) *Ionic mobility at low values of* E/p_0

(i) *The Langevin theory*

Langevin (1903), on the basis of the kinetic theory, obtained the well known expression

$$\mathscr{K} = 0{\cdot}815 \frac{e}{M}\frac{L}{C}\left[1+\frac{M}{m_i}\right]^{\frac{1}{2}} \tag{1}$$

for the mobility $\mathscr{K}$ of positive ions in terms of M and m_i the masses of the gas molecules and positive ions respectively, C the root mean square agitational velocity of the molecules, L the mean free path of the ions and e the electronic charge. The mean free path is given by

$$L = [N\pi\sigma_{12}^2]^{-1}, \tag{2}$$

where σ_{12} is the sum of the ionic and molecular radii and N is the number of molecules per unit volume.

Equations (1) and (2) represent the best solution to the problem using the kinetic theory and the elastic sphere model. However, equation (1) is not consistent with the results of experimental investigations. For example, the values obtained for $\mathscr{K}$ by means of equations (1) and (2) are about four times higher than the experimental values, and do not have the correct temperature dependence.

Subsequently, Langevin (1905) assumed a model in which the ions possessed a Maxwellian distribution of velocities. The gas molecules were considered to be elastic spheres of radius σ which were polarizable in the field of an ion of charge e. The force of attraction between ion and molecule was shown to be

$$\frac{2e^2\sigma^3}{r^5} = \frac{(K-1)\,e^2}{2\pi N r^5} = \frac{2e^2 P_e}{r^5}, \tag{3}$$

where r the distance of the ion from the centre of the sphere is assumed to be large compared with σ, K is the dielectric constant of the gas containing N molecules per unit volume and P_e the total effective molecular polarizability.

For the mobility, Langevin obtained the expression

$$\mathscr{K} = \frac{A(\lambda)}{[\rho(K-1)]^{\frac{1}{2}}}\left[1+\frac{M}{m_i}\right]^{\frac{1}{2}}, \tag{4}$$

where ρ is the gas density and $$\lambda^2 = \frac{8\pi\rho\sigma_{12}^4}{(K-1)\,e^2}. \tag{5}$$

When the polarization forces are of much greater importance than the repulsive forces, $A(\lambda)$ tends to the limiting value of 0·5105 at $T = 0\,^\circ\mathrm{K}$ and the expression for mobility becomes

$$\mathscr{K} = \frac{0{\cdot}5105}{[\rho(K-1)]^{\frac{1}{2}}}\left[1+\frac{M}{m_i}\right]^{\frac{1}{2}}. \tag{6}$$

However, when the polarization forces are weak and elastic scattering predominates, $A(\lambda)\,\lambda$ tends to 0·75 and the mobility is given by

$$\mathscr{K} = \frac{0{\cdot}75\,e}{\sigma_{12}^2\,(8\pi p\rho)^{\frac{1}{2}}}\left[1+\frac{M}{m_i}\right]^{\frac{1}{2}}. \tag{7}$$

Equations (4), (6) and (7) have been extensively applied to calculate mobilities of molecular ions in atomic gases and of species of atomic ions not of the same nature as the gas in which they travel. However, in most cases considerable doubt arises as to what value of the cross-section $\pi\sigma_{12}^2$ should be used in the formulae, especially for molecular ions which cannot be expected to be spherically symmetric. Values of mobility calculated from equation (4) for values of cross-sections obtained from atomic wavefunctions (Slater 1930) are in better agreement with experiment than those computed for cross-sections obtained from values of viscosity.

In a treatment due to Hassé & Cook (1931) and Hassé (1926), the Langevin theory was modified by replacing the hard sphere repulsion by a force inversely proportional to the ninth power of the distance. The total force between the ion and molecule was then expressed as

$$f(r) = \frac{s}{r^5}-\frac{t}{r^9}, \tag{8}$$

where s and t are constants.

Values of mobility calculated from the expression derived by Hassé & Cook have been tabulated by Chanin & Biondi (1957) for molecular ions in the rare gases. These values are shown in table 4 from which it will be seen that the usual Langevin theory gives closer agreement with experiment (see table 3).

The most recent development in the classical treatment of mobility at low field strength is that due to Kihara (1953). On the basis of an extension of the Chapman–Enskog theory (see Chapman & Cowling 1939) an expression for mobility can be obtained in the form

$$\mathscr{K} = \mathscr{K}_0+\mathscr{K}_2E^2+\mathscr{K}_4E^4+\ldots,$$

where $\mathscr{K}_n$ are complicated functions of the temperature, the mass ratio of the ions and molecules and of the force law between the ions and molecules. For a pure polarization interaction all $\mathscr{K}_n$ with $n > 0$ vanish so that the mobility remains constant and independent of E. Dalgarno (see Bates 1962) considers that the expansion should be useful for E/p_0 up to about 10 V cm^{-1} mmHg^{-1}, but at present the comparison of the expansion with experiment is not possible, because no measurements have been made for systems to which the theory is applicable and for which the force laws between the ions and molecules are known (Mason & Schamp 1958).

(ii) *Modification of the Langevin theory for atomic ions in their parent monatomic gas*

The Langevin theory is not directly applicable in the case of atomic ions moving in the parent monatomic gas where the phenomenon of charge exchange occurs. However, since the variation of charge exchange cross-section with relative velocity is small, attempts have been made to estimate the mobility for such ions by inserting into the Langevin equation (4) an appropriate cross-section which includes the effects of both hard sphere scattering and charge exchange. For the hard sphere model and for high electric fields Wannier (1953) derived an expression relating the ionic drift velocity to the hard sphere cross-section (see equation (20)). This equation was subsequently shown to be incorrect and was modified by Wannier (1954) to that given by equation (21).

Equations (20) and (21) both predict that the drift velocity W should be proportional to $(E/p_0)^{\frac{1}{2}}$ which has been confirmed experimentally (Hornbeck 1951 *b*). Inserting the experimentally observed values of W into equation (20), Hornbeck calculated the cross-section to be used in the Langevin equation (4). Fair agreement with experiment was found (see tables 1 and 2).

