Aust. J. Phys., 1974, **27**, 211–25

Pressure Dependence and End Effects in Precision Ion Mobility Studies

M. T. Elford and H. B. Milloy

Ion Diffusion Unit, Research School of Physical Sciences, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600.

Abstract

The mobilities of K^+ ions have been measured by the Bradbury–Nielsen method in He, Ar, H_2 and N_2 at 293 K at pressures and E/N values in the range 1·4–190 torr and 1–28 Td respectively. Three drift tubes were used with drift lengths of 3·395, 9·076 and 50·00 cm. The anomalous variation of the reduced mobility with E/N at low values of E/N reported by Elford (1971) has been shown to be due to the presence of charged surface layers on the first grid of the time-of-flight system. The dependence of the reduced mobility on pressure also reported by Elford has been confirmed, and an explanation of the pressure dependence in He, Ar and H_2 is proposed in terms of the formation of ion–atom or ion–molecule complexes in orbiting resonant states. The zero-field reduced mobilities in the zero-pressure limit have been derived by a fitting procedure and found to be $21·3 \pm 0·2$, $2·64 \pm 0·02$ and $12·8 \pm 0·1$ $cm^2 V^{-1} s^{-1}$ for He, Ar and H_2 respectively. The pressure dependence of the reduced mobility for K^+ ions in N_2 is shown to be of a different form from the other gases investigated and to be due to the formation of the cluster ion $K^+.N_2$. The present data are consistent with the equilibrium constant of Beyer and Keller (1971) for the reaction $K^+ + N_2 + N_2 \rightleftarrows K^+.N_2 + N_2$. The zero-field reduced mobility for K^+ ions in N_2 in the zero-pressure limit has been found to be $2·50 \pm 0·02$ $cm^2 V^{-1} s^{-1}$.

1. Introduction

In a series of experimental measurements of the reduced mobility of potassium ions in various gases, Elford (1971) found two effects which are not predicted by mobility theories based on the Boltzmann equation. The first was a small but significant dependence of the reduced mobility on the gas number density and the second an increase in the reduced mobility at a given gas number density as E/N decreased towards zero, an effect which was termed upcurving (E is the electric field strength and N the gas number density). After a series of experimental tests, Elford could find no explanation of these effects and in particular concluded that the formation of stable ion–atom clusters could not satisfactorily account for the experimental data. This conclusion was disputed by Gatland (1972) who proposed an explanation of both the pressure dependence and upcurving in terms of non-equilibrium clustering reactions and a correction which arises from the diffusion of the ions in the direction of the electric field.

Both the anomalous effects have now been re-examined experimentally using a wider range of experimental conditions and three different drift tubes, including one with a drift length of 50 cm. The experimental details of these measurements are given in Section 2 and the results are discussed in Section 3. One of the anomalous effects, the upcurving, has been found to be due to an experimental defect and data have now

been obtained in which no observable upcurving exists. The pressure dependence of the reduced mobility, however, has been confirmed. An explanation of the observed pressure dependence is advanced in Section 4 together with a detailed discussion of the explanation by Gatland (1972). The pressure dependence of the reduced mobility of K^+ ions in N_2 is of a different form and magnitude compared with the other cases investigated, and this case is discussed separately in Section 5.

The experimental data are given in terms of the reduced mobility κ, which is the mobility $K = W/E$ (where W is the drift velocity) in a gas at a standard number density N_s. This standard gas number density is chosen to be $2{\cdot}6866 \times 10^{19}$ cm^{-3} (i.e. that of a gas at 273·16 K and 760 torr). Thus the reduced mobility can be written

$$\kappa = (N/N_s)W/E = \{W/(E/N)\} \times 3{\cdot}7215 \times 10^{-3} \text{ cm}^2\,\text{V}^{-1}\,\text{s}^{-1},$$

where W is in units of cm s^{-1} and E/N is in units of townsends (1 townsend (Td) = 10^{-17} V cm^2). All mobility values quoted in this paper are in units of cm^2 V^{-1} s^{-1}.

2. Experimental Details

The ionic drift velocity was measured by the Bradbury–Nielsen method. This technique has been discussed in detail by many authors (e.g. Crompton and Elford 1959; Elford 1972; Huxley and Crompton 1974) and will not be further considered here. The three drift tubes used in the present work were a modified version of the system A described by Elford (1971), system C also described by Elford (1971) and a 50 cm drift length tube described by Crompton and Elford (1973). The very long drift tube enables ionic drift velocity data to be taken at low values of E/N while maintaining a relatively large potential difference across the drift length.

System A of Elford (1971) was modified to the extent that a separate collector electrode was attached below the main electrode system. In the work of Elford with system A, which incorporates three shutter grids with spacings of 9·076 cm and 2·965 cm, the ion current was collected on the lowest of the three shutters. This restricted measurements to one drift length (9·076 cm) only. With a separate collector it became possible to make measurements using two different drift lengths without changing any other experimental parameters. In this paper the modified version of system A will be referred to as system A_1.

A quartz spiral manometer (Texas Instruments Type 141) was used to measure the gas pressures. This pressure gauge was calibrated using the apparatus and techniques described by Gascoigne (1972) and the errors in pressure measurement are estimated to be less than $\pm 0{\cdot}25/p$ % or 0·1 % whichever is the greater (p being the gas pressure in torr). Copper–constantan thermocouples situated on electrodes adjacent to the shutters in the 50 cm drift tube and system A were used to measure the gas temperature and also to detect any temperature gradients across the drift length. The temperature difference between the two thermocouples was less than 0·5 K in any mobility measurement. The temperature used in the calculation of the gas number density was taken to be the mean of the two temperature measurements. In the case of system C the temperature of the gas was taken to be that of the water in the thermal jacket surrounding the drift tube; the temperature change of the water was less than 0·1 K per hour. The hydrogen used was purified by passage through heated silver–palladium. All other gases were Matheson Research Grade and were let into the system using the

techniques described by Elford (1972). In all cases the ions were obtained by heating tungsten filaments coated with the appropriate alkali alumino-silicate glass (Blewett and Jones 1936).

