THE MOTION OF LOW ENERGY ALKALI IONS
IN GASES

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H.B. MILLOY
STATEMENT

Except where acknowledgements are made in the text all the material contained in this thesis was the work of the candidate.

H.B. Milloy.

H.B. Milloy.
ABSTRACT

The motion of low energy Li\(^+\), K\(^+\) and Cs\(^+\) ions in inert and light diatomic gases has been studied, with particular emphasis on the reduced mobility $\kappa$, the longitudinal diffusion coefficient, $D_L$, and the formation of ion-atom clusters. If accurate experimental data are available it is possible to use an iterative fitting procedure to determine the ion-atom forces. In a previous attempt to obtain mobility data for this purpose, Elford (1971) observed two anomalous effects, a dependence of $\kappa$ on pressure and an increase in $\kappa$ as $E/N$ was decreased towards zero. These effects have been investigated by measuring the reduced zero field mobility over an extended range of pressures (typically 5-180 torr) and by measuring $\kappa$ at two different drift distances (3 and 50 cm). It was found that the anomalous mobility results at low $E/N$ were due to effects at the shutters caused at least partly by the bombardment of the shutter wires with alkali ions. A separate investigation into these effects was carried out. The pressure dependence observed by Elford was partly due to these end effects but even after correction the data still exhibit a significant pressure dependence (~1% between 10 and 100 torr for K\(^+\) ions in Ar). It is postulated that this residual pressure dependence is due to the formation of unstable ion-atom complexes with lifetimes comparable with the mean free time between collisions at gas pressures of a few torr. Predictions based on this hypothesis agree with the experimental data in all cases to better than ±0.2% over the full pressure range. By examining the sensitivity of the mobility to changes in the magnitude of the ion-atom forces it was established that data in error by less than about ±0.3% are required if analytical theories are to be used to give accurate estimates of the interaction potential. Such data are not currently available and it is therefore essential to understand effects of the type and order observed by Elford if such data are to be obtained.

In measurements of the longitudinal diffusion coefficient, $D_L$, other sources of error mask the effects of the formation of ion-atom complexes. This coefficient has been measured for K\(^+\) ions in He, Ar and N\(_2\) in the range $0 < E/N \ (Td) < 30$ and the results, which are estimated to be in error by less than ±3%, have been compared with the theoretical predictions of Kumar and Robson (1973) and Wannier (1953). There is found...
to be a significant disagreement between theory and experiment. In the case of the inert gases there are no published experimental data available for comparison.

Recent theoretical work by Robson made it possible to predict the mobility of ions in gas mixtures at intermediate and high $E/N$ values. To test this theoretical work, which is based on a constant mean free time model, the reduced mobility of $K^+$ ions in Ne, Ne, Ar, $H_2$ and $N_2$ and in mixtures of He-Ne, Ne-Ar and $H_2$-$N_2$ was measured in the range $20 \leq E/N$ (Td) $\leq 100$. It was found that there was good agreement between theory and experiment. An alternative theory, developed by Mason and Hahn (1972) is shown to be invalid.

At the present time there are no published data for the formation or break-up of alkali ion-inert gas atom clusters. The difficulties associated with these measurements have been investigated by using a drift-tube quadrupole mass spectrometer system. It has been shown that large errors can be introduced by mass discrimination effects at the exit aperture and at the conical skimmer. Methods of overcoming these problems are discussed. The formation of clusters in the jet of gas escaping from the drift tube is also shown to be a serious source of error.
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Rₘ for K⁺ ions in H₂, He and Ar

Reduced mobility of K⁺ ions in N₂

Computer control circuit

Contact potential apparatus

Surface charging with electron bombardment
LIST OF SYMBOLS

= ion acceleration.

= impact parameter.

= ion velocity after collision.

= ion velocity before collision.

= velocity of neutral particles after collision.

= velocity of neutral particles before collision.

= differential scattering cross section.

= mutual diffusion coefficient.

= diffusion tensor.

= longitudinal diffusion coefficient.

= transverse or lateral diffusion coefficient.

= zero field diffusion coefficient.

= diffusion coefficient in mixture.

= ionic charge.

= electric field.

= ion distribution function.

= frequency of \( n \)th maximum in an ion current frequency spectrum

= neutral distribution function.

= force.

= perturbation to ion velocity distribution function caused by spatial gradients.

= relative velocity.

= Planck's constant.

= drift distance.

= ion velocity distribution function when spatial density is uniform.

= current.

= flux density of ions.

= angular momentum.

= Boltzmann's constant.

= reaction rate for conversion of species B to A.

= mobility = W/E.
$K_0$ = zero field mobility.
$K_E$ = equilibrium constant.
$m$ = ionic mass.
$M$ = mass of neutral particle.
n(r,t) = number density of ions.
$N$ = number density of neutral particles.
$N_s$ = number density of neutral particles at 273.16 K and 760 torr = $2.687 \times 10^{19}$ cm$^{-3}$.
p = gas pressure.
P$_{273.16}$ = reduced pressure.
P$_V$ = $P_{273.16}$ = Legendre polynomials.
$Q^g(r)$ = collision cross sections.
$Q_D$ = diffusion cross section.
$Q_m$ = momentum transfer cross section.
r = position vector of ion.
r$_b$ = position of minimum for 12-4 potential.
r$_m$ = position of minimum for 12-6-4 potential.
r$_o$ = distance of closest approach.
$R_{12}$ = sum of radii of ion and atom.
S$_{k+1/2}$ = Sonine polynomials.
t = time.
t$_m$ = effective transit time.
T = gas temperature.
V = potential difference.
V(r) = interaction potential.
$V_{eff}(r,J)$ = effective potential.
$V_{re}(r)$ = repulsive part of interaction potential.
W = drift velocity.
$x,y$ = cartesian coordinates at right angles to the field direction.
z = cartesian coordinate in direction of $E$.
$\alpha$ = polarizability of neutral particles.
$\alpha_{AB}$ = collision frequency of conversion of species B to A.
\( \varepsilon \) = depth of minimum for 12-6-4 potential.

\( \varepsilon_1 \) = depth of minimum for 12-4 potential.

\( \theta \) = angle between velocity vector and field direction.

\( \kappa \) = reduced mobility.

\( \kappa_0 \) = reduced zero field mobility.

\( \kappa_{\text{mix}} \) = reduced mobility in mixture.

\( \lambda \) = mean free path.

\( \mu \) = reduced mass = \( mM/(M+m) \).

\( \nu_{\text{m}}(g) \) = collision frequencies.

\( \nu_{\text{m}} \) = momentum transfer collision frequency.

\( \nu_{\text{vis}} \) = viscosity collision frequency.

\( \rho \) = radial distance = \( (x^2 + y^2)^{1/2} \).

\( \sigma \) = cross section.

\( \tau \) = mean free time.

\( \chi \) = angle of scattering in centre of mass system.

\( \psi_r(r) \) = Burnett function.

\( \Omega \) = solid angle.

In the consideration of the problem of an ion in a gas with this average velocity, and with a mean energy equal to \( \varepsilon \) of the gas particles, when the electric field is applied in equilibrium, it is assumed that the energy the ions gain from the field is dissipated in collisions. The result is an expression in the form of a series in the random motion. In any case, if the velocity of the ions was only two bodies and there are no interactions have a negligible effect, then the transport properties of the ions depend on the density \( \bar{n} \) and the magnitude of the electric field strength \( E \). It is to this parameter and for a gas temperature \( T \) is 300 K, that \( \varepsilon/n \) will be expressed in units of “amperes” (where \( \varepsilon = 8.85 \times 10^{-14} \text{ V cm}^2 \)).

The motion of an ion under the influence of an electric field is usually described in terms of the drift velocity, \( \varepsilon \), which is defined as the average velocity of the ions under conditions where the ion number density is spatially independent. In many cases it is found that the drift velocity \( \varepsilon \) is, to first order, proportional to the electric field strength \( E \), and for this reason it has been convenient to define the mobility \( \kappa \) by the relation \( \varepsilon = \kappa E \). To facilitate the comparison of data at different pressures, a quantity called the reduced mobility has been introduced. The reduced mobility \( \kappa_0 \) is defined to be the mobility at a gas number density \( \bar{n}_0 = 2.67 \times 10^{13} \text{ cm}^{-3} \) (that of a gas at 373.15 K and 760 torr) and can therefore be written

\[ \kappa_0 = \frac{\kappa}{n_0^2} \]

This normalization procedure can also be expressed in terms of the reduced pressure \( P_{\text{red}} = \frac{P}{P_0} \), which is given by

\[ P_{\text{red}} = \frac{P}{P_0} \]
CHAPTER 1

INTRODUCTION

1.1 GENERAL CONSIDERATIONS

In the absence of an external field, ions in a gas move in a random manner with no net displacement and with a mean energy equal to that of the gas particles. If a static and uniform electric field is applied an equilibrium is established between the energy the ions gain from the field and lose to the neutral particles. The result is an increase in the average ion energy and, superimposed on the random motion, a net velocity of the ions in the field direction. If it is assumed that the collision times are much shorter than the time between collisions, that only two body collisions occur and that ion-ion interactions have a negligible effect on the ion motion, then the transport properties of the ions depend on the gas number density \( N \) and the magnitude of the electric field strength \( E \) only through the ratio \( E/N \). It is this parameter and the gas temperature, \( T \), which together determine the mean ion energy for a given ion-atom combination. In this thesis \( E/N \) will be expressed in "townsends" (where 1 townsend (Td) = \( 10^{-17} \text{ V cm}^2 \)).

The net motion of the ions under the influence of an electric field is usually described in terms of the drift velocity, \( \mathbf{W} \), which is defined to be the average velocity of the ions under conditions where the ion number density is spatially independent. In many cases it is found that the drift velocity is, to first order, proportional to the electric field strength, \( E \), and for this reason it has been convenient to define the mobility, \( \mathbf{K} \) by the relation \( \mathbf{W} = \mathbf{KE} \). To facilitate the comparison of data at different pressures a quantity called the reduced mobility has been introduced. The reduced mobility, \( \kappa \), is defined to be the mobility at a gas number density \( N_s = 2.687 \times 10^{19} \text{ cm}^{-3} \) (that of a gas at 273.16 K and 760 torr) and can therefore be written

\[
\kappa = \frac{KN}{N_s} = \frac{W}{(E/N)N_s}. \tag{1.1.1.}
\]

This normalization procedure can also be expressed in terms of the reduced pressure \( p_{273.16} \), which is given by
where $p_T$ is the pressure at temperature $T$. The reduced mobility can then be written,

$$K = \frac{K_{273.16}}{760} = \frac{W}{(E/p_{273.16}) 760}, \quad 1.1.3.$$  

where the reduced pressure is in torr.

The mobility at vanishingly small $E/N$ values is known as the zero field mobility and is defined by the relation,

$$K_0 = \lim_{E/N \to 0} K. \quad 1.1.4.$$ 

Similarly the reduced zero field mobility is defined to be

$$K_0 = \lim_{E/N \to 0} K. \quad 1.1.5.$$ 

If the number density of ions is spatially independent the ion flux density, $j(r,t)$, across any plane in space is given by

$$j = n W, \quad 1.1.6.$$ 

where $n$ is the ion density. If there are small spatial gradients in the distribution of ions there is an additional contribution to the flux, which now becomes (Wannier 1953),

$$j(r,t) = n(r,t) W - \mathbf{D} \cdot \nabla n(r,t), \quad 1.1.7.$$ 

where $\mathbf{D}$ is the diffusion tensor. A tensor quantity is required to describe the diffusion because in general it is anisotropic. The components of the diffusion tensor in the directions parallel and perpendicular to the field are known as the longitudinal and lateral (or transverse) diffusion coefficients, $D_L$ and $D_T$ respectively. At low values of $E/N$, where the ion motion is dominated by the random motion of the neutral particles, the
diffusion coefficients are equal and related to the zero field mobility by the Nernst-Townsend relation,

\[ \frac{D_t}{K_0} = \frac{kT}{e}, \]

where \( D_t \) is the zero field diffusion coefficient, \( k \) is Boltzmann's constant and \( e \) is the ionic charge. It can be seen from equation 1.1.8 that in the zero field limit the motion of the ions can be described by one parameter. At higher values of \( E/N \) the motion of the ions cannot be fully described unless \( D_L, D_T \) and \( \kappa \) are known.

1.2 BACKGROUND TO PRESENT WORK

One of the long term aims of low energy ion swarm research is to obtain accurate quantitative information about the nature of long-range ion-atom forces by comparing the transport coefficients measured experimentally with those predicted theoretically. In principle the experimental measurements are not difficult. The theory is more complicated and until recently the treatment of Kihara (1953) was the only one available. However in the past few years Kumar and Robson (1973) have developed an alternative and less restrictive approach.

The mathematical difficulties involved in the iterative fitting procedure could in principle be bypassed by using beam techniques to measure the collision cross sections directly. Unfortunately there are severe difficulties associated with low energy beam experiments, such as the influence of stray electric fields and low beam intensities and at the present time it is not a comparable technique.

Although swarm techniques have been used to estimate the interaction potential for several ion-atom combinations there appears to have been no adequate discussion of the errors involved and in particular the errors associated with uncertainties in the experimental data have been neglected. This is an important omission as small changes in the form of the variation of the transport coefficients with \( E/N \) lead to very much larger errors in the magnitude of the derived ion-atom forces.

A fundamental limitation to the use of swarm techniques for determining ion-atom forces was recently discussed by Elford (1971) who reported measurements of the reduced mobility in which anomalous
dependences on the gas number density and E/N were observed. Elford argued that the available theories should not be used until these effects were satisfactorily explained. These measurements raised the important questions of whether the basic assumptions in the theory of ion transport were valid for experiments carried out at a few torr, the normal pressure region for ion swarm experiments, and also cast doubts on the previously unquestioned assumption that potassium ions do not form clusters with inert gas atoms at room temperature. The formation of these clusters is the subject of controversy at the present time as there is evidence from some experiments that they are significant at room temperature and contradictory evidence from other experiments. The understanding of the formation and stability of clusters is very limited. This is partly due to the complexity of the theoretical problem and partly due to the difficulties inherent in the experimental measurements, many of which are only now being fully appreciated.

1.3 AIMS OF PRESENT RESEARCH

The majority of the work reported in this thesis is part of a research programme to determine the magnitude of the forces between alkali ions and inert gas atoms as a function of internuclear separation. The particular aims of the present work were,

1) to explain the effects observed by Elford (1971),

2) to investigate the feasibility of using the theory of Kumar and Robson (1973) to determine the magnitude of the ion-atom forces,

3) to measure the variation of the longitudinal diffusion coefficient of alkali ions in inert gases in the E/N range for which the theory of Kumar and Robson is valid and to compare the results with the theoretical predictions,

4) to measure the mobility of ions in gas mixtures at high E/N values and to compare the results with the theories of Mason and Hahn (1972) and Robson,
(5) to assess the significance of the formation of ion-atom clusters in the measurement of the transport coefficients of alkali ions in inert gases.

The results of these investigations are reported in Chapters 6 to 10. No attempt has been made to give an overall conclusion to the work in this thesis. Instead the conclusions from each investigation are given in the relevant chapter.
CHAPTER 2

A REVIEW OF IONIC TRANSPORT THEORY

At the present time there is no general theory which can predict ionic transport coefficients as a function of E/N and gas temperature. However under certain circumstances it is possible to determine the long-range ion-atom forces by comparing the experimentally measured transport properties with the theoretical predictions. Except in the simplest cases ab initio calculations of the ion-atom forces have not been carried out and thus the procedure of comparing the measured transport properties with theory is usually the only one available.

There are three stages in the procedure for predicting the macroscopic properties of the ion motion. Assuming the interaction potential has not been calculated from first principles by quantum mechanics, the first step is to choose an algebraic form for the potential by considering the general characteristics of the ion-atom forces. The second step is to calculate the collision cross sections either by quantum or classical mechanics. Usually this can be carried out sufficiently accurately with classical mechanics but a quantum mechanical description is necessary if very low energies or very light ion-atom combinations are involved. The third step is to use the collision cross sections with an adequate transport theory to predict the variation of the transport coefficients as a function of E/N and T. In this chapter the formal theory involved in these three steps will be described and an outline given of the various attempts which have been made to predict the transport coefficients. Some of these attempts are general in the sense that no restriction is placed on the form of the interaction potential. These general theories are all based on the works of Chapman and Enskog and are limited to relatively small values of E/N. The other theories which will be discussed are limited to particular scattering models. One of these, the constant mean free time model, is particularly relevant to this work as it has been used by Robson to predict in a qualitative way the mobility of ions in gas mixtures. The computer simulation techniques used by Skullerud will also be discussed. These techniques, which are not restricted to a particular form of the interaction potential, are particularly useful at high values of E/N because for a given computing time the accuracy increases with increasing E/N and because there
are no other quantitative theories to predict the motion of ions at high values of E/N.

2.1 ION-ATOM FORCES

The only ab initio calculations of the interaction potential for an ion-atom combination relevant to this work are those for the case of lithium ions in helium. Since the advent of high speed computers calculations of the interaction potential for this case have been made several times. The most extensive of these calculations, in that they cover all internuclear separations, are those of Catlow et al. (1970) and Junker and Browne (1969). Fischer (1968) and Schneiderman and Michels (1965) have also considered aspects of the problem. For other alkali ion-atom combinations the complexity of the quantum mechanical calculations is severe and the interaction potential is assumed to have an algebraic form consistent with the known long-range and expected short-range forces acting between an ion and a neutral particle. These forces will now be considered in detail.

2.1.1 Repulsive forces

Repulsive forces between an ion and a neutral particle are significant when the particle separation is sufficiently small that the electron clouds of the two particles interact. There are two contributions to this repulsive interaction, one of which is the direct Coulomb interaction and the other, which is sometimes called an exchange interaction, is a consequence of the Pauli Exclusion Principle. Since the repulsive forces have not in general been calculated, model potentials are often used to describe this complex interaction. The models which have been most commonly used are

(a) hard sphere model

(b) \( V_{\text{rep}}(r) = r^{-2N} \) where \( N \) is an integer and \( r \) is the internuclear separation

and

(c) \( V_{\text{rep}}(r) = \exp (- \xi r) \).

These models will be discussed more fully in section 2.1.3.

2.1.2 Attractive forces

When an ion interacts with a neutral particle the electron cloud of the neutral particle becomes polarised and the magnitude of the resultant
attractive force between the induced dipole and the ion can be written,

\[ F = \frac{2 e^2 a}{r^5} \quad \text{2.1.1.} \]

where \( a \) is the polarizability of the gas particle, \( e \) is the ionic charge and \( r \) is the particle separation. In writing eqn. 2.1.1. it is assumed that the distance \( r \) is much greater than the diameters of the particles. Maxwell pointed out that for an inverse fifth power law of force the mean free time spent by the ions between collisions is constant and that as a result all the transport properties can be calculated without a knowledge of the ion velocity distribution function. For this reason the special case of an interaction potential due solely to the polarization force is often referred to as the Maxwellian model.

The ion not only induces a dipole moment on the atom but also forces arising from quadrupole, octupole and other moments (Margenau 1941). Of these higher order interactions the only one usually considered is the quadrupole for which the interaction force is proportional to \( r^{-7} \). There is, however, a further contribution to the net \( r^{-7} \) force, for the ion is polarized by the dipole which it induces in the atom.

2.1.3 Algebraic forms of the interaction potential

It is usually assumed, although with doubtful validity, that the interaction potential for any realistic case can be represented by the algebraic sum of the interactions discussed above and consequently the most general of these algebraic forms can be written,

\[ V(r) = \frac{a}{r^{2N}} - \frac{b}{r^6} - \frac{c}{r^4} \quad \text{2.1.2.} \]

and

\[ V(r) = a \exp(-\xi r) - \frac{b}{r^6} - \frac{c}{r^4} \quad , \quad \text{2.1.3.} \]

where \( a, b \) and \( \xi \) are fitting parameters and \( N \) is an integer. The constant \( c \) is determined by the polarizability of the atom. Equation 2.1.2. has been used (with \( N = 6 \)) by Mason and Schamp (1958), Creaser (1969) and Robson and Kumar (1973) to predict the transport coefficients of alkali ions in inert
gases. Equation 2.1.3. has been used (with \( b = 0 \)) by Dalgarno et al. (1958) and Creaser (1969).

Simpler forms for the interaction potential have also been used. For example it has sometimes been assumed that the particles are hard elastic spheres, that is,

\[
V(r) = \begin{cases} 
\infty & r \leq R_{12} \\
0 & r > R_{12}
\end{cases}
\]

where \( R_{12} \) is the sum of the radii of the particles. This interaction results in isotropic scattering in the centre of mass frame of co-ordinates and in a mean free path between collisions which is independent of the relative velocity of the particles. Langevin (1905) assumed that the repulsive interaction could be approximated by a hard sphere and the attractive interaction by the dipole polarization force, that is

\[
V(r) = \begin{cases} 
\infty & r \leq R_{12} \\
cr^{-6} & r > R_{12}
\end{cases}
\]

This potential is commonly referred to as a Sutherland potential. The constant mean free time model (of which the Maxwellian model is a special case) has also been commonly used.

### 2.2 DETERMINATION OF COLLISION CROSS-SECTIONS

Once the interaction potential has been determined or an approximate algebraic form for it has been assumed the differential scattering cross section, \( dI(g,\chi) = I(g,\chi) \, d\Omega \) can then be calculated. \( I(g,\chi) \, d\Omega \) is the area presented by each target particle for scattering into the element of solid angle \( d\Omega \) about an angle \( \chi \) in the centre of mass system to an incident beam of particles of velocity \( g \). It is assumed that the scattering is independent of the azimuthal angle and thus only central forces are considered.

In a quantum mechanical description of the collisions the Schrödinger wave equation is often solved by the method of partial waves and the differential scattering cross section calculated in terms of the phase shifts of the partial waves \( \eta_\chi \), from the relationship
\[ I(g,\chi) = \frac{1}{4k^2} \left| \sum_{l=0}^{\infty} (2l+1)(\exp(2in\chi) - 1) P_l^2(\sin \chi) \right|^2 , \]  

where \( k = 2\pi \mu g/h \), and \( P_l^2(\chi) \) are the Legendre polynomials.

On the other hand if a classical description of the collisions is adequate the scattering angle is expressed in terms of the impact parameter \( b \) and the interaction potential \( V(r) \) by the relation,

\[ \chi(b,g) = \pi - 2b \int_{r_0}^{\infty} \frac{dr/r^2}{[1-b^2/r^2 - V(r)/0.5\mu g^2]^{1/2}} , \]

where \( r_0 \), the distance of closest approach, is found from

\[ 1 - b^2/r^2 - V(r)/0.5\mu g^2 = 0 . \]

The differential scattering cross section can then be calculated from the classical formula,

\[ I(g,\chi) = \frac{b}{\sin \chi} \left| \frac{d}{d\chi} \right| . \]

The full derivation of the relations 2.2.2, 2.2.3, and 2.2.4. can be found in several standard texts (Hirschfelder et al. 1964, Kennard 1938, McDaniel 1964) and will not be given here.

A number of other cross sections are involved in calculations of transport coefficients. These cross sections \( Q^\lambda(g) \), are defined in terms of the differential scattering cross section by the relationship,

\[ Q^\lambda(g) = 2\pi \int_0^\pi (1-\cos^\lambda \chi) I(g,\chi) \sin \chi \, d\chi , \]

where \( \lambda = 1, 2, 3 \ldots \).

The cross section \( Q^1(g) \) is referred to as either the momentum transfer cross section, \( Q_m^1 \), or the diffusion cross section, \( Q_p^1 \). The cross section \( Q^2(g) \) is known as the viscosity cross section. The transport collision frequencies are also frequently used. These are defined by,
\[ \nu_k(g) = 2\pi N \int_0^\pi (1 - \cos^2 \chi) g I(g, \chi) \sin \chi \, d\chi . \] 2.2.6.

2.3 THE BOLZMANN EQUATION

The motion of the ions in a gas may be described in terms of the distribution function \( f(r, c, t) \), which is formally defined to be the number of ions per unit volume of phase space which are located in a small volume element \( dr \) at \( r \) in position space and which have a velocity vector in the range \( dc \) about \( c \) in velocity space. From this definition it follows that the number density, \( n \), of ions in position space is given by

\[ n(r, t) = \int f(r, c, t) \, dc . \] 2.3.1.

In order to determine the distribution function of the ions under the conditions investigated in this work the following assumptions are normally made.

1. The effects of three body collisions are negligibly small.
2. The collision times are negligibly small compared with the times between collisions.
3. The ion density is sufficiently low that the effects of ion-ion interactions can be neglected. This makes the Boltzmann equation linear in the ion distribution function.
4. The only external force acting on the ions is a constant and uniform electric field, but it is assumed that this field is not strong enough to significantly polarize the neutral gas particles.
5. The distribution function of the neutral particles, \( F \), is independent of time and position space and the velocity dependence is assumed to have a Maxwellian form,

\[ F(c) = N \left( \frac{M}{2\pi kT} \right)^{3/2} \exp \left( - \frac{Mc^2}{2kT} \right) , \] 2.3.2.

where \( N \) is the number density of neutral particles in position space. In writing 2.3.2, it is implicitly assumed
that the passage of ions through the gas has a negligible effect on the gas temperature.

(6) The ion-atom forces are always directed along the line of centres and as a consequence the differential scattering cross sections are independent of the azimuthal angle.

(7) All collisions are elastic.

With these assumptions the Boltzmann equation can be written

$$\frac{\partial f}{\partial t} + \frac{eE}{m} \cdot \nabla f + c \cdot \nabla f = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}}$$

where

$$\left( \frac{\partial f}{\partial t} \right)_{\text{coll}} = -\int \int [f(c) F(C) - f(c') F(C')] g I(g,\lambda) \, d\Omega \, d\zeta$$

where the primed quantities refer to pre-collision conditions.

The Boltzmann equation is solved in two stages. In the first stage it is assumed that the ion velocity distribution function is independent of time and of position space and thus,

$$f(r,\zeta, t) = n \, h(\zeta)$$

where $n$ is a constant and $h(\zeta)$ satisfies the equation

$$\frac{eE}{m} \cdot \nabla h(\zeta) + \int \int [h(\zeta) F(C) - h(\zeta') F(C')] g I(g,\lambda) \, d\Omega \, d\zeta = 0.$$  

with the normalization condition,

$$\int h(\zeta) \, d\zeta = 1.$$  

Under these conditions of spatial uniformity only one transport coefficient is needed to describe the behaviour of the ion swarm. This is the drift velocity, $\bar{W}$, which is defined by,

$$\bar{W} = \int h(\zeta) \, \zeta \, d\zeta.$$  

In the second stage the effects of small density gradients are taken into account by considering the full equation (2.3.3.) and taking the new terms as perturbations. The theory for this has been developed by Wannier (1953) who assumed that

\[ n(r,t) = \exp(k \cdot \mathbf{r} - \langle c \rangle t), \quad 2.3.9. \]

where

\[ k = \frac{1}{n} \frac{\partial n}{\partial r} = \text{const.} \]

and

\[ f(r,\zeta,t) = n(r,t) \{ h(\zeta) + g(\zeta) \} \quad 2.3.10. \]

where \( g(\zeta) \) is the perturbation to the velocity distribution function caused by the density gradient. Using this approach Wannier showed that a small density gradient will give rise to a diffusion flux density which can be described by a density independent diffusion tensor. The expression for the total flux density at any point in space can then be written,

\[ j(r,t) = j_{\text{drift}} + j_{\text{diff}} \]

\[ = n(r,t) \mathbf{w} - \hat{\mathbf{D}} \cdot \nabla n(r,t) \quad 2.3.11. \]

where

\[ \hat{\mathbf{D}} = \begin{pmatrix} D_T & 0 & 0 \\ 0 & D_T & 0 \\ 0 & 0 & D_L \end{pmatrix} \quad 2.3.12. \]

in a Cartesian co-ordinate system. The expressions for \( D_T \), the transverse or lateral diffusion coefficient and for \( D_L \), the longitudinal diffusion coefficient are given by,
\[ D_T = \int \phi_T(c) \, dc \] 2.3.13.

\[ D_L = \int \phi_L(c) \, dc \] 2.3.14.

where \( c_T = c_x \) or \( c_y \) and \( c_L = c_z \). The functions \( \phi_T \) and \( \phi_L \) are determined by the equations,

\[
eE \frac{\partial \phi_L}{\partial c_L} + \int \left[ \phi_L(c) F(c') - \phi_L(c') F(c) \right] g \, d\Omega \, dc = -(W-c_L) h(c) 2.3.15
\]

\[
eE \frac{\partial \phi_T}{\partial c_L} + \int \left[ \phi_T(c) F(c') - \phi_T(c') F(c) \right] g \, d\Omega \, dc = c_T h(c) 2.3.16.
\]

On substituting the expression for \( j \) given by equation 2.3.11. into the continuity equation,

\[
\frac{\partial n(r,t)}{\partial t} + \nabla \cdot j(r,t) = 0 , 2.3.17.
\]

an expression governing the ionic number density at any point in position space can be derived,

\[
\frac{\partial n(r,t)}{\partial t} - \nabla^2 n(r,t) + W \cdot \nabla n(r,t) = 0 . 2.3.18.
\]

This equation, which is often referred to as the diffusion equation, is the link between the Boltzmann level of description and the experimental measurements and will be discussed in Chapter 4.