However, when the correct equation (21) is used to determine the cross-section (McDaniel 1958), the agreement between theory and experiment is not satisfactory.

(iii) *Quantum mechanical calculations*

For a rigorous calculation of the mobility when charge exchange occurs, a wave mechanical treatment is necessary. Massey & Mohr (1934) used a quantum mechanical method to determine the mobility of He^+ ions in helium where the interaction between ion and atom is fairly well known.

The mobility was evaluated from the Einstein relation

$$\mathscr{K} = eD/kT, \tag{9}$$

which holds for a Maxwellian distribution of velocities. The coefficient of diffusion D was obtained by determining the momentum transfer cross-section Q_d and inserting it into the Chapman–Enskog formula

$$D = \frac{3\pi^{\frac{1}{2}}}{16}\left[\frac{M+m_i}{jMm_i}\right]^{\frac{1}{2}}\frac{1}{NP_{12}(1-\epsilon_0)}, \tag{10}$$

where M and m_i are the masses of gas atom and ion, N is the concentration of the gas atoms. ϵ_0 is a small corrective constant which is usually ignored.

$$P_{12} = 2\int_{-\infty}^{\infty} u^5 Q_d \exp\left[-\frac{jMm_i u^2}{M+m_i}\right]\mathrm{d}u, \tag{11}$$

where $j = 1/2kT$ and u is the relative velocity of an ion and gas atom before impact and

$$Q_d = 2\pi\int_0^{\pi} I(\theta)\,(1-\cos\theta)\,\mathrm{d}\theta, \tag{12}$$

where $I(\theta)$ is the angular scattering distribution function for collision between ion and atom.

For the computation of Q_d it is necessary to know the nature of the interaction between ion and gas molecule. On account of the occurrence of charge exchange, the interaction takes one of two forms depending on whether the electronic wavefunction is symmetric or antisymmetric with respect to the interchange of nuclei. The antisymmetric interaction potential $V_a(R)$ of an ion and atom at a separation R is similar to that between an atom and an ion of unlike gas, whereas the symmetric interaction $V_s(R)$, while also behaving as $-Pe^2/R^4$ at large values of R (where P, the polarizability of the atom is given by

$$P = (K-1)/4\pi N$$

has an attractive component which persists to much smaller separations. In calculating the mobility of atomic ions in their parent gases, the cross-section included in equation (11) is the mean of two cross-sections $Q_d(a)$ and $Q_d(s)$ calculated from the respective interactions $V_a(R)$ and $V_s(R)$.

In the case considered, i.e. the mobility of He^+ ions in helium, the computed value of $12\,cm^2\,V^{-1}\,s^{-1}$ at 760 mmHg and 20 °C did not agree with the value of $21{\cdot}4\,cm^2\,V^{-1}\,s^{-1}$ observed experimentally (Tyndall & Powell 1932). However, this discrepancy was resolved by Meyerott (1946) who suggested that Tyndall and Powell determined the mobility of the molecular ion He_2^+. An ion of lower mobility which agrees with the theoretical value has since been observed (see table 1, p. 314).

Using a method similar to that of Massey & Mohr (1934), Dalgarno, McDowell & Williams (1958) calculated the momentum transfer cross-section Q_d for ions moving in unlike gases and obtained values which agreed satisfactorily with the classical value. This is to be expected because the quantum mechanical modifications to the classical theory are only important at small angles of scattering, and the term $(1-\cos\theta)$ in equation (12) ensures that the contribution of smaller angle scattering to the value of Q_d is small. Having demonstrated the suitability of the technique in this way, Dalgarno (1958) extended the method to calculate the value of Q_d for ions in the parent gas where charge exchange occurs. However, since the energies of interaction between ion and molecule were not accurately known, he selected interactions which reproduced experimental data on charge exchange cross-sections and used them to predict values for the mobility (see table 2).

For the calculation of values of mobility for Ar^+ in Ar, He^+ in He and Ne^+ in Ne, Holstein (1952) has employed a quantum mechanical procedure differing from that of Massey & Mohr. A suitable cross-section taking charge exchange and polarization forces into consideration was evaluated, and the mobility was derived from this cross-section by means of the kinetic theory analysis given by Massey (1949). The average cross-section required in this analysis is related to the momentum transfer cross-section Q_d which is a function of the impact parameter b. Holstein showed that there is a critical impact parameter b_c inside which the probability of charge transfer P_r is a rapidly oscillating function of b with extremes at 0 and 1 and having an average value of $\frac{1}{2}$. For $b > b_c$, P_r rapidly decreased to zero with increasing b. Wave mechanical methods were used to compute the probability P_r as a function of the impact parameter b, and from this a value for b_c and the required cross-section were found.

The only application of wave mechanics to the determination of the mobility of molecular ions in atomic gases is due to Geltman (1953), who calculated the mobility of He_2^+ ions in helium as a function of temperature. The computed values are, however, not in very good agreement with the experimental values of Tyndall & Pearce (1935) or of Chanin & Biondi (1957), being about 10% higher and having a different dependence on temperature.

In hydrogen, Mason & Vanderslice (1959) used quantum mechanical theory to calculate the mobility of H^+, H_2^+ and H_3^+ ions. In these calculations the long range ion-molecule forces were derived theoretically, while the more difficult short range forces were estimated from an analysis of the measurement of scattering of low velocity beams in hydrogen carried out by Simons, Fontana, Francis & Unger (1943) and by Simons, Fontana, Muschlitz & Jackson (1943). The short range forces for H_3^+ ions are repulsive, for H_2^+ ions are essentially determined by electron charge transfer, and for H^+ ions have a strongly attractive component.