3. Experimental Results

The experimental results fall into two groups: those concerned with the investigation into upcurving and those concerned with the pressure dependence. These will be considered separately.

(*a*) *Investigation of Upcurving*

Measurements with system A_1 and the 50 cm drift length tube

In order to investigate upcurving, measurements were made with system A_1 over a range of pressures and at E/N values between 1 and 4 Td. The data were taken using both drift lengths and in each case plots of κ versus E/N at a given pressure exhibited upcurving, as had been observed previously by Elford (1971). However, the degree of upcurving was significantly different for each drift length, in contrast to Elford's measurements, although it should be noted that one of the electrode systems he used in making the comparison of data taken at two drift lengths was different from those used in the present work.

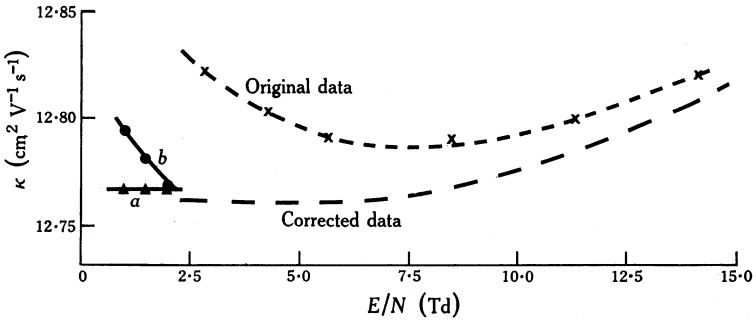

Fig. 1. Reduced mobility κ of K^+ ions in H_2 as a function of E/N at 5·1 torr. The full curves, which are data taken with the 50 cm drift length tube, show (*a*) the initial results and (*b*) the results after several hours of operation. The dashed curves are the original and corrected 5·1 torr data of Elford (1971).

When the data of system A_1 were examined it was found to be possible to remove the upcurving obtained at each drift length by assuming a small potential to exist at the upper shutter in addition to the applied potential. The corrected κ versus E/N curves for each drift length were in excellent agreement. However, the small potentials required to remove the upcurving in the data obtained at the two drift lengths were significantly different and were also a function of gas pressure and of the nature of the gas. These results suggested that the upcurving was a complex phenomenon caused by the presence of charged surface layers on the upper shutter grids of the drift tube systems.

To test this hypothesis, additional data were obtained for K^+ ions in H_2 using the 50 cm drift length tube. In this tube, data can be taken at very low values of E/N where

the intrinsic variation of the reduced mobility with E/N can be neglected while at the same time maintaining a relatively large potential difference across the drift length in order to reduce the effects of charged surface layers on the upper shutter grid. Before the tube was assembled the shutter grids, which had previously been used for ion mobility measurements in another drift tube, were sand-blasted to remove all traces of alkali ions or contaminant layers and then coated in turn with copper and gold. The initial data taken with the 50 cm drift length tube are shown in Fig. 1 together with the data of Elford (1971) for the same gas pressure. It can be seen that the two sets of data differ significantly and that the results of the 50 cm drift length tube show no evidence of upcurving (curve *a*, Fig. 1). However, it was possible to obtain upcurving in the data of the 50 cm drift length tube by exposing the top shutter to an ion current of approximately 10^{-10} A for many hours (curve *b*, Fig. 1). When such upcurving was produced it remained stable for several weeks of operation and it was only after the total number of ions collected by the upper shutter became very large that the magnitude of the upcurving increased further. When this occurred the upper shutter was removed, sand-blasted clean, regilded, vapour degreased and replaced. The results at 5·1 torr were in excellent agreement with the previous initial results which showed no upcurving.

Finally, the effect of bombarding metal surfaces with low energy K^+ ions was investigated using a modified form of the apparatus described by Crompton *et al.* (1965) to determine the change in contact potential difference between a probe and an extended surface. The results were qualitatively consistent with the hypothesis of a charged surface layer and the magnitude of the changes in the surface potential due to the ion bombardment were adequate to explain the magnitude of the upcurving observed in the mobility measurements.

As a result of these investigations it was concluded that upcurving was predominantly due to the formation of charged surface layers on the upper shutter grid. The nature of the contaminant layer is open to speculation but is most probably due to polymerized hydrocarbon molecules. This is consistent with the known history of the shutter grids, the conditions under which the surface potential measurements were made and the results of many previous investigations of surface layer effects (see Petit-Clerc and Carette 1968; Lindholm 1960).

Contact potential differences and diffusive effects

The presence of charged layers on the shutters is only one of three effects which may give rise to upcurving. Both the existence of a contact potential difference between the two grids and diffusive effects can also cause upcurving. However, since both grids are gilded, the contact potential difference between them should be small and certainly much less than the potential differences required to correct for upcurving.

It is known that a number of diffusion processes can affect the shape of the ion-current peaks obtained in the Bradbury–Nielsen method. These processes have been discussed in detail by Lowke (1962), Huxley and Crompton (1974) and D. S. Burch (personal communication) who show that the true reduced mobility κ is approximately related to the measured reduced mobility κ_m by

$$\kappa \sim \kappa_m\{1-C(D_L/K)/V\},$$

where D_L is the longitudinal diffusion coefficient, V is the potential difference between the shutter grids and C is a constant. Lowke concluded that C had the value 3 but

there are at least two effects which are not taken into account in any of the analyses: the variable transmission of the shutters to ions of different energies (Lowke 1962), and the back diffusion to the second shutter (D. S. Burch, personal communication). Since there is no complete analysis available, the value of C must be regarded with caution. It is therefore not possible to determine to what extent diffusive errors contribute to upcurving although it is clear that the upcurving cannot be entirely attributed to this cause.