2.4 CALCULATION OF TRANSPORT COEFFICIENTS

The formal theory of the motion of low energy ions in gases has been outlined in the first three sections of this chapter. Unfortunately there is no general method for either solving the Boltzmann equation or for calculating the drift velocity or the diffusion coefficients. However,
various theories have been developed to describe the ion motion under certain restrictive conditions and a summary of these theories is given in this section. The more general theories are described first. These theories are not restricted to a particular form of the ion-atom interaction potential, although they are restricted to a relatively small range of ion energies. In the final part of this section a description is given of the theories which use more restrictive scattering models.

2.4.1 General theories

The general theories are based on the work of Chapman (1912), and Enskog (1911a, 1911b) who independently developed a theory which describes the diffusion of particles in a gas in the absence of an electric field. The resultant expression for the diffusion coefficient under the conditions applicable to this work is

\[ D = \frac{3}{16} \left( \frac{2\pi kT}{\mu} \right)^{1/2} \frac{(1+e_o)}{NP_{12}} \]

where \( P_{12} = \frac{1}{2} \int_0^\infty w^2 Q_0(g) \exp(-w) \, dw \) and \( w = \frac{\mu g^2}{2kT} \).

The factor \( e_o \) is a calculable correction which is zero for the Maxwellian model and a maximum of 0.136 for hard sphere scattering. Recently Mason et al. (1972) used the predictions of Chapman and Enskog as the basis of a theory for the mobility of polyatomic ions.

Kihara (1953) and Kumar (1967) have extended Chapman and Enskog's work to the case of ions moving under the influence of a constant electric field by expanding the ion velocity distribution function in terms of Burnett functions, \( \psi_\lambda^{(r)} \),

\[ f(c) = f_{\text{Max}} \left( \frac{mc^2}{2kT} \right) \sum_{\lambda r} a_{\lambda r} \psi_\lambda^{(r)} \]

where

\[ \psi_\lambda^{(r)} = \frac{(mc^2)^{\lambda/2}}{2kT} \left( \frac{c}{c} \right)_\lambda S^{(r)}_{\lambda} \left( \frac{mc^2}{2kT} \right) \]

and \( f_{\text{Max}} \) is a Maxwellian velocity distribution.
In equation 2.4.3, the preferred direction of motion caused by the electric field is taken into account by the inclusion of the Legendre polynomials $P_l(cz/c)$. The functions $S_{l,r}^{(r)}$ are Sonine polynomials. A consequence of this expansion technique is that the first approximation to the transport coefficients are those predicted by the Maxwellian model. The use of Burnett functions is both the strength and the weakness of these theories. The strength lies in the relative ease with which the collision integrals can be evaluated. The weakness is that the theory is limited to those situations where the ion velocity distribution function is not greatly perturbed from a Maxwellian distribution. Thus the method is restricted to those conditions where the mean energy of the ions does not differ greatly from the mean thermal energy.

In the remaining part of this section an outline of Kihara's approach is given and the advantages of the matrix formalism developed by Kumar are discussed.

**A. Kihara's theory**

Kihara has extended the method of Chapman and Enskog for obtaining the transport properties of binary gas mixtures to the calculation of the drift velocity of ions in atomic gases. The general expression for the drift velocity can be found by considering equation 2.4.3. It follows that if $l = 1, r = 0$, then

$$
\psi_1^{(0)} = \left( \frac{m}{2kT} \right)^{1/2} c_z,
$$

and therefore

$$
<\psi_1^{(0)}> = \left( \frac{m}{2kT} \right) W
$$

2.4.4.

In order to obtain an expression for $<\psi_1^{(0)}>$ the Boltzmann equation, as given by equation 2.3.6., is multiplied by Burnett functions and the resultant expression integrated over all velocity space. Thus no attempt is made to solve the Boltzmann equation directly, but instead a form of the general moment equation is used. This results in an infinite set of coupled integral equations for $<\psi_{l}^{(r)}> \psi_{l}^{(r)}$, which can be expanded as an infinite sum of $<\psi_{l}^{(r)}> \psi_{l}^{(r)}$ over the index $s$ to give the following doubly infinite set of coupled
algebraic equations,

\[(\ell+\delta) a_{rr}(\ell) \psi_{\ell}^{(r)} = \varepsilon [\ell(\ell+\delta+r) \psi_{\ell-1}^{(r)} - (\ell+1) \psi_{\ell+1}^{(r-1)}] \]

- \[(\ell+\delta) \sum_{s=0}^{\infty} (1-\delta) a_{rs}(\ell) \psi_{s}^{(s)}, \]

where \(\psi_{\ell+1} = 0\) and \(\varepsilon = \left( \frac{eE}{mN} \right) \left( \frac{m}{2kT} \right)^{\ell} \). The expansion coefficients \(a_{rs}(\ell)\)
are multiple integrals over all the variables specifying an ion-atom collision. The set of equations 2.4.5. cannot in general be solved exactly, but a convergent successive approximation scheme can be developed. This scheme is based on the observation that for the constant mean free time model the coefficients \(a_{rs}(\ell) = 0\) for \(r \neq s\). The results of this model are used as a first approximation to \(\psi_{\ell}^{(r)}\), which can be written

\[ (\ell+\delta) a_{rr}(\ell) \psi_{\ell}^{(r)} = \varepsilon [\ell(\ell+\delta+r) \psi_{\ell-1}^{(r)} - (\ell+1) \psi_{\ell+1}^{(r-1)}] \]

Higher approximations for \(\psi_{\ell}^{(r)}\) and in particular for \(\psi_{\ell}^{(0)}\) can be obtained by inserting lower approximations for other \(\psi_{\ell}^{(r)}\) in the terms containing the off-diagonal \(a_{rs}(\ell)\).

Mason and Schamp (1958) have taken these general expressions from Kihara's theory and presented them in a form applicable to the analysis of experimental data. They showed that the mobility can be expressed in the form

\[ K = K_1 (g_0 + g_1 (\varepsilon/a_{oo}(1))^2 + g_2 (\varepsilon/a_{oo}(1))^4 + \ldots) \]

and evaluated the coefficients \(g_0\), \(g_1\), and \(g_2\) in the third approximation.

In equation 2.4.7. \(K_1\) is the first (constant mean free time) approximation. The coefficients, \(g\), are complicated functions of the \(a_{rs}(\ell)\). Using the expansion 2.4.7. and a 12-6-4 interaction potential, Creaser (1969) has estimated the potential parameters for several ion-atom combinations by comparing the predictions of Kihara's theory with experimental mobility data over a range of temperatures and values of \(E/N\).
Kihara did not consider diffusion processes but Whealton and Mason (1972b) and Skullerud (unpublished) have extended the theory to enable diffusion coefficients to be calculated.

B. Kumar's theory

Kumar has shown that if the distribution function of the ions is expanded in terms of Burnett functions the coefficients can be expressed as the elements of a matrix. The mobility and both the longitudinal and the lateral diffusion coefficients can then be expressed in matrix formalism (Kumar and Robson 1973). The main advantage of this approach is that the algebraic difficulties which beset Mason and Schamp can be overcome and transport coefficients can be accurately determined at higher values of E/N than were possible with the approach adopted by Mason and Schamp.

This theory has been used by Robson and Kumar (1973) and by Robson (1973) to predict the transport coefficients of alkali ions in rare gases. The values of the diffusion coefficients predicted by this work are the only quantitative ones available for comparison with the experimental values reported in Chapter 8. Robson (1972) has also used Kumar's theory to calculate the velocity distribution function of the ions.

2.4.2 Theories based on restrictive scattering models

A. Constant mean free time model

Although the constant mean free time model is a specialized case it is of general interest as it is the zeroth order approximation for the more general theories. This model was also used by Robson as a first approximation for the theoretical work on deviations from Blanc's Law (section 2.6).

The main results of this model are given below. Apart from the expression for the ionic mobility, which has also been derived by Langevin (1905) the results are those of Wannier (1953).

The mobility is given by

$$K = \frac{e}{(\nu_m \mu)}$$

where \(\nu_m\) is the constant collision frequency for momentum transfer.
The mean kinetic energy of an ion is given by

\[(K.E.)_{tot} = \frac{1}{2} m \langle c^2 \rangle = \frac{3}{2} kT + \left[ \frac{1}{2} m W^2 + \frac{1}{2} M W^2 \right] \] 2.4.9.

The first term on the right hand side is the energy of the ions due to the thermal motion of the neutral gas atoms. The second term is the energy gained from the field. The first component of the field term may be identified as the energy of the drift motion and the second component is the contribution to the random motion caused by the electric field. From equation 2.4.9, it can be seen that

\[
\frac{\text{random energy induced by field}}{\text{directed energy induced by field}} = \frac{\text{atomic mass}}{\text{ion mass}} \] 2.4.10.

That is light ions in a heavy gas (electron case) have very little capacity for storing energy in the field direction but when heavy ions move in a light gas very little of the field energy is stored in random motion.

Wannier has also shown that the random energy due to the field is distributed anisotropically. For the case of an induced dipole interaction this can be written,

\[
\frac{\text{[(K.E.)}^{\text{random}}_T - \frac{1}{2} kT]}{\text{[(K.E.)}^{\text{random}}_L - \frac{1}{2} kT]} = \frac{(M+m)}{(M+3.72m)} \] 2.4.11.

The diffusion coefficients are given by the equations

\[
\frac{D_L}{K} = \frac{2}{e} (K.E.)^{\text{random}}_L = \frac{kt}{e} + \frac{MW^2}{e} \frac{(M \nu_v + 2m(2 \nu_m - \nu_v))}{(4m \nu_m + 3M \nu_v)} \] 2.4.12.

\[
\frac{D_T}{K} = \frac{2}{e} (K.E.)^{\text{random}}_T = \frac{kt}{e} + \frac{(M+m) W^2 M \nu_v}{e} \frac{1}{(4m \nu_m + 3M \nu_v)} \] 2.4.13.

B. Constant cross section model at high E/N

It was pointed out in the previous section that the expansion of the distribution function in terms of Burnett functions is inappropriate.
at high E/N as the ion velocity distribution function is severely distorted from the thermal Maxwellian distribution. In principle it should be possible to use an alternative expansion scheme for the high field case, but as yet this has not been done for a realistic scattering model. However, Wannier (1953) has considered the case of hard sphere scattering and m=M and the results are given below.

The mobility is given by,

\[ K = \frac{1.147}{N} \left( \frac{e}{m \sigma E/N} \right)^{\frac{1}{2}} \]  

where \( \sigma \) is the hard sphere collision cross section. The expressions for the kinetic energy of the ions are given by,

\[ (K.E.)_{\text{tot}} = \frac{1}{2} m \langle c^2 \rangle = 0.898 \text{ mW}^2 \]  
\[ (K.E.)_{L} = \frac{1}{2} m \langle c^2 \rangle^z = 0.673 \text{ mW}^2 \]

\[ \frac{(K.E.)_{\text{random}}}{(K.E.)_{L}} = 0.65 \]  

Wannier also calculated the longitudinal diffusion coefficient for this case:-

\[ D_L = \frac{0.22}{N} \left[ \frac{eE/N}{m \sigma^3} \right]^{\frac{1}{2}} \]

C. The work of Dalgarno, McDowell and Williams

The quantum mechanical determination of the collision cross sections, as described in section 2.2, has been used by Dalgarno et al. (1958) together with equation 2.4.1. to predict the zero field mobility of ions in unlike gases and ions in their parent gases. This work was carried out before the general use of high speed computers, and to simplify the calculations the following form of the potential was used,
\[ V(r) = A \exp(-r) - \frac{b}{r^4}. \quad 2.4.19. \]

It was also necessary to make other simplifying assumptions.

Creaser (1969) has used this method to fit a potential of the form \(2.4.19\) to the experimentally measured temperature variation of the reduced zero field mobility of \(K^+\) ions in He.

**D. Theories of Langevin**

Langevin (1903) pioneered ionic mobility theory with a constant mean free path theory. Both ions and atoms were considered to be hard elastic spheres of equal mass, their only distinguishing feature being the charge on the ion. As poor agreement with experiment was obtained Langevin revised his assumptions and in 1905 published a second theory which took account of the polarization force between the ion and the atom as well as the hard sphere repulsion (see section 2.1.3.). The mobility was given by

\[ K = \frac{A(\lambda)}{N(4\pi \alpha \mu)^{\frac{1}{2}}}, \quad 2.4.20. \]

where \(A\) is a function of the parameter \(\lambda\), defined by the relation,

\[ \lambda^2 = \frac{2kT R_{12}^4}{\alpha e^2} \]

and \(R_{12}\) is the sum of the radii of the ion and the atom. The value of \(A(\lambda)\) is a measure of the relative importance of elastic sphere and polarization scattering. When the polarization term in the interaction potential dominates equation \(2.4.20\) becomes

\[ K = \frac{0.5105}{N} \frac{1}{(4\pi \mu \alpha)^{\frac{1}{2}}} \quad 2.4.21. \]

and when the hard sphere repulsion dominates the mobility becomes

\[ K = 0.75 \left( \frac{e}{NR_{12}^2 (8\pi \mu kT)^{\frac{1}{2}}} \right) \quad 2.4.22. \]
In an attempt to improve Langevin's theory, Hasse and Cook (1931) replaced the concept of polarizable elastic spheres by point centres of force with an interaction potential of the form,

\[ F(r) = \frac{a}{r^8} - \frac{b}{r^4}. \]

However, this did not significantly improve the agreement between theory and experiment.

2.5 A MONTE CARLO INVESTIGATION

In this method statistical information is gained about the swarm by following individual ions through a large number of stochastically chosen free paths. The great advantage of this technique is that it can be used when analytical theory fails and thus is particularly useful at high E/N values. The problems of calculating the scattering angles analytically still remain but once these are known the transport coefficients can be calculated and thus the problems outlined in sections 2.3. and 2.4. can be by-passed. The main drawback is that the accuracies obtainable, with reasonable computing times, may be rather poor.

Skullerud (1973a, 1973b) has used this method to investigate the general motion of ions in atomic gases and in particular to study the transport of K⁺ ions in Ar. The general results of this work will be outlined below in a summary of the form of the variation of the transport coefficients with the experimental parameters.

2.5.1 General form of the variation of the transport coefficients with E/N and T

In this work Skullerud used an interaction potential of the form,

\[ V(r) = \frac{3}{2} \varepsilon_1 \left[ \frac{4}{n} \left( \frac{r_b}{r} \right)^n - \delta \left( \frac{r_b}{r} \right) - \frac{r_b^6}{r^6} \right], \]

2.5.1.

where \( \delta \) is a constant, \( \varepsilon_1 \) is the depth of the potential minimum when \( \delta = 0 \) and \( r_b \) is the position of the minimum when \( \delta = 0 \). It will be assumed in this discussion that \( m = M \) and that the thermal motion of the gas atoms can be ignored. Figs. 2.1a and 2.1b show the variation of the
Fig. 2.1a

Fig. 2.1b

The curves show potential functions plotted as $D/(E/N)^{2}$ as functions of $E/N$ for a $n=8$ potential. The curves show a similar deviation to the mobilities, but with relatively higher peaks.

The largest deviation in the case of the $n=8$ potential was observed due to the fact that $D/E$ is almost proportional to $E^{2}$ and $N$, and so $D/(E/N)^{2}$ is roughly proportional to $n^{2}$. The decrease of mobility is approximately to the $n^{2}$ term at higher values of $E/N$. The mobility is only an $n^{2}$ term in the interaction potential to a large extent. In this case the collision frequency increases with increasing energy, the potential becomes more strongly attractive than a pure repulsive potential. There is no known instance of combination which attains a marked increase of $K$ with increasing energy, but it seems that the potential has been observed in the case of some ions in gas in [4]. A paper by D. E. Page by B. G. S. is pointed out that if due to the cancellations of the effects of the attractive and repulsive terms in the interaction potential. The attractive and repulsive terms define the ions in opposite directions and this causes a dip in the mobility. The dip is larger if the attractive force is more strongly dominant. For this is that a soft repulsive term is needed to define over a wider range of speeds than a sum curve. As the value of $D/E$ is increased still further the repulsive term dominates and the mobility is free from the collision process. It can be shown that the asymptotic behaviour of the mobility in this region is
mobility - $E/N$ curve with changes in $n$ and $\delta$. At low values of $E/N$ the collisions are dominated by the polarization term in the interaction potential and thus the mobility is only a slowly varying function of $E/N$. The largest variation of $K$ with $E/N$ in this range occurs when the $r^{-6}$ term in the interaction potential is large. In this case the collision frequency increases with increasing energy as the potential becomes more strongly attractive than a pure polarization potential. There is no known ion-atom combination which exhibits this initial decrease of $K$ with increasing $E/N$ but it seems likely that this effect has been observed in the case of Li$^+$ ions in $N_2$ (see section 5.4.3.). The maximum in the mobility - $E/N$ curve at higher values of $E/N$ is the subject of a paper by Wannier (1970) where it is pointed out that it is due to the partial cancellation of the effects of the attractive and repulsive terms in the interaction potential. The attractive and repulsive terms deflect the ions in opposite directions and this causes a dip in the momentum transfer cross section at certain energies. It can be seen from Fig. 2.1a that the bump is larger if the repulsive force is soft. The reason for this is that a soft repulsion compensates the attractive contribution over a wider range of speeds than a hard force. As the value of $E/N$ is increased still further the repulsive term dominates and the mean free time between collisions decreases. It can be shown that the asymptotic behaviour of the mobility in this region is,

$$K = \text{const. } (E/N)^{(4-n)/(2n-4)}$$  \hspace{1cm}  \text{2.5.2.}$$

The diffusion coefficients, plotted as $D/(E/N)^2$ are shown as functions of $E/N$ in Fig. 2.2 for a 12-4 potential. The curves show similar behaviour to the mobilities, but with relatively higher peaks. The larger maxima in the case of the diffusion coefficients are partly due to the fact that to first order $D/(E/N)^2$ is proportional to $v_m^{-3}$, as can be seen from equations 2.4.12. and 2.4.13., whereas the mobility is proportional to $v_m^{-1}$. The decrease of $D/(E/N)^2$ at high values of $E/N$ is again due to the increase in the collision frequencies.

It is interesting to note that at low values of $E/N$, $D_L > D_T$, 


12-4 potential

\[ \frac{D}{(E/N)^2} \text{ (arb. units)} \]

\[ \frac{D}{(E/N)^2} \text{ (arb. units)} \]

Fig. 2.2.

Fig. 2.3 shows the effect of temperature on the mobility - E/N curve for a 12-4 potential at 300 K. The curves at intermediate values of E/N at 100 K and 0 K, show that at a given value of E/N the curves are independent of temperature. Thus the repulsive term in the internuclear potential influences the work at lower values of E/N at high temperatures than it does at low temperatures. At high values of E/N the thermal contribution to the ion motion is negligible and thus the curves nicely come together.

Mobility (arb. units)

\[ \text{E/N (arb. units)} \]

Fig. 2.3.
but the inequality is reversed at high values of E/N. There are two reasons why the diffusion of ions is anisotropic about the field direction. The first of these arises from the anisotropy of the ion velocity distribution function. Under circumstances where the collision frequencies are independent of the relative velocity this is the only contribution. The second contribution has been explained by Skullerud (1969) in the following way. Consider the case of the collision frequencies increasing with velocity. An ion diffusing against the field vector will lose energy, its collision frequency will therefore decrease and the "instantaneous drift velocity" will increase. Similarly, an ion diffusing in the direction of the field vector will acquire a lower "instantaneous drift velocity". Thus, if this were the only contribution, D_L would be less than D_T. This contribution dominates the diffusion processes in the case of electrons at any E/N value as the electron velocity distribution function is approximately isotropic.

Fig. 2.3 shows the effect of temperature on the mobility - E/N curve for a 12-4 potential. It can be seen that the curves of Fig. 2.3 cross at intermediate values of E/N. This is due to the fact that at a given value of E/N the mean relative energy increases with increasing temperature. Thus the repulsive term in the interaction potential influences the swarm at lower values of E/N at high temperatures than it does at low temperatures. At high values of E/N the thermal contribution to the ion motion is negligible and thus the curves slowly come together.

2.6 TRANSPORT COEFFICIENTS IN MIXTURES

Until recently the only research carried out into the transport properties of ions in gas mixtures was confined to the region of E/N where the motion of the ions is dominated by the thermal motion of the gas particles. The experimental results were compared with the phenomenological relation derived by Blanc (1908),

\[ \frac{1}{\kappa_{B}^{\text{mix}}} = \sum_{i} x_{i} / \kappa_{i} \]  

2.6.1.

where \( \kappa_{B}^{\text{mix}} \) is the reduced mobility in a mixture in which the concentration of the \( i^{\text{th}} \) component is \( x_{i} \), the reduced mobility for this component being \( \kappa_{i} \). In the derivation of equation 2.6.1. it was assumed that the effect
of the electric field was negligibly small and it therefore follows from the Nernst-Townsend relation (equation 1.1.8.) that Blanc's Law can also be written

\[
\frac{1}{D_B^{\text{mix}}} = \sum_i x_i/D_i, \tag{2.6.2}
\]

where \(D_B^{\text{mix}}\) and the \(D_i\) are normalized to the same gas number density. Both equations 2.6.1. and 2.6.2. simply state that in this zero field limit the ions can be treated as passing first through a region containing only one gas and then through another region containing another gas and so on. At higher values of \(E/N\) deviations from Blanc's Law are expected because the velocity distribution function and therefore the velocity averages are functions of the field strength and this simple picture is no longer valid.

Apart from the work of Robson (1973), which is restricted to relatively low values of \(E/N\), there are no quantitative theories of ion motion in gas mixtures. The theories which have been developed (Mason and Hahn 1972, Robson (Milloy and Robson 1973) and Whealton and Mason 1972a) are based on the use of the momentum and energy balance equations and simple scattering models. Before these qualitative theories are discussed the momentum and energy balance equations will be derived as there is no known concise deviation of these equations in the literature.

The mobility of ions in gas mixtures is further discussed in Chapter 9.

2.6.1 Derivation of momentum and energy balance equations

It is assumed that the distribution of ions is time and spatially independent. Thus the Boltzmann equation can be written,

\[
\frac{eE}{m} \cdot \nabla f = - \int \int \left[ f(c) F(C) - f(c') F(C') \right] g I(g,\lambda) \, d\Omega \, dc. \tag{2.6.3}
\]

We require to find an expression for the mean velocity of the ions. To do this we consider the balance between the momentum and energy the ions gain from the field and lose the neutral particles. First we multiply the Boltzmann equation by \(c\) (in fact \(mc\) for convenience) and integrate over all \(c\). The integration on the LHS can be done by parts, while for the RHS we invoke a theorem on the symmetry of the collision
integral with respect to pre-collision and post-collision velocities (see, e.g. Chapman and Cowling 1952, Sec. 3.53). The result is

$$n eE = \int f(c) F(C) [mc - mc'] g I(g, x) d\Omega dc dC .$$  \hspace{1cm} \text{(2.6.4)}

The integration over scattering angles can be done by transforming to centre of mass and relative velocities $G, g$ respectively:

$$C = G + \frac{M}{m+M} g$$  \hspace{1cm} \text{(2.6.5)}

$$\zeta = G - \frac{m}{m+M} g$$  \hspace{1cm} \text{(2.6.6)}

with

$$(m+M) G = mc + MC$$

and

$$g = \zeta - \zeta .$$  \hspace{1cm} \text{(2.6.6)}

Furthermore, since energy and momentum are conserved in a collision, we have

$$G' = G, \quad g' = g.$$  \hspace{1cm} \text{(2.6.7)}

With this transformation equation 2.6.4. becomes

$$n eE = \int f(c) F(C) [\mu g - \mu g'] g I(g, x) d\Omega dc dC .$$  \hspace{1cm} \text{(2.6.8)}

The integration over $d\Omega = 2\pi \sin x \, dx$ can now be performed by noting that $\cos x = \hat{g} \cdot \hat{g}'$ and by taking a co-ordinate frame in which $g$ is directed along the $z$-axis. Thus we obtain

$$\int (g-g') I(g, x) d\Omega = g \times 2\pi \int (1 - \cos x) I(g, x) \sin x \, dx$$

$$= g Q_m(g)$$  \hspace{1cm} \text{(2.6.9)}
where $Q_m$ is the momentum transfer cross section. The momentum balance equation 2.6.8. then becomes

$$n eE = \int f(c) F(C) \mu g g Q_m(g) \, dc \, dC$$

2.6.10.

$$\equiv n N \mu \langle g g Q_m(g) \rangle$$

2.6.11.

By multiplying 2.6.3. by $\frac{1}{2} mc^2$ and integrating over all $c$, the energy balance equation can be written

$$n eE.\tilde{W} = \int f(c) F(C) \frac{\mu}{m+M} [mc^2-Mc^2 + (M-m) c.C] g g Q_m(g) \, dc \, dC$$

2.6.12.

$$= \frac{nN\mu}{m+M} \langle [mc^2-Mc^2 + (M-m) c.C] g g Q_m(g) \rangle$$

2.6.13.

The analysis so far has been rigorous and equations 2.6.11. and 2.6.13. are exact. Unfortunately these equations are also, in general, intractable and to evaluate the averages it is necessary to make certain simplifying assumptions. The assumptions made in the various theories will now be discussed.

2.6.2 Mobilities of ions in mixtures

Robson's Theory

Robson has assumed that the averages of functions of velocity may be replaced by functions of averages of velocity. This operation may be represented for any function $\psi$ by

$$\langle \psi(c) \rangle = \psi(\langle c \rangle)$$

2.6.14.

and similarly for averages over the neutral velocities $C$.

Equation 2.6.11. can now be written,
In equation 2.6.15, the collision frequency for momentum transfer has been normalized to unit number density.

Similarly, equation 2.6.13, can be written

$$eE \bar{\nu} = \frac{N_m}{m+M} \left[ m \langle c^2 \rangle - M \langle C^2 \rangle + (M-m) \langle C \rangle \cdot \langle \epsilon \rangle \right] \nu_m \langle \epsilon \rangle.$$ 2.6.16.

Since $M \langle C^2 \rangle = 3kT$, equation 2.6.16, can be written

$$eE \bar{\nu} = \frac{N_m}{m+M} \left[ m \langle c^2 \rangle - 3kT \right] \nu_m \langle \epsilon \rangle.$$ 2.6.17.

Note that while equations 2.6.15 and 2.6.17, are in general only approximate, they are exact for one particular molecular model, namely, the constant mean free time model ($Q_m \cdot g^{-1}$). The degree of approximation associated with these equations therefore depends upon how closely the true ion-molecule interaction can be represented by this model.

Robson (see Appendix A) has used the approximate forms of the momentum and energy balance equations (2.6.15 and 2.6.17) together with the assumption that $\nu_1 \langle \epsilon_{\text{mix}} \rangle$ is a slowly varying function of energy to derive an expression for the deviations from Blanc's Law. The resultant expression is,
where \( \frac{1}{\kappa_{\text{mix}}} \) is given by equation 2.6.1.

**Theory of Mason and Hahn**

It was also assumed in this theory that the averages of functions of velocity may be replaced by functions of averages of velocity. This assumption can only be justified for situations where the constant mean free time model is a good first approximation. However, a more stringent condition was also introduced: this was to assume that the momentum transfer cross section is independent of the relative velocity. Thus this theory is only known to be valid when both the constant mean free time and the constant cross section models are applicable. This does not correspond to any known ion-atom interaction.

### 2.6.3 Diffusion of Ions in Mixtures

It is possible to obtain an expression for the diffusion coefficients of ions in gas mixtures under conditions where the constant mean free time model is a good first approximation. To do this it is necessary first to consider the constant mean free time case.