(*c*) *Ionic mobility at high values of* E/p_0

The theoretical treatments of mobility already considered are applicable only at low values of E/p_0, i.e. when the energy gained by the ions from the electric field is negligible compared with their thermal energy. To obtain a theory applicable at high values of E/p_0, Wannier (1953) discussed the solution of the Boltzmann equation in conditions when the Maxwellian distribution of velocities could not be considered to be an approximation to the distribution of velocities of the ions, because of the high field.

Three types of ion-molecule interactions were considered. Polarization forces were accounted for by a mean free time model, while gas kinetic repulsion and symmetry forces were accounted for by a hard sphere model. The method Wannier used was to solve the Boltzmann equation for the velocity distribution, or, if this was impossible, to extract from the equation certain averages such as the drift velocity. The form of the dependence of the drift velocity W and the diffusion coefficient D of the ions on E/p_0 and on the temperature of the gas, for both low and high fields, was first deduced from a qualitative discussion of the appropriate Boltzmann equation by considering dimensional analysis.

For high fields Wannier found that if polarization forces were predominant then

$$W \propto E/p_0 \tag{13}$$

and

$$Dp_0 \propto (E/p_0)^2; \tag{14}$$

whereas for the elastic sphere model

$$W \propto (E/p_0)^{\frac{1}{2}} \tag{15}$$

and

$$Dp_0 \propto (E/p_0)^{\frac{1}{2}}. \tag{16}$$

These expressions compare with the well known relations at low fields that

$$W \propto E/p_0 \tag{17}$$

and

$$Dp_0 = \text{constant}. \tag{18}$$

In a more detailed study the constant of proportionality in equation (13) was found and the full equation for W then becomes

$$W = \frac{0{\cdot}9048}{2\pi}\left[\frac{1}{M}+\frac{1}{m_i}\right]^{\frac{1}{2}}\frac{E}{(P)^{\frac{1}{2}}N}. \tag{19}$$

Equation (19) is identical with the Langevin equation (6) which is therefore applicable at both high and low fields when polarization forces predominate.

Using numerical methods, the constant in equation (15) may also be evaluated. Wannier (1953), considering the special case when the ions and gas atoms have the same mass, first obtained the expression

$$W = 1{\cdot}147\left[\frac{eE}{4MN\pi\sigma}\right]^{\frac{1}{2}}, \tag{20}$$

where σ is the atomic radius. Later Wannier (1954) stated that, owing to an error in the derivation, equation (20) was incorrect and that the correct equation should be

$$W = \left(\frac{2}{\pi}\right)^{\frac{1}{2}}\left[\frac{eE}{4MN\pi\sigma}\right]^{\frac{1}{2}}. \tag{21}$$

This equation has also been obtained by Perel (1957).

3. Previous experimental investigations

Detailed descriptions of the early investigations concerning the mobility of positive ions in gases have been given (see, for example, Thomson & Thomson 1928; Loeb 1955). Owing to impure gas samples and the relatively long lifetimes of the ions on which measurements were made, the effect of clustering, particularly when polar molecules were present, seriously affected the early measurements of drift velocity. For drift velocity and other measurements to be significant, it is essential that the identity of the particular group of ions studied should be known. Even in highly purified gases uncertainty still remains, since it is possible to have either atomic or molecular ions or both present, and these may change in nature as conditions such as field and gas pressure are altered.

(a) *Experimental methods for the measurement of mobilities*

(i) *Electrical shutter methods*

One of the most accurate and versatile methods of determining the drift velocity of ions of short age (*ca.* 10^{-6} s) is due to Tyndall, Starr & Powell (1928); Tyndall & Powell (1930, 1932); Tyndall (1938). The method had also been independently developed by Van de Graaff (1929). Recently Beaty (1961) and Beaty & Patterson (1963, 1965), using an apparatus basically the same as that of Tyndall & Powell but with a more refined gas handling system and electronic timing techniques, have measured mobilities of argon, helium and neon ions in their parent gases. In a modified form, the method was also used for the measurement of electron drift velocities by Nielson & Bradbury (1936, 1937), for the measurement of mobilities of potassium ions in nitrogen and in neon by Crompton & Elford (1959) and for the measurement of mobilities of positive and negative ions in oxygen by Eiber (1963*b*)

The principle of this method is to measure the interval which the ions take to traverse a known distance between two electrical shutters. In the apparatus of Tyndall & Powell, a shutter consisted of two electrodes about 2 mm apart, each electrode having a central gauze mesh. A reverse field between these electrodes prevented ions passing through the shutter. If alternating sinusoidal or square wave voltage pulses were applied to open both shutters a narrow band of ions could pass through them during the advancing phase of the alternation when the amplitude was sufficient to overcome the reverse field. The frequency of the pulses was varied until maximum ion current flowed to a collecting electrode placed beyond the second shutter.

A difficulty with electrical shutters is to assess the effect of the pulses on the uniform field in which the ions are drifting. The use of square wave pulses with the four gauze method should, however, make this a negligible source of error, and even with sinusoidal pulses absolute calibration of such an apparatus is possible by arranging the second shutter to be movable (Tyndall & Powell 1932). It has also been shown (Crompton & Elford 1959) that, despite the relatively higher potential pulses in the Bradbury–Nielson type shutter (which consists of a simple grid between alternate wires of which an alternating voltage is applied) and the fact that the pulses are not screened from the drift region, there is no appreciable distortion of the drift field by the pulses in this case either.

Electrical shutter methods can be applied to ions both in like and unlike gases and are the most accurate available (error ~ 1 %) for the determination of mobilities. Furthermore, these methods give considerably better resolution between ions of differing mobilities than do the other methods to be discussed.

(ii) *Microwave methods*

Ionic mobilities have also been obtained from measurements of ambipolar diffusion coefficients in gaseous afterglows. Biondi & Brown (1949) measured this coefficient in helium and obtained a value of $13 \cdot 7\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for the mobility of helium ions in helium at 20 °C and 760 mmHg in fair agreement with the value of 12 obtained by Massey & Mohr. This method has also been used by Persson & Brown (1955) and by Richardson and Holt (1951) for the measurement of the mobility of hydrogen ions in hydrogen. Recently both Mulcahy & Lennon (1962) and Oskam & Mittelstadt (1963) have measured the mobilities of atomic and molecular helium, neon and argon ions in their parent gases by this method; the values obtained (see tables 1 and 3) agree fairly well with those obtained using other methods.