Both contact potential differences between the shutters and diffusive effects were examined by Elford (1972) as possible causes of the upcurving and pressure-dependent effects which he observed in his mobility measurements. However, he found no significant difference between mobility data for K^+ ions in H_2 and Ar taken with drift tubes which varied by a factor of three in drift length and thus concluded that contact potential difference and diffusive effects, which both vary with drift length, could not be significant. In the light of the present investigation it would appear that when Elford's measurements were made, the upper grid of system A was fortuitously subject to a much larger charged layer effect than the upper grid of system C. It should be noted that as they stand Elford's data preclude any explanation which requires them to be a function of drift length. The two processes invoked by Gatland (1972) to explain Elford's results both require a dependence of the reduced mobility on drift chamber length. Other defects in Gatland's analysis are discussed in Section 4.

(b) Pressure Dependence

It was found that after corrections for upcurving had been applied the reduced mobility of K^+ ions in He, Ar and H_2 was still a function of the gas pressure. In the investigation of this effect, particular emphasis was placed on obtaining data at low E/N values in order to obtain the zero-field reduced mobility, as this quantity can be studied over the largest pressure range. The experimental tubes used in these measurements were system C (drift length 3·395 cm) and the 50 cm drift length tube. Before carrying out the investigation into the dependence of the reduced mobility on pressure, the shutter grids of both tubes were cleaned and regilded and the accuracy of the measuring equipment checked by determining the drift velocity of electrons in hydrogen at several values of E/N. The electron drift velocity values agreed to within $\pm 0{\cdot}1\%$ with those taken with other drift tubes (Elford and Robertson 1973).

The lower limit to the usable pressure range of the ion mobility measurements was determined by two factors. The first was the increasing error in the measurement of the gas pressure as the pressure was reduced and the second was the difficulty in estimating the zero-field reduced mobility from results which not only exhibited upcurving but also a small intrinsic variation of κ with E/N. The second of these factors was unimportant when the 50 cm drift tube was used and for this reason lower pressures were used in this case. The upper limit to the usable pressure range was determined by such factors as low ion currents, electrical breakdown at the high voltage feed-throughs and clustering with impurities.

The results fall mainly into two groups, those taken at values of E/N which are sufficiently low that the intrinsic change of κ with E/N can be ignored and those taken at E/N values where the change of κ with E/N is significant. The data taken at pressures greater than about 40 torr fall into the first group, since the values of E/N which could be used were less than about 3 Td. The zero-field reduced mobility was

taken to be the value of κ measured at the highest E/N value, and it is estimated that there is a maximum error of $\pm 0{\cdot}1\%$ introduced in the value of κ_0 obtained by this procedure as a result of upcurving. The data taken at pressures less than about 40 torr fall into the second group. The value of κ_0 was obtained by applying a correction to remove upcurving and then extrapolating the corrected data to zero E/N. The maximum error incurred in the value of κ_0 by the correction and extrapolation procedure is estimated as $\pm 0{\cdot}2\%$.

The data were highly repetitive, the maximum difference between values of κ measured at the same E/N and p values on different days and with different gas samples was $\pm 0{\cdot}15\%$. The relative errors in the values obtained for κ_0 are therefore expected to be less than $\pm 0{\cdot}15\%$. The absolute error in the values of κ_0 obtained at each pressure is estimated as less than $0{\cdot}8\%$. A detailed discussion of experimental errors is given by Milloy (1973). The estimated values of κ_0 for K^+ ions in He, Ar and H_2 are shown in Figs 2*a*, 2*b* and 2*c* respectively as a function of the reduced pressure $p_{273.16}$ (torr). The largest pressure dependence observed was in argon: between 5 and 183 torr the value of κ_0 changed by $1{\cdot}3\%$.

Before considering a possible mechanism to explain the pressure dependence it is necessary to consider experimental errors which might give rise to the observed pressure dependence. Two such errors are:

(1) *End effects.* In order to investigate the possibility that the residual pressure dependence, i.e. the pressure dependence obtained after corrections for upcurving, was not due to an end effect of unknown origin, the values of the estimated zero-field reduced mobilities for K^+ ions in H_2 and Ar obtained with the 3 and 50 cm drift tubes were compared. It can be seen from Fig. 2 that there is no significant difference between the values obtained with drift tubes which differ by a factor of 15 in drift length. End effects may therefore be discounted.

(2) *Error in pressure measurement.* Although the precision of the pressure measurement and the calibration procedure make this a very unlikely explanation of the pressure dependence, further evidence against an error in the pressure measurement is provided by the fact that the pressure dependence varies from gas to gas although the same pressure gauge was used throughout.

We now consider the formation of ion–atom complexes as an explanation of the observed residual pressure dependence.

4. Formation of Ion–Atom Complexes and their Significance in Ion Mobility Studies

In all ion mobility theories it is assumed that the collisions take place in times negligibly small compared with the time between collisions. In the present work the mean free time for momentum transfer varied between about 10^{-9} and 10^{-7} s. The only published data for ion–atom collision times based on the assumptions of classical mechanics appear to be those of Miller *et al.* (1968), which show a value of approximately 10^{-13} s for the case of protons in hydrogen. However, as Miller *et al.* only considered the times spent by ions inside the radius for classical orbiting, their estimates are probably low. R. E. Robson (personal communication) removed this restriction but found that, classically, an insignificant number of ions had collision times greater than 10^{-11} s, assuming the ions to have a thermal energy distribution. The assumption of a negligible collision time in ion mobility theories based on a classical description is