Wannier (1953), using the technique developed by Maxwell, derived the following expressions for the constant mean free time model,

\[
D_L = \frac{kT}{N \mu \nu_m} + \frac{m}{\mu} \frac{<c_{z}^{2}> - <c_{z}>^{2}}{N \nu_m} \tag{2.6.19}
\]

and

\[
D_T = \frac{kT}{N \mu \nu_m} + \frac{m}{\mu} \frac{<c_{x}^{2}>}{N \nu_m} \tag{2.6.20}
\]

where the averages are over the ion velocity distribution function. In
the case of mixtures equation 2.6.19. becomes

\[ D_{L}^{\text{mix}} = \sum N_{i} \mu_{i} v_{mi} = kT + m \left< \frac{c_{z}^{2}}{z} \right>_{\text{mix}} - \frac{W_{2}}{\text{mix}} \]  

2.6.21.

where \( \left< \right>_{\text{mix}} \) represents the average over the velocity distribution function in the mixture and \( W_{2} \) is given by Blanc's Law. Substituting the value of \( \mu_{i} \), the reduced mass of the ion in the \( i \)th gas, from equation 2.6.19. into equation 2.6.21. we have

\[ \frac{1}{D_{L}^{\text{mix}}} = \sum \frac{x_{i}}{D_{L}^{i}} \cdot \frac{kT + m \left< \frac{c_{z}^{2}}{z_{i}} \right>}{kT + m \left< \frac{c_{z}^{2}}{z_{i}} \right>_{\text{mix}} - \frac{W_{2}}{\text{mix}}} \]  

2.6.22.

In a similar way the transverse diffusion coefficient in a mixture can be written

\[ \frac{1}{D_{T}^{\text{mix}}} = \sum \frac{x_{i}}{D_{T}^{i}} \cdot \frac{kT + m \left< \frac{c_{x}^{2}}{x_{i}} \right>}{kT + m \left< \frac{c_{x}^{2}}{x_{i}} \right>_{\text{mix}}} \]  

2.6.23.

The expressions 2.6.22. and 2.6.23. only reduce to the form of Blanc's Law given by 2.6.2. in the limit of zero \( E/N \), in contrast to the expression for the mobility of ions in gas mixtures (equation 2.6.18.). The diffusion coefficient can be evaluated once the energy partition of the ions in the pure gases and in the mixture has been determined.

Wannier (1953) has considered the energy partition for the pure gas case and his analysis can easily be extended to the case of mixtures.

We have

\[ m \left< \frac{c_{z}^{2}}{z_{i}} \right> = kT + (M_{i} + m) \frac{W_{2}}{M_{i} v_{i}^{2}} \left[ \frac{4m v_{i} + M_{i} v_{i}}{4m v_{i} + 3M_{i} v_{i}} \right] \]  

2.6.24.

\[ m \left< \frac{c_{x}^{2}}{x_{i}} \right> = kT + (M_{i} + m) \frac{W_{2}}{M_{i} v_{i}^{2}} \left[ \frac{M_{i} v_{i}}{4m v_{i} + 3M_{i} v_{i}} \right] \]  

2.6.25.
where $\nu_{vi}$ is the viscosity collision frequency (see section 2.2.). In the case of mixtures these expressions become

$$ m<\frac{c^2}{z}_{\text{mix}} = kT + m \left\{ \sum_{i} \frac{x_i \nu_{mi}}{M_i W_i^2} \left[ \frac{4m \nu_{mi} + 3M_i \nu_{vi}}{4m \nu_{mi} + M_i \nu_{vi}} \right] \right\}^{-1} $$ \hspace{1cm} 2.6.26. \\

$$ m<\frac{c^2}{x}_{\text{mix}} = kT + m \left\{ \sum_{i} \frac{x_i \nu_{mi}}{M_i W_i^2} \left[ \frac{4m \nu_{mi} + 3M_i \nu_{vi}}{M_i \nu_{vi}} \right] \right\}^{-1} $$ \hspace{1cm} 2.6.27.

So far the analysis has been exact for the constant mean free time model. Since this model would appear to be a good first approximation in many cases, it is worthwhile to develop expressions for the diffusion coefficients analogous to those developed by Robson for the mobility of ions in gas mixtures. In these circumstances the diffusion coefficients can be written

$$ D_L = \frac{kT}{\mu N \nu_m(<\epsilon>)} + \frac{m}{\mu} \left[ \frac{<c^2_z> - <c^2_z>}{N \nu_m(<\epsilon>)} \right] $$ \hspace{1cm} 2.6.28. \\

and

$$ D_T = \frac{kT}{\mu N \nu_m(<\epsilon>)} + \frac{m}{\mu} \frac{<c^2_x>}{N \nu_m(<\epsilon>)} $$ \hspace{1cm} 2.6.29.

The diffusion coefficients in a mixture of gases can then be written

$$ \frac{1}{D_{L_{\text{mix}}}} = \sum \frac{x_i \nu_{mi}(<\epsilon_i>_{\text{mix}})}{D_{L_i \nu_{mi}(<\epsilon_i>)}} \cdot \frac{kT + m [<c^2_{zi}> - W^2_i]}{kT + m [<c^2_{zi}>_{\text{mix}} - W^2_{\text{mix}}]} $$ \hspace{1cm} 2.6.30. \\

$$ \frac{1}{D_{T_{\text{mix}}}} = \sum \frac{x_i \nu_{mi}(<\epsilon_i>_{\text{mix}})}{D_{T_i \nu_{mi}(<\epsilon_i>)}} \cdot \frac{kT + m c^2_{xi}}{kT + m c^2_{xi_{\text{mix}}}} $$ \hspace{1cm} 2.6.31.
These expressions can be easily evaluated since \[ v_{mi} \left( \langle \epsilon_i^{\text{mix}} \rangle / v_{mi} \langle \epsilon_i \rangle \right) \]
and \( W_{\text{mix}} \) can be written in terms of quantities measured experimentally (see Appendix A).

Wheaton and Mason (1972a) have also derived expressions for the diffusion coefficients of ions in gas mixtures. They assume that even at high values of \( E/N \) the diffusion is isotropic and that the mean energy of the ions is equal to the mean energy of the neutral particles. These assumptions cannot be justified. With these assumptions it is predicted that for the constant mean free time case the diffusion coefficients are given by Blanc's Law, in contradiction to the exact analysis given earlier in this section.
CHAPTER 3

REVIEW OF PREVIOUS EXPERIMENTAL WORK

This chapter is devoted principally to a description of some of the methods which have recently been used to investigate the motion of low energy ions in gases. After a brief summary of the development of the subject the methods which have been used to measure mobilities, diffusion coefficients and reaction rates will be separately described.

3.1 HISTORICAL SUMMARY

The study of ion motion in gases began in the late 1890's at the Cavendish Laboratory when J.J. Thomson, E. Rutherford and J.S. Townsend observed that passing X-rays through gases made the gases conduct. The early studies were understandably crude and the results of the experimental investigations carried out before 1928 are today of little more than historical interest. The experiments which can be recognized as the forerunners of modern work were performed in 1928. In that year Van de Graaff (1928) devised an electrical shutter method which is in many ways identical to the method developed independently at Bristol by Tyndall, Starr and Powell (1928). Although Van de Graaff did not continue his ion mobility work the techniques developed at Bristol were used in a very notable series of experiments during the period 1928-1941. During this period Bradbury and Nielsen (1936) also developed an effective electrical shutter method and applied it to the determination of electron drift velocities. This method, which was used in the present work, is described in more detail later in this chapter and also in Chapter 4.

Much of the early work was designed to determine the interaction potential between ions and neutral particles. For example Pearce (1936) was able to estimate the interaction potential between caesium ions and helium atoms by using the theory of Hassé and Cook (1931) to analyse his measurements of the variation of the zero field mobility with temperature. At about the same time Hershey (1939a, 1939b) attempted to determine the interaction potential of $K^+$ ions in several gases by analyzing mobility data as a function of $E/N$ with generalized forms of the theories of both Langevin (1905) and Hassé and Cook (1931).

During the 1940's the subject was largely in abeyance but in
the 1950's interest again began to grow and in particular several investigations were carried out with the aim of understanding discharge phenomena. In the 1960's several mobility studies were carried out and the first measurements of the longitudinal diffusion coefficient were made, but large research efforts were also devoted to measurements of ion-molecule reaction rates. There are two main reasons for the development of this branch of the subject. The first of these was the development of the quadrupole mass spectrometer by Paul and his colleagues at the University of Bonn, Germany in the 1950's (see for example Dawson and Whetten 1969). This instrument which is small in size and relatively easy to operate has largely solved the problems of ion identity which plagued early investigators. The other important impetus for ion-molecule reaction studies came in 1963 when Narcisi and Bailey investigated the ionic composition of the lower atmosphere with a rocket-borne mass spectrometer (Narcisi and Bailey 1965). Since that time many laboratory experiments have been carried out to investigate the production, transport and properties of the ions observed in the first and subsequent rocket flights.

Even more recently there has been considerable interest in measurements of all the transport coefficients with a view to determining ion-atom interaction potentials. This interest has largely been stimulated by the theoretical work of Kumar and Robson (Kumar and Robson 1973, Robson and Kumar 1973), Skullerud (1973a, 1973b) and Whealton and Mason (1972b).

3.2 METHODS USED TO DETERMINE α

3.2.1 Tyndall-Powell method

The four gauze method of Tyndall and Powell has been used in many investigations of ion transport in gases and for this reason will be described in some detail.

A schematic diagram of the apparatus used at Bristol (Tyndall 1938) is shown in Fig. 3.1, where the source of ions is denoted by the letter A and CD and EF are the electrical shutters, each of which comprises a pair of thin and closely spaced metal gauzes. The electric field is maintained uniform in the drift space, M, by a series of guard rings. The
shutters are operated by applying an alternating potential difference between
the gauges and by also applying a small retarding d.s. potential between the
gauges it is arranged that the shutter open time is a short fraction of the
period of the alternating potential. This results in improved peak resolution.
A pulse emitted by the first shutter will, owing to the residual field
towards the second shutter, delay the signals to the shutters are
in phase the ion arrival times. A shutter signal has been transmitted if the
shutter signal has positive correlation with the ion signal. Thus by
noting the signal frequency of the ion and the frequency spectrum
are observed the transition probability can be calculated from the relation

\[ \text{transition probability} = \frac{\text{ion frequency}}{\text{oscillator frequency}} \]

where \( f_n \) is the frequency of the \( n^{th} \) peak maximum. In ions of different
mobilities are present, each ion will give rise to a different current-
frequency spectrum. A typical current-frequency spectrum observed by the
Bristol group is shown in Fig. 3.2.

The most serious disadvantage of this method in its original form
is the problem of determining the exact position of the plane at which the
group originates and the plane at which the group is sampled. Tyndall
and Powell (1934) sought to overcome this difficulty by building an apparatus
of variable length. The current in the collector was monitored as the drift
distance was varied, field strength and frequency being kept constant. A
series of peaks was obtained, and on the distance travelled by the ions in
one period of oscillator signal corresponded to the distance between two
peaks, the mobility could be determined.

In this way Tyndall and Powell measured the zero field reduced
mobility of an ion in He at 19.9 cm² V⁻¹ s⁻¹ and used this value to calibrate
the drift distance in their tubes. Unfortunately this calibration procedure
cannot be generally used for the many kinds of the end effects, and hence the
effective drift distance will depend on the gas-gas combination, the value
of E/H, the pressure and the distance of the plane. Despite these drawbacks
it is noticeable that the mobility results obtained by this group are usually
in agreement with the results obtained by other workers within ± 22.

Fig. 3.1.

Fig. 3.2.
shutters are operated by applying an alternating potential difference between the gauzes and by also applying a small retarding d.c. potential between the gauzes it is arranged that the shutter open time is a short fraction of the period of the alternating potential. This results in improved peak resolution. A pulse emitted by the first shutter drifts under the action of the field towards the second shutter and if the alternating signals to the shutters are in phase the ions arriving at the second shutter are only transmitted if the shutter signal has passed through an integral number of cycles. Thus by noting the signal frequencies at which maxima in the current-frequency spectrum are observed the transit time, $t_m$, can be calculated from the relation

$$t_m = \frac{n}{f_n},$$

where $f_n$ is the frequency of the $n^{th}$ peak maximum. If ions of different mobilities are present, each ion will give rise to a different current-frequency spectrum. A typical current-frequency spectrum observed by the Bristol group is shown in Fig. 3.2.

The most serious disadvantage of this method in its original form is the problem of determining the exact position of the plane at which the ion group originates and the plane at which the group is sampled. Tyndall and Powell (1931) sought to overcome this difficulty by building an apparatus of variable length. The current to the collector was monitored as the drift distance was varied, field strength and frequency being kept constant. A series of peaks was obtained, and as the distance travelled by the ions in one period of oscillator signal corresponded to the distance between two peaks, the mobility could be determined. In this way Tyndall and Powell measured the zero field reduced mobility of an ion in He $(19.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ and used this value to calibrate the drift distance in other tubes. Unfortunately this calibration procedure cannot be generally used as the magnitude of the end effects, and hence the effective drift distance, will depend on the ion-gas combination, the value of $E/N$, the pressure and the design of the gauzes. Despite these drawbacks it is noticeable that the mobility results obtained by this group are usually in agreement with the most accurate present day work to within $\pm 2\%$. 
There have been several other uses of the Tyndall-Powell method. For example Beaty, by taking advantage of advances in electronic techniques, was able to reduce the end effects which troubled Tyndall and Powell. Square wave pulses were used to ensure that when the shutters were open the field between the grids comprising one shutter was equal to the field between the shutters. After Beaty (1961) investigated the mobility of positive argon ions in argon, Beaty and Patterson (1965, 1968) used the apparatus to study helium and neon ions in their parent gases. Mobilities and reaction rates for conversion of atomic to molecular ions were obtained.

Varney used a Tyndall-Powell type of drift tube coupled with a quadrupole mass spectrometer to investigate the mobility and reactions of positive nitrogen ions in nitrogen (Varney 1968) and positive and negative oxygen ions in oxygen (Varney 1970). The apparatus developed by Sinnott (1964) and subsequently used by Saporoschenko (1965a, 1965b) was similar to that used by Varney, but lacked facilities for direct mass identification.

3.2.2 Bradbury-Nielsen method

Van der Graaff was one of the first to suggest the type of shutter used in this method (Van der Graaff 1929). Thus although he never published the results of any mobility measurements Van der Graaff suggested both the Bradbury-Nielsen and Tyndall-Powell shutter techniques. The Bradbury-Nielsen type of shutter was also used by Cravath (1929), on the suggestion of Loeb.

Fig. 3.3 shows a schematic diagram of the method. $S_1$ and $S_2$ are the shutters. Each shutter consists of a coplanar set of parallel wires with alternate wires connected together. Ions are only transmitted when the potential difference between the two sets of wires is small. If a sine wave signal is used to gate the shutters, as is usually the case, it is arranged that there is a phase difference of $\pi$ between the signals applied to each set of wires in one shutter. Thus an ion will be transmitted by the second shutter if its transit time corresponds to an integral number of half cycles of the gating signal and hence by noting the signal frequencies at which maxima in the current-frequency spectrum are observed, the transit time can be calculated from the relation
where \( f_n \) is the frequency of the \( n \)th peak maximum.

After Bradbury and Nielsen (1956) used this method to measure electron drift velocities it was not used again until Milford (1957) and Crompton and Milford (1959) took up Tyndall's suggestion and used it to measure the mobility of ions in gases. Since then the method has been used by several authors to measure electron drift velocities and by Milford (1967, 1971) and Fleming, Tomsick and Austin (1969a, 1969b) to measure alkali ion mobilities. The drift tubes used by Nees et al. at the University of Liverpool are smaller in many respects to the tubes used in this work and for this reason will not be described separately.

### 3.1.3 Oscillographic method

If ions are drifting in a gas under the action of a potential difference applied between two plane parallel electrodes, the current in the external circuit will vary periodically with time at a frequency given by

\[
\omega = \frac{1}{2} \left( \frac{V_1 - V_2}{d} \right)
\]

where \( V_1 \) and \( V_2 \) are the potentials of the two electrodes, \( d \) is the electrode spacing, \( \omega \) is the angular frequency and \( V_1 \) and \( V_2 \) are the applied potentials. The method described in this section relies on the analysis of the current waveform of a pulse in section 3.2.

**Schematic diagram of the Bradbury-Nielson method**

Fig. 3.3.
\[ t_m = \frac{n}{2f_n} \]

where \( f_n \) is the frequency of the \( n \)th peak maximum.

After Bradbury and Nielsen (1936) used this method to measure electron drift velocities it was not used again until Elford (1957) and Crompton and Elford (1959) took up Tyndall's suggestion and used it to measure the mobility of ions in gases. Since then the method has been used by several authors to measure electron drift velocities and by Elford (1967, 1971) and Fleming, Tunnicliffe and Rees (1969a, 1969b) to measure alkali ion mobilities. The drift tubes used by Rees et al. at the University of Liverpool are similar in many respects to the tubes used in this work and for this reason will not be described separately.

3.2.3 Oscillographic method

If ions are drifting in a gas under the action of a potential difference applied between two plane parallel electrodes, the current in the external circuit is given by

\[ i(t) = N(t) \frac{eW}{h} \]

where \( N(t) \) is the number of ions moving in the drift space at time \( t \), \( e \) is the ionic charge, \( W \) the ionic drift velocity and \( h \) the electrode spacing. The method described in this section relies on the analysis of the current waveform of a pulse of ions, as given by equation 3.2.3. The current waveform is displayed on an oscilloscope.

Consider that a pulse of positive non-reacting ions is introduced at \( t = 0 \) in the region immediately adjacent to the anode. The ions will drift across to the cathode and will be neutralized at the surface of the cathode. If diffusion is ignored and the time constant of the measuring circuit is ignorably small the oscilloscope trace would be as shown in Fig. 3.4a. However, in practice the diffusion of the ions in the field direction results in the ions arriving at the cathode with a spread of arrival times. Also some of the ions initially injected into the drift space diffuse back to the anode and this results in the current decreasing with time, the largest rate of decrease being at short times. These
effects give rise to a current waveform of the type shown in Fig. 3.4b. In practice the effects of diffusion and the finite time constant of the measuring circuit make the waveform difficult to analyse.

Hornbeck (1951) was the first to use this method. His apparatus is shown in Fig. 3.3. A discharge was initiated by a short burst of photoelectrons from the cathode C. After the discharge the electrons were quickly collected leaving an exponential distribution of ions in the chamber. The drift velocity of the ions was then determined by measuring, from the oscilloscope trace, the time taken for the current in the gap to reduce to zero, since this time is related to the time taken for ions to travel from anode to cathode. This method was limited to high values of $E/N$ and to the type of wave which could be studied.

Blond and Chanin (1955) used a similar detector system and also used a discharge to produce the ions. However, by restricting the discharge to a small section of the tube these workers were able to use much lower values of $E/N$. The apparatus is shown in Fig. 3.5a. The discharge was created between two bent tungsten sheets. Ions formed in the discharge were injected into the drift space and a current transient was recorded on the oscilloscope. The drift distance was varied to reduce errors due to end effects and the like.

Oscillographic techniques have also been used by Thallerud (1954), Dahlquist (1953) and Wei (1963).

### 3.2.6 Variable drift distance method

(1) The method of McDaniel et al.

The group at Georgia Institute of Technology, led by Professor E.W. McDaniel, has been concerned mainly with investigations of gas phase ions in diatomic gases but some results for molecules ions in various gases have also been published. Some of the first results of mobility measurements with a mass spectrometer coupled to the drift tube were reported by this group at the Sixth International Congress on Phenomena in Ionsized Gases (Martin et al., 1963). McAfee and Maloney (1962) also reported similar results at this conference. The prototype apparatus used in the experiments...
effects give rise to a current waveform of the type shown in Fig. 3.4b. In practice the effects of diffusion and the finite time constant of the measuring circuit make the waveform difficult to analyse.

Hornbeck (1951) was the first to use this method. His apparatus is shown in Fig. 3.5. A discharge was initiated by a short burst of photoelectrons from the cathode C. After the discharge the electrons were quickly collected leaving an exponential distribution of ions in the chamber. The drift velocity of the ions was then determined by measuring, from the oscilloscope trace, the time taken for the current in the gap to reduce to zero, since this time is related to the time taken for ions to travel from anode to cathode. This method was limited to high values of E/N and to the type of ions which could be studied.

Biondi and Chanin (1954) used a similar detection system and also used a discharge to produce the ions. However, by restricting the discharge to a small section of the tube these workers were able to use much lower values of E/N. The apparatus is shown in Fig. 3.6. The discharge was created between the electrode on the left and the grid. Some of the ions formed in the discharge were injected into the drift space and a current transient was recorded on the oscilloscope. The drift distance was varied to reduce errors due to end effects at the grid.

Oscillographic techniques have also been used by Skullerud (1966), Dahlquist (1963) and Woo (1965).

3.2.4 Variable drift distance methods

(1) The method of McDaniel et al.

The group at Georgia Institute of Technology, led by Professor E.W. McDaniel, has been concerned mainly with investigations of gaseous ions in diatomic gases but some results for potassium ions in various gases have also been published. Some of the first results of mobility measurements with a mass spectrometer coupled to the drift tube were reported by this group at the Sixth International Conference on Phenomena in Ionized Gases (Martin et al. 1963). McAfee and Edelson (1963) also reported similar results at this conference. The prototype apparatus used in the experiments
reported above was not built to U.H.V. specifications and the construction of a new and more sophisticated version was begun in early 1968. Fig. 3.7 is a sectional drawing of the more recent apparatus. It is the only apparatus which can be used to determine not only the mobility but also the longitu
dinal diffusion constant in gases.

Detailed aspects of these measurements and techniques are described by Small et al. (1972). Measurements were also made over almost the entire length of the 44 cm drift tube, by electron-impact excitation or in the drift tube by a microscopically created source of alkali ions, by thermionic emission from a filament placed just inside it, and gated into the drift tube with a Thyristor to reach the end of the drift tube. A 32-channel analyzer was swept out through the entire range of the emission spectrum. A 236-channel analyzer measured the arrival time spectrum to determine the majority of drift tube velocity effects. First the time-of-flight of the ions as measured for a given drift distance. The drift distance was then varied, all other experimental parameters being kept constant, and the new time-of-flight measured. The drift velocity can then be calculated.

(2) Skullerud's method

The drift tube used by Skullerud (1972b) is shown in Fig. 3.5. The tube was operated with the Tyndall–Stark effect in a feedback circuit. Experimental values of the mobility were obtained by introducing the effects.
reported above was not built to U.H.V. specifications and the construction of a new and more sophisticated version was begun in early 1964. Fig. 3.7 is a sectioned drawing of the more recent apparatus. It is the only apparatus which can be used to determine not only the mobility but also the longitudinal and lateral diffusion coefficients of ions in gases. Detailed accounts of the development of this apparatus and the measurement techniques are given by Albritton et al. (1967), Miller, Martin et al. (1968), Moseley, Martin et al. (1968), Snuggs et al. (1970) and Schummers et al. (1972). The ion source is moveable over almost the entire length of the 44 cm cylindrical drift tube. Ions are created either by electron-impact with the gas or in the case of alkali ions, by thermionic emission from a filament coated with Kingman feldspar. The ions are then gated into the drift tube with a Tyndall-Powell shutter. When the ions reach the end of the drift tube, some of those close to the axis are swept out through the exit aperture and mass analysed by a quadrupole mass spectrometer. A 256 channel time-of-flight analyzer is used to measure the arrival time spectrum of the ions. The ionic drift velocity is found by a difference measurement to eliminate the majority of end effects. First the time-of-flight of the ions is measured for a given drift distance. The drift distance is then changed, all other experimental parameters being kept constant, and the new time-of-flight measured. The drift velocity can then be calculated.

(2) Skullerud's method

The drift tube used by Skullerud (1973b) is shown in Fig. 3.8. The drift length is variable from 0 to 5 cms. The triple grid shutters were operated in the Tyndall-Powell mode. As is discussed later (section 4.3) Tyndall-Powell shutters are very suitable for high values of E/N. Experimental values of the mobility of K+ ions in Ar over the range 23 \( \leq E/N(Td) \leq 793 \) were obtained by a difference method to avoid serious end effects.

3.2.5 Ambipolar diffusion method

It is possible to determine the zero field mobility of positive gaseous ions in their parent gases from measurements of electron concentrations in afterglows produced by microwave breakdown. This
The apparatus used by McDaniel et al.

Fig. 3.7.
method was first developed by Munds and Brown (1941). Although the quantity measured experimentally is the diffusion coefficient at zero gradient, the data are reported in terms of mobility and for this reason this method is described in this section.

It can be shown that the number density of electrons in a highly ionized gas must approximately equal the number density of positive ions. Any deviation from charge equality produces electric forces which oppose the charge separation and tend to restore charge equality. Both species of charged particles contribute to the ion gas number density, which is described by the motional diffusion equation (Scheffer, 1928), which is defined by

\[ \frac{D_n}{D_e} \frac{d}{dx} \left( \frac{d}{dx} \left( n_n \frac{dx}{D_n} \right) \right) = \frac{D_e}{D_n} \frac{d}{dx} \left( \frac{d}{dx} \left( n_e \frac{dx}{D_e} \right) \right) \]

where the subscript \( n \) and \( e \) refer to ions and electrons, respectively.

In the decaying plasma of a fusion reactor, the electron density decreases as an exponential function of decay time, and the decay rate of the electron density is a function of the experimental geometry. The electron density in the plasma is measured by an electron recombination probe.
method was first developed by Biondi and Brown (1949). Although the quantity measured experimentally is the diffusion coefficient at zero E/N, the data are reported in terms of mobility and for this reason this method is described in this section.

It can be shown that the number density of electrons in a highly ionized gas must approximately equal the number density of positive ions. Any deviation from charge equality produces electric forces which oppose the charge separation and tend to restore the equality. Both species of charged particles thus diffuse together. This linked diffusion process is described by the ambipolar diffusion coefficient (Schottky, 1924), which is defined to be

\[ D_A = \frac{D_i K_i + D_e K_e}{K_i + K_e} \]

where the subscripts \( i \) and \( e \) refer to the ions and electrons respectively. In the decaying plasma, if there is no source of ionization and no volume recombination,

\[ \frac{\partial n}{\partial t} = \nabla \cdot (D_A \nabla n) \]

where \( n \) is the common number density of electrons and positive ions. If an exponential time rate of decay is assumed, the solution of this equation gives \( D_A \) in terms of the decay constant and a diffusion length (which is a function of the experimental geometry). To determine the decay constant the electron density in the plasma is measured by noting the changes in the resonant frequency of the microwave cavity as a function of time.

If the decay of the electron density is observed after the electrons and ions have come into thermal equilibrium with the gas, then

\[ \frac{D_i}{K_i} = \frac{D_e}{K_e} = \frac{kT}{e} \]

and therefore

\[ D_A = \frac{2D_i K_e}{(K_i + K_e)} = 2D_i \]
Thus

\[ K = e^{D_A/2kT} \]  \hspace{1cm} 3.2.6.

Although this method has been extensively used, it is one of the less accurate methods available. Errors can arise from the presence of several ion species, recombination, diffusion cooling, heating of the gas and approximations in the theory.

3.3 METHODS USED TO DETERMINE $D_L/K$

The only method which has been used to measure diffusion coefficients directly is the ambipolar diffusion method described in the preceding section. At finite values of $E/N$ it is not possible to measure diffusion coefficients directly and only the ratio of the diffusion coefficient to the mobility can be determined. This restriction results from the fact that the diffusion of the swarm is measured with respect to the centroid of the swarm and unless the position of the centroid in space is known the diffusion cannot be determined absolutely. A consequence of this is the fact that all the methods used to determine $D_L/K$ were first used to measure mobilities.

3.3.1 Bradbury-Nielsen method

This method has been used in this laboratory to measure $D_L/K$ for $K^+$ ions in He, Ar and $N_2$. A full description of this work is given in Chapters 4 and 8.

3.3.2 Method of McDaniel et al.

A description of the apparatus used by the group at Georgia Institute of Technology has been given in section 3.2.4. The longitudinal diffusion coefficient is determined by comparing the measured arrival time spectrum with that predicted by theory and adjusting $D_L$ until the agreement is satisfactory. Thus $D_L$ can be determined from a single arrival time spectrum once the mobility has been determined.