The principle of the method is to produce a plasma in a quartz vessel situated in a microwave cavity. After the ionizing pulse ceases, the ion and electron concentrations decrease because of diffusion to the walls, recombination or attachment to neutral particles. The mean decay time of electron density (when ambipolar diffusion is the predominant loss mechanism) is measured by observing the change of the resonant wavelength of the cavity by means of a weak microwave probing signal. From this the ambipolar diffusion coefficient D_a may be found and

$$D_a = 2D_+ = 2\mathscr{K}kT/e.$$

Since there are no internal electrodes, a high vacuum $\sim 10^{-9}$ mmHg may be attained in the quartz tube and very high purity gas samples may be used. Further, since the microwave probing signal is weak and the electric field in the apparatus is due only to space charge, no extrapolation of the experimental results is needed for comparison with those predicted by theory for $E/p_0 = 0$. The method has the disadvantage, however, that the exact interpretation of the electron concentration decay curve is difficult, since, although one loss mechanism can be made to predominate, other processes also contribute (Oskam 1958). Other complicating factors include the influence of metastable atoms and the initial concentration of ions and electrons (Oskam 1958).

(iii) *Pulse methods*

In recent years, high speed pulse techniques have been used to obtain values for the mobility of positive ions by analysing the current transient resulting from a group of ions drifting a measured distance in the field between a pair of plane parallel electrodes. The ions may be produced in two ways. In the first method (Hornbeck 1951 *a*, *b*) a short (*ca.* 0·1 s) pulse of photoelectrons liberated from the cathode created ions in a Townsend type discharge. The current-time traces produced were rather difficult to analyse, being generally complicated by secondary electron avalanches, photoelectric emission from the cathode and by the action of metastable atoms. It was possible, however, to obtain values of the mean drift velocity of positive ions accurate to about 5 % over a wide range of values of E/p_0. In this way, Hornbeck determined the mobilities of both atomic and molecular ions of helium, neon and argon in their parent gases. Using the same technique, Varney (1952, 1953) studied drift velocities in krypton, xenon, oxygen, nitrogen and carbon monoxide. Frommhold (1960), using a similar technique, studied drift velocities of ions in hydrogen, nitrogen and oxygen, Beaty (1956) studied the temperature dependence of the mobility of positive ions in krypton and argon, while Kovar, Beaty & Varney (1957) studied the temperature dependence of the mobility of nitrogen ions in nitrogen.

The method has the advantages that measurements may be made on pure gases admitted into baked out systems evacuated to a residual pressure $\sim 10^{-9}$ mmHg, that ion drift velocities may be obtained at high values of E/p_0, and that, due to the extremely short lifetimes of the ions, impurity effects are eliminated as much as possible. The disadvantages are that measurements can only be made on ions of the parent gas, and that the resolution between ions of different species is not as high as that of the electrical shutter method, and that to determine zero-field mobilities a lengthy extrapolation is needed, since relatively high values of E/p_0 are required to produce ionization.

Biondi & Chanin (1954) and Chanin & Biondi (1957) introduced an improvement on the Hornbeck method. They used an ion source external to the drift space; ions were created in the source by means of a short (*ca.* 0·5 μs) high voltage (*ca.* 1000 V) pulse and were then allowed to diffuse through a grid in the anode into the drift region. The motion of the ions in the drift space induced a current $i(t)$ in the external circuit. When the ions reached the cathode $i(t)$ became zero and this gave a measure of the transit time. This technique was used extensively to measure drift velocities at various temperatures in the rare gases and hydrogen (Chanin 1961). Biondi & Chanin (1961) have also extended their investigations to check the validity of Blanc's law (1908).

This method has the additional advantage over the Hornbeck method that the drift field is not likely to be distorted since lower concentrations are used. Further, it is possible to prevent the penetration of negatively charged particles into the drift region, and the current-time traces obtained are therefore easier to analyse.

(iv) *Other methods*

Bradbury (1932), with a modified form of the apparatus initially developed by Tyndall & Grindley (1926) measured the absolute mobilities of oxygen nitrogen, hydrogen and helium ions in their parent gases. A thin layer of gas between parallel plate electrodes was ionized by means of X-rays passing through a narrow slit. The application of a suitably designed potential cycle removed the electrons and allowed ions to cross the gap under the influence of a uniform electric field. From the time taken to cross and the distance between the electrodes, the drift velocity was calculated. Hershey (1939), using the lateral diffusion method of Townsend (1925) in which the ion beam was deflected by means of a magnetic field, determined the mobilities of potassium ions in hydrogen, helium, nitrogen and argon.

Lauer (1952), following the procedure of Colli, Facchini & Gatti (1950), used a cylindrical cathode and wire anode arrangements to investigate drift velocities and other discharge mechanisms in argon and hydrogen. The discharge was initiated by means of α-particles projected near to the cathode and parallel to the anode wire from a polonium source. The method has also been extended by Huber (1955) in an investigation of ions in nitrogen.

Vogel (1957) has measured the mobility of positive ions in nitrogen at high values of pd (200 to 1000 cm mmHg). The method used is very similar to Hornbeck's method. The main difference between the two methods lies in the mode of initiation of the discharge. Whereas Hornbeck maintained a steady potential difference between the anode and cathode and initiated the discharge by allowing a short (*ca.* 0·1 μs) pulse of ultraviolet light to fall on the cathode, Vogel maintained a steady potential difference across the gap until one electron leaving the cathode initiated the discharge. The motions of the ions and electrons in the gap induced a current transient in the external circuit similar to that observed by Hornbeck. In most cases, however, interpretation of the oscilloscope traces was complicated by secondary avalanches stimulated by electron emission from the cathode.