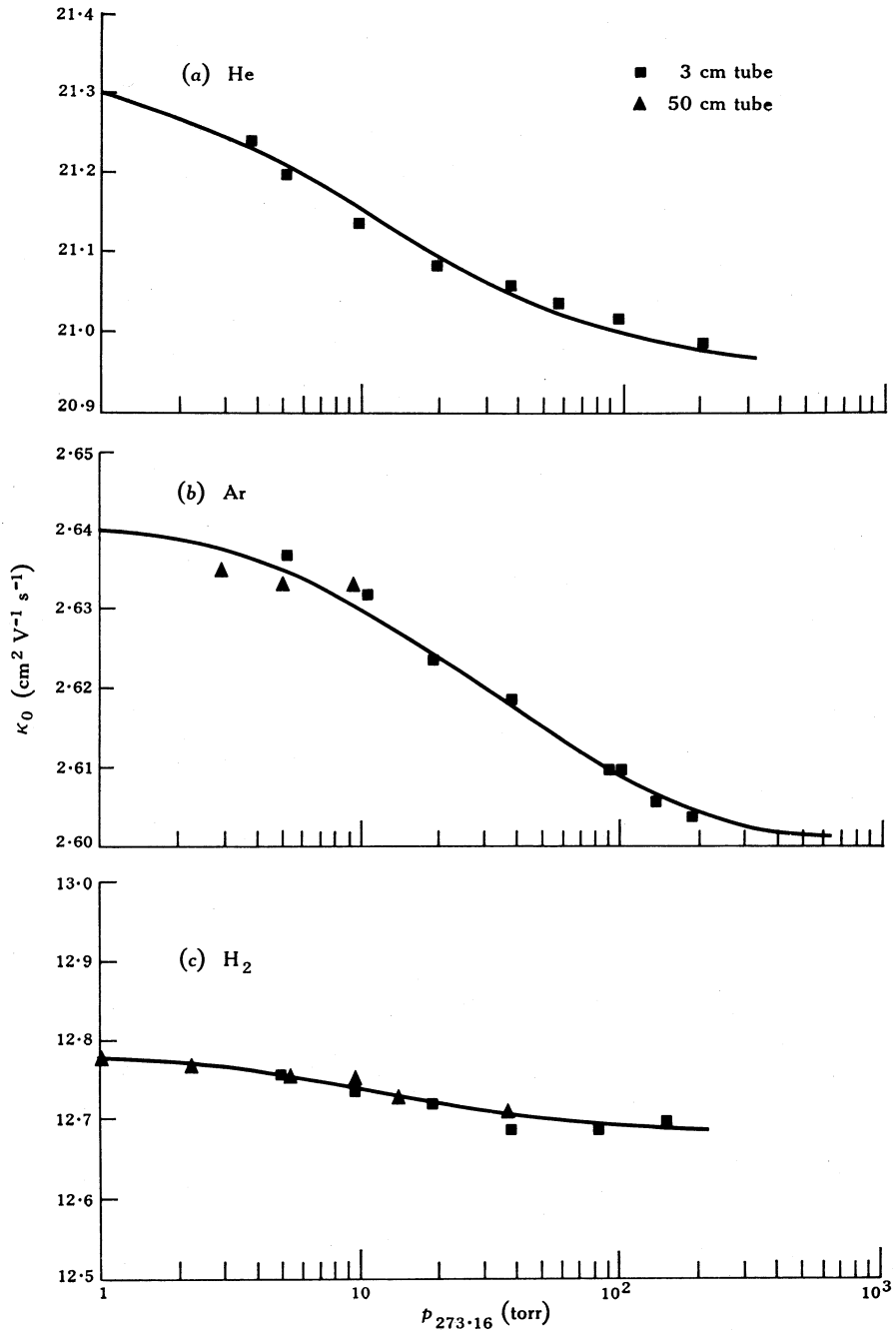

Fig. 2. Reduced zero-field mobility κ_0 of K^+ ions in He, Ar and H_2 as a function of gas pressure. The experimental data were obtained using the 3 cm and 50 cm drift length tubes. The continuous curves are the predictions of equation (1) with the parameters given in Table 1.

therefore justified. However, in a quantum mechanical description of low energy heavy particle scattering it is known that ion–atom complexes can have lifetimes very much longer than those found in calculations based on classical mechanics (Dickinson and Dalgarno 1968, cited after McDaniel *et al.* 1970).

The dynamics of ion–atom scattering can be simplified by considering the equivalent one-dimensional motion of a particle of reduced mass μ moving in a central field of force about the origin of coordinates. The effective potential can then be written (McDaniel 1964)

$$V_{\text{eff}}(r,J) = V(r) + J^2/2\mu r^2,$$

where $V(r)$ is the interaction potential of the ion and atom, r the internuclear spacing and J the angular momentum in the centre of mass frame. A typical set of effective potential curves for a fixed value of the centre of mass energy but for different values

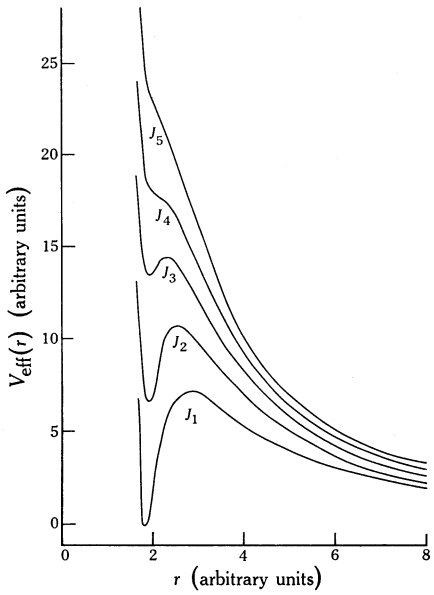

Fig. 3. Typical curves of effective potential V_{eff} at an internuclear spacing r for a given centre of mass energy. Each curve corresponds to a different value of the angular momentum J.

of J are shown in Fig. 3, and it can be seen that for certain values of J the effective potential contains a well. In a quantum mechanical description of an ion–atom collision there may be a number of quasi-bound states in this well of the effective potential. Those states which decay by tunnelling through the centrifugal barrier are known as orbiting resonances and have associated with them lifetimes T which are related to the energy widths Γ of the states by $T = \hbar/\Gamma$. The widths of the states can be obtained from the phase shifts η_l by the relation

$$(\partial\eta_l/\partial\varepsilon)_{\text{max}} = 2/\Gamma,$$

where l is the angular momentum quantum number.