In the derivation of the expression for the arrival time spectrum it is assumed that the ions are produced in an axial thin disk of constant number density $s$ ions per unit area and radius $r_0$ and are collected over a small axial area $A$ in free space. The flux of ions on axis can then be
written for a non-reacting species, Moseley, Martin et al. (1968)

\[ \phi(o,z,t) = \frac{As}{4(\pi D_L t)^{3/2}} (W+z/t) \left[ 1 - \exp - \frac{r^2}{4D_L t} \right] \times \exp - \frac{(z-Wt)^2}{4D_L t} \].

3.3.1. In practice it is found that \( D_L \) can be determined without knowledge of \( D_T \) as the fits are relatively insensitive to values of \( D_T \). This will always be the case if the width of the arrival time spectrum is small compared with the average flight time of the ions or if the source area is large. If the species is being depleted by ion molecule reactions \( D_L \) can still be determined if the resolution of the current-time curve is large.

3.3.3 Skullerud's Method

The apparatus described in section 3.2.4. has been used by Skullerud (1973b) to measure the ratio \( D_L/K \) for \( K^+ \) ions in Ar over the range \( 86 \leq E/N(Td) \leq 793 \). Due to the rather large initial width of the current pulses the values of \( D_L/K \) were obtained from the broadening of the current waveforms with increasing drift distance.

3.4 METHODS USED TO DETERMINE \( D_T/K \)

The motion of non-reacting low energy ions in a gas cannot be fully described unless the lateral diffusion coefficient is known as well as the mobility and the longitudinal diffusion coefficient. The methods used to measure the mobility and the longitudinal diffusion coefficient have already been described. Thus for completeness a brief description will be given of the methods which have been used to measure the ratio \( D_T/K \), although no measurements of this quantity are reported in this thesis.

3.4.1 Townsend-Huxley method

In 1908 Townsend described a method for the measurement of the ratio \( D_T/K \). The technique, modified as suggested by Huxley (1940) and known as the Townsend-Huxley method, has been extensively used to determine
\( \frac{D_T}{K} \) for electrons (Huxley and Crompton 1973), but less frequently for measurements with positive ions.

Fig. 3.9 shows the geometry of a Townsend-Huxley diffusion chamber. Ions enter the chamber through a small hole 0. As the ions drift in the direction of the applied constant electric field they diffuse laterally. The ions are collected at an electrode which consists of a central disk and surrounding annuli, each portion insulated from the others. By measuring the ratios of the currents to various parts of the collector, \( \frac{D_T}{K} \) can be determined. For example if the length of the diffusion chamber is much greater than the diameter of the central collector, the ratio, \( R \), of the current to the central collector to the total current is given by (Huxley 1940),

\[
R = 1 - \frac{h}{d} \exp \left( \frac{- (d-h)}{W/2D_T} \right)
\]

Then since \( K = W/E \) and \( E \) is known the ratio \( \frac{D_T}{K} \) can be found.

This technique has been used by Crompton and Elford (1963) to investigate \( \frac{D_T}{K} \) for \( K^+ \) ions in \( H_2 \), by Dutton and Williams (1964) (\( Ne^+ \) in Ne) and by Fleming et al. (1969a \( K^+ \) in \( H_2 \), 1969b, \( K^+ \) in \( N_2 \)). The earlier work of Llewellyn-Jones (1935) on \( \frac{D_T}{K} \) for positive ions in Ar was based on Townsend's method.

3.4.2 Skullerud's method

Skullerud (1966) has developed a method for measuring values of \( \frac{D_T}{K} \) which is also based on Townsend's original suggestion. The apparatus used by Skullerud is shown in Fig. 3.10. The ions, from a filament source, enter the diffusion chamber through a narrow slit. The gap can be varied from 0 - 5 cms. The circular collector is divided into two halves by a narrow slit parallel to the entrance slit and can be moved in the direction normal to the entrance slit (x direction). The currents, \( I_1 \) and \( I_2 \), to the two halves of the collector are measured by means of two electrometers. Experimental values of \( \frac{D_T}{K} \) are obtained by recording the ratio \( \frac{I_1}{I_1 + I_2} \) as a function of \( x \) for various gap distances. Using this apparatus Skullerud has measured values of \( \frac{D_T}{K} \) for \( K^+ \) ions in Ar in the range \( 10 \leq E/N(Td) \leq 1151 \).

This method is particularly suitable for coupling to mass identification facilities (Gray and Rees 1972) as the collector can be
Schematic diagram of the Townsend-Huxley method

Fig. 3.9.
moved laterally with respect to the source. Thus it can be arranged that high ion-current densities fall on a small sampling hole situated in the semi-circular collector. A similar sampling arrangement would be difficult to incorporate in the small central collector of a Tandem-Buckley apparatus.

3.4.2 Variable drift distance method

A variable drift distance method has been used by McDermal at al., using the apparatus described in section 3.4.1. In this method, the ion pulses from the source are counted and measured by the position of the detector in front of the spectrometer. The position of the detector at the position at which the current is given by

\[ I(z) = A e^{-\frac{z}{\lambda}} \]

where \( A \) is the ion current and \( \lambda \) is the drift distance of strength \( e \).

3.5 Determination of reaction rates

Although there have been a number of studies of reaction rates over the last 1930s, most work has been concerned with ions in their own gases and it is only recently that attention has been paid to the theoretical study of reaction rates in inert systems. Isotopic drift tubes have been used to determine reaction rates and ranges of \( E/N \) and \( p \), mass identification facilities can easily be incorporated and the gas temperature readily measured. Although many of these advantages are also inherent in some of the other possible techniques, the use of drift tubes is certainly one of the most versatile ways of tackling the problem of measuring reaction rates.
moved laterally with respect to the source. Thus it can be arranged that high ion current densities fall on a small sampling hole situated in the semi-circular collector. A similar sampling arrangement would be difficult to incorporate in the small central collector of a Townsend-Huxley apparatus.

3.4.3 Variable distance method

A variable drift distance method has been used by McDaniel et al. using the apparatus described in section 3.2.4.

As the arrival time spectrum is insensitive to $D_T$ this parameter has to be determined in another way. The method involves holding the source output constant and measuring the ion current detected by the mass spectrometer as a function of drift distance. The current at the position $z$ is given by

$$I(z) = A \cdot S \left[ 1 - \frac{z}{\left( z^2 + r_o^2 \frac{D_s}{D_T} \right)^{\frac{1}{2}}} + 1 \right] \exp \left\{ -\left[ \frac{z^2 W^2}{4 D_s^2} + \frac{r_o^2 W^2}{4 D_s^2 D_T} \right]^{\frac{1}{2}} - \frac{z W}{2 D_s} \right\} ,$$

where $A$ is the area of the exit aperture and $r_o$ is the radius of the source of strength $s$. $D_T$ can be determined by comparing the experimentally observed variation of $I(z)$ with $z$ with the predictions of equation 3.4.2.

3.5 DETERMINATION OF REACTION RATES WITH DRIFT TUBE TECHNIQUES

Although drift tubes have been used in the determination of reaction rates since the late 1950's the early work was concerned with ions in their own gases and it is only recently that attention has been paid to the theoretically more simple situation of alkali ions in inert and simple diatomic gases.

There are several advantages of using drift tubes for reaction rate studies. For example the reaction rates can be studied over wide ranges of $E/N$ and $p$, mass identification facilities can easily be incorporated and the gas temperature can be varied. Although many of these advantages are also inherent in some of the other possible techniques, the use of drift tubes is certainly one of the most versatile ways of tackling the problem of measuring reaction rates.
Almost all the methods which have been used to determine reaction rates with drift tubes can be divided into two categories. The first and most general method is called the "conversion of ion types" or "current ratio" method. The second is called the "curve fitting" method. The only exceptions are the "additional residence time" method used by Biondi's group and one of the methods used by McDaniel's group which depends on varying the drift chamber length. Of the two main methods, curve fitting, which does not necessarily require the use of a mass spectrometer, is probably the more accurate at the present time but its use is restricted to situations in which the mobilities of the parent and product ion species are significantly different. The accuracy of the current ratio method is limited primarily by mass discrimination in the ion extraction and detection system.

3.5.1 Current Ratio Method

Consider two species of ion, \( A^+ \) and \( B^+ \), which react with the neutral gas in a forward and backward reaction scheme of the form,

\[
A^+ \rightarrow B^+. 
\]

The nature of the reactions does not have to be specified at this stage. The time rate of change of the total population of the two species, \( N_A \) and \( N_B \), can be described by the following coupled equations,

\[
\frac{\partial N_A}{\partial t} = - \alpha_{BA} N_A + \alpha_{AB} N_B \quad 3.5.1.
\]

\[
\frac{\partial N_B}{\partial t} = - \alpha_{AB} N_B + \alpha_{BA} N_A , \quad 3.5.2.
\]

where \( \alpha_{BA} \) and \( \alpha_{AB} \) are the reaction frequencies of the conversion of species \( A \) to \( B \) and \( B \) to \( A \) respectively. The solution for \( N_B \) is
\[ N_B = \frac{\alpha_{BA} N_{\text{tot}}}{\alpha_{AB} + \alpha_{BA}} \left[ \left( \frac{\alpha_{BA} N_{\text{tot}}}{\alpha_{AB} + \alpha_{BA}} - N_{BO} \right) \exp \left( -t(\alpha_{AB} + \alpha_{BA}) \right) \right], \quad 3.5.3. \]

where \( N_A + N_B = N_{\text{tot}}, \)

and \( (N_B)_{t=0} = N_{BO}. \)

Under normal circumstances only one species, say A, is produced in the source and \( N_B \) and \( N_A \) can be written,

\[ N_B = \frac{\alpha_{BA} N_{\text{tot}}}{\alpha_{BA} + \alpha_{AB}} \left( 1 - \exp \left( \frac{1}{a_{BA} + a_{AB}} \right) \right) \quad 3.5.4. \]

\[ N_A = N_{\text{tot}} \left[ 1 - \frac{\alpha_{BA} N_{\text{tot}}}{\alpha_{BA} + \alpha_{AB}} \left( 1 - \exp \left( \frac{1}{a_{AB} + a_{BA}} \right) \right) \right]. \quad 3.5.5. \]

Combining these equations the reaction frequency \( \alpha_{BA} \) can be written,

\[ \alpha_{BA} \left( a_{BA} \right) = \frac{K_E}{1 + K_E} \ln \left[ \frac{N_B}{N_A} \right], \quad 3.5.6. \]

where \( K_E = \alpha_{BA}/\alpha_{AB} = (N_B/N_A)_{t=\infty}. \) Thus the reaction frequency \( \alpha_{BA} \) can be determined if the ratio of the two ions species is measured at a given time and the equilibrium ratio \( K_E \) is known. \( \alpha_{AB} \) can then be found from the relation \( \alpha_{AB} = \alpha_{BA}/K_E. \)

Apart from the problems of mass discrimination effects in the ion sampling process there is another important source of error in this method. It is not generally valid to assume that the currents of species A and species B sampled through a small axial aperture in the drift tube are related to the total number of ions in each species, \( N_A \) and \( N_B, \) in the same way. The fraction of say, \( N_A, \) which is collected by the small axial hole in the cathode depends on the ratio \( D_T/K \) for ions of species A.
ratio $D_T/K$ is itself closely related to the mean energy of the ions in the direction transverse to the electric field and varies from one ion species to another when $E/N > 0$. Errors from this cause increase with increasing $E/N$ and consequent increasing ion energy. An approximate procedure for reducing this error was developed by Kaneko et al. (1966) but most authors have neglected the problem. However, it is very doubtful if errors introduced by the effects of lateral diffusion are as large as the errors introduced by mass discrimination effects.

3.5.2 Curve fitting

In this method reaction rates are determined by comparing the measured arrival time spectrum of the ions with the theoretically calculated spectrum and adjusting the rates until there is good agreement between experiment and theory. The method is therefore very similar to the methods used to determine the longitudinal diffusion coefficient, as described in section 3.3.

The two most complete analyses of the transport and reactions of ions in gases are those of Woo and Whealton, and Gatland. The former authors (Whealton and Woo, 1968, Woo and Whealton 1969 and Woo and Whealton 1971) include in their analysis the effects of radial diffusion to the walls of the drift chamber, a forward reaction to a secondary species and the effects of different radial ion density distributions at the source. Gatland (1972b) has formulated the general solution to the problem, including the effects of both forward and backward reactions. Further details of Gatland's analysis have been given by Snuggs et al. (1970) and Schummers et al. (1972).

Although the theory is available there has only been one determination of both the forward and backward reaction rates with a curve fitting technique. McKnight et al. (1967) compared the arrival time spectra of nitrogen ions in nitrogen with the theoretical predictions of Edelson et al. (1967), who solved the diffusion equation numerically. On the other hand curve fitting techniques have been extensively used under conditions where the reverse reaction is negligible (for example Beaty and Patterson 1965, Heimerl et al. 1969, Snuggs et al. 1970, Schummers et al. 1972).
3.5.3 Additional residence time technique

This technique has been developed by Biondi and others at the University of Pittsburgh, (Heimerl et al. 1969, Johnsen et al. 1970, 1971) to study both two and three body reactions. A pulse of positive ions is extracted from the source region and the ions drift in a mixture of two gases, one of which is chosen so that it does not react with the ions. Helium is often chosen as the buffer gas. After the ions have travelled a certain distance the field is either reduced to zero or reversed for a short time. By varying the residence time in this way the reaction rate can be determined by noting the decrease in parent ion population as a function of time. The net loss of parent ions due to reaction with the reactant gas molecules is separated from the loss due to lateral diffusion by repeating the experiment without the reactant gas. This technique is useful when the mobilities of the parent and product species are similar.

3.5.4 Parent ion attenuation

This method is similar to the one described above in that the reduction of the parent ion population is monitored as a function of time. However, in this method, which has been used by Miller, Moseley et al. (1968) Moseley, Snuggs et al. (1969), Snuggs, Volz, Catland et al. (1971) and Schummers et al. (1972), the time-of-flight of the ions is varied by changing the drift distance rather than by reversing or reducing the electric field. The losses due to diffusion are calculated by computing the collected ion count at each drift distance, as outlined in section 3.4.3. The disadvantage of this method is that it is sometimes difficult to determine both $D_T$ and the reaction rates, although, in general, it is usually possible to do this by using the different dependencies of $D_T$ and the reaction frequencies on gas number density.
CHAPTER 4

THE BRADBURY-NIELSEN METHOD

The Bradbury-Nielsen method was used in this work to measure the mobility and longitudinal diffusion coefficient of ions in gases. In this chapter a description is given of the methods used to determine these transport coefficients from an examination of the peaks in the current-frequency spectrum.

4.1 THEORY

The mathematical description of a travelling group of charged particles in a drift tube given in this section is based on the work of Huxley (1972) and Huxley and Crompton (1973).

The number density \( n(x,y,z,t) = n \) of the ions is assumed to be a solution of the diffusion equation,

\[
\frac{\partial n}{\partial t} = D_T \left( \frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) + D_L \frac{\partial^2 n}{\partial z^2} - W \frac{\partial n}{\partial z}. \tag{4.1.1}
\]

It was shown in Chapter 2 that this equation, although not exact, is a good approximation in the case of small density gradients. A solution of 4.1.1. that represents an isolated travelling group of \( n_0 \) ions produced at the origin at time \( t = 0 \) is

\[
n = \frac{n_0}{(4\pi D_T t)(4\pi D_L t)^{1/2}} \left( \exp - \frac{\rho^2}{4D_T t} \right) \left( \exp - \frac{(z-Wt)^2}{4D_L t} \right), \tag{4.1.2}
\]

where \( \rho^2 = x^2 + y^2 \). If this distribution were measured at any time, \( t \), it would be symmetrical in both the axial and transverse directions about the point \( (z = Wt, \rho = 0) \) but in general the width of the distribution is different in the different directions. On the other hand if the number density were measured at a fixed position as a function of time then the distribution would be distorted, being broader at longer times.

The physically realistic boundary conditions which are imposed on the solution are that \( n = 0 \) for \( t > 0 \) at the first shutter \( (z = 0) \).
and that \( n = 0 \) at the second shutter \((z = h)\). The boundary condition at the first shutter is imposed by adding to the solution representing an isolated swarm a second solution representing a delta function dipole distribution with a strength chosen so that \( n = 0 \) at \( z = 0 \). Thus since the sum of solutions is also a solution we can write,

\[
n = \frac{n_0}{(4\pi D_T t)(4\pi D_L t)^{1/2}} \left\{ \exp - \frac{\rho^2}{4D_T t} \left[ \exp - \frac{(z-Wt)^2}{4D_L t} \right] \right. \\
- \left( \frac{2D_L}{Wt} \frac{\partial}{\partial z} \left[ \exp - \frac{(z-Wt)^2}{4D_L t} \right] \right) \right\}
\]

4.1.3.

\[
n = \frac{n_0}{(4\pi D_T t)(4\pi D_L t)^{1/2}} \frac{z}{Wt} \left( \exp - \frac{(z-Wt)^2}{4D_L t} \right).
\]

4.1.4.

The boundary condition at the second shutter is met by adding a term which is analytically the same as equation 4.1.4. except that this image group starts at \((0,0,2h)\) at \( t = 0 \) so that \( z \) is replaced by \((z-2h)\). This additional term is weighted so that \( n = 0 \) at \( z = h \). The equation for \( n \) within the drift space then becomes,

\[
n = \frac{n_0}{(4\pi D_T t)(4\pi D_L t)^{1/2}} \frac{1}{Wt} \left[ \frac{z}{Wt} \left( \exp - \frac{(z-Wt)^2}{4D_L t} \right) \right. \\
+ \left( \frac{z-2h}{4D_L t} \right) \left. \left[ \exp - \frac{(z-Wt)^2 + 4h(h-z)}{4D_L t} \right] \right]. \quad 4.1.5.
\]

With the addition of this image term the boundary condition at the first shutter is no longer strictly satisfied. However, in practice the value of \( n \) at \( z = 0 \) predicted from equation 4.1.5. is negligibly small. If required an exact solution can be obtained with an infinite set of images (Huxley 1972).

In an experimental tube the ions are not emitted from a point on the first shutter. The ions enter the drift chamber through an
aperture typically 5 mm in diameter and 1 cm above the first shutter. Thus a more applicable form for \( n \) than that given by equation 4.1.5. is the solution to the one dimensional diffusion equation,

\[
\frac{\partial n}{\partial t} = D_L \frac{\partial^2 n}{\partial z^2} - W \frac{\partial n}{\partial z},
\]

which is

\[
n = \frac{N_0'}{(4\pi D_L t)^{1/2}} \frac{1}{Wt} \left[ z \left( \exp - \frac{(z-Wt)^2}{4D_L t} \right) + (z-2h) \left( \exp - \frac{(z-Wt)^2 + 4h(h-z)}{4D_L t} \right) \right] \]

where \( N_0' \) is the number of ions per unit area which are released by the first shutter each time it opens. The quantity \( N_0' \) is directly proportional to the open time of the shutter which, for sine-wave gating, is taken to be inversely proportional to the gating frequency. Under these conditions the number of ions emitted per pulse therefore depends on the time between the opening of the first shutter and the opening of the second shutter. It follows that \( N_0' \) can be written

\[
N_0' = \text{const.} \cdot x \cdot t.
\]

It is not necessary to include the effect of the shutter transmission factor when considering the second shutter since the inverse dependence of \( N_0' \) on gating frequency is cancelled by the direct dependence on the number of pulses transmitted per unit time. Thus \( n \) has the form,

\[
n = \frac{\text{const.}}{(4\pi D_L t)^{1/2}} \frac{1}{Wt} \left[ z \left( \exp - \frac{(z-Wt)^2}{4D_L t} \right) + (z-2h) \left( \exp - \frac{(z-Wt)^2 + 4h(h-z)}{4D_L t} \right) \right].
\]
Note that equation 4.1.8. does not satisfy the diffusion equation. This is because this expression for n does not describe the transport of a single ion swarm.

We now require to find the form of the current-frequency curve which is appropriate to the Bradbury-Nielsen experiment. If a swarm is in the vicinity of the second shutter and this shutter is closed the density gradient will be high since \( n = 0 \) at the shutter surface. It is therefore assumed that when the shutter opens for a brief interval of time the contribution to the total current transmitted by the shutter from the gradient term is much greater than the contribution from the drift term. That is

\[
\frac{\partial n}{\partial z} \gg n W. \tag{4.1.9}
\]

As a consequence the flux density transmitted by the second shutter may be written to a good approximation by

\[
j(h,t) = D_L \left( \frac{\partial n}{\partial z} \right)_{z=h}. \tag{4.1.10}
\]

To show the validity of the approximation 4.1.9. and to illustrate the form of a swarm of ions as it drifts and diffuses in a drift tube, equation 4.1.7. was computed and the results for a typical situation are shown in Fig. 4.1.

The current incident on a collector of area A can be obtained by combining equations 4.1.8. and 4.1.10. and is given by

\[
I = eA_j = \text{const.} \cdot t^{-\frac{1}{2}} \left[ (h^2/4D_L t) - 2 \right] \exp - (h-Wt)^2/4D_L t. \tag{4.1.11}
\]

In the derivation of equation 4.1.11. it has been assumed that the pulses travelling down the drift tube do not overlap.

4.1.1 Determination of the ionic drift velocity

When an experiment is carried out the variation of the tube current, as given by 4.1.11. is examined to determine the effective transit time, \( t_m \), that is the time at which the collected current is a maximum.
Fig. 4.1

\[(D_L/K)/V = 0.001\]
To a close approximation the drift velocity, $W$, is then given by $W = \frac{h}{t_m}$. In practice, however, it is necessary to recognize that $t_m$ does not correspond to the time at which the centroid of the group passes the second shutter. This error will be discussed in section 4.2.

A typical current-frequency spectrum of the first two peaks is shown in Fig. 4.2. The plot refers to $K^+$ ions in 9.68 torr He at $E/N = 5.66$ Td. and a drift distance of 3.395 cm. It can be seen that the resolution of the second peak is larger than the first. This is a result of the way in which the shutters are operated. To a first approximation the shutters are open for a constant fraction of the period of the gating signal and consequently the second peak is more clearly resolved as the open time of the shutter is a smaller fraction of the total drift time.

4.1.2 Determination of the longitudinal diffusion coefficient

It is also possible to measure the longitudinal diffusion coefficient, $D_L$, in a Bradbury-Nielsen type of experiment. This transport coefficient is determined by examining the width of the peaks in the current-frequency spectrum.

Under normal experimental conditions $\frac{h^2}{4D_L t} \gg 2$ and thus equation 4.1.11. can be written

$$I = \text{const. } t^{-3/2} \exp - \frac{(h-Wt)^2}{4D_L t} .$$  \hspace{1cm} 4.1.12.

The experimentally measured quantity is the resolving power, $R$, which is defined as the ratio of the time at which the maximum current occurs divided by the time spread at half the maximum current. To derive an expression for the resolving power it is assumed that the distribution of current as a function of time is affected to an insignificant extent by the coefficient $t^{-3/2}$ in equation 4.1.12., that is the current peak is described by

$$I = \text{const. } \exp - \frac{(h-Wt)^2}{4D_L t} .$$  \hspace{1cm} 4.1.13.

It has been shown (Milloy 1973) that under normal experimental conditions this assumption introduces a negligible error in the determination of $D_L$. 
$k^+$ in He

$E/N = 5.66 \text{Td}$

$h = 3.395 \text{ cm}$

$p_{273.2} = 9.68 \text{ torr}$

shutter signal = 12 V peak to peak
Following Lowke (1962a), the time difference at half the maximum current is \( t'' - t' \) where \( t'' \) and \( t' \) are the roots of

\[
\text{const. exp} - \left( h - Wt \right)^2 / 4D L t = I_{\text{max}} / 2. \quad 4.1.14.
\]

The resolving power, \( \delta r \), can then be written (Elford, 1966)

\[
\delta r = \frac{\frac{t_m}{t'' - t'}}{4} = \frac{1}{4} \left( \frac{hW}{D L \ln 2} \right)^{1/2} \quad 4.1.15.
\]

where \( t_m \) is the time corresponding to the peak maximum.

For the purposes of comparison of results taken at different pressures it is convenient to tabulate the data as the product of the diffusion coefficient and the gas number density, i.e. \( N D L \), and thus the resolving power is written in the form

\[
\delta r = \frac{1}{4} \left[ \frac{hE N_s \kappa}{\ln 2 D L N_s} \right]^{1/2} \quad 4.1.16.
\]

or

\[
N D L = \frac{hE N_s \kappa}{16 \ln 2 \delta r^2} \quad 4.1.17.
\]

4.2 DIFFUSIVE EFFECTS

Duncan (1957) was the first to consider the effects of diffusion processes on drift velocity data taken in a Bradbury-Nielsen type of experiment. His analysis was extended and modified by Lowke (1962b). More recently Huxley and Crompton (1973) have further refined the analysis.

When the effects of diffusion are considered it is found that the maxima in a current-frequency spectrum do not correspond to the centroid of the peaks. The error introduced by calculating \( W \) from the position of the peak maxima is referred to as the diffusion error. The magnitude of this error can be derived by equating to zero the derivative of the collector current (given by equation 4.1.11.) with respect to time, and so finding an analytical form for \( t_m \). It can then be easily shown that the drift velocity
can be expressed as,

\[ W = \frac{h}{t_m} \left(1 - \frac{3D_L}{hW}\right) = \frac{h}{t_m} \left(1 - \frac{3D_L/K}{V}\right), \]

4.2.1.

where \( V \) is the potential difference between the planes of the shutters. Similarly by using equation 4.1.5. it can be shown that if the ions are transmitted into the drift space from an axial point on the first shutter an error of \( 5D_L/hW \) is introduced if the current is monitored at a point on axis and an error of \( 3D_L/hW \) is introduced if all the current is collected. For all the experiments reported in this work the experimental geometry was such that an error of \( 3D_L/hW \) would be expected on the basis of this theory.

It is important to note that there are several factors which have not been included in the analysis of diffusion errors. No account has been taken of the diffusion of ions to the second shutter after it has closed or of the fact that the transmission of a shutter depends on the ion energy. The assumptions that \( n = 0 \) at a shutter when the shutter is closed and that the ion velocity distribution function is unaffected by the presence of the shutters may be unrealistic. It is also suspected that the neglect of higher order density gradients in equation 4.1.1. is a significant source of error. The analysis may therefore be an oversimplification of the complex effects introduced at the shutters. On the other hand the analysis does indicate the order of magnitude of the effects and their dependence on the experimental parameters.

4.3 LIMITATIONS OF METHOD

The Bradbury-Nielsen method is restricted to a moderately low range of \( E/N \) values. At high \( E/N \), when the mean energy of the ions is significantly greater than thermal energies it becomes more difficult to form discrete pulses and to reduce the transmitted current between the peaks to zero. Eventually the peaks become so broad that they are difficult to measure accurately.

The difficulties of forming well defined pulses at high values of \( E/N \) were also experienced by Blevin and Hasan (1967) in their experiments to measure electron drift velocities but they overcame the problem by using Tyndall-Powell shutters.
CHAPTER 5

APPARATUS AND MOBILITY RESULTS

Three drift tubes were used in this work in order to cover a large range of experimental parameters. Two of these tubes are very similar in design and construction but differ considerably in length (3 cms. and 50 cms.), while the third is more sophisticated and includes facilities for mass identification of the ions and for work at temperatures down to 77 K. Before these tubes are described in detail and the results discussed an outline will be given of the features common to all tubes and of the experimental tests which were carried out in order to check both the operation of the shutters and the overall accuracy of the method.

5.1 EXPERIMENTAL DESIGN

The following design factors and experimental techniques were common to all three drift tubes.

5.1.1 Production of uniform electric field, E

The electric field was established and held uniform by guard electrodes at potentials appropriate to their position in the electrode system. Although it may be thought desirable to use a large number of thin guard rings and so have good field uniformity throughout virtually all of the drift space, in practice this is not possible due to the mechanical instability of the thin rings. A more satisfactory alternative is to use a smaller number of "thick" rings (Crompton, Elford and Gascolgne 1965) and all the drift tubes used in the present work were of this latter type. These rings can be seen in Fig. 5.5. The use of thick guard rings results in large field distortion close to the rings but a high degree of uniformity in the axial region of the tube. Thus the diameter of the drift tube must be sufficiently large that a very small fraction of the ions pass close to the guard rings. The advantages of thick guard ring systems are that they are easily manufactured and assembled and act as electrostatic screens for the ion swarms. It should be noted that in drift velocity measurements small non-uniformities in the electric field strength are unimportant. Since the total potential drop across the tube is known, an increase in \( W \) due to an increased value of \( E/N \) in one part of
the electrode system is to a first order cancelled by the corresponding decrease in \( W \) in another section of the system.