An important recent development has been the measurement* in nitrogen (McAfee & Edelson 1963; Martin, Barnes, Keller, Harmer & McDaniel 1963; Keller, Martin & McDaniel 1965) of the drift velocities of species of ions identified in a mass spectrometer incorporated into the detection system. In these experiments, the drift velocities were measured either by a development of the Hornbeck method (McAfee & Edelson 1963), or by a pulse method using a large (*ca.* 20 cm) drift space and low pressures ($\sim$ 0·1 mmHg) (Martin *et al.* 1963; Keller *et al.* 1965).

The problem of analysing the species of ions on which the drift velocity measurements have been made is an extremely difficult one, because as Eiber (1963*a*) has pointed out the identity of the ion may change in passing from the relatively high pressure region in which the measurements are made to the very low pressures ($\sim 10^{-6}$ mmHg) in the mass spectrometer. Eiber (1963*a*) has shown that a Bradbury–Nielson type shutter with sufficiently small spacing between alternate wires can be used for mass analysis at gas pressures of a few millimetres of mercury. It would be extremely interesting to incorporate such a device together with a shutter type mobility apparatus, and an apparatus of this sort is at present being constructed in this Department.

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* [*Note added in proof* 2 *December* 1965.] More recently, Saporoschenko (1965*b*, *c*) measured the mobility of mass spectrometrically identified hydrogen and nitrogen ions in their parent gases.

(*b*) *Measurements of diffusion coefficient and mean energy*

Very few data concerning diffusion coefficients, velocity distributions, mean free paths or mean energies of positive ions have been published. The only values published for diffusion coefficients of positive ions in gases are due to Townsend (1915) and other experimenters (see Thomson & Thomson 1928) who used the same method as Townsend, i.e. diffusion of ions through narrow tubes. In addition to these measurements, Llewellyn Jones (1935) using the lateral diffusion method of Townsend, examined the variation of mean energy with E/p_0 for argon ions in argon. He showed that for pressures in the range 3 to 0·24 mmHg and for values of E/p_0 less than about 20 V cm^{-1} mmHg^{-1} the mean energy of the ions was equal to that of the gas atoms. In pure gas samples the mean energy of the ions exceeded that of the gas atoms, for E/p_0 greater than 20 V cm^{-1} mmHg^{-1}, but the mean energy was found to be very sensitive to any impurities present and was considerably reduced at gas pressures $\gtrsim$ 0·5 mmHg.

The lateral diffusion method is currently being used in this Department to obtain further information about the collisional properties of positive ions (see part IV).

4. DATA FOR MOBILITIES

(*a*) *The variation of mobility with temperature and E/p_0 for ions in their parent monatomic gases*

Experimental zero-field mobilities (obtained by extrapolating the curves of $\mathcal{K}$ against E/p_0 back to $E/p_0 = 0$) have been reduced to standard gas density of $2{\cdot}69 \times 10^{19}$ atoms cm^{-3}, corresponding to 0 °C and 760 mmHg, and are shown for various gas temperatures in tables 1 and 3. Theoretical values for the zero-field mobility of atomic and molecular ions are shown in tables 2 and 4, respectively.

(i) *Atomic ions*

In the case of atomic ions, for all gases there is excellent agreement between the various experimental values except for those of Biondi and Brown in He, and the values obtained are also in good agreement with the calculated values of Dalgarno at all temperatures studied. The quantum mechanical computations of Holstein (1952) for helium, neon and argon and the extension of these computations by Bernstein (see Biondi & Chanin 1954) to krypton and xenon (for which the wavefunctions are only approximately known), give good agreement with the experimental values at various temperatures. The only exception is for helium where the computed values lie 10 to 20 % above the experimental values. The reason for this discrepancy is not clear, since the treatment of Holstein is particularly applicable to cases such as helium, for which the outer atomic shell is an *S*-shell. For helium the calculations of Dalgarno (1958), Massey & Mohr (1934), and Lynn & Moiseiwitsch (1957) are in much closer agreement with experiments than those of Holstein.

It is interesting to note that the values quoted for atomic ions by the Bristol school actually refer to molecular ions for helium, neon and argon and to atomic ions for krypton and xenon.

The mobility of atomic ions decreases with E/p_0 becoming proportional to $(E/p_0)^{-\frac{1}{2}}$ for high values of E/p_0.

Table 1. Experimental values of zero-field mobility (cm^2 V^{-1} s^{-1}) at standard gas density for atomic ions in their parent monatomic gases

gas	temperature (°K)	Biondi & Chanin (1954, 1957)	Hornbeck (1951 *b*)	Beaty (1956) Hornbeck method	Beaty (1961) Tyndall method	Varney (1952) Hornbeck method	Munson & Tyndall (1941)	Biondi & Brown (1949)	Mulcahy & Lennon (1962)	Oskam & Mittelstadt (1963)	Beaty & Patterson (1963 and 1965)
helium	300	10·8	10·8	—	—	—	—	12·8	10·2	10·7	10·5
	195	12·1	—	—	—	—	—	—	—	—	—
	77	13·5	—	—	—	—	—	—	—	—	—
neon	300	4·2	4·4	—	—	—	—	—	3·9	4·1	4·0
	195	4·5	—	—	—	—	—	—	—	—	—
	77	5·2	—	—	—	—	—	—	—	—	—
argon	300	1·6	1·63	1·38	1·54	—	—	—	1·4	1·6	—
	195	1·95	—	—	—	—	—	—	—	—	—
	77	2·2	—	1·88	—	—	—	—	—	—	
krypton	300	0·90	—	—	—	0·9 to 0·95	0·88	—	—	—	—
	195	—	—	—	—	—	—	—	—	—	—
	77	—	—	—	—	—	—	—	—	—	—
xenon	300	0·58	—	—	—	0·6 to 0·65	0·61	—	—	—	—
	195	—	—	—	—	—	—	—	—	—	—
	77	—	—	—	—	—	—	—	—	—	—