The lifetimes of ion–atom complexes in orbiting resonant states have been calculated by Dickinson and Dalgarno (McDaniel *et al.* 1970) for the case of Li^+ ions in He and by Watts (1974) for K^+ ions in Ar. Watts has used the best available estimates of the

interaction potential and has shown that there are eight states whose energies and lifetimes are such that they could significantly affect the ion mobility at room temperature. It now remains to show how the existence of such complexes can explain the observed pressure dependence of the reduced mobility.

It is assumed that the formation and breakup of the complexes are described by the equations

$$X^+ + Y \underset{k_{01}}{\overset{k_{10}}{\rightleftarrows}} (X^+ . Y)^* \qquad \text{and} \qquad (X^+ . Y)^* + Y \underset{k_{12}}{\overset{k_{21}}{\rightleftarrows}} X^+ + Y + Y,$$

where X^+ is an ion, Y is a neutral particle, $(X^+ . Y)^*$ is an ion–neutral complex and the k's are the reaction rates. If the pressure dependence is independent of drift distance, the reactions must be in equilibrium and the principle of microscopic reversibility satisfied. The ratio of the abundances of the parent ions and the ion–neutral complexes is given by

$$[X^+]/[(X^+ . Y)^*] = (k_{01} + k_{21} N)/(k_{12} N^2 + k_{10} N).$$

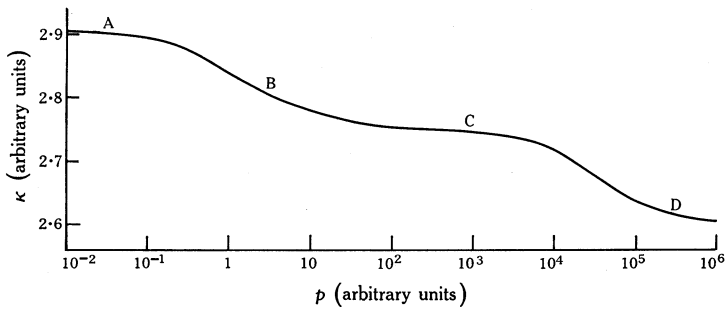

Fig. 4. Typical variation of the reduced mobility κ with gas pressure p when ion–neutral complexes are formed.

If the reduced mobilities of X^+ and $(X^+ . Y)^*$ are given by κ_1 and κ_2 the apparent or measured reduced mobility can be written

$$\kappa_m = \frac{\kappa_1[X^+] + \kappa_2[(X^+ . Y)^*]}{[X^+] + [(X^+ . Y)^*]} = \frac{\kappa_1 + \kappa_2\{(k_{12} N + k_{10})/(\tau^{-1} + k_{21} N)\}N}{1 + \{(k_{12} N + k_{10})/(\tau^{-1} + k_{21} N)\}N}, \qquad (1)$$

where $\tau = 1/k_{01}$ is the lifetime of a complex in the absence of collisions.

The general form of equation (1) is shown in Fig. 4:

In region A of this figure the gas number density is very low and the time between collisions is long compared with the complex lifetime. The time spent by an ion as a heavier complex is therefore negligible compared with that spent as a single particle and as a result the measured reduced mobility is that of X^+ and is independent of gas number density. In this region the approximations made in a theoretical treatment based on the Boltzmann equation are valid.

In region B the gas number density is sufficiently high for τ to be comparable with the mean free time between collisions and the time spent by X^+ as a heavier complex is now no longer negligible. Thus the measured reduced mobility decreases.

Region C corresponds to conditions in which τ is now greater than the mean free time between collisions. Each complex is broken up by collision with a neutral particle and the spontaneous breakup of a complex becomes a very unlikely event. The two dominant reactions are the formation and breakup of complexes by two-body collisions. Since both these reaction rates depend linearly on the pressure, the reduced mobility again becomes pressure independent and can be written

$$\kappa_m = \frac{\kappa_1 + \kappa_2(k_{10}/k_{21})}{1+(k_{10}/k_{21})}.$$

At still higher pressures the true three-body reaction finally dominates and the measured mobility is the mobility of the complex. This corresponds to region D.

Table 1. Parameters used to obtain curves of best fit

Gas	κ_1 ($cm^2 V^{-1} s^{-1}$)	κ_2 ($cm^2 V^{-1} s^{-1}$)	τ (s)	k_{10} ($cm^3 s^{-1}$)	k_{12} ($cm^6 s^{-1}$)	k_{21} ($cm^3 s^{-1}$)
He	21·33	20·04	$1{\cdot}75\times10^{-9}$	$4{\cdot}00\times10^{-10}$	1×10^{-32}	1×10^{-9}
Ar	2·642	2·360	$9{\cdot}14\times10^{-10}$	$1{\cdot}75\times10^{-10}$	1×10^{-32}	1×10^{-9}
H_2	12·79	12·60	$1{\cdot}00\times10^{-9}$	$1{\cdot}38\times10^{-9}$	1×10^{-32}	1×10^{-9}

It is possible, in the region B of Fig. 4, to fit the measured variation of κ_0 with pressure for K^+ ions in He, Ar and H_2 with a curve of the form of equation (1) by adjusting the various rate constants. The calculated curves, as shown by the continuous lines in Figs 2*a*, 2*b* and 2*c* are consistent with the experimental data to within the scatter of the measurements. The values of the parameters used to obtain the fits are given in Table 1. It can be seen that the rate constants used lie within the range observed experimentally for ion–molecule reactions and the complex lifetimes are consistent with the work of Watts (1974). The only parameter which can be determined with reasonable accuracy by this fitting procedure is κ_1, the reduced zero-field mobility of the ion in the zero-pressure, or Boltzmann limit. As it is not possible to vary κ_1 by more than $\pm 0{\cdot}2\%$ and still fit the data to within the scatter of the measurements the absolute error in κ_1 for the three cases investigated is estimated as less than $\pm 1\%$. The rate constants cannot be uniquely determined from the fitting procedure.