Contact potential differences may introduce an error when the applied field is calculated. Errors due to contact potential differences were reduced by coating the shutter wires with gold and by using large potential differences between the two shutters: no results were taken with less than 15 V between the shutters, and only a very few with less than 25 V. Contact potential differences and other surface effects are discussed in more detail in Chapter 6.

The electrode potentials were supplied by a highly stabilized power supply (Fluke model 415B) and a precision voltage divider, the potential of all electrodes being within ±0.1% of the values calculated from their position in the electrode system. The potential difference between the planes of the shutters which, together with the drift distance, determines the value of \( E \), was measured with a Fluke model 891AR differential voltmeter. This differential voltmeter was calibrated with an error of less than ±0.01% with a Guildline 9160 potentiometer. However it was found that the long term calibration of the Fluke drifted slightly and for this reason it is estimated that the error in the d.c. potential difference applied between the shutters was somewhat higher but still less than ±0.05%.

5.1.2 Gas number density, \( N \)

Once the temperature and pressure are known the gas number density can be calculated from the perfect gas law,

\[
p = \frac{NkT}{p} \quad 5.1.1.
\]

In this work the gas number densities were sufficiently low that departures from ideal gas behaviour were insignificant.

It was necessary to use more than one gauge as a wide range of pressures (0.2 to 200 torr) were used in these investigations. A quartz spiral manometer (Texas Instrument type 141B, capsule type 5) was used to measure pressures in the range 1-200 torr and a capacitance manometer (MKS Baratron type 90H-3E) was used in the range 0.2 to 3.1 torr. Both gauges were calibrated by, and periodically checked against, a double
dead weight primary pressure standard. This calibrator, which incorporates two Consolidated Electrodynamics Corporation type 6201 piston-cylinder combinations, has been described by Gascoigne (1972). The errors in the calibration procedure are considered to be less than ± 0.05% or $5 \times 10^{-4}$ torr, whichever is greater. The sensitivity of the quartz spiral manometer did not change by more than ± 0.1% over a period of several years but both long and short term changes in the sensitivity of the capacitance manometer were observed. It is estimated that these changes in the sensitivity of the capacitance manometer introduced errors of less than ± 0.2%. Gascoigne (to be published) has investigated the difficulties of using this gauge as a precision instrument.

The major source of error in the measurement of low pressures with the quartz spiral gauge was the limited resolution of this instrument. The gauge could only be read to one dial unit and this introduced an error of ± 0.25/p%, where p is the gas pressure in torr.

5.1.3 Gas temperature, $T$

The gas temperature affects measurements of ion transport coefficients in two ways. First a knowledge of the temperature is required to calculate the gas number density and hence $E/N$ and secondly the transport coefficients are intrinsic functions of the gas temperature.

The details of the temperature measurement varied from one drift tube to another and are given in the descriptions of each tube (sections 5.3, 5.5 and 5.7).

5.1.4 Drift distance, $h$

The drift distance, which is taken to be the distance between the centre plane of each shutter is one of the most crucial parameters since both the electric field strength and the drift velocity involve this parameter. This distance was measured in the following way. First a fine wire probe was used to locate a single wire in each shutter, contact with the wire being confirmed electrically. The height of this single wire from a reference plane was then measured by using a Mitutoya Height Master. A number of such measurements were made and averaged in order to establish the height of the shutter plane above the reference plane. This procedure was repeated for the other shutter and the drift distance
calculated. The total error in the determination of a drift distance is estimated to be less than ± 40µm, or ± 0.04% in a 10 cm drift distance.

5.1.5 Effective transit time, \( t_m \)

The effective transit time is most accurately measured by measuring the gating frequencies \( f_1 \) and \( f_2 \) on either side of the peak at some arbitrary fraction (usually greater than 0.8) of the maximum current. \( t_m \) is then given by

\[
\frac{1}{t_m} = \frac{1}{f_1} + \frac{1}{f_2} \quad \text{5.1.2.}
\]

If the peak is narrow and \( |f_1 - f_2| \ll f_{\text{max}} \), \( t_m \) can be written

\[
\frac{1}{t_m} = \frac{1}{f_m} = \frac{1}{(f_1 + f_2)/2} \quad \text{5.1.3.}
\]

In all previous work in this group equation 5.1.3. was used (Elford, 1966). The error introduced by this approximation is given accurately by

\[
\frac{1}{4} \left( \frac{|f_1 - f_2|}{f_m} \right)^2
\]

This error is insignificant under normal experimental conditions.

The frequencies \( f_1 \) and \( f_2 \) are measured near the peak maximum as the peak is slightly asymmetric and the further down the peak the frequencies are measured, the larger the error introduced. On the other hand the frequencies can be determined more accurately if measurements are made where \( \text{di/df} \) is large. In practice a compromise is made and \( t_m \) is measured at two or three different positions near the top of the peak and these values averaged. The procedure is then repeated at another peak and the average value taken.

The frequencies were measured with a Hewlett-Packard 3734A Electronic Counter which was periodically checked using its inbuilt standard frequency. The counter error was always found to be less than ± 0.001%.

5.1.6 Electrical shutters

The electrical shutters are required to meet a stringent set of
conditions. The wires must be accurately coplanar in order for the drift distance to be well defined, the materials used must be compatible with UHV practice and the wire diameter and wire spacing must be chosen so that the gating signals do not produce significant end effects. Apart from one shutter, which is described in section 5.5, the shutters were made with nichrome wire according to the procedure described in detail by Crompton, Elford and McIntosh (1968). If made to this design the shutters can be outgassed and cooled to liquid nitrogen temperatures. The dimensions of the shutters were,

\[
\begin{align*}
\text{Inner diameter} & = 5.6 \text{ cm} \\
\text{Wire diameter} & = 0.008 \text{ cm} \\
\text{Wire separation} & = 0.04 \text{ cm}
\end{align*}
\]

After alternate wires were connected together by spot welding to constantan wire leads, the wires were vacuum coated with gold to reduce contact potential differences. A typical shutter is shown in Fig. 5.1.

5.1.7 Current measurement

A Keithley Model 600A electrometer was used to measure the ion currents. This instrument has a full scale reading of \(1 \times 10^{-13} \text{ A}\) on the most sensitive range. The maxima in the current-frequency spectra normally corresponded to currents of about \(10^{-11} \text{ A}\).

5.1.8 Production of ions

The alkali ions were produced by heating an appropriate alkali alumino-silicate bead, as described by Blewett and Jones (1936). The beads were formed on coils of 30µm diameter tungsten wire (torch bulb filaments). If the coils were to be used for Li\(^+\) or Cs\(^+\) filaments they were run at bright red heat in vacuum until the ion current, as measured by a collector situated near the filament, fell by two orders of magnitude. This usually took about twelve hours. Unless this ageing process was carried out the abundance of K\(^+\) ions from a new filament could exceed the abundance of the desired ion for many hours. If the filaments were aged before coating only trace quantities of K\(^+\) ions were observed.
5.1.9 Gases and gas handling equipment

Hydrogen was admitted through a heated silver-palladium osmosis tube. All other gases were Matheson Research Grade and were admitted from high pressure cylinders attached by means of a modified conflat flange directly to a Granville-Phillips UHV variable leak valve. This procedure avoided the use of regulators containing greases or elastomer materials which could be sources of contamination.

5.2 EXPERIMENTAL TESTS

The Bradbury-Nielsen method has the advantage that there are a number of tests which can be carried out to check the operation of the shutters and the overall accuracy of the method. These tests are now considered.

5.2.1 Measurement of several peaks in the current-frequency spectrum

There are several factors which can cause distortion of the peaks in the current-frequency spectrum and hence errors in the drift velocity measurements.

(a) Variation of the shutter signal amplitude with changing frequency.

As the transmission of a shutter is very sensitive to changes in the amplitude of the gating signal even small changes in the signal amplitude with changing frequency can significantly distort the peak.

(b) Peak overlap.

Under certain circumstances the peaks may overlap, causing the peak maximum of the first peak to be displaced to a higher frequency. The frequency of the maximum of the second peak is displaced by a smaller amount since both the low and high frequency sides are influenced by neighbouring peaks. As the peak number is further increased the disagreement between the values of $t_m$ measured from adjacent peaks decreases but unless an asymptotic value of $t_m$ is obtained $W$ cannot be accurately measured when such overlap occurs.

(c) Peak distortion due to the presence of more than one ion.

Errors may be introduced if the ions react with the neutral
gas atoms or if more than one ion is emitted from the source. The distortion of the first peak may not be noticed if the mobilities of the parent and product ion species are similar but if another peak is examined the distortion becomes more evident as peak resolution increases with peak number. In a system without mass identification facilities, peak disagreement is often the first evidence that there is more than one ion species present.

To ensure that there were no significant errors from the effects listed above the effective transit time was always measured by examining at least two of the peaks. It was usually found that the value of $t_m$ was independent of peak number to within ±0.1%. An example of the peak agreement which was obtained under good experimental conditions is given in the following table.

<table>
<thead>
<tr>
<th>Peak number (m)</th>
<th>$f_m/m$ (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4735</td>
</tr>
<tr>
<td>2</td>
<td>4736</td>
</tr>
<tr>
<td>3</td>
<td>4736</td>
</tr>
<tr>
<td>4</td>
<td>4736</td>
</tr>
<tr>
<td>5</td>
<td>4735</td>
</tr>
<tr>
<td>6</td>
<td>4736</td>
</tr>
</tbody>
</table>

The data in this table refer to $K^+$ ions in He at $E/p_{273.2} = 2.0 \text{ V cm}^{-1} \text{torr}^{-1}$ and at a pressure of 9.68 torr. The amplitude of the sine-wave signal applied to the shutters was 6 V peak to peak.

5.2.2 Variation of shutter signal amplitude

If the results are independent of shutter signal amplitude it can be concluded that the shutter signal causes negligible distortion of the electric field in the drift region. It can also be concluded that there are no end effects due to "heating" of the ion swarm by the high fields in the vicinity of the shutter wires.

A typical plot showing the value of $f_m$ to be independent of shutter signal amplitude is shown in Fig. 5.2. The experimental conditions were the same as those in the table above.
As an indication of the transmissive characteristics of a shutter, we sometimes use an indication of the presence of anomalous surface effects. This can be seen in Fig. 5.3 in which the transmitted fraction of a particular ion beam was measured at a range of different potentials. The presence of what we believe to be cut-off curves is a shutter which had been used for several months. When this shutter was replaced, the results were unstable with time and it was necessary to build the shutter wires to remove this effect and improve the transmission characteristics. Curve B in Fig. 5.3 shows the cut-off curve after replacement.

Unfortunately this test was not always a sensitive test of the condition of the shutter wires. In some cases normal cut-off curves were observed although the results of utility experiments indicated that the behaviour of the surfaces was far from ideal.

3.3 DISCUSSION OF MASS SPECTROMETER SYSTEM A

This apparatus, which was initially designed by Dr. B.P. Alfred and Mr. E.P. Greaves, has been described in detail by Greaves (1960). Although no major structural alterations were made for the work, several modifications and additions were carried out after a brief general description of the apparatus these changes may be described in detail.

3.3.1 General description of the apparatus

[Diagram showing the apparatus with labeled parts]
5.2.3 Examination of shutter transmission characteristics

An investigation of the transmission characteristics of a shutter can sometimes give an indication of the presence of anomalous surface effects. This can be seen in Fig. 5.3 in which the transmitted fraction of the incident ion current is plotted as a function of a d c potential difference applied between adjacent wires. Plots of this type will be referred to as cut-off curves. Curve A in Fig. 5.3 shows the anomalously broad cut-off curve of a shutter which had been used for several months. When this shutter was used the results were unstable with time and it was necessary to regild the shutter wires to remove this effect and improve the transmission characteristics. Curve B in Fig. 5.3 shows the cut-off curve after regilding. The effects of bombarding low energy alkali ions onto metal surfaces are described in Chapter 6.

Unfortunately the form of the cut-off curve of a shutter was not always a sensitive test of the condition of the shutter wires. In some cases normal cut-off curves were observed although the results of mobility experiments indicated that the behaviour of the surfaces was far from ideal.

5.3 DRIFT TUBE - MASS SPECTROMETER. SYSTEM A

This apparatus, which was initially designed by Dr. M.T. Elford and Dr. R.P. Creaser, has been described in detail by Creaser (1969). Although no major structural alterations were necessary for this work, several modifications and additions were made and after a brief general description of the apparatus these changes will be described in detail.

5.3.1 General description

The apparatus is shown schematically in Fig. 5.4 and in detailed cross section in Fig. 5.5. It consists of three sections, the drift section, the transition section and the analyser section. The drift section consists basically of an ion source and a guard ring system with three Bradbury-Nielsen shutters. The distances between the planes of the shutters are 9.076 cm and 2.965 cm. All electrical connections to the guard ring system are made through seals in flange A (Fig. 5.5). The ion source (B in Fig. 5.5) is supported by a long glass stem attached to the small flange above A. The guard ring system is surrounded by a dewar, C, which for measurements
to pressure gauge and pressure controller

from gas inlet system

DRIFT SECTION

TRANSITION SECTION

ANALYSER SECTION

Cryosorb trap

water baffle

4" diff. pump

rotary pump

Cryosorb trap

water baffle

6" diff. pump

rotary pump

Fig. 5.4.
at room temperature is filled with alcohol to remove the effects of room
temperature fluctuations but which contains liquid nitrogen and other cooling fluids. A appropriate
pressure of 30 torr is used, an arrangement for the pressure in
the region. The pressure is kept at this level by using the output of
the capacitance manometer to control 213.

A beam enters through an aperture (typically 50 mm diameter) and enters the transition region. It is then passed through a conical skimmer and into the quadrupole mass spectrometer. The potentials of the quadrupole rods are supplied by an ion source. The ion pulses from this source are detected with a high speed oscilloscope, the drift section both horizontal and vertical. The transition section is used to drift section the ions. This facility was used to determine mass/charge ratios in this work (see Chapter 10).

The whole drift section was built on a stainless steel plate in the analyzer section. The drift section plate was calibrated copper-constant temperature and to the electrodes above the top shutter and below the bottom shutter. The ion source was developed. The pressures were measured by a Leeds and Northrup K-3 potentiometer. The temperature recorded by each thermocouple was set 0.1 K each the thermocouple temperature by a Leeds and Northrup K-3 potentiometer. Since no results were obtained with a potentiometer, the maximum error in the temperature measurement at room temperature is 0.2 K or ± 0.1 K.

As both the ion source and the drift system are supported by flanges A in Fig. 5.5, the whole drift system is used without modification in another manifold. Several experiments were carried out in this way.

Fig. 5.5.
at room temperature is filled with alcohol to reduce the effects of room temperature fluctuations but which can also be filled with liquid nitrogen and other cooling fluids. A capacitance manometer with a maximum differential pressure of 3.1 torr is used to measure and monitor the pressure in this region. The pressure is kept stable with time by using the output of the capacitance manometer to control a Granville-Phillips leak valve model 213.

A small fraction of the ions in the drift tube pass through an aperture (typically 0.5 mm diameter) in the centre of the exit plate D, and enter the transition region. They then pass through the conical skimmer E into the quadrupole mass spectrometer. The potentials of the quadrupole rods are supplied by an E.A.I. Quad 150A power supply. The ions resolved by the quadrupole are detected by a particle multiplier and the pulses from this are further amplified and counted. It is possible, by means of micrometer screw drives, to move the position of the analyser section both horizontally and vertically with respect to the drift section. This facility was used extensively in various aspects of this work (see Chapter 10).

The whole system was built to U.H.V. specifications. Base pressures of \(1 \times 10^{-9}\) torr in the transition section and \(2 \times 10^{-9}\) torr in the analyser section were routinely achieved without baking. With 3.1 torr of argon in the drift region and a 0.2 mm diameter exit hole, the pressure measured in the transition section at F was \(4 \times 10^{-5}\) torr and that measured in the analyser section at G was \(4 \times 10^{-6}\) torr.

The temperature of the gas in the drift section was measured by two calibrated copper-constantan thermocouples, one attached to the electrode above the top shutter and one attached to the electrode beneath the bottom shutter. The e.m.f's developed by the thermocouples were measured by a Leeds and Northrup K-3 potentiometer. The temperature recorded by each thermocouple was measured with an error of less than \(\pm 0.1\) K, and since no results were taken when the difference between the thermocouple temperature exceed 0.5 K it is estimated that the maximum error in the temperature measurement at room temperature was \(\pm 0.25\) K or \(\pm 0.1\%\).

As both the ion source and the guard ring system are supported by flange A in Fig. 5.5, the whole drift section can be used without modification in another manifold. Several experiments were carried out in this way
by placing the drift section in a stainless steel manifold and connecting the apparatus to the vacuum system shown in Fig. 5.6. The main advantage of this arrangement, which will be referred to subsequently as System A (1), is that a larger range of pressures can be used.

5.3.2 Modifications to the drift section

A. Reduction of thermal gradients.

In previous work with this apparatus (Creaser 1969) thermal gradients caused significant errors, especially at liquid nitrogen temperatures.

The alkali ion source, which was usually operated at dull red heat, gave rise to significant thermal gradients at all temperatures. In an effort to overcome this problem a cylindrical copper can was placed round the filament assembly. The aperture of this radiation shield was covered in a fine wire mesh to improve the field uniformity in the region above the entry hole of the drift tube.

At 77 K thermal gradients were also caused by radiation from the stainless steel and glass walls situated above the dewar (Fig. 5.5). This problem was partially overcome by inserting a copper cylinder above the guard ring system (H in Fig. 5.5). However, the most effective method of reducing the temperature gradients at liquid nitrogen temperatures was to fill the glass filament stem with liquid nitrogen. With this technique even continuous operation of a Li\(^+\) filament in Ar did not result in a temperature difference across the electrode stack of more than 1 K. If the filament was switched off the temperature difference fell to less than 0.1 K.

B. Multi-filament source.

A four filament source was used. It has the following advantages.

(a) The transport properties of several alkali ion species can be investigated without letting the system up to atmospheric pressure.

(b) If one ion species is being used for the first time the general performance of the apparatus can be checked by using another ion species to take an accurately known value.
A schematic diagram of the vacuum system is shown in Fig. 5.6. The capillary entrance to the probe section can be seen in Fig. 5.8. The cylindrical electrode, filament, central electrode and additional shield are all connected to separate power supplies so that potential differences between these components and with the ion source can be adjusted. The potentials of ions from the drift section were the subject of separate discussion. In addition, the drift section was the site for the subsequent gas feed. The drift section was located at least an order of magnitude below the exit plate and the entire guard ring was biased to a few volts above ground. To do this a gridless anode was inserted between the drift plate and the dewar wall. A potential difference of 25 to 30 V was applied between the exit plate and earth. This gave both good transmission and adequate mass spectrometer resolution. The transmission also made it possible to continuously monitor the current in the drift tube.

Fig. 5.6.
(c) The control settings of the quadrupole mass spectrometer can be adjusted by comparing the resolution of ions of different masses. With the present quadrupole mass spectrometer it was quite possible to have a large variation in transmission over the mass scale and thus this check was essential.

A schematic diagram of the source is shown in Fig. 5.7. The position of the source with respect to the drift section can be seen in Fig. 5.5. The cylindrical electrode, filament, central electrode and radiation shield are all connected to separate power supplies and the potential differences between these components adjusted to give good transmission of ions into the drift section.

Usually two potassium, one lithium and one caesium filaments were used. Drift tube currents of \(10^{-9}\) A could be easily obtained under normal operating conditions but to avoid significant space charge repulsion effects ion currents of about \(10^{-11}\) A were normally used. Although the short term stability of the currents emitted from the filaments tended to deteriorate slowly with time, useful filament lifetimes of many months were not uncommon.

Other but more minor modifications to the drift section were the insertion of a liquid nitrogen trap on the low pressure side of the gas inlet line and the tie rods which hold the guard rings and shutters in position were changed from ceramic to stainless steel.

5.3.3 Modifications to the ion detection system

Several modifications were carried out to improve the transmission of ions from the drift section to the quadrupole mass spectrometer and to increase the signal to noise ratio in the counting circuit. The transmission was improved by at least an order of magnitude by insulating the exit plate of the drift tube from earth and floating the entire guard ring system a few volts above ground. To do this a soda glass annulus was inserted between the exit plate and the dewar wall. A potential difference of between 3 and 20 V was usually applied between the exit plate and earth as this gave both good transmission and adequate mass spectrometer resolution. This modification also made it possible to continuously monitor the current in the drift tube.
The transmission was further improved by changing the design of the conical skimmer. Cremer (1969) used a skimmer with an included angle of $120^\circ$. This resulted in poor transmission, due to a shock wave set up in front of the skimmer (Anderson et al., 1966). A new skimmer with a $60^\circ$ included angle was found to improve the transmission by about a factor of ten (Alford, private communication).

With these changes, and by careful tuning of the mass spectrometer power supply, good transmission was obtained over the whole mass range which it was possible to check (v=133 m. s.$^{-1}$). Fig. 5.6 shows the peaks observed when a Li$^+$ and a Ce$^{4+}$ filament were used in nitrogen at a pressure of 1 torr. The ion current spectrum was taken with a potential of $+5$ V on the exit plate, $-30$ V on the conical skimmer, L/H = 30:24 and a total drift tube current of $2 \times 10^{-8}$ amp from each filament. Fig. 5.7 shows the peak shapes more clearly under normal operating conditions. This spectrum shows the 39 and 41 amu isotopes of potassium, taken under the same conditions as the data in Fig. 5.6.

The data shown in Fig. 5.7 were taken with large drift tube currents to enable the peak shapes to be investigated without significant signal noise. Under normal conditions a pulse counting system was used. This system used a preamplifier with a gain of 10x, an amplifier, also with a gain of 10x, a pulse height analyser and a scaler. Count rates of $3 \times 10^9$/sec could be used without significant dead time losses.

3.3.4 Computer control of the quadrupole mass spectrometer

The quadrupole mass spectrometer was controlled by a small computer (model 7090/E, manufactured by the Digital Equipment Corporation) to facilitate the data collection and analysis. With this system the amount of information which could be obtained in a given amount of time was increased by about a factor of 3. A schematic diagram of the logic circuits and a brief description of the functions of the components are given in Appendix 5.

The computer was programmed to sweep through one mass peak in a series of steps. Figure 5.10 shows the variation of the output of the control circuit and the equivalent mass numbers in a typical measurement, the determination of the currents of $^7\text{Li}^+$ and $^7\text{Li}^{1+}.\text{H}_2$. In any experiment the sequence shown in Fig. 5.10 was repeated many times to reduce the statistical errors.

Schematic diagram of four filament ion source.  

Fig. 5.7.
The transmission was further improved by changing the design of the conical skimmer. Creaser (1969) used a skimmer with an included angle of 120°. This resulted in poor transmission, due it is suspected, to a shock wave set up in front of the skimmer (Anderson et al. 1966). A new skimmer with a 60° included angle was found to improve the transmission by about a factor of ten (Elford, private communication).

With these changes, and by careful tuning of the mass spectrometer power supply, good transmission was obtained over the whole mass range which it was possible to check (6-133 a.m.u.). Fig. 5.8 shows the peaks observed when a Li⁺ and a Cs⁺ filament were used in nitrogen at a pressure of 1 torr. The ion current spectrum was taken with a potential of +5 V on the exit plate, -23 V on the conical skimmer, $E/N = 30$ Td and a total drift tube current of $2 \times 10^{-9}$ A from each filament. Fig. 5.9 shows the peak shapes more clearly under normal operating conditions. This spectrum shows the 39 and 41 a.m.u. isotopes of potassium, taken under the same conditions as the data in Fig. 5.8.

The data shown in Figs. 5.8 and 5.9 were taken with large drift tube currents to enable the peak shapes to be investigated without significant signal noise. Under normal operating conditions a pulse counting system was used. This system consists of a preamplifier with a gain of 10x, an amplifier, also with a gain of 10x, a pulse height analyser and a scalar. Count rates of $8 \times 10^5$/sec could be used without significant dead time errors.

5.3.4 Computer control of the quadrupole mass spectrometer

The quadrupole mass spectrometer was controlled with a small computer (model PDP.8/E, manufactured by Digital Equipment Corporation) to facilitate the data collection and analysis. With this system the amount of information which could be obtained in a given amount of time was increased by about a factor of 3. A schematic diagram of the logic circuits and a brief description of the functions of the components are given in Appendix B.

The computer was programmed to sweep through one mass peak in a series of steps. Figure 5.10 shows the variation of the output of the control circuit and the equivalent mass numbers in a typical measurement, the determination of the currents of $^7$Li⁺ and $^7$Li⁺H₂. In any experiment the sequence shown in Fig.5.10 was repeated many times to reduce the statistical errors.
The peaks observed at the output of the particle multiplier when a Li\(^+\) and a Cs\(^+\) filament were used in N\(_2\). The peaks formed by both the 6 a.m.u. and 7 a.m.u. Li\(^+\) isotopes can be clearly seen.

Fig. 5.8.

Fig. 5.9.
The system was tested by measuring the ratio of the two isotopes of potassium at 39 a.m.u. and 41 a.m.u. The measured ratio of the 41 a.m.u. isotope to the 39 a.m.u. isotope was 7.42 ± 0.22. The standard value is 7.38.

5.4 RESULTS TAKEN WITH SYSTEM A

System A was used to investigate the reduced mobility of alkali ions in various gases and the clustering of alkali ions to neutral gas particles. The clustering studies are described in Chapter 10.

In this section, the reduced mobilities are slowly-varying functions of the gas density. This phenomenon is discussed in Chapter 6, where the relative errors in the measurements at different pressures are described in detail. In this chapter only the total errors are discussed.

5.4.1 The reduced mobility of Li⁺ ions in helium, neon and argon

The reduced mobility of Li⁺ ions in helium was measured in the range 2.82 < $E/N$ (Td) < 68.8 and at pressures between 0.44% and 2.90 Torr. The data are listed in Table 6.1 and are presented in graphical form in Fig. 5.11. The large minimum in the $\mu/E$ curve is due to the fact that in this case the repulsive part of the interaction potential is a relatively slowly-varying function of the particle separation. No product ions were observed with the quadrupole mass spectrometer and only one ion was observed in the current-frequency spectrum.

The reduced mobility of Li⁺ ions in neon and argon was measured during an investigation of the clustering of Li⁺ ions to atoms of these gases. The measurements were taken with the ionization source in the stainless steel manifold, as described in Section 3.3. The data, which are presented in Tables 6.1 and 6.2 for Ne and Ar respectively, are restricted to limited ranges of $E/N$ and are not of the clustering reactions. However, it was possible to estimate the reduced zero field mobility in each case and these, together with the value of $\alpha_0$ for ions in helium, are given in Table 5.1. Also given in Table 5.1 are the dipole polarization limits of $\alpha$ and the values of $\alpha_0$ obtained by the Bristol group (Tyndall 1938). The only other data for comparison is the value of $4.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the reduced zero field mobility of Li⁺ ions in argon reported by Keller (1972).
The system was tested by measuring the ratio of the two isotopes of potassium at 39 a.m.u. and 41 a.m.u. The measured ratio of the 41 a.m.u. isotope to the 39 a.m.u. isotope was 7.4%± 0.2%. The standard value is 7.39%.

5.4 RESULTS TAKEN WITH SYSTEM A

System A was used to investigate the reduced mobility of alkali ions in various gases and the clustering of alkali ions to neutral gas particles. The clustering studies are described in Chapter 10.

It will be seen from the results discussed in this section that the reduced mobilities are slowly varying functions of the gas number density. This phenomenon is discussed in Chapter 6, where the relative errors in the measurements at different pressures are described in detail. In this chapter only the total errors are discussed.

5.4.1 The reduced mobility of Li+ ions in helium, neon and argon

The reduced mobility of Li+ ions in helium was measured in the range 2.83 ≤ E/N (Td) ≤ 84.8 and at pressures between 0.498 and 2.90 torr. The data are listed in Table C.1 and are presented in graphical form in Fig. 5.11. The large maximum in the κ-E/N curve is due to the fact that in this case the repulsive part of the interaction potential is a relatively slowly varying function of the particle separation. No product ions were observed with the quadrupole mass spectrometer and only one ion was observed in the current-frequency spectrum.