Table 2. Theoretical values of zero-field mobility (cm^2 V^{-1} s^{-1}) at standard gas density of atomic ions in their parent monatomic gases

gas	temperature (°K)	Holstein (1952)	Dalgarno (1958)	Massey & Mohr (1934)	Lynn & Moiseiwitsch (1957)	equations (4) and (20)	equations (4) and (21)	Bernstein†	Langevin polarization equation (6)*
helium	300	12·16	10·4	11·2	10·2	13·4	23·1	—	
	195	13·75	11·6	—	11·5	—	—	—	22
	77	17·11	14·2	—	14·1	—	—	—	
neon	300	4·12	4·0	—	—	4·85	7·8	—	
	195	4·64	4·4	—	—	—	—	—	7·0
	77	5·54	5·2	—	—	—	—	—	
argon	300	1·65	1·6	—	—	1·67	2·7	—	
	195	1·85	1·8	—	—	—	—	—	2·4
	77	2·16	2·3	—	—	—	—	—	
krypton	300	—	0·9	—	—	1·01	1·5	1·0	
	195	—	1·0	—	—	—	—	—	
	77	—	1·3	—	—	—	—	—	
xenon	300	—	0·6	—	—	0·77	0·96	0·66	
	195	—	0·68	—	—	—	—	—	
	77	—	0·84	—	—	—	—	—	

* The Langevin polarization equation refers to the temperature $T = 0$ °K.

† See Biondi & Chanin (1954).

Table 3. Experimental values of zero-field mobility ($\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$) at standard density for molecular ions in their parent monatomic gases

gas	temp. (°K)	Biondi & Chanin (1954 and 1957)	Hornbeck (1951 *b*)	Beaty (1956) Hornbeck method	Beaty (1961) Tyndall method	Varney (1952) Hornbeck method	Tyndall *et al.* (1935 and 1941)	Lauer (1952)	Mulcahy & Lennon (1962)	Oskam & Mittelstadt (1963)	Beaty & Patterson (1963, 1965)
helium	300	20·3	19·0	—	—	—	20·6*	—	20·3	16·2	16·7, 20
	195	21·7	—	—	—	—	20·6*	—	—	—	—
	77	18·0	—	—	—	—	18·7*	—	—	—	—
neon	300	6·5	6·4	—	—	—	5·84†	—	7·5	6·5	6·2 (two ions with mobility of this order)
	195	7·5	—	—	—	—	—	—	—	—	
	77	6·7	—	—	—	—	—	—	—	—	
argon	300	2·7, 1·9	1·9	1·8	2·6, 1·83	—	1·81†	1·81	2·6	1·9	—
	195	2·9	—	—	—	—	—	—	—	—	—
	77	2·7	—	1·8	—	—	—	—	—	—	—
krypton	300	1·2	—	—	—	1·1 to 1·2	—	—	—	—	—
	195	—	—	—	—	—	—	—	—	—	—
	77	—	—	—	—	—	—	—	—	—	—
xenon	300	0·79	—	—	—	0·67 to 0·77	—	—	—	—	—
	195	—	—	—	—	—	—	—	—	—	—
	77	—	—	—	—	—	—	—	—	—	—

* Tyndall & Pearce (1935). † Munson & Tyndall (1941).

Table 4. Theoretical values of zero-field mobility ($\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$) at standard gas density for molecular ions in their parent monatomic gases

gas	temperature (°K)	Langevin* equation (4)	Hassé & Cook*	Geltman (1953)	Langevin polarization equation (6)†
helium	300	21·3	35·1	22·7	18·5
	195	21·5	36·2	22·0	
	77	21·1	31·2	20·7	
neon	300	6·82	11·0	—	6·0
	195	6·92	11·6	—	
	77	6·86	10·3	—	
argon	300	2·35	3·79	—	2·1
	195	2·42	4·02	—	
	77	2·41	3·77	—	
krypton	300	—	—	—	1·18
	195	—	—	—	
	77	—	—	—	
xenon	300	—	—	—	0·74
	195	—	—	—	
	77	—	—	—	

* See Chanin & Biondi (1957).
† The Langevin polarization equation refers to a temperature $T = 0$ °K.

(ii) *Molecular ions*

In addition to the atomic ion, two other species of ion (see table 3) have been observed in helium and neon (Beaty & Patterson 1963) and in argon (Biondi & Chanin 1954, 1957; Beaty 1961) and one other species in krypton and xenon (Varney 1952; Biondi & Chanin 1954).

In helium, the ion most generally observed (Tyndall & Pearce 1935; Hornbeck 1951*b*; Biondi & Chanin 1954; Mulcahy & Lennon 1962) has been the faster ion with zero-field mobility $\simeq 20\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ and this ion was until recently considered to be He_2^+. A slower ion with zero-field mobility $\simeq 16{\cdot}5\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ has, however, since been observed by Oskam & Mittelstadt (1963) and by Beaty and Patterson who consider that this slower ion is in fact He_2^+. If this is the case the identity of the faster ion has yet to be established.

In argon, the two ion species with zero-field mobilities $\simeq 1{\cdot}8$ and $2{\cdot}7\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ have been observed by Chanin & Biondi (1957) and by Beaty (1961). With the exception of Mulcahy & Lennon (1962), all other investigators have observed the slower ion species in argon. The identities of these ions in argon are uncertain.

In neon, the situation is even more confused; Hornbeck, Biondi & Chanin and Oskam and Mittelstadt studied an ion with zero-field mobility $\simeq 6{\cdot}5\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$, but values of 5·84 and $7{\cdot}5\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ were obtained by Munson & Tyndall (1941) and by Mulcahy & Lennon. More recently, Beaty and Patterson have observed two species of ion with nearly the same zero-field mobility $\simeq 6{\cdot}2\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. The identity of none of these ions has yet been established.