The present values of κ_0 ($p = 0$) for K^+ ions in He, Ar and H_2 may be compared with the values of κ_0 obtained by previous workers if the pressures used in their earlier studies were sufficiently small for the difference between κ_0 (at pressure p) and κ_0 (at $p = 0$) to be much less than the experimental error. This condition holds for all comparisons made with previous data for these three cases.

There is only one earlier value of κ_0 available for the case of K^+ ions in He, namely $21{\cdot}5$ from Tyndall (1938). This is in good agreement with the present value of $21{\cdot}3 \pm 0{\cdot}2$. In the case of K^+ ions in Ar, the values of Tyndall (1938) of $2{\cdot}63$, Hoselitz (1941) of $2{\cdot}64$ and James *et al.* (1973) of $2{\cdot}66 \pm 0{\cdot}05$ are also in good agreement with the present value of $2{\cdot}64 \pm 0{\cdot}02$. In the case of K^+ ions in H_2 the values of κ_0 available are: $12{\cdot}7$ (Tyndall 1938), $12{\cdot}75 \pm 0{\cdot}04$ (Elford 1967), $12{\cdot}7 \pm 0{\cdot}1$ (Fleming *et al.* 1969*a*) and $12{\cdot}8 \pm 0{\cdot}6$ (Miller *et al.* 1968). These values are in good agreement with the present value of $12{\cdot}8 \pm 0{\cdot}1$.

Although there is excellent agreement between the experimental results and the theoretical predictions of equation (1), there are a number of criticisms that may be levelled at this proposed explanation:

(1) it might be expected that the magnitude of the pressure dependence would vary more from gas to gas;

(2) it might also be expected that the pressure region in which the effect is observed might vary more from gas to gas, i.e. one might expect the factor τk_{10} (which controls the position of region B in Fig. 4) to be a stronger function of the nature of the gas;

(3) it has not been conclusively shown that regions A and C in Fig. 4 exist;

(4) although all the rate constants used in the fitting procedures are reasonable, they are all relatively large for such simple systems.

It can be seen from Fig. 2 that a more complete test of this explanation would be possible if accurate experimental data were available at both higher and lower pressures, but unfortunately this is not possible at the present time. At low pressures the pressure measurement itself imposes a severe limitation if random errors of about $\pm 0{\cdot}1\,\%$ are required and a shorter drift tube would be needed for measurements at higher pressures. However, even if sufficiently accurate measurements could be taken with a shorter drift tube it would seem likely that gas contamination giving rise to clustering would become a limiting factor at higher pressures.

In the analysis developed above it has been assumed that the complexes are not stabilized by reactions of the type

$$(X^+ . Y)^* + Y \rightarrow X^+ . Y + Y,$$

i.e. stable cluster ions $X^+ . Y$ are not formed. There were no indications from this work that stable clusters were formed in He, Ar or H_2. The peaks in the ion current–frequency spectrum were symmetrical, the mobility was independent of drift distance, no clusters were observed when a mass spectrometer was used in conjunction with electrode system A (although $K^+ . N_2$ clusters were observed) and, as pointed out by Elford (1971), the magnitude of the pressure dependence was too small to be consistent with an equilibrium clustering reaction. However, our conclusion that stable clusters are not formed in these gases at room temperature is inconsistent with the work of Thomson *et al.* (1973), who observed clustering of single molecules of CO_2, NO, CO, N_2, O_2, Ar, D_2, Ne and He to K^+ ions and concluded that clustering is likely to be important in studies of the transport properties of K^+ ions in all these gases except D_2, Ne and He. The conclusion of Thomson *et al.* was the basis of an explanation of the pressure dependence of K^+ ions in Ar proposed by Gatland (1972). This will now be considered.

Explanation Proposed by Gatland (1972)

By assuming the existence of a diffusive correction $2(D_L/K)/V$ in magnitude and the existence of a non-equilibrium clustering reaction

$$K^+ + Ar + Ar \rightleftarrows K^+ . Ar + Ar, \qquad (2)$$

Gatland (1972) has attempted to fit the pressure dependence reported by Elford (1971)

for K^+ ions in Ar, using the rate constants as fitting parameters. The fit he obtained is unsatisfactory, as the predicted curves are not only different in form to the experimental curves but differ from them over a significant pressure range by an amount which is much larger than the experimental error. Such a disagreement is not unexpected in view of the assumptions which Gatland made. He derived the correction $2(D_L/K)/V$ by ignoring boundary conditions, and thus ignoring diffusion to the shutters which is a physically unrealistic assumption. Gatland also assumed that there are no clustered ions when the ions leave the first shutter, i.e. he ignored any clustering reactions which may occur between the ion source and the first shutter. If Gatland's postulated rate constants are used it can be shown that a very high proportion of the ions would be clustered by the time they reach the first shutter, invalidating the assumption that no cluster ions exist at the first shutter.

There remains, of course, the possibility that some of the upcurving can be attributed to diffusive effects, although the magnitude assumed by Gatland (1972) for such effects is open to dispute. In view of the experimental tests reported in Section 3 it would appear that the dominant cause of upcurving in Elford's measurements was a surface effect at the first shutter grid and not diffusive errors. There is also a further objection to Gatland's explanation in addition to those already raised.

If the reaction (2) is in equilibrium, the measured mobility κ_m is related to the mobilities κ_1 and κ_2 of the unclustered and clustered ions respectively by the relation

$$\kappa_m = (\kappa_1 + K_e N \kappa_2)/(1 + K_e N), \tag{3}$$

where K_e is the equilibrium constant. At very high values of N, κ_m approaches κ_2, the mobility of the clustered ion. Elford (1971) found that his data could be fitted satisfactorily by equation (3) but that the estimated value of κ_2 was too close to the value of κ_1 for the ion at high N to be $K^+.Ar$. The same conclusion has been reached in the present work. In view of this and the alternative explanation of the data for K^+ ions in Ar which has been discussed here, doubt must be cast on Gatland's (1972) assumption of reaction (2).