The reduced mobility of Li+ ions in neon and argon was measured during an investigation of the clustering of Li+ ions to atoms of these gases. The measurements were taken with the drift section placed in a stainless steel manifold, as described in Section 5.3. The data, which are presented in Tables C.2 and C.3 for Ne and Ar respectively, are restricted to limited ranges of E/N and p because of the clustering reactions. However, it was possible to estimate the reduced zero field mobility in each case and these, together with the value of κ₀ for ions in helium, are given in Table 5.1. Also given in Table 5.1 are the dipole polarization limits of κ and the values of κ₀ obtained by the Bristol group (Tyndall 1938). The only other data for comparison is the value of 4.6 cm² V⁻¹ s⁻¹ for the reduced zero field mobility of Li+ ions in argon reported by Keller (1972).
Table 5.1

The reduced zero field mobility of Li$^+$ ions in helium, neon and argon

<table>
<thead>
<tr>
<th>Gas</th>
<th>Present work</th>
<th>Bristol Group</th>
<th>Polarization limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>23.05</td>
<td>24.2</td>
<td>19.1</td>
</tr>
<tr>
<td>Ne</td>
<td>10.6</td>
<td>11.1</td>
<td>9.52</td>
</tr>
<tr>
<td>Ar</td>
<td>4.64</td>
<td>4.66</td>
<td>4.44</td>
</tr>
</tbody>
</table>

All mobilities are in units of cm$^2$ V$^{-1}$ s$^{-1}$.

From the data in Table 5.1 it can be seen that the fractional difference between the value of $K_0$ and the value of $K$ in the polarization limit decreases as the mass of the gas atom increases. For a given ion the depth of the minimum in the interaction potential increases with increasing atomic mass and consequently the relative importance of the attractive forces also increases with increasing atomic mass.

5.4.1.1 Experimental errors

The reduced mobility can be expressed in terms of the experimental parameters by the relation,

$$\kappa = \frac{h^2}{Vt} \frac{p}{760} \frac{273.16}{T}.$$ 5.4.1.

The details of measurement of the experimental parameters in equation 5.4.1. have already been discussed in this chapter and will not be repeated here. The largest source of systematic error was due to the possibility of diffusion errors and other end effects, which are discussed in more detail in Chapter 6. Table 5.2 lists the sources of error and the estimated maximum magnitude of their effect on $\kappa$. 

It is concluded from the present work, and it was also observed by Tyndall (1938), Dalgaro et al. (1956), and Miller, Mosley et al. (1968), that the value of $K_0$ for Li$^+$ ions in hydrogen is about 43 smaller than the value of $K_0$ for K$^+$ ions in hydrogen. Although this is contrary to elementary theory (see equation 2.4.20) which predicts that the mobility decreases with increasing reduced mass, no satisfactory explanation was offered by
Table 5.2

Estimated total errors in the reduced mobility of Li⁺ ions in He, Ne and Ar

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Type of error</th>
<th>Maximum effect on κ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>Ne</td>
</tr>
<tr>
<td>p.d. between shutters</td>
<td>random</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.05</td>
</tr>
<tr>
<td>Temperature</td>
<td>random</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.08</td>
</tr>
<tr>
<td>Pressure</td>
<td>random</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.2</td>
</tr>
<tr>
<td>Drift distance</td>
<td>systematic</td>
<td>0.08</td>
</tr>
<tr>
<td>End effects</td>
<td>random</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.4</td>
</tr>
<tr>
<td>Effective transit time</td>
<td>random</td>
<td>0.1</td>
</tr>
<tr>
<td>Estimated total uncertainty</td>
<td></td>
<td>1.0%</td>
</tr>
</tbody>
</table>

5.4.2 The reduced mobility of Li⁺ ions in hydrogen

The reduced mobility of Li⁺ ions in hydrogen was measured in the range \( 2.12 \leq \frac{E}{N} (\text{Td}) \leq 50.9 \) and at pressures between .817 and 37.9 torr. The measurements were taken with the drift section placed in the stainless steel manifold (i.e. System A (1)). The data are listed in Table C.4 and are shown in Fig. 5.12. As only one ion was observed in the current-frequency spectrum at all values of \( \frac{E}{N} \) and \( p \) and as the reduced mobility shows no significant pressure dependence there is no evidence from these experiments for the formation of lithium-hydrogen clusters at room temperature. The present value for the reduced zero field mobility (12.24 cm² V⁻¹ s⁻¹) compares favourably with the previous measurements of Tyndall (1938) (12.4 cm² V⁻¹ s⁻¹) and Miller, Moseley et al. (1968) (12.3 cm² V⁻¹ s⁻¹).

It is concluded from the present work, and it was also observed by Tyndall (1938), Dalgarno et al. (1958) and Miller, Moseley et al. (1968), that the value of \( \kappa_0 \) for Li⁺ ions in hydrogen is about 4% smaller than the value of \( \kappa_0 \) for K⁺ ions in hydrogen. Although this is contrary to elementary theory (see equation 2.4.20) which predicts that the mobility decreases with increasing reduced mass, no satisfactory explanation was offered by
The reason would appear to be that at low values of E/N at room temperature the repulsive forces in the interactions between Li$^+$ ions and hydrogen molecules are more significant than the repulsive forces between Li$^+$ ions and hydrogen molecules. This causes the mobility to increase at lower mass for energies in the barrierless case.

As Li$^+$-H$_2$ clusters form readily at room temperature, data could only be taken over a restricted range of E/N and y values. The data for the reduced mobility of Li$^+$ ions in nitrogen are listed in Table 5.3. The variation of $\kappa$ with E/N is shown in Fig. 5.12. All the points are within the thickness of the line. The mobility was monitored by monitoring the current of Li$^+$ ions at the output of the quadrupole mass spectrometer as a function of the frequency of the electron gating signal. At low values of E/N, it was impossible to detect the current. The measurements were taken at 300°C and the mobility is difficult to estimate at zero field.

The form of the variation of $\kappa$ with E/N, as shown in Fig. 5.13, has not previously been observed for any gas-atom combination (Li$^+$ ions in nitrogen have not previously been investigated except by Tyndall (1936) who obtained a value of 3.95 cm$^2$ V$^{-1}$ s$^{-1}$ for $\kappa$). The initial decrease in $\kappa$ with increasing E/N is due to the repulsive term in the interaction potential as E/N (and hence the relative energy) increases. This causes the repulsive force between the ion and the molecule to be greater than the polarization force alone. Under these conditions the collision frequency for momentum transfer increases with increasing relative energy. There is always a contribution from this effect but in all other cases it is masked by the effect of the repulsive forces.

![Fig. 5.12.](image-url)
these authors. The reason would appear to be that at low values of E/N at room temperature the repulsive forces in the interactions between K+ ions and hydrogen molecules are more significant than the repulsive forces between Li+ ions and hydrogen molecules. This causes the mobility to increase at lower mean ion energies in the heavier ion case.

5.4.2.1 Experimental errors

The sources of error are identical to those outlined in section 5.4.1.1 for the case of Li+ ions in neon. Thus the data are considered to be in error by less than ±1.2%.

5.4.3 The reduced mobility of Li+ ions in nitrogen

As lithium-nitrogen clusters form readily at room temperature data could only be taken over a restricted range of E/N and p values. The data for the reduced mobility of 7Li+ ions in nitrogen are listed in Table C.5 and the variation of κ with E/N is shown in Fig. 5.13. All the data points lie within the thickness of the line. The mobility was measured by monitoring the current of 7Li+ ions at the output of the quadrupole mass spectrometer as a function of the frequency of the shutter gating signal. At low values of E/N there was insufficient current to carry out the measurements and for this reason it is difficult to estimate the zero field reduced mobility. As only a small dependence of κ on gas pressure was observed (~ 0.1% when pressure varied from 0.5 to 1.44 torr) and as the measured mobility did not depend on which peak in the current frequency spectrum was measured, it was concluded that the 7Li+ ions detected at the mass spectrometer did not spend a significant fraction of their drift time as clusters.

The form of the variation of κ with E/N, as shown in Fig. 5.13, has not previously been observed for any ion-gas combination (Li+ ions in nitrogen have not previously been investigated except by Tyndall (1938) who obtained a value of 3.95 cm2 V−1 s−1 for κo). The initial decrease in κ with increasing E/N is probably due to the increasing relative importance of the r−6 term in the interaction potential as E/N (and hence the relative energy) increases. This causes the net attractive force between the ion and the molecule to be greater than the dipole polarization force alone. Under these conditions the collision frequency for momentum transfer increases with increasing relative energy. There is always a contribution from this effect but in all other cases it is masked by the effect of the repulsive
The reduced mobility of Ca$^+$ ions in neon was measured over the range 11.3 \( \text{E/N} \) (Td) \( \leq \) 30.9 at pressures of 0.502, 0.933, 1.94 and 2.87 torr. The data are listed in Table 5.12 and are presented in graphical form in Fig. 5.14. Also shown in this figure are the data taken with System B (see Section 5.6). The low \( \text{E/N} \) data are used in Chapter 7 to obtain an estimate of the \( \text{Ca}^+\)-Ne interaction potential. The height of the mobility maximum is only 17\% above the polarization limit whereas in the case of Li$^+$ ions in helium the mobility maximum is about 60\% above the polarization limit. This is shown in Chapter 2 to be due to a larger \( r^{-6} \) term in the interaction potential or to a smaller repulsive core. No product ions were observed in the quadrupole mass spectrometer and only one ion was observed in the current-frequency spectrum.

Tyndall (1935) obtained a value of 4.1 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) for the reduced mobility at 291 K which compares favourably with the present value of 3.99 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \). There are unpublished data for the variation of the reduced mobility with \( \text{E/N} \).

**Experimental errors**

The sources of error are identical to those outlined in Section 5.4.3.1 except that the error due to the distance measurement is larger due to the shorter drift distance (2.965 cm) used in this investigation. It is estimated that the total uncertainty is less than \( \pm 1.3\% \).

It was necessary to use a short drift tube in some aspects of this work in order to make measurements at high values of \( \text{E/N} \) without electrical discharge occurring. In other cases, this drift tube was the most suitable of the three for the investigation of deviations from Blaun's Law and for work at high gas pressures.

---

**Fig. 5.13.**
ion-atom forces which tend to increase the mobility. It can be seen from Fig. 5.13 that in this case the effect of the repulsive forces is not obvious until about $E/N = 100 \text{Td}$.

5.4.3.1 Experimental errors

The data are estimated to be in error by less than $\pm 1.5\%$.

5.4.4 The reduced mobility of Cs$^+$ ions in neon

The reduced mobility of Cs$^+$ ions in neon was measured over the range $11.3 \leq E/N (\text{Td}) \leq 50.9$ at pressures of 0.502, 0.932, 1.94 and 2.87 torr. The data are listed in Table E.2 and are presented in graphical form in Fig. 5.14. Also shown in this figure are the data taken with System B (see section 5.6). The low $E/N$ data are used in Chapter 7 to obtain an estimate of the Cs$^+$-Ne interaction potential. The height of the mobility maximum is only 17% above the polarization limit whereas in the case of Li$^+$ ions in helium the mobility maximum is about 60% above the polarization limit. This is shown in Chapter 2 to be due to a larger $r^{-6}$ term in the interaction potential or to a harder repulsive core. No product ions were observed in the quadrupole mass spectrometer and only one ion was observed in the current-frequency spectrum.

Tyndall (1938) obtained a value of $6.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the reduced mobility at 291 K which compares favourably with the present value of $5.98 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. There are no published data for the variation of the reduced mobility with $E/N$.

5.4.4.1 Experimental errors

The sources of error are identical to those outlined in section 5.4.1.1 except that the error due to the distance measurement is larger due to the shorter drift distance (2.965 cms) used in this investigation. It is estimated that the total uncertainty is less than $\pm 1.3\%$.

5.5 3CM DRIFT TUBE. SYSTEM B

It was necessary to use a short drift tube in some aspects of this work in order to make measurements at high values of $E/N$ without electrical discharge occurring. In particular, this drift tube was the most suitable of the three for the investigation of deviations from Blanc's Law and for work at high gas pressures.
Fig. 5.14.

Cs$^+$ in Ne

- $\nabla$ .502 torr System A
- • .932 System A
- ▲ 1.03 System A
- × 1.94 System A
- ■ 2.10 System B
- ○ 2.87 System A

$\kappa$ (cm$^2$V$^{-1}$s$^{-1}$) vs. $E/N$ (Td)
A schematic diagram of this tube is shown in Fig. 5.15. The guard rings (inner diameter 9.5 cm) were constructed of brass and a glass bell jar was used as a vacuum envelope. The vacuum seals at the base of the bell jar and at the filament stem were made with Apiezon N grease. The system was connected via a liquid nitrogen trap to an 8 l/s ion pump and a gas inlet system. This ancillary vacuum system is shown schematically in Fig. 5.6. Pressures of about $5 \times 10^{-8}$ torr and adequately low out-gassing rates were achieved after pumping for a few days. However, because of the risk of gas contamination this apparatus was only used for measurements with potassium and caesium ions as the probability of these ions forming clusters is low. With these ions gas samples could be used for several hours before there was evidence of contamination. The top shutter was identical in construction to those used in System A and described in section 5.1.6 but the lower shutter was of the type used by Jory (1964).

The glass bell jar was surrounded by a water bath. Due to the large heat capacity of the bath and the fact that the tube was operated in an air-conditioned room the variation of bath temperature with time was small ($< 0.3$ K per hour). Errors due to the heating effects of the filament were considered negligible as the results were stable with time.

5.6 RESULTS TAKEN WITH SYSTEM B

System B was used to measure the longitudinal diffusion coefficient of $K^+$ ions in various gases, deviations from Blanc's Law at relatively high values of $E/N$ and the reduced mobility of $K^+$ and $Cs^+$ ions in various gases. The determination of $D_L$ is the subject of Chapter 8 and the deviations from Blanc's Law are discussed in Chapter 9.

5.6.1 The reduced mobility of $K^+$ ions in helium, argon, hydrogen and nitrogen

The reduced mobility of $K^+$ ions in helium, argon, hydrogen and nitrogen was measured as a function of pressure in the range $3 < p_{273.16} \text{(torr)} < 200$. Particular emphasis was placed on taking data at low values of $E/N$ in order to obtain the reduced zero field mobilities. The data are listed in Tables D.1, D.2, D.3 and D.4 and are discussed in detail in Chapters 6 and 10.
Schematic diagram of System B - 3 cm drift tube

Fig. 5.15.
5.6.1.1 Experimental errors

Table 5.3 lists the sources of error in the measurements and the estimated maximum magnitude of their effect on $\kappa$.

Table 5.3

The estimated total errors in the reduced mobility of $K^+$ ions in He, Ar, $H_2$ and $N_2$

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Type of error</th>
<th>Maximum effect on $\kappa$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p.d. between shutters</td>
<td>random</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.05</td>
</tr>
<tr>
<td>Temperature</td>
<td>random</td>
<td>0.2</td>
</tr>
<tr>
<td>Pressure</td>
<td>random</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.1</td>
</tr>
<tr>
<td>Drift distance</td>
<td>systematic</td>
<td>0.24</td>
</tr>
<tr>
<td>End effects</td>
<td>random</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
<td>0.4</td>
</tr>
<tr>
<td>Effective transit time</td>
<td>random</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Estimated total uncertainty</td>
</tr>
</tbody>
</table>

5.6.2 The reduced mobility of $Cs^+$ ions in helium and neon

The reduced mobility of $Cs^+$ ions in helium was measured in the range $1.41 \leq E/N \ (Td) \leq 45.3$ and at pressures between 1.68 and 37.5 torr. The data are listed in Table E.1 and are presented in graphical form in Fig. 5.16. It can be seen that at room temperature the repulsive ion-atom forces are dominating the motion of the ions. Tyndall (1938) has reported the value of $K_0$ for caesium ions in helium to be $18.4 \ cm^2 \ V^{-1} \ s^{-1}$ at 291 K. This is in good agreement with the present estimate of $18.3 \ cm^2 \ V^{-1} \ s^{-1}$ at 293 K.

The reduced mobility of caesium ions in neon was measured over the range $45.3 \leq E/N \ (Td) \leq 96.2$ to complement the low $E/N$ data discussed in section 5.4. Pressures of 1.03 and 2.10 torr were used. These data are listed in italics in Table E.2 and are shown in Fig. 5.14. It can be seen that the agreement between the two sets of data is better than 0.4% in the region of overlap.
3.6.2.1 Experimental error

The sources of error in the measurements are identical with those outlined in Table 3.3.

3.6.3 The reduced mobility of Cs⁺ ions in oxygen

The reduced mobility of Cs⁺ ions was obtained by using a quadrupole mass spectrometer and comparing these results for Cs⁺ ions with those of negative ions in oxygen (Elford and Gump 1971) with those of Elford, Voss, and Scheinman et al. (1971). It was found that the values of \( \frac{E}{N} \) for Cs⁺ ions were slightly lower in agreement with the values obtained for negative ions, as are listed in Table 3.3. A Cs⁺ ion source was connected to the drift tube and the ion source was located on the side of the drift tube. The ion source was used to measure the temperature of the gas. The structure was the same as that used in the experiment with Cs⁺ ions in He. The inner diameter of the drift tube was 19 cm and the drift distance was 295 cm ± 0.1 cm. A more detailed description of the experiment will be given by Gump and Elford (1973).

### Fig. 5.16

- 1.68 torr
- 2.41
- 3.69
- 5.05
- 9.37
- 18.7
- 37.5

#### E/N (Td)

\( \kappa (\text{cm}^2 \text{v}^{-1} \text{s}^{-1}) \)

\( \text{Cs}^+ \text{ in He} \)
5.6.2.1 Experimental errors

The sources of error in the measurements are identical with those outlined in Table 5.3.

5.6.3 The reduced mobility of $K^+$ ions in oxygen

The reduced zero field mobility of $K^+$ ions in oxygen was measured to assist Elford and Rees compare their results for the mobilities of negative ions in oxygen (Elford and Rees 1973) with those of Snuggs, Volz, Schummers et al. (1971). It was found that the value of $\kappa_0$, $2.69 \pm 0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was in excellent agreement with the value of $2.68 \pm 0.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ obtained by Snuggs. The data are listed in Table D.5.

5.7 50CM DRIFT TUBE. SYSTEM C

A 50 cm tube was constructed to enable accurate values of electron and ion transport coefficients to be made at low values of E/N. It was used in this work to investigate the phenomena observed by Elford (1971). A photograph of this tube is shown in Fig. 5.17. A bell jar is used as a vacuum envelope for this tube and the vacuum seals at the base and at the filament are made with Apiezon W40 wax. The tube was connected to the vacuum system shown in Fig. 5.6.

Two copper constantan thermocouples attached to the electrodes beneath the top shutter and above the bottom shutter were used to measure the temperature of the gas. The shutters are the same as those used in System B. The inner diameter of the guard rings is 10 cm and the drift distance is $49.995 \text{ cm} \pm 0.01\%$. A more detailed description of the apparatus will be given by Crompton and Elford (1973).

5.8 RESULTS TAKEN WITH SYSTEM C

5.8.1 The reduced mobility of $K^+$ ions in hydrogen

The reduced mobility of $K^+$ ions in hydrogen was measured in the range $0.5 \leq E/N(Td) \leq 7.0$ and at pressures between 1.03 and 37.4 torr. These data are listed in italics in Table D.3 and are discussed fully in Chapter 6. It is estimated that the total uncertainty in the data is $\pm 1.0\%$. 
CHAPTER 6

PRESSURE DEPENDENCE AND END EFFECTS IN PRECISION ION MOBILITY STUDIES

6.1 STATEMENT OF PROBLEM

All theoretical treatments based on the form of the Boltzmann equation given by equation 2.3.6 predict that the reduced mobility is a function of \( E \) and \( N \) only in the combination \( E/N \). This is a result of the assumptions that only two-body collisions occur and that collision times are negligibly small compared with the time between collisions. The first experimental evidence that these assumptions may not be valid in ion mobility experiments at gas pressures of a few torr was published in 1971 when Elford reported measurements of the reduced mobility of potassium ions in various gases in which a small dependence of the reduced mobility on gas pressure was observed. It was found that the magnitude of the pressure dependence was similar for all gases but that the pressure dependence in nitrogen was of a different form from the dependence in the other gases, helium, neon, argon and hydrogen. Elford also found that at low values of \( E/N \), where the ion motion is dominated by the thermal motion of the neutral particles and is influenced only slightly by the presence of the electric field, the measured values of the reduced mobility did not become independent of \( E/N \) as expected from theory. Instead it was found that the reduced mobility increased as \( E/N \) decreased. This phenomenon is referred to as upcurving in this thesis.

Elford carried out various experimental tests to determine the cause of the pressure dependence and upcurving. Three drift tubes with widely varying dimensions were used and experimental parameters such as the amplitude of the signal applied to the shutters and the magnitude of the current in the tube were varied by large amounts. However, it was concluded that there was no significant dependence of the reduced mobility on any of these parameters. Elford could also find no evidence that the effects were due to the formation of stable ion-atom clusters.

6.1.1 Gatland's explanation

Gatland (1972a) has proposed an explanation of the pressure dependence and upcurving in terms of non-equilibrium clustering reactions and a correction to the measured mobility data which arises from the
diffusion of the ions in the direction of the electric field. This explanation was based on the results of Thomson et al. (1972) who observed ion-neutral clusters with $K^+$ ions in $CO_2$, $NO$, $CO$, $N_2$, $O_2$, $D_2$, $Ar$, $Ne$ and $He$. It seems probable, however, that many of the clusters observed by Thomson et al. may have been produced not in the drift tube but in the jet of isentropically cooled gas escaping from the hole used to sample the ions. Evidence for this conclusion is given in Chapter 10. Thomson et al. did not show that the abundance of the clustered ion depends on the drift time. However, even without any additional evidence it can be shown that Gatland's proposals do not explain the pressure dependence, although the upcurving effects may partly be due to diffusion errors. It was pointed out in section 4.2.1 that the magnitude of the diffusion correction is not known with any certainty and for this reason it is not possible to determine to what extent diffusion effects contribute to the phenomenon of upcurving.

One of the assumptions made by Gatland is that non-equilibrium ion-molecule reactions take place in the space between the shutters. This would give rise to asymmetrical peaks in the current-frequency spectrum unless the drift velocities of the parent and product ions were identical. A typical current-frequency spectrum taken at a pressure in the range where the reduced mobility is pressure dependent, has already been shown in Fig. 4.2. Close examination of the peaks in this figure indicate that there are no anomalous asymmetries. Another assumption made by Gatland is that no ions are clustered by the time they reach the first shutter. If ion-molecule reactions were responsible for the effects then, since the value of $E/N$ and $N$ was constant in Elford's experiments for at least 1 cm before the first shutter, the reaction frequencies would have been the same before and after the first shutter. Using Gatland's assumed figures for the reaction rates it can be shown that for $K^+$ ions in argon at a pressure of 0.937 torr and $E/N = 5.66$ Td, the relative abundance of the clustered ions at the first shutter is within 10% of the equilibrium value. At higher pressures the approach to equilibrium will be even closer. Thus as Gatland has neglected the possibility of ion-molecule reactions occurring before the first shutter the comparison between his predicted mobilities and Elford's measured mobilities is invalid.
The remainder of this chapter describes the results of an experimental investigation into the effects reported by Elford. It is shown that except for the case of potassium ions in nitrogen the results cannot be explained by the formation of stable clusters. It is also shown that the upcurving effects are due to end effects at the shutters caused at least partly by the action of alkali ions on the gold coated shutter wires. An explanation for the pressure dependence is proposed.

6.2 **UPCURVING**

To determine whether upcurving was a fundamental property of the ion motion or was due to an unknown experimental error, the reduced mobility of $K^+$ ions in various gases was measured at two different drift distances in the same tube. In this way an accurate comparison between the results of the two drift distances could be made as most of the experimental parameters remained constant during the course of the experiment. To do this the drift section of System A (see section 5.3) was placed in a stainless steel manifold and connected to the vacuum system shown in Fig. 5.6. The current was collected by a metal plate which was supported beneath the bottom shutter. The mobility values taken with the two shutters nearest the filament were compared with the results taken with the two lower shutters and in this way two drift distances varying by a factor of 3.1 were obtained.

A typical set of results is shown in Fig. 6.1 where the measured reduced mobility of potassium ions in hydrogen at a pressure of 9.37 torr is plotted as a function of $E/N$ for the two drift distances. It can be seen that the upcurving in both sets of results differ by a factor of about two whereas the drift distances are a factor of three different. If it is assumed that the potential difference between the planes of the shutters is 350 mV larger than the applied potential difference between the top two shutters and 200 mV larger in the case of the bottom two shutters, the corrected data (shown by crosses in Fig. 6.1) are independent of $E/N$ and show no significant dependence on the drift distance. It was found that a similar procedure could be used to correct other sets of data but that in general the magnitude of the correction factor depended on the gas pressure and on the nature of the gas. Thus upcurving alone can cause a dependence of the measured reduced mobility on pressure and
Fig. 6.1.

$\kappa^+ \text{ in } H_2$

- $9.076 \text{ cm}$
- $2.965 \text{ cm}$
it is pointed out later in this chapter that part of the pressure dependence observed by Elford (1971) was caused by this effect. The residual pressure dependence, that is the pressure dependence which remains after the data have been corrected to remove upcurving, is discussed in section 6.3.

It was concluded from this investigation that upcurving is due to anomalous effects at the shutters. In an attempt to understand and remove these effects two further investigations were carried out. One of these was a study of the effects of bombarding low energy potassium ions onto various metal surfaces and the other investigation involved the use of the 50 cm drift tube (System C). These investigations will now be described in more detail.

6.2.1 Investigation of surface effects

The surface effects were studied by measuring the change in contact potential difference between a probe and a metal surface after the surface had been bombarded with charged particles. Details of the apparatus and method are given in Appendix H.

It was found that if low energy (< 13 eV) K\(^+\) ions were collected on either gold, copper, aluminium or stainless steel surfaces the surface potential of the metal increased positively. It was not possible to make a quantitative comparison between the magnitude of the effects on different metals, but qualitatively the effects were the same for each surface. In view of this it seems unlikely that the upcurving problems could be eliminated by using different shutter materials. The results of a typical experiment are shown in Fig. 6.2 where the potential difference between the probe and a gold surface is plotted as a function of time. The charge collected at each bombardment is shown on the figure together with the accelerating voltages. It can clearly be seen that although the surface potential initially decreased with time after the filament was switched off, the potential did not return to the level prior to the first bombardment. This characteristic is consistent with upcurving. Apart from one experiment all the potassium ion work was carried out in vacuum. The exception was one of the runs shown in Fig. 6.2 in which 5 torr of hydrogen was admitted into the apparatus. The hydrogen neither affected the decay rate nor the charge up characteristics of the surface. This experiment also
showed that ions of near thermal energies were as effective in changing the surface properties as ions of a few electron volts energy.

Similar experiments were carried out with electrons and these are discussed in Appendix H. Certain metal surfaces were found to charge positively when bombarded with electrons.

The effect which causes the time dependence of the patch potential has not been observed in ion mobility experiments using freshly gilded shutters. However, time dependence of the mobility of potassium ions was once observed using shutters which had been used for many months after they had been gilded. It seems more likely that the effect which causes a permanent change of the equilibrium potential of the surface after bombardment is connected with the upcurving effects. Although the exact mechanism of this change is unknown, the presence of contaminant hydrocarbon molecules on the metal surfaces is thought to be a contributing factor (Petit-Clerc and Carette 1968). It can be concluded from this work that anomalous changes in surface potentials can occur when ions are collected by nominally clean metal surfaces and that the magnitude of these effects are quite consistent with the upcurving effects.

6.2.2 Experiments with the 50 cm tube

The construction of the 50 cm drift tube made it possible to investigate upcurving at sufficiently low values of E/N that the intrinsic dependence of the reduced mobility on E/N could be neglected. Before the tube was assembled the shutters, which had previously been used for ion mobility work with another tube, were sandblasted to remove all traces of alkali ions and then the wires (nichrome) were coated first with copper and then with gold.

At pressures greater than about 4 torr, no upcurving was observed in the initial results. This is shown in Fig. 6.3 in which the reduced mobility of potassium ions in hydrogen at a pressure of 5.1 torr is plotted as a function of E/N. The initial results (triangles) were confirmed by quickly repeating the measurements in another sample of gas (squares). However, after measurements had been taken for about six hours upcurving was observed (circles in Fig. 6.3). The magnitude of the upcurving then remained constant to within ± 0.05% for a period of several days and it was not until the tube had been used for several weeks that a significant increase in the magnitude of the upcurving was observed.
$k^+$ in $H_2$

Elford (1971)

corrected data

Fig. 6.3.
At this time the shutter nearest the filament was cleaned by sandblasting and regilded and the first results taken after the cleaning operation again showed no upcurving effects.