It is interesting to note that the faster of the two ions observed by Beaty and Patterson in helium and neon, and by Beaty and by Biondi & Chanin in argon disappeared at the higher gas pressures investigated in the experiments. Under the conditions of Beaty's and of Beaty & Patterson's experiments, the atomic ions were observed to convert into the slower molecular species in all gases. In helium and neon the rate of conversion was shown to be dependent on the square of the gas pressure, and Beaty & Patterson consequently suggested that the slower species was the diatomic ion, formed from the atomic ion according to three-body impact processes.

On the other hand, if the slower species in helium and argon are diatomic ions then the measured zero-field mobilities lie below the corresponding values predicted for diatomic ions by the Langevin theory. In fact, the Langevin equation gives values for the mobility of diatomic ions much nearer to the observed zero-field mobility of the faster species; the variation with the temperature predicted by the Langevin equation is not exactly that observed experimentally, but lies in much closer agreement with the experimental values than either the Hassé-Cook theory or the quantum mechanical calculations of Geltmann.

(*b*) *The variation of mobility with temperature and E/p_0 for nitrogen, oxygen and hydrogen ions in their parent gases*

Initial studies (Tyndall & Powell 1930; Bradbury 1932) of the drift of nitrogen ions in nitrogen gave a value for the zero-field mobility $\simeq 1{\cdot}8\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Later measurements (Tyndall & Pearce 1935; Mitchell & Ridler 1934; Huber 1955; Vogel 1957) were made on a species of ion with zero-field mobility $\simeq 2{\cdot}5\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. McAfee & Edelson (1963), who incorporated a mass analyser in their measuring apparatus, identified the species with zero-field mobility $\simeq 1{\cdot}8\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ as N_4^+; the mobilities of N^+, N_2^+ and N_3^+ were also measured but not at sufficiently low values of E/p_0 to obtain zero-field values. Keller *et al.* (1965), also using a mass analyser in their apparatus, recently corrected earlier data from their laboratory (Martin *et al.* 1963) and now obtain values of 1·5, 1·85 and 2·5 cm^2 V^{-1} s^{-1} for the zero-field mobilities of N_2^+, N_4^+ and N^+, respectively. As well as the species discussed above, ion species with higher values of zero-field mobility have been observed by Dahlquist (1963), who obtained a value for $\mathscr{K}$ of 3·2 cm^2 V^{-1} s^{-1}, and by Woo (1965) who obtained zero-field mobilities of 2·9 and 3·4 cm^2 V^{-1} s^{-1}. These ions have not as yet been identified.

In addition to the measurements of zero-field mobility, there has been considerable investigation of the variation of drift velocity with E/p_0. In the investigation of Varney (1953) and of Kovar, Beaty & Varney (1957), values of drift velocity appropriate to a single ion species were observed over the range $40 < E/p_0 < 1000\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$. However, over the range $50 < E/p_0 < 80\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ the drift velocity was found to remain practically constant. To account for this Varney postulated that two ions N_2^+ and N_4^+ were involved in the experiment, the N_4^+ ions being stable at the lower range of E/p_0, and the N_2^+ ions being stable at the higher range of E/p_0. At intermediate values of E/p_0, Varney postulated that the ions repeatedly interchanged their identity during their passage through the measuring system, giving a drift velocity which was an average of the values for the individual ions. Direct evidence of a reaction between the N_2^+ and N_4^+ ions has now been obtained from measurements of the mobility of identified ions by McAfee & Edelson and by Keller *et al.* From the measurements of McAfee & Edelson at high values of E/p_0 (*ca.* 200 V cm^{-1} mmHg^{-1}) it has been suggested that a similar reaction between N^+ and N_3^+ ions also occurs in this range. At low values of E/p_0, Keller *et al.* have found evidence that the N_3^+ ion reacts with the gas molecules and suggest that the end product of this reaction is either N_2^+ or N_4^+. Measurements of the mobility of nitrogen ions in nitrogen have also been made in the present work, and are compared with the above results and with theoretical values in part II.

In all the recent investigations of the mobility of positive oxygen ions in oxygen undertaken by Varney (1953), Frommhold (1960) and Eiber (1963*b*) a single ion species was observed. Eiber's investigation covered the range of E/p_0 from about 0·1 to 250 V cm^{-1} mmHg^{-1} and gave a value of zero-field mobility of 2·2 cm^2 V^{-1} s^{-1}. The data of Frommhold & Varney obtained at values of E/p_0 above 40 V cm^{-1} mmHg^{-1} are in very good agreement with those of Eiber, and extrapolate to the same zero-field mobility. The ion is considered to be O_2^+ since no other ion species was observed in the mass spectrometer investigations of Luhr (1933) and of Knewstubb, Dawson & Tickner (1963). The variation of mobility with E/p_0 observed in the three investigations is in close agreement and is similar to that found for atomic ions in the rare gases, i.e. the drift velocity is proportional to $(E/p_0)^{\frac{1}{2}}$ at high values of E/p_0.

Both experimental and theoretical values of the zero-field mobility of hydrogen ions in hydrogen are shown in table 5. At least three different species of ion seem to have been observed. Lauer (1952), Mitchell (see Tyndall 1938), and Bradbury (1932) observed species with zero-field mobility $\simeq 12{\cdot}5\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. This value agrees with that obtained

Table 5. Experimental and theoretical values of zero-field mobility at standard gas density for hydrogen ions in hydrogen

	Bradbury (1932)	Mitchell (1938)	Lauer (1952)	Richardson & Holt (1951)	Persson & Brown (1955)	Chanin (1961)	Sinnott (1964)
	—	—	—	—	—	—	11·8 (470 °K)
	—	—	—	—	—	—	11·5 (380 °K)
experimental (cm^2 V^{-1} s^{-1})	12·3 (300 °K)	12·8 (300 °K)	12·5 (300 °K)	14·0 (300 °K)	16·5 (300 °K)	12·3 (300 °K)	10·2 (300 °K)
	7·6 (300 °K)	—	—	—	—	13·3 (195 °K)	10·1 (195 °K)
	two ions	—	—	—	—	13·0 (77 °K)	10·0 (77 °K)
theoretical $\mathscr{K}$ (cm^2 V^{-1} s^{-1})	ion	Mason & Vanderslice* (1959)	Langevin equation† (6)	—	—	—	—
	H^+	18·3	19·2	—	—	—	—
	H_2^+	13·9	—	—	—	—	—
	H_3^+	22·0	14·3	—	—	—	—