5. Mobility of K^+ Ions in N_2

The results of Elford (1971) for the reduced mobility of K^+ ions in N_2 extend from 1·44 to 18·8 torr and show a dependence on pressure which is significantly different from the form of the pressure dependence observed in He, Ne, Ar and H_2. However, he reached no conclusions about the reason for this difference. With the observation of the formation of the $K^+.N_2$ cluster by many workers it seemed possible that the pressure dependence observed was due to an equilibrium clustering reaction. The present data were taken with the aim of establishing the form of the pressure dependence, to see if it was satisfactorily fitted by equation (3) and to determine the zero-field reduced mobility for K^+ ions in N_2.

The mobility of K^+ ions in N_2 at 293 K was measured using system C and the 50 cm tube at pressures ranging from 2·9 to 190 torr and at E/N values from 1·3 to 28 Td. The values of the zero-field reduced mobilities, plotted in Fig. 5 as a function of the reduced pressure, were obtained from these data by the method described in Section 3*b*. At pressures greater than about 50 torr there was some evidence of the presence of more than one ion in the ion current–frequency spectrum but as the magnitude of the

subsidiary system of peaks increased slowly with time it was concluded that this peak system was due to a cluster ion formed by K^+ ions combining with impurity molecules, probably water vapour. As the measured mobility of the major ion species did not change by more than $\pm 0{\cdot}1\%$ over a period of several hours it was concluded that the results were not significantly affected by impurities. In the case of K^+ ions in N_2 the errors involved in estimating κ_0 are smaller than in the cases considered in Section 3 since the intrinsic variation of κ with E/N at values < 15 Td is insignificant. For this reason it is estimated that the maximum random errors in the measurements are less than $\pm 0{\cdot}2\%$ at all pressures. Since the total systematic error on each datum point is estimated as less than $\pm 0{\cdot}8\%$, the total error of any datum point in Fig. 5 is less than $\pm 1\%$. It can be seen that the variation of κ_0 with pressure is $4{\cdot}1\%$ between 5 and 190 torr, about 4 times larger than that observed with K^+ ions in Ar over the same pressure range and about 20 times larger than the random error of the measurements.

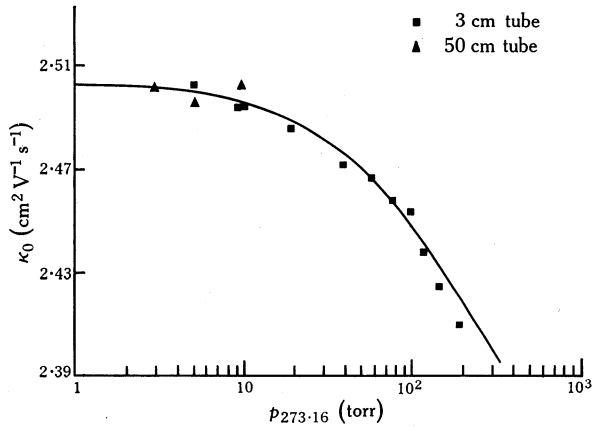

Fig. 5. Reduced zero-field mobility κ_0 of K^+ ions in N_2 as a function of gas pressure. The experimental data were obtained using the 3 cm and 50 cm drift length tubes. The continuous curve is the prediction of equation (3) with the parameters given in the text.

If the reactions

$$K^+ + N_2 + N_2 \rightleftarrows K^+.N_2 + N_2$$

are occurring and are in equilibrium, the variation of κ_0 with gas pressure will be given by equation (3). Equilibrium was assumed to have been reached under the conditions used in the present work since the results were independent of drift distance and the peaks of the ion current–frequency spectrum were symmetrical.

The curve of best fit of relation (3) to the present data for K^+ ions in N_2 was obtained with the parameters:

$$\kappa_1 = 2{\cdot}504, \qquad \kappa_2 = 2{\cdot}320, \qquad K_e = 1{\cdot}27 \times 10^{-19}\ \text{cm}^3,$$

and is shown by the continuous curve in Fig. 5. The maximum deviation of the experimental points from the curve is $0{\cdot}2\%$. Although the value of K_e used in the fitting

procedure is in good agreement with the experimental value of 2×10^{-19} cm^3 quoted by Beyer and Keller (1971), it is not possible to determine either K_e or κ_2 accurately by this fitting procedure and thus the agreement may be fortuitous. On the other hand, κ_1 can be obtained with good precision. If κ_1 is varied by more than $\pm0{\cdot}2\%$ an adequate fit cannot be obtained.

There have been a number of previous derivations of κ_0 for K^+ ions in N_2 although in none of this earlier work was a dependence of κ on p reported. However, it can be seen from Fig. 5 that at pressures less than about 20 torr the values of κ_0 are within $0{\cdot}5\%$ of the value of κ_0 at zero pressure. Since all previous data were taken at pressures less than 20 torr, a comparison is possible with the present value of κ_0 ($p = 0$) to within this limit. The values obtained were: 2·53 (Mitchell and Ridler 1934), $2{\cdot}54\pm0{\cdot}01$ (Crompton and Elford 1959), $2{\cdot}55\pm0{\cdot}07$ (Davies *et al.* 1966), $2{\cdot}55\pm0{\cdot}1$ (Moseley *et al.* 1969) and $2{\cdot}53\pm0{\cdot}02$ (Fleming *et al.* 1969*b*). The present value of $2{\cdot}50\pm0{\cdot}02$ is, in general, lower than these and in particular is $1{\cdot}4\%$ lower than the 'standard value' of $2{\cdot}54\pm0{\cdot}01$ estimated by McDaniel and Martin (1971).