The 5.1 torr results of Elford (1971) are also shown in Fig. 6.3. It can be seen that when a correction of 90 mV is applied to his data to remove the upcurving the estimated zero field reduced mobility is less than 0.1% lower than the results of this work.

At pressures lower than about 4 torr upcurving was observed even with clean shutters but this has not been investigated further.

It was concluded from the results summarized in this section that the upcurving effects observed by Elford (1971) and also observed in this work are at least partly caused by the presence of potassium ions on the shutter wires but it also seems likely that the presence of contaminant hydrocarbon molecules is a contributing factor. Only one method of removing the effect proved successful but as this only appeared to be effective at pressures greater than about 4 torr and involved dismantling the drift tube to clean the shutter it is obviously impractical. An alternative method of overcoming the problem would be to use Tyndall-Powell shutters. If these shutter systems were used a large percentage of the ions would be collected by the top gauze of the shutter nearest the filament and even if the surface potential of this gauze increased by several hundred millivolts the ions in the drift space would not be significantly affected.

6.3 PRESSURE DEPENDENCE OF REDUCED MOBILITY

The variation of the reduced mobility of $K^+$ ions in various gases was studied over as large a pressure range as possible while still maintaining sufficient accuracy to allow useful conclusions to be drawn. Particular emphasis was placed on taking results at low values of $E/N$ in order to obtain the zero field reduced mobility as this quantity can be studied over the largest range of pressures; at high pressures the onset of electrical breakdown in the gas restricts the useful $E/N$ range. The 3 cm and 50 cm drift tubes were used in these experiments. Before the investigations began the shutters were regilded and the equipment checked by measuring the drift velocity of electrons in hydrogen at several values of $E/N$. The electron data agreed to within ± 0.1% with the standard values (Elford and Robertson 1973).
The results for the reduced mobility of K⁺ ions in helium, argon and hydrogen have been briefly discussed in sections 5.6.1 and 5.8.1 and are tabulated in Appendix D. The low pressure limit to the data was determined by two factors, the increasing error in the pressure measurement as the pressure was reduced and the difficulty in estimating the zero field reduced mobility from results which not only exhibited upcurving but also a small intrinsic variation of χ with E/N. The second of these factors was unimportant when the 50 cm tube was used and for this reason lower pressures were used with this tube. At high gas pressures it was necessary to use low E/N values, and at the low chopping frequencies required the amplitude of the sine wave signal applied to the shutters varied with frequency. This made it difficult to measure the effective transit time to better than ± 0.1% and introduced upper pressure limits of approximately 38 torr with the 50 cm tube and 200 torr with the 3 cm tube.

As a result of the investigation into the cause of upcurving the following procedure was developed to estimate the zero field reduced mobilities from the experimental data. At pressures greater than approximately 40 torr it was not possible to use values of E/N greater than 3 Td. The intrinsic variation of χ with E/N could therefore be neglected at these pressures and the zero field reduced mobility was taken to be the value of χ measured at the highest value of E/N used. It is estimated that a maximum error of ± 0.1% was introduced by upcurving at these pressures. At lower pressures it was more difficult to estimate χ₀ not only because of upcurving but also because the intrinsic variation of χ with E/N had to be considered. It is estimated that these factors introduced a maximum error of ± 0.2% in the determination of χ₀.

The estimated values of χ₀ for potassium ions in helium, argon and hydrogen are plotted as a function of pressure in Figs. 6.4, 6.5 and 6.6 respectively. Many of the data points represent the average of the results taken with several gas samples. In order to determine the error in the magnitude of the pressure dependence it is only necessary to consider the random errors and these are listed in Table 6.1.
Fig. 6.4.  

\[ k^+ \text{ in He} \]

\[ \kappa_0 \text{ (cm}^2\text{V}^{-1}\text{s}^{-1}) \]

\[ P_{273.2} \text{ (torr)} \]

Fig. 6.5.  

\[ k^+ \text{ in Ar} \]

\[ \kappa_0 \text{ (cm}^2\text{V}^{-1}\text{s}^{-1}) \]

\[ P_{273.2} \text{ (torr)} \]

Fig. 6.6.  

\[ k^+ \text{ in H}_2 \]

\[ \kappa_0 \text{ (cm}^2\text{V}^{-1}\text{s}^{-1}) \]

\[ P_{273.2} \text{ (torr)} \]
Table 6.1

Random errors in determination of $\kappa_o$

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Magnitude of error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 cm tube</td>
</tr>
<tr>
<td>p.d. between shutters</td>
<td>0.01</td>
</tr>
<tr>
<td>Pressure</td>
<td>0.25/p (torr)</td>
</tr>
<tr>
<td>Estimation of $\kappa_o$ from data</td>
<td>0.2 (p &lt; 40 torr)</td>
</tr>
<tr>
<td></td>
<td>0.1 (p &gt; 40 torr)</td>
</tr>
<tr>
<td>Effective transit time</td>
<td>0.1</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.2</td>
</tr>
</tbody>
</table>

It can be seen from this table that the maximum random error on any single data point was usually greater than about ± 0.3%. It was found in practice, however, that even at the lowest pressures the scatter in the measurements with different gas samples was always less than ± 0.15%. For this reason the error bars on the data in Figs. 6.4, 6.5 and 6.6 were determined by adding ± 0.1% to the errors involved in estimating $\kappa_o$ from the data. However, as the scatter about the line of best fit in each of these figures is in general less than ± 0.1% it would appear that the error estimates are conservative. The largest pressure dependence is observed in argon - 1.3% between 5 and 183 torr. Elford (1971) reported the magnitude of the pressure dependence to be somewhat larger than that concluded from this investigation as no corrections for upcurving were applied in the earlier work.

Several experimental tests were carried out to ensure that the pressure dependence was not due to an experimental error.

6.3.1 Experimental tests

To investigate the possibility that the residual pressure dependence shown in Figs. 6.4, 6.5 and 6.6 is due to an error of the type which causes upcurving the zero field reduced mobility of potassium ions in hydrogen was measured as a function of drift distance by comparing the results taken with the 3 cm tube with those taken with the 50 cm tube. It can be seen from Fig. 6.6 that in the region of overlap (5-38 torr) there is no significant difference between the 50 cm tube results (triangles).
and the 3 cm tube results (squares). Also as the magnitude of the pressure dependence was the same both before and after upcurving was observed there is no evidence to suggest that the pressure dependence is due to an end effect.

Additional checks included varying the ion current, the collector geometry and the time-of-flight of the ions before the first shutter, but neither these nor the tests outlined in section 5.2 gave any indication of error. The possibility that the pressure dependence is due to an error in the calibration of the pressure gauge was discounted as the magnitude, and to a lesser extent the form, of the pressure dependence varies from gas to gas.

As there was no evidence to suggest that the residual pressure dependence is due to an experimental error an explanation of the effect was sought in terms of the fundamental properties of the ion motion.

6.3.2 Fundamental property of ion motion

In all ion mobility theories it is assumed that the collisions take place in times negligibly small compared with the time between collisions. It is postulated that the pressure dependence is caused by the breakdown of this assumption and that ion-neutral complexes are formed with lifetimes comparable with the mean time between collisions. Similar complexes have been frequently discussed in relation to neutral-neutral scattering phenomena. For example, Roberts et al. (1969) have based a successful theory of termolecular recombination on neutral-neutral complexes. Before it is shown how this hypothesis can explain the observed pressure dependence the formation of ion-atom complexes will be briefly discussed.

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

\[
V_{\text{eff}}(r,J) = V(r) + \frac{J^2}{(2\mu r^2)} ,
\]

where \(V(r)\) is the interaction potential of the ion and atom and \(J\) is the angular momentum in the centre of mass frame. A typical form of the effective potential is shown in Fig. 6.7. A maximum can occur for certain
values of $\theta$ when the energy of relative motion, $E$, is less than $E_c$, the critical energy. At values of $E > E_c$ there can be no maxima in the effective potential curve. If the collision dynamics are such that the energy of relative motion is approximately equal to the height of the centrifugal barrier (i.e., $V_{max}$). In Fig. 6.7 then in a classical description of the collision the time is long. In the limiting case when $E = V_{max}$, the collision time is infinite.

In a quantum mechanical description of an ion-stone collision there may be a number of accessible energy levels in the well of the effective potential and it is necessary to take into account tunnelling through the centrifugal barrier. These energy states are known as orbiting resonances and have associated with them lifetimes, $\tau$, which are related to the energy levels $E_n$ of the states, $\gamma$, by $1 = E_n \gamma$. The widths of the states can be calculated from $\Gamma$ by the relation,

$$\Gamma = 4\hbar^2 \kappa^2 / 4132 \text{eV}$$

where $\kappa$ is the angular momentum quantum number.

As far as is known the only published data for ion-surface collision lifetimes are the classical calculations of Miller, Nisbet and Searle (1968). However as Miller has pointed out the time spent by ions inside the radius $r_c$ his estimates are probably low. Robma (private communication) removes this restriction but found that classically an insignificant number of ions had collision times greater than $10^{-1} \text{s}$ for a thermal energy swarm. Thus, as the lifetime for ion-stone complexes would have to be comparable with the mean free time between collisions, it was concluded that a classical description was inadequate.

A quantum mechanical calculation of the collision lifetimes for the K'-Ar combination has recently been performed by Watts and Iford (1973). In this work the phase shifts were calculated in the manner described in section 2.2 and it was found that there were about 100 resonances in the energy range 10-50 meV with lifetimes between $10^{-11}$ and $10^{-7}$s. Unfortunately the mean collision time for a thermal energy swarm cannot be calculated from Watts' data as the probability of an ion
values of $J$ when the energy of relative motion, $\varepsilon$, is less than $\varepsilon_{c}$, the critical energy. At values of $\varepsilon > \varepsilon_{c}$ there can be no maximum in the effective potential curve. If the collision dynamics are such that the energy of relative motion is approximately equal to the height of the centrifugal barrier (i.e. $V_{\text{max}}$ in Fig. 6.7) then in a classical description of the motion the particles spiral about each other and the collision time is long. In the limiting case when $\varepsilon = V_{\text{max}}$, the collision time is infinite.

In a quantum mechanical description of an ion-atom collision there may be a number of allowable energy levels in the well of the effective potential and it is necessary to take into account tunnelling through the centrifugal barrier. These energy states are known as orbiting resonances and have associated with them lifetimes, $\Gamma$, which are related to the energy widths of the states, $\Gamma$, by $\Gamma = h/\Gamma$. The widths of the states can be obtained from the phase shifts $\eta_{\lambda}$ by the relation,

$$\left(\frac{3\eta_{\lambda}}{\delta \varepsilon}\right)_{\text{max}} = \frac{2}{\Gamma},$$

where $\lambda$ is the angular momentum quantum number.

As far as is known the only published data for ion-atom collision times are the classical calculations of Miller, Moseley et al. (1968). However as Miller only considered the time spent by ions inside the radius $r_{c}$ his estimates are probably low. Robson (private communication) removed this restriction but found that classically an insignificant number of ions had collision times greater than $10^{-11}$ s for a thermal energy swarm. Thus, as the lifetimes of ion-atom complexes would have to be comparable with the mean free time between collisions to significantly affect the mobility, it was concluded that a classical description was inadequate.

A quantum mechanical calculation of the collision lifetimes for the K$^+$-Ar combination has recently been performed by Watts and Elford (1973). In this work the phase shifts were calculated in the manner described in section 2.2 and it was found that there were about 100 resonances in the energy range 10-50 meV with lifetimes between $10^{-10}$ and $10^{-7}$ s. Unfortunately the mean collision time for a thermal energy swarm cannot be calculated from Watts' data as the probability of an ion
penetrating the centrifugal barrier to form an orbiting resonance has not been determined. However, Watts' calculations do show that there are several ion-atom complexes with life-times comparable with the mean free time between collisions at pressures of a few torr. This is consistent with the earlier work of Dickenson and Dalgarno (quoted as private communication by McDaniel et al. 1970). Catlow et al. (1970) only considered the effect of resonances on the momentum transfer cross section and took no account of the time spent by the ions in the resonant states.

In the remaining part of this section it will be shown how the pressure dependence of the reduced mobility can be explained in terms of the formation of ion-atom complexes in orbiting resonant states. As there have been no theoretical estimates of average collision lifetimes these will be treated as adjustable parameters.

The formation and properties of ion atom complexes may be described by the following rate equations,

\[ \frac{k_{10}}{k_{01}} X^+ + Y \rightarrow (X^+.Y)^* \]

6.3.2.

and

\[ \frac{k_{21}}{k_{12}} (X^+.Y)^* + Y \rightarrow X^+ + Y + Y \]

6.3.3.

where \( X^+ \) is an ion, \( Y \) is a neutral particle, \( (X^+.Y)^* \) is an ion neutral complex and \( k \) is a reaction rate. Since the pressure dependence is independent of drift distance the reactions 6.3.2 and 6.3.3 must be in equilibrium and the principle of microscopic reversibility satisfied (Klots 1970). For this reason the true three body rate constant \( k_{12} \) is included for completeness in the analysis although it will later be assumed to be vanishingly small. The ratio of the abundances of the parent ions and the ion-neutral complexes is given by,

\[ \frac{[X^+]}{[X^+.Y]^*] = \frac{(k_{01} + k_{21}N)/(k_{12}N^2 + k_{10}N)}{1 + (k_{01}/k_{10})} \]

6.3.4.
If the reduced mobilities of $X^+$ and $(X^+.Y)^*$ are given by $\kappa_1$ and $\kappa_2$ the apparent or measured mobility can be written

$$
\kappa_m = \frac{\kappa_1 [X^+] + \kappa_2 [(X^+.Y)^*]}{[X^+] + [(X^+.Y)^*]}
$$

6.3.5.

The general form of equation 6.3.6 is shown in Fig. 6.8. In region A of Fig. 6.8 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 $\tau$ to be comparable with the mean free time between collisions and the time spent by $X^+$ in the heavier complex is now no longer negligible. Thus the measured reduced mobility decreases.

Region C corresponds to conditions in which $\tau$ is now greater than the mean free time between collisions. Each complex is broken up by collision with a neutral particle and the spontaneous break-up of a complex becomes a very unlikely event. The two dominant reactions are the formation and break up 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

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

6.3.7.
Fig. 6.8.
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.

It is possible to fit the measured variation of $k_0$ with pressure for $K^+$ ions in He, Ar and $H_2$ with a curve of the form of equation 6.3.6. by adjusting the various rate constants. The calculated curves, as shown by the continuous lines in Figs. 6.4, 6.5 and 6.6 are consistent with the experimental data to within the scatter in the measurements. The values of the parameters used to obtain the fits are given in Table 6.2. 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 and Elford. The only parameter which can be determined with reasonable accuracy by this fitting procedure is $K_1$, the reduced mobility of the ion in the zero pressure, or Boltzmann limit. It is not possible to vary $K_1$ by more than ± 0.2% and still fit the data to within the scatter on the measurements. The other rate constants cannot be uniquely determined.

<table>
<thead>
<tr>
<th>$K_1$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>He</th>
<th>Ar</th>
<th>$H_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2$ (cm$^2$V$^{-1}$s$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_0$ (cm$^3$s$^{-1}$)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$k_{12}$ (cm$^6$s$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{21}$ (cm$^3$s$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Although there is excellent agreement between the experimental results and the theoretical predictions of equation 6.3.6 the following doubts about this explanation of the pressure dependence remain.

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

(2) It might be expected that the pressure region in which the effect is observed might vary more from gas to gas,
that is one might expect the factor $\tau k_{10}$ (which controls the position of region B in Fig. 6.8) 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. 6.8 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 clearly be seen from Figs. 6.4, 6.5 and 6.6 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 accuracies of about ±0.1% are required and a shorter drift tube would be required 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 would become a limiting factor at higher pressures.

Unfortunately, there is no known way of observing the ion-atom complexes directly. The possibility of using both mass spectrometer and ion cyclotron resonance techniques were investigated but both are unsuitable for measuring species with lifetimes of this order. Finally, it is worth noting that it cannot be determined whether the effects described in this section are due to an intrinsic pressure dependence or to an intrinsic dependence on the electric field. However, field dependence was thought to be unlikely as the polarization force induced by the ion is very much greater than that induced by the drift field even at ion-atom separations of about 100Å.

In the analysis developed in this section it has been assumed that the complexes are not stabilized by reactions of the type,

$$(X^+Y)^* + Y \rightarrow X^+Y + Y$$  \hspace{1cm} 6.3.8.$$

that is stable clusters are not formed. The formation of clusters will be fully discussed in Chapter 10. It has already been shown that non-equilibrium clustering cannot explain the pressure dependence but an explanation based on clustering reactions in equilibrium must also be
considered as many of the characteristics of the effect are consistent with such an explanation. For example the symmetrical peak shapes and the independence of the results on drift distance are both consistent with equilibrium clustering reactions. On the other hand there are two objections to this explanation. The first of these is that there was no evidence from experiments with the quadrupole mass spectrometer incorporated in System A that potassium ions cluster to a significant extent at room temperature to atoms of He or Ar or to H\textsubscript{2} molecules. A fuller discussion of this point is given in Chapter 10. The second argument against an explanation in terms of equilibrium clustering is that the pressure dependence, particularly in Ar, is too small. If a stable cluster was formed it would seem most unlikely that the mobility of the cluster would only be about 1-2\% smaller than the mobility of the parent ion.

It is of interest to note, however, that the pressure dependence of K\textsuperscript{+} ions in N\textsubscript{2} is probably due to the formation of the stable cluster K\textsuperscript{+}.N\textsubscript{2} (see Chapter 10).
CHAPTER 7

DETERMINATION OF INTERACTION POTENTIALS BY ANALYTICAL TECHNIQUES

One of the main objectives of a study of the motion of ions in gases is to determine the force between an ion and an atom as a function of particle separation. To determine this force with swarm methods it is necessary to use iterative fitting techniques in which the interaction potential is adjusted until there is good agreement between the transport coefficients measured experimentally and those predicted theoretically.

The principle of the iterative fitting technique will be described with the aid of Fig. 7.1, where the interaction potential is plotted as a function of particle separation for a typical ion-atom combination. An assumed distribution of $r_0$ (the distance of closest approach in an ion-atom collision) in a swarm is also shown in Fig. 7.1 and it will be assumed for the purposes of this discussion that the form of the distribution of $r_0$ is independent of $E/N$ and $T$. As the mean energy of the ions in a swarm is varied the position of the average distance of closest approach ($r_{av}$ in Fig. 7.1) moves along the abscissa. At high mean energies the repulsive forces play a dominant part in determining the ion motion and at low energies the collisions are dominated by the attractive polarization force. Thus by varying the experimental parameters $E/N$ or $T$ the ion-atom forces can be determined as a function of particle separation. If data could be obtained with zero error it would seem likely that only two experimental points would be required to determine the entire interaction potential but in practice the range of ion-atom separations which can be examined depends on the range of $E/N$ and $T$ for which there is data available and also on the accuracy of the data.

There are two ways in which the ion transport coefficients can be calculated as a function of $E/N$ and $T$ from a knowledge of the interaction potential. First, the motion of the ions can be simulated with the aid of a large computer. This approach, which has been used by Skullerud (1973b) (see also section 2.5) to study potassium ions in argon, has the advantage that it is not restricted to low values of $E/N$ and in fact for a given amount of computer time the accuracy increases with increasing $E/N$. The second approach is based on the analytical work of either
Interaction Potential

Fig. 7.1.

typical distribution of $r_0$ in a swarm

Internuclear Spacing

The form of the interaction potential used by Reibens and Kamar can be written:

$$V(r) = \frac{1}{2} \left( 1 - 4\gamma(r) - (1-\gamma)^2 \right) ,$$

where $r$ is the depth of the potential well, and $\gamma(r)$ is the position of the minimum for a given $r$ value. $0 < \gamma < 1$ determines the relative weight of the $-4\gamma(r)$ and $-1$ terms.

For other potentials, the abscissa are not strictly different free $\gamma$ and $\gamma'$. The coefficients of the dipole polarization term can be written in terms of the position, $\gamma$, an experimentally known quantity, in the following way:

$$\frac{\partial \gamma}{\partial \tau} = \frac{1}{2} \left( 1 - 4\gamma - (1-\gamma)^2 \right) .$$

Interaction Potential

Potential

Fig. 7.1.
Kihara (1953) or Kumar (1967) and has been described in section 2.4. The analytical approaches are restricted to a relatively small range of E/N values as the velocity distribution function of the ions is assumed to be only slightly perturbed from the zero-field Maxwellian distribution. It follows that even with extremely accurate data the interaction potential can only be determined over a small range of particle separations.

The technique of fitting to the measured variation of $\kappa$ with E/N has been used by Creaser (1969) and Robson and Kumar (1973) but no attempts have been made to estimate the range of ion-atom separations for which the derived potential is accurate. It was also assumed in the fitting procedure that there were negligible errors associated with the curve of best fit to the experimental data and no estimates of accuracy of the derived potential were made. However, Robson and Kumar (1973) do point out in their paper that a study of the accuracy of the technique is necessary and the work reported in this chapter was carried out for this reason. The computer programmes used in this work were those of Robson and required only trivial modifications

7.1 THE EFFECT ON THE TRANSPORT COEFFICIENTS OF VARYING THE POTENTIAL PARAMETERS

The form of the interaction potential used by Robson and Kumar can be written,

$$V(r) = \frac{\epsilon}{2} \left[ (1+\gamma) \left(\frac{r_m}{r}\right)^2 - 4\gamma \left(\frac{r_m}{r}\right)^6 - 3(1-\gamma) \left(\frac{r_m}{r}\right)^4 \right],$$

where $\epsilon$ is the depth of the potential minimum for a 12-6-4 potential, $r_m$ is the position of the minimum for a 12-6-4 potential and $\gamma$, where $0 \leq \gamma < 1$ determines the relative strength of the $r^{-6}$ and $r^{-4}$ terms. Mason and Schamp (1958) suggested this form of the potential with N = 6. For other values of N the depth and position of the minimum are not greatly different from $\epsilon$ and $r_m$. The coefficient of the dipole polarization term can be written in terms of the polarizability, $\alpha$, an experimentally known quantity, in the following way,

$$3\epsilon(r_m^{4}(1-\gamma) = e^2\alpha.$$

7.1.2.
Mason and Schamp suggested that one further restriction on the parameters could be imposed; they stated that \( \gamma \) could be estimated from a consideration of the \( r^{-6} \) potential assuming that both the ion and the atom could be treated as point masses. The contributions to the \( r^{-6} \) term in the interaction potential have been discussed in Chapter 2. However, Skullerud (1973b) has pointed out that this is an invalid procedure as at ion-atom separations where the \( r^{-6} \) term is significant the dimensions of the particles are comparable with their separation.

It is difficult to determine the effect on a transport coefficient of the variation of a particular potential parameter as at least two parameters must be varied if equation 7.1.2 is to be satisfied. However, it can be seen from equation 7.1.2 that the interaction potential is more sensitive to some parameters than others. For example, if \( \varepsilon \) is varied by \( x \% \) and \( \gamma \) is held constant, \( r_m \) need only be varied by \( \frac{x}{\gamma} \% \) to satisfy the polarizability restriction. Using this feature of the sensitivity of the parameters it was possible to estimate the effect on the transport coefficients of varying \( \varepsilon \) and \( \gamma \). The effect on the mobility of varying \( \varepsilon \), holding \( \gamma \) constant and varying \( r_m \) by a small amount is shown in Fig. 7.2. The continuous curve is the estimated line of best fit to the data for the reduced mobility of \( \text{Cs}^+ \) in Ne. The broken lines in Fig. 7.2 illustrate the effect of varying \( \varepsilon \) by \( \pm 1 \) mV from the line of best fit. A 12-6-4 potential and a value of \( \gamma \) equal to 0.444 was used for each curve. It can be seen that to a first approximation varying \( \varepsilon \) changes the position of the hump in the mobility-E/N curve. As \( \varepsilon \) is increased the mobility maximum is situated at higher E/N values.

The effect of varying \( \gamma \), holding \( \varepsilon \) constant and varying \( r_m \) to satisfy equation 7.1.2 is shown in Fig. 7.3. The continuous curve is again the curve of best fit to the experimental data. The broken curves illustrate the effect of varying \( \gamma \) by \( \pm 0.2\% \) from the best fit condition. The effect of changing \( \gamma \) is therefore to vary the height of the mobility maximum above the polarization limit.

Robson and Kumar (1973) came to significantly different conclusions about the effects of varying the potential parameters as they varied each parameter independently and did not enforce the polarization restriction.
It can be concluded from Figs. 7.2 and 7.3 that the potential parameters given in this chapter that give the best fit to the available experimental data for Cs⁺ in Ne are:

- $\gamma = 0.444$
- $\varepsilon = 26$ mV

and no attempt has been made to estimate the errors in the potential parameters associated with the uncertainties in the experimental data.

7.2.1 Potassium ions in halides

It will be shown in this chapter that it is not possible to obtain accurate potential parameters with such data, and so the accuracy of the potential parameters associated with the errors in the experimental data is not known.

7.2.2 Potassium ions in air

The experimental data obtained with a 12-6-4 potential, such as shown in Fig. 7.4, is also not accurate enough to be an adequate fit. The best fit obtained with an 12-6-4 potential, which cannot be distinguished from the figure, is given by $E/N = 15$ Td.

The data were also fitted with a 12-6-4 potential and the calculated variation of $\varepsilon$ with $E/N$ for each value of $\gamma$ could not be distinguished from the lines of best fit. Hence the experimental data in these three potentials are plotted in Fig. 7.4 and it can be seen that the wall positions of the minima are such as to be much less long than the experimental data used to be much less long.

The case of potassium ions in air is similar. The above illustrations do not lead to the potentials accurately the errors in the experimental data used to be much less long.
It can be concluded from Figs. 7.2 and 7.3 that the following parameters for a 12-6-4 potential give the best fit to the available data for Cs⁺ in Ne,

\[\varepsilon = 27 \text{ mV}\]
\[\gamma = 0.444\]
\[r_m = 3.370 \text{ Å}\]

However, as pointed out earlier in this chapter the range of ion-atom separations for which this potential is accurate is not known and no attempt has been made to estimate the errors in the potential parameters associated with uncertainties in the line of best fit.

7.2 ACCURACY OF THE DERIVED POTENTIAL

It will be shown by means of two examples that it is not possible to obtain accurate potential parameters using Kumar and Robson's theory with even the most accurate experimental data available at the present time.

7.2.1 Potassium ions in helium

It will be assumed for the purposes of this discussion that the curve of best fit to the experimental data for the reduced mobility of potassium ions in helium (see Chapter 6) is everywhere accurate to ± 0.3%. This curve is shown as a continuous line in Fig. 7.4. The best fit to the experimental data obtained with a 12-6-4 potential, as shown in Fig. 7.4 lies everywhere within the experimental error and thus can be said to be an adequate fit. The best fit obtained with an 8-6-4 potential, which cannot be distinguished on the figure from the 12-6-4 curve at E/N < 15 Td, is also an adequate fit. The data were also fitted with a 16-6-4 potential and the calculated variation of \(\kappa\) with E/N for this potential cannot be distinguished from the line of best fit to the experimental data. These three potentials are plotted in Fig. 7.5 and it can be seen that the well depths vary by as much as 80% and the positions of the minima by as much as 20%. Thus in order to determine the potential accurately the errors in the experimental data would need to be much less than 0.3%.

7.2.2 Potassium ions in argon

The case of potassium ions in argon clearly illustrates the errors which can be introduced by attempting to predict the short range
Fig. 7.4.

$\kappa (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$

- 16-6-4 and experimental curve
- 12-6-4
- 8-6-4

$E/N (\text{Td})$

Fig. 7.5.

$V(r)$ (eV)

- 8-6-4
- 12-6-4
- 16-6-4

$r (\text{Å})$

There are three approaches that could be used to determine at least part of the interaction potential:

1. If a thorough study of the transport coefficients over a range of $E/N$ were extended, it would be possible to use reliable data. Wannier (1953) has outlined a possible approach for such a theoretical treatment.

2. Computer simulation techniques could be used to predict the transport coefficients.

3. There have been attempts to determine accurate interaction potentials at lower values of $E/N$ through computational methods.
ion-atom forces with low energy swarms. Unless the data are extremely accurate it is not possible to gain information from the tails of the distribution functions.