* These values refer to $T = 300$ °K. † These values refer to $T = 0$ °K.

at 300 °K by Chinin (1961) who determined the mobility at 77, 195 and 300 °K. On the other hand, Bennett (1940) observed a species having a zero field mobility of 10·0 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ which is in close agreement with the value of 10·2 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ at room temperature recently obtained by Sinnott (1964), in an investigation of the mobility as a function of the gas temperature. Higher values of mobility 16·5 and 14 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ were obtained in the microwave experiments of Persson & Brown (1955) and of Richardson & Holt (1951).

Theoretical calculations of Mason & Vanderslice (1959) indicate that the ion species with zero-field mobility $\simeq$ 12·5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ is H_2^+, and that the ion species with zero-field mobility of 16·5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, as observed in the experiments of Richardson and Holt, is H^+. Varney (1960) has, however, suggested that the value of mobility calculated by Mason & Vanderslice for H_3^+ ions may be incorrect as no account was taken of the possibility of a proton charge transfer reaction (see also Hasted 1965). In view of this and mass spectrometric work in hydrogen (Luhr 1933; Hirschfelder, Curtiss & Bird 1954; Barnes, Martin & McDaniel 1961), which shows that H_3^+ ions are abundant at pressures $\sim 10^{-1}$ mmHg, Chanin considered the species with mobility $\simeq$ 12·5 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ to be H_3^+.

Since measurements on hydrogen form part of the present investigation, motions of ions in this gas are discussed further in part IV.

(c) *Mobility of alkali ions in gases*

The data on the zero-field mobility of alkali ions in gases, obtained by the Bristol School (Tyndall 1938; Hoselitz 1941) have been analysed by Dalgarno, McDowell & Williams (1958) and by Mason & Schamp (1958). Dalgarno *et al.* have shown that the behaviour of alkali ions in atomic gases of high polarizability is qualitatively in accordance with theory if the interaction between ion and gas atom is due to polarization of the atom. Quantitatively, however, a consistent 8 % discrepancy exists between theory and experiment. Dalgarno *et al.* suggested that this 8 % discrepancy was due to a systematic error in the Bristol data; but in a more detailed analysis Mason & Schamp have shown that if the influence of short range forces are considered then satisfactory agreement between theory and experiment may be obtained. It thus appears that measurements of the mobility of alkali ions in these gases have not been made at sufficiently low temperatures to enable the true polarization limit to be attained. This view is reinforced by the results of recent measurements of the mobility of alkali ions in gases (Crompton & Elford 1959) which gave values of zero-field mobility in very good agreement with those published by the Bristol group.

In atomic gases of lower polarizability (e.g. neon and helium), the mobilities of alkali ions are no longer independent of the gas temperature. Dalgarno *et al.* and Mason & Schamp have analysed this data using trial interaction functions, and in general they have been able to reproduce most of the experimental data.

In the case of alkali ions in the molecular gases nitrogen, hydrogen and carbon monoxide, Dalgarno *et al.* have shown that the mobilities are qualitatively in accordance with theory if the interaction between ion and gas molecule is assumed to be due to polarization. For nitrogen and carbon monoxide the results are also quantitatively reconcilable with this theory, but in hydrogen (the molecular gas of least polarizability) this is not so.

A characteristic feature of the data on mobility of alkali ion versus E/p_0 published by the Bristol group is the sudden increase in mobility above the constant value obtained at low values of E/p_0. Recent measurements of Crompton & Elford (1959) show, however, that for potassium ions in nitrogen and in neon the breakdown is not as sharp as that obtained by the Bristol group, and Crompton & Elford suggested that the four gauze method used with sinusoidal pulses gives erroneous results in this region.

5. CONCLUSIONS

Analysis of the theoretical and experimental data available for slow ions shows the position is not satisfactory and that further research is needed. There is a particular need for measurements of diffusion and mean energy of positive ions moving in low uniform electric fields, on which there is a dearth of experimental data.

For atomic ions in the inert gases, the experimental values for the zero-field mobility are consistent, and there is good agreement between these values and the theoretical quantum mechanical values. On the other hand, the modification of the Langevin theory by inserting into equation (4) a suitable cross-section obtained from Wannier's equation (21) does not appear to be satisfactory.

The situation for the case of molecular ions in the inert gases is far less clear. Values of mobility have been obtained for two species of ion in addition to the atomic species in helium, neon and argon. No positive identification of the ions involved has been made and there is some conflict of evidence concerning the species of ion to which these values of mobility refer. It seems likely that one of the ions is the diatomic ion, but whereas comparison with the Langevin theory suggests that the diatomic ion is the faster species, experimental evidence on reactions between the various species and the gas atoms has led to a suggestion that the slower species is the diatomic ion. Further measurements of mobility using an apparatus incorporating a mass analyzer are required in order to resolve the problem.

In the diatomic gases oxygen, nitrogen and hydrogen the experimental situation is clear only in the case of oxygen, and it would be interesting to have quantum mechanical computations for comparison. For nitrogen and hydrogen ions in their parent gases further data both theoretical and experimental are required. Further measurements of the mobility of N_3^+ ions in nitrogen are needed in order to obtain the zero-field mobility of this species as well as additional information about possible reactions between these ions and molecules of the gas. In hydrogen a large range of mobility values have been obtained. It is clear that these must refer to different ion species, but positive identification of which mobility refers to which species has yet to be made.* Although there are theoretical values available for comparison with the experimental data, the situation is complicated by the possibility of proton charge transfer. Further theoretical computation taking this process into account would be helpful in identifying the ion species involved.

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* See, however, footnote p. 312.