6. Conclusions

Although one of the anomalous effects in the ion mobility measurements of Elford (1971) has been shown to be due to a combination of diffusive effects and the effect of a charged contaminant layer, the other effect, namely that of a pressure dependence in the reduced mobility, has been found to be present in all the cases examined and as far as can be ascertained is not due to experimental defects. An explanation of this pressure dependence in terms of orbiting resonances is found to satisfactorily account for the observed effects in those cases where stable cluster ions do not form. The formation of complexes makes the measurement of the classical reduced mobility (i.e. the value of κ obtained at $p \to 0$) as a function of E/N very difficult as it is necessary to obtain data at each value of E/N over a range of gas number densities. In the present work the only classical reduced mobilities obtained were those at E/N zero. The values for K^+ ions in He, Ar and H_2 at 293 K were $21{\cdot}3\pm0{\cdot}2$, $2{\cdot}64\pm0{\cdot}02$ and $12{\cdot}8\pm0{\cdot}1$ respectively. At high ionic speeds, orbiting resonances cannot be formed because the energies of the quasi-bound states are too low. It would therefore be expected that at high E/N values the dependence of the reduced mobility on pressure will vanish. There is some data to support this conclusion (note added in proof by Elford 1971) but further data are desirable.

In the case of K^+ ions in N_2 the stable ion cluster $K^+.N_2$ is formed and the pressure dependence has a different form to that found in both He, Ar and H_2. The present data for K^+ ions in N_2 can be fitted to within the experimental scatter by assuming an equilibrium reaction scheme $K^+ \rightleftarrows K^+.N_2$. The equilibrium constant cannot be rigorously obtained by the fitting procedure but it is found that the value quoted by Beyer and Keller (1971) of 2×10^{-19} cm^3 is consistent with the present data. The estimated zero-field reduced mobility for K^+ ions in N_2 is $2{\cdot}50\pm0{\cdot}02$.

It should be noted that with the exception of the pressure dependence observed for the mobility of K^+ ions in N_2 the other pressure dependences are small, the largest observed being $1{\cdot}3\%$ for K^+ ions in Ar. However, if accurate interaction potentials are to be derived from ion mobility data, the experimental errors must be very small and such effects as discussed in the present work become important.

Acknowledgments

The authors wish to express their thanks for the comments and suggestions of Dr H. R. Skullerud and for discussions with members of the Ion Diffusion Unit. The technical assistance of Mr J. Gascoigne, Mr F. Johnson and Mr K. Roberts is gratefully acknowledged.

References

Beyer, R. A., and Keller, G. E. (1971). *Trans. Am. geophys. Un.* **52**, 303.
Blewett, J. P., and Jones, E. J. (1936). *Phys. Rev.* **50**, 464.
Crompton, R. W., and Elford, M. T. (1959). *Proc. phys. Soc.* **74**, 497.
Crompton, R. W., and Elford, M. T. (1973). *Aust. J. Phys.* **26**, 771.
Crompton, R. W., Elford, M. T., and Gascoigne, J. (1965). *Aust. J. Phys.* **18**, 409.
Davies, P. G., Dutton, J., and Llewellyn-Jones, F. (1966). *Phil. Trans. R. Soc.* A **1100**, 321.
Elford, M. T. (1967). *Aust. J. Phys.* **20**, 471.
Elford, M. T. (1971). *Aust. J. Phys.* **24**, 705.
Elford, M. T. (1972). *In* 'Case Studies in Atomic Collision Physics' (Eds E. W. McDaniel and M. R. C. McDowell), Vol. 1, Ch. 2 (North-Holland: Amsterdam).
Elford, M. T., and Robertson, A. G. (1973). *Aust. J. Phys.* **26**, 685.
Fleming, I. A., Tunnicliffe, R. J., and Rees, J. A. (1969*a*). *J. Phys.* B **2**, 780.
Fleming, I. A., Tunnicliffe, R. J., and Rees. J. A. (1969*b*). *J. Phys.* D **2**, 551.
Gascoigne, J. (1972). *Vacuum* **21**, 21.
Gatland, I. R. (1972). *Phys. Rev. Lett.* **29**, 9.
Hoselitz, K. (1941). *Proc. R. Soc.* A **177**, 200.
Huxley, L. G. H., and Crompton, R. W. (1974). 'The Diffusion and Drift of Electrons in Gases' (Wiley: New York) (in press).
James, D. R., Graham, E., Thomson, G. M., Gatland, I. R., and McDaniel, E. W. (1973). *J. chem. Phys.* **58**, 3652.
Lindholm, E. (1960). *Rev. scient. Instrum.* **31**, 210.
Lowke, J. J. (1962). *Aust. J. Phys.* **15**, 39.
McDaniel, E. W. (1964). 'Collision Phenomena in Ionised Gases' (Wiley: New York).
McDaniel, E. W., Cermak, V., Dalgarno, A., Ferguson, E. E., and Friedman, L. (1970). 'Ion Molecule Reactions' (Wiley: New York).
McDaniel, E. W., and Martin, D. W. (1971). *Rev. scient. Instrum.* **42**, 157.
Miller, T. M., Moseley, J. T., Martin, D. W., and McDaniel, E. W. (1968). *Phys. Rev.* **173**, 115.
Milloy, H. B. (1973). Ph.D. Thesis, Australian National University.
Mitchell, J. H., and Ridler, K. E. W. (1934). *Proc. R. Soc.* A **146**, 911.
Moseley, J. T., Gatland, I. R., Martin, D. W., and McDaniel, E. W. (1969). *Phys. Rev.* **178**, 234.
Petit-Clerc, Y., and Carette, J. D. (1968). *Vacuum* **18**, 7.
Thomson, G. M., *et al.* (1973). *J. chem. Phys.* **58**, 2402.
Tyndall, A. M. (1938). 'The Mobility of Positive Ions in Gases' (Cambridge Univ. Press).
Watts, R. O. (1974). *Aust. J. Phys.* **27**, 227.

Manuscript received 20 August 1973