There have been two recent attempts to determine the interaction potential for K\(^+\) ions in Ar, those of Robson (1972) and Skullerud (1973b). A 12-6-4 potential was used in both cases at particle separations greater than 2.5 Å. The derived potentials are shown in Fig. 7.6 and it can be seen that the well depths differ by 20%. If the potential parameters derived by Skullerud are used in Kumar and Robson's theory the reduced mobility is at most 0.5% greater than that predicted by Robson's interaction potential in the range E/N < 30 Td and is still an adequate fit to the data of Elford (1971) and Skullerud (1973b). This agreement is due to the fact that at low values of E/N at room temperature the mobility of potassium ions in argon is dominated by long range collisions and relatively few of the ions have sufficient energy to probe the potential about the minimum. The difference between the potentials becomes more apparent at higher values of E/N and Skullerud has shown that at about 100 Td the difference between the mobility values predicted from the two interaction potentials is 6%, a difference well outside the experimental error.

### 7.3 CONCLUSION

The following conclusion was drawn from this investigation.

It is not possible at the present time to accurately determine any part of the interaction potential using the analytical methods of either Kihara or Kumar as in the E/N range for which the theories are applicable the errors in all the available transport data are significant compared with the change in the transport coefficients with E/N.

There are three approaches which could be used to determine at least part of the interaction potential.

1. If a theory capable of predicting the transport coefficients over a larger range of E/N were developed it would be possible to use available data. Wannier (1953) has outlined a possible approach for such a theoretical treatment.

2. Computer simulation techniques could be used to predict the transport coefficients.
Fig. 7.6.

Robson (1972)

Skullerud (1973b)

K\textsuperscript{+} in Ar

If the errors in transport coefficient measurements were reduced it would be possible to obtain the interaction potential from the analytical theories of Kummer and Skwara.

If appropriate experimental data were available it would probably be necessary to solve numerical rather than analytical forms for the interaction potential and for certain ion-atom combinations the collision cross sections would have to be calculated quantum mechanically.
If the errors in transport coefficient measurements were reduced it would be possible to obtain the interaction potential from the analytical theories of Kumar and Kihara.

If more accurate experimental data were available it would probably be necessary to use a numerical rather than an analytical form for the interaction potential and for certain ion-atom combinations the collision cross sections would have to be calculated quantum mechanically.
THE LONGITUDINAL DIFFUSION COEFFICIENT OF K⁺ IONS IN He, Ar, N₂

Whereas the mobility is dominated largely by the momentum transfer cross section and is influenced to only a small extent by the viscosity cross section, both cross sections are important in determining the longitudinal diffusion coefficient, \( D_L \). A result of this is that \( D_L \) is more sensitive than \( \kappa \) to variations in the interaction potential and thus if both \( D_L \) and \( \kappa \) could be determined with the same accuracy a more accurate estimate of the interaction potential could be obtained by fitting to the variations of \( D_L \) with \( E/N \) and \( T \) rather than to the variation of \( \kappa \). Unfortunately, due to the low drift tube currents which must be used to avoid space charge broadening of the diffusing pulses and to the difficulty of fitting a theoretical arrival time spectrum to the spectrum measured experimentally it is not possible at present to measure \( D_L \) as accurately as \( \kappa \).

In the first two determinations of the longitudinal diffusion coefficient for alkali ions in gases (Moseley, Gatland et al. 1969, K⁺ in N₂ and Snuggs, Volz, Schummers et al. 1971, K⁺ in O₂) the value of the coefficient extrapolated to zero \( E/N \) disagreed by as much as 25% with the predictions of the Nernst-Townsend relation and thus little confidence could be placed in the data. The aim of the present work was to obtain accurate values of \( D_L \) and also to investigate ion-atom combinations for which there were quantitative predictions available for comparison with experiment (Robson and Kumar 1973). The experimental techniques were developed by considering K⁺ in N₂ (Milloy 1973).

The measurements were made with a Bradbury-Nielsen drift tube apparatus (System B, described in section 5.5). The theory of the method of determining \( D_L \) from the current-frequency spectrum has been described in section 4.1.2 and only the final result will be quoted here. Since diffusion coefficients are inversely proportional to the gas number density it is convenient to work in terms of the product \( ND_L \) which can be written,

\[
ND_L = \frac{\hbar E N S \kappa}{16 \ln 2 \delta^2}
\]
8.1 EXPERIMENTAL DETAILS

8.1.1 Method

It was necessary to ensure that the experimental conditions were consistent with the assumptions made in the derivation of equation 4.1.17. The most crucial assumptions were that the initial pulse closely resembles a delta function and that ion-ion interactions could be neglected.

To ensure that the initial pulse was a good approximation to a delta function the effective open time of the shutters was changed by varying the amplitude of the gating signal to the shutters and by investigating more than one peak in the current-frequency spectrum. It was found that errors introduced by finite initial pulse widths could be reduced to less than the experimental scatter. The variation of the measured value of $D_L/K$ with signal amplitude is shown for a typical case in Fig. 8.1. The data are for the fifth peak in the current-frequency spectrum of $K^+$ ions in He at $E/N = 18.4$ Td. Each data point is the average of five individual measurements, the maximum scatter about the mean being ± 3%.

To ensure that the peaks were not anomalously broadened by space charge effects the resolving power was measured as a function of tube current. It was found that when the maximum currents were less than $10^{-12}$ A there was no detectable space charge broadening, even at the lowest $E/N$ values.

A further experimental check which was carried out was to investigate the full arrival time spectrum of the ions. A typical spectrum is shown in Fig. 8.2 in which the experimental points are shown together with the spectrum predicted by equation 4.1.12 using the measured values of $D_L$ and $W$. It can be seen that the agreement between experiment and theory is very satisfactory.

8.1.2 Results and Errors

The values of $N_D L$ and $D_L/K$ for $K^+$ ions in He, Ar and $N_2$ are tabulated as a function of $E/N$ in Appendix G, and are plotted in Figs. 8.3, 8.4 and 8.5 respectively. Also shown in these figures are the values of $N_D L$ predicted by the Nernst-Townsend relation using the average of the
$K^+$ in He
$E/N=18.4\text{Td}$
peak 4
$P_{273.2}=3.66\text{torr}$

\[ \text{Current (arbitrary units)} \]

$K^+$ in $N_2$
$E/N=5.66\text{Td}$
$P_{273.2}=5.09\text{torr}$
Fig. 8.3. Present research compared to data from Wannier (1953) and Robson and Kumar. The graph shows the number density of $K^+$ in He as a function of $E/N$ (Td). The data points at 3.66 torr and 5.15 torr are indicated.

$NDL \left(10^{18} \text{ cm}^{-2} \cdot \text{s}^{-1}\right)$
Fig. 8.4.
The two major errors are considered to be the possibility of a temperature gradient between the water jacket and the drift tube and the difficulty in measuring the resolving power of the current probe. The random error is to the temperature measurement is estimated to be about 1%. It is believed that the resolving power measurement to be approximately 1%. In the case of nitric oxide the error limit of ±3% has been put on the values of \( N_{\text{D}} \). Due to the uncertainties in the determination of the relative cross sections of the relevant states it is not possible to estimate the error in the predicted values of \( N_{\text{D}} \). The only high precision cross section data available is for K⁺ in nitrogen (Sawyer and Zeller 1971, also see reaction 2.23).

It can be seen from Figs. 8.4 and 8.5 that a curve can be drawn through each set of experimental points which has approximately the same initial slope and curvature as in the case of nitric oxide, which demonstrates the validity of the assumptions made in the theoretical calculation. The general consistency with the Born-Oppenheimer relation is evident in the case of nitric oxide, and the Born-Oppenheimer value of \( 1.1 \times 10^{-18} \) cm·s is in good agreement with the Born-Oppenheimer value of \( 1.1 \times 10^{-18} \) cm·s.

The results in Figs. 8.4-8.5 are compared with values calculated from Sawyer and Zeller's work. The interaction potentials which predict the right temperature dependence of \( N_D \) with \( E/N \) most accurately (Zeller 1972) were used in these theoretical calculations. The results in the inert gases are also compared with the predictions of the constant mean free time, isotropic scattering model (Wannier 1953, equation 131). For this model \( N_D \) can conveniently be written,
reduced mobilities measured at each of the two gas pressures used (the difference between the mobilities is at most 0.2%). No dependence of ND\textsubscript{L} on gas pressure was observed within the experimental scatter. The lack of an observable pressure dependence in the values of ND\textsubscript{L} is a strong indication that the measurements were not seriously affected by "end effects" as all errors due to "end effects" are thought to scale inversely with the pressure at a given value of E/N.

The two major errors are considered to be the possibility of a temperature gradient between the water jacket and the drift tube and the difficulty in measuring the resolving power of the current peak. The maximum error due to the temperature measurement is estimated to be ± 0.5 K and that in the resolving power measurement to be approximately ± 1%. An error limit of ± 3% has been put on the values of ND\textsubscript{L}. Due to the estimated uncertainty of ± 1% in the values of the reduced zero field mobilities there are corresponding errors in the values of ND\textsubscript{L} predicted from the Nernst-Townsend relation. If higher pressures had been used there would have been an error due to the clustering of K\textsuperscript{+} ions to N\textsubscript{2} molecules (Beyer and Keller 1971, see also section 10.2).

8.2 DISCUSSION

It can be seen from Figs. 8.3, 8.4 and 8.5 that a curve can be drawn through each set of experimental points that has zero initial slope and is consistent at zero E/N with the Nernst-Townsend relation to within the combined experimental errors. In the case of nitrogen the line of best fit to the present data intersects the ordinate at \(1.77 \times 10^{18} \text{cm}^{-1} \text{s}^{-1}\) which is only 4% higher than the Nernst-Townsend value of \(1.70 \times 10^{18} \text{cm}^{-1} \text{s}^{-1}\). The general consistency with the Nernst-Townsend relation is strong evidence for the reliability of the data.

The results in Figs. 8.3 and 8.4 are compared with values calculated from Kumar and Robson's theory. The interaction potentials which predict the room temperature variation of \(\kappa\) with E/N most accurately (Robson 1972) were used in these theoretical calculations. The results in the inert gases are also compared with the predictions of the constant mean free time, isotropic scattering model (Wannier 1953, equation 151). For this model ND\textsubscript{L} can conveniently be written,
where the constant mean free time between collisions, \( \tau \), has been calculated from the relation

\[
\tau = \frac{\mu_K}{e},
\]

in order to normalise the theoretical curve at zero \( E/N \).

In the case of helium (Fig. 8.3) there is good agreement between the experimental data and the predictions of Wannier but the difference between the experimental data and the predictions of Kumar and Robson is as large as 11\% at the highest value of \( E/N \). The good agreement with Wannier's predictions is probably due to the fact that at room temperature and low \( E/N \) values there is a partial cancellation between the attractive and repulsive forces. This results in a weak dependence of the collision frequencies on the relative velocities of the colliding particles. It has already been shown in Chapter 2 that this effect gives rise to a maximum in the mobility-\( E/N \) curve. In the case of argon (Fig. 8.4) the constant mean free time model is not an accurate description of the ion motion as the partial cancellation of the attractive and repulsive forces does not occur until much higher \( E/N \) values. There is also a significant discrepancy in this case between the experimental data and the values of \( N_{D_L} \) predicted by the quantitative theory of Kumar and Robson. The cause of the discrepancy between Kumar and Robson's theory and the experimental values is not known. It may be due to the difficulty of obtaining an accurate interaction potential, as discussed in Chapter 7, but to ensure that it is not due to an experimental error the values of \( N_{D_L} \) should be measured at a different and preferably longer drift distance (present distance is 3.395 cm). It would also be desirable to use a larger range of gas pressures but the onset of electrical breakdown would make it impossible to take higher pressure measurements at values of \( E/N \) where there is a significant discrepancy between theory and experiment. If the discrepancy is due to an experimental error this error must not only increase with increasing \( E/N \) but also be independent of the gas pressure. No such error has been observed in mobility measurements.
The fact that ND is a more strongly varying function of E/N in helium than in argon arises from the more efficient transfer of energy from an ion to an atom when the masses of the particles are equal. Thus at a given value of E/N the total energy of the ions is greater in helium than in argon and it can be seen in a qualitative way from equation 2.4.12 that this gives rise to a higher value of D_L.

The data for K+ ions in nitrogen (Fig. 8.5) are compared with the line of best fit to the recent data of Thomson et al. (1972) who quote error limits of ± 5% for each experimental point. Thomson et al. used the technique described in section 3.3.2. In early work with this technique it was found that the values of D_L when extrapolated to zero E/N did not agree with the predictions of the Nernst-Townsend relation. The results for positive ions were higher than the values predicted theoretically (Moseley, Snuggs et al. 1968, Moseley, Gatland et al. 1969, Snuggs et al. 1971 and Volz et al. 1971) while those for negative ions were lower than the predicted values (Snuggs, Volz et al. 1971). Schummers et al. (1972) overcame this problem by refining the analysis of the arrival time spectra and by further development of the experimental techniques.

Although Wannier's analysis of the constant mean free time model is not strictly applicable to diatomic molecules the predictions of equation 8.2.1 are included for comparison in Fig. 8.5. There is seen to be a significant difference between the present results and the results of Thomson et al., which agree closely with the predictions of Wannier's qualitative theory.
Although there has been considerable interest over the years in the mobility of ions in gas mixtures at low E/N values McDaniel (1964), it is only recently, with the publication of a theoretical paper by Mason and Hahn (1972), that attention has been paid to the high E/N region. Unfortunately Mason and Hahn's theory is invalid under all circumstances as both the constant cross section and constant mean free time models were used. Robson (Milloy and Robson 1973, Appendix A) has developed an alternative treatment valid under circumstances where the constant mean free time model is a good first approximation and the work described in this chapter was carried out primarily to test the accuracy of Robson's approach.

9.1 EXPERIMENTAL DETAILS AND RESULTS

9.1.1 Experimental details

The drift tube used in this investigation has been described in section 5.5 (System B). This tube was especially suitable for work with gas mixtures because it operates under static gas conditions. The type of apparatus more frequently used for ion mobility work has a constant flow-through of gas as the ions are sampled and mass analysed. However, Heimerl et al. (1969) have found that such dynamic mode systems are unsuitable for use with gas mixtures because of mass discrimination effects at the sampling apertures and errors in gas composition of 25% have been estimated by these workers.

Before the commencement of the present series of measurements the shutter wires were regilded and the general performance of the tube checked by measuring the drift velocity of electrons in hydrogen at various values of E/N. The results obtained agreed with the values taken with other drift tubes in this laboratory (Robertson 1970, Elford and Robertson 1973) to within ± 0.1%.

Two factors had to be considered when choosing the gas pressures to be used. It was necessary to choose pressures low enough that high values of E/N could be obtained without the risk of electrical breakdown at the high voltage lead throughs, but not so low that the pressure could
not be accurately measured with the pressure gauge available (Texas Instruments type 141B). In all cases the final pressures were measured by a volume sharing technique as this gave increased accuracy both in the pressure measurement and in the measurement of the mixture concentrations. The total gas pressures used in these experiments ranged from .823 torr to 1.11 torr, measured at approximately 293 K. To reduce the possibility of significant errors from contact potential differences and other "end effects" no measurements were taken with a potential difference of less than 15 V between the planes of the shutters. It was noted that at high values of E/N, and especially in mixtures containing a large fraction of He, the efficiency of the Bradbury-Nielsen shutters decreased. This effect, which results in a background current on which the peak system is superimposed, and thus in a decrease in the signal to noise ratio, has previously been discussed by Blevin and Hasan (1967) (see also section 4.3). In the present work this effect did not introduce a significant source of error as the frequency of the peak maxima was measured a sufficient number of times to reduce the statistical error.

9.1.2 Experimental results

The reduced mobility of $K^+$ ions in He, Ne, Ar, H$_2$ and N$_2$, and in mixtures of He-Ne, Ne-Ar and H$_2$-N$_2$ were measured as a function of E/N in the range $20 \leq E/N (T_d) \leq 100$ and these data are listed in Appendix F.

9.1.3 Analysis of experimental errors

In addition to the errors in mobility measurements normally associated with this apparatus (see section 5.6) there were additional minor errors incurred by the use of gas mixtures and volume sharing techniques. The errors in the mobility measurements in the mixtures are given in Table 9.1.
Table 9.1
Estimated total errors in mobility measurements

<table>
<thead>
<tr>
<th>Source of error</th>
<th>Maximum effect on $\kappa$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p.d. voltage between shutters</td>
<td>random</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
</tr>
<tr>
<td>Temperature</td>
<td>random</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
</tr>
<tr>
<td>Pressure</td>
<td>random</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
</tr>
<tr>
<td>Drift distance</td>
<td>random</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
</tr>
<tr>
<td>End effects</td>
<td>random</td>
</tr>
<tr>
<td></td>
<td>systematic</td>
</tr>
<tr>
<td>Effective transit time</td>
<td>random</td>
</tr>
</tbody>
</table>

Total uncertainty ± 1.5%

The errors in the composition of the gas mixtures were estimated to be less than ± 0.4%.

If higher pressures had been used there would have been an error due to the clustering of $K^+$ ions to $N_2$ molecules (Beyer and Keller 1971), (see also Chapter 10). However, at a pressure of 1 torr of $N_2$ the effects of clustering result in the measured mobility being only about 0.1% smaller than the zero pressure limit.

The errors in the deviations from Blanc's Law are less than the errors in the mobility values since systematic errors cancel when the deviations are calculated. Also to a first approximation the deviations from Blanc's Law are not affected by diffusion errors and "end effects" of the type discussed in section 6.2. It is estimated that the deviations from Blanc's Law are in error by less than ± 0.4%.

9.1.4 Comparison with previous work

Measurements of the mobility of ions in gas mixtures at high E/N values have not previously been reported. It is possible, however, to compare some of the present mobility data for $K^+$ ions in the pure gases with previous work and when such a comparison is possible the mobility measurements reported here agree with the results of all previous work published in the past decade to within the combined experimental errors.
The H₂ data are in excellent agreement with the results of Elford (1967) at the lower values of E/N, but lie approximately 1.8% below Elford's data at the highest value of E/N. The present results are less than 1% higher than the curve of best fit to the data of Fleming et al. (1969a) at \( E/N \leq 80 \text{Td} \) but by 100 Td the discrepancy has increased to 2.5%. The curve of best fit to the data of Miller, Moseley et al. (1968) agrees with the present work to within the combined experimental errors. A graphical comparison of these sets of data is given in Fig. 9.1.

The agreement with previous work in N₂ is not as good as in H₂, but again all differences are much smaller than the combined experimental errors. There is a 1.3% systematic difference between the present work and the work of Moseley, Gatland et al. (1969) who quote a ± 3.9% error limit for their determination of the zero field reduced mobility. The maximum differences between the present work and the curves of best fit to the data of Crompton and Elford (1959) and Fleming et al. (1969b) are 0.9% and 0.4% respectively. The various sets of experimental data for this case are shown in Fig. 9.2.

Elford (1971) extended his measurements of \( \kappa \) for \( K^+ \) ions in Ar to \( E/N = 184 \text{Td} \) and in the region of overlap his results are systematically 1.1% higher than the present values. There is also satisfactory agreement between the present work and the results of Skullerud (1973b), which extend to \( E/N = 783 \text{Td} \).

9.2 COMPARISON OF THEORY AND EXPERIMENT

The deviations of the experimental results from Blanc's Law for mixtures of He-Ne and Ne-Ar are shown in Figs. 9.3 and 9.5. The difference between the reciprocals of the reduced mobility predicted from Blanc's Law \( 1/\kappa_B^{\text{mix}} \), and the reduced mobility measured experimentally, \( 1/\kappa^{\text{mix}} \), that is \( \Delta(1/\kappa^{\text{mix}}) \), expressed as a percentage of \( 1/\kappa_B^{\text{mix}} \) is plotted as a function of E/N for various mixtures. The figures beside the curves refer to percentages of Ne and Ar respectively.

Figures 9.4 and 9.6 show the predictions of Robson, who has shown that if the mean free time for momentum transfer collisions is approximately independent of the relative velocity of the colliding particles then the deviations from Blanc's Law can be written, (Appendix A)
Fig. 9.1.

Fig. 9.2.
Fig. 9.3.

Fig. 9.4.
where $\kappa$ is the ion mass. When the experimental and theoretical curves are compared it can be seen that in most cases the curves of best fit are not of equal quality and experimental deviations quantitatively would not be expected in view of the approximations in the theory. In Fig. 9.6, the large disagreement of theory and experiment in the case of $K^+$ ions in Ne-Ar is indicated. Whence the lines of best fit in the experimental data are plotted in Fig. 9.6. The large discrepancy with the approximations used in the theory.

9.3 DISCUSSION

The agreement between the results of this work and Johnson's theoretical predictions is due in the fact that in each of the inert gases used the mobility of $K^+$ ions is only a slowly varying function of $E/N$. In the case of the noble gases, the electron distribution is such that the small deviation $E/N$-curve occurs in the range of $E/N$ used in this investigation. If higher values of $E/N$ were used, the electron distribution would be more rapidly influenced by the repulsion part of the interaction potential and it would be expected that the agreement between theory and experiment would not be as good. At very high values of $E/N$ a constant cross section is an approximation which does not hold even under these conditions, as the theory of Hasegawa and Slichter points out. It is also a valid assumption which usually varies for the case of free electron motion as discussed in Section 4.1. A more interesting fact is that the only enclosed curve is the only one capable of predicting the ion motion at high $E/N$ values. A realistic interaction potential (computer simulation technique) would be quite useless in this situation as extremely long computer times would be required to predict the deviation from Blanc's ion mobility data.
\[ \frac{1}{\kappa_{\text{mix}}} - \frac{1}{\kappa_B} = \frac{1}{\kappa_{\text{mix}}} - \frac{1}{\kappa_{\text{mix}}} \]

\[ = \frac{1}{\kappa_B} \sum \frac{x_i^{3\lambda n} \kappa_i}{\kappa_i^{3\lambda n}} \frac{1}{E/N} \left\{ \left( \frac{m+M}{m} \right)^2 \frac{x_j^{\lambda n}}{\kappa_j} \frac{x_k^{\lambda n}}{\kappa_k} \left( \frac{m+M}{m} \right)^{-1} \right\}^{-1} \]

where \( \kappa_{\text{mix}} \) is given by equation 2.6.1. When the experimental and theoretical curves are compared it can be seen that in each case the curves of best fit to the data points are consistent with Blanc's Law at low values of \( E/N \). This is a convenient experimental check. It can also be seen that there is good qualitative agreement between theory and experiment. Good quantitative agreement would not be expected in view of the approximations in the theory.

Mason and Hahn computed the deviations from Blanc's Law for the case of \( K^+ \) ions in \( H_2-N_2 \) mixtures and their predictions together with the lines of best fit to the experimental data are plotted in Fig. 9.7. The large disagreement between theory and experiment is not surprising considering the approximations made in the theory.

9.3 DISCUSSION

The agreement between the results of this work and Robson's theoretical predictions is due to the fact that in each of the inert gases used the mobility of \( K^+ \) ions is only a slowly varying function of \( E/N \). In the cases of He and Ne this is due partly to the fact that the hump in the mobility-\( E/N \) curve occurs in the range of \( E/N \) used in this investigation. If higher values of \( E/N \) were used the motion of the ions would be more strongly influenced by the repulsive part of the interaction potential and it would be expected that the agreement between theory and experiment would not be as good. At very high values of \( E/N \) a constant cross section model might be a good approximation but even under these conditions the theory of Mason and Hahn would not be applicable because it also embodies assumptions which are only valid for the constant mean free time model, as discussed in Section 2.6.

It is interesting to note that the only method capable of predicting the ion motion at high \( E/N \) for a realistic interaction potential (computer simulation technique) would be unsuitable in this investigation as extremely long computing times would be required to predict the deviations from Blanc's Law with sufficient accuracy.
It was observed that there are two methods which can be used with utmost care to investigate a reaction system in which both the forward and reverse reactions are significant. In the first, the reaction rates are measured by conventional methods on a single spectrometer. In the second, when the concentration of one reactant is very much greater than that of the other, the reaction may proceed to completion, and the concentration of this species may be measured by an ordinary spectrophotometer. In both cases, the reaction mixture was kept at constant temperature, and the absorbance was measured as a function of time. In general, the reaction was stopped by the addition of an appropriate reagent at the appropriate time. Although this method is limited to reactions that can be stopped immediately, it is useful for reactions that proceed to completion, and the concentration of the species of interest can be measured accurately.

The project is largely devoted to a description of the drift tube. It is shown that, by using the drift tube method, it is possible to obtain a more accurate determination of the concentration of the ions in the drift tube. It is also shown that this method has advantages to be gained by using an electrical shunt technique where the ions are not extracted from the drift tube to investigate non-collision reactions and ion-molecule reactions.
CHAPTER 10

THE STUDY OF CLUSTERING REACTIONS WITH DRIFT TUBES

It was pointed out in Chapter 3 that there are two methods which can be used with drift tubes to investigate a reaction scheme in which both the forward and reverse reactions are significant. In one of these the reaction rates are determined by comparing the measured ion arrival time spectrum with the spectrum predicted theoretically. Unfortunately when the mobilities of the parent and product species are similar the fitting procedure becomes inaccurate and in fact this method has only been used once (McKnight et al. 1967). The other method, which involves measuring the relative abundance of the parent and product species as a function of time, is of general applicability but is subject to mass discrimination errors in the ion sampling and detection system. Although this has been acknowledged for several years (Moruzzi and Phelps 1966, McDaniel 1970) it is only recently that serious consideration has been given to the magnitude and characteristics of the errors involved in typical drift tube experiments (Kinsman and Rees 1970, Parkes 1971).

Another serious source of error involved in reaction rate determinations is the possibility of the formation and break-up of clusters as the ions pass from the drift region to the particle multiplier. Errors of this type, which can be incurred in both the curve fitting and current ratio methods, have been considered by Cuthbert (1966) and by Parkes (1971) but generally have received scant attention in the literature. Although it would seem likely that ion-neutral clusters would in general form more easily than neutral-neutral clusters, there appears to be more information about neutral clusters (see for example Golomb et al. 1970, Milne et al. 1970 and Kleppner 1970).

The present chapter is largely devoted to a description of an investigation into the problems of mass discrimination and cluster formation in the ion detection region of System A, a typical mass analysis system. It is shown that, if used alone, the current ratio method can lead to totally misleading conclusions about the ion motion in the drift tube. It is also shown that there are considerable advantages to be gained by using an electrical shutter technique where the ions are not extracted from the drift tube to investigate ion-molecule reactions and
this is demonstrated by the results of an investigation into the pressure dependence of the reduced mobility of \( K^+ \) ions in \( N_2 \).

10.1 MASS DISCRIMINATION AND THE FORMATION OF PRODUCT IONS IN THE SAMPLING REGION

There were two main reasons for carrying out an investigation of the problems of mass discrimination and cluster formation in the analyser section of System A. The first was that there is a conflict between the results of experiments carried out with System A and the results reported by Thomson et al. (1972). Whereas Thomson observed clusters of \( K^+ \) ions with neutral particles of \( CO_2 \), \( NO \), \( CO \), \( N_2 \), \( O_2 \), \( Ar \), \( D_2 \), \( Ne \) and \( He \) at room temperature and concluded that "clustering is likely to be of importance in studies of the transport properties of \( K^+ \) ions in all of these gases except \( D_2 \), \( Ne \) and \( He \)," no \( K^+ \) ion clusters were observed in this work when experiments of similar sensitivity were carried out with \( Ar \), \( Ne \) and \( He \), although \( K^+.N_2 \) clusters were observed. This discrepancy is important as Thomson's conclusion is the basis of Gatland's (Gatland 1972a) explanation of the pressure dependence of the reduced mobility of \( K^+ \) ions in \( Ar \). Gatland's explanation has already been criticized in Chapter 6 where it was also pointed out that an explanation of the pressure dependence in terms of the formation of stable clusters is unlikely because of the small magnitude of the effect.

The second reason for this study was that there was a disagreement between the results of experiments carried out with the mass identification facilities incorporated in System A and the results of time-of-flight experiments at higher pressures with System A(1). For example it was found that when the reduced mobility of \( Li^+ \) ions in \( H_2 \) was measured in the range \( 0.817 \leq p \leq 37.9 \text{ torr} \) only one peak system was measured in the ion current-frequency spectrum and the estimated zero field reduced mobility did not vary by more than 0.3% over the full pressure range. These data have been discussed in Section 5.4 and are listed in Table C.4. On the other hand when a lithium filament was used in \( H_2 \) with System A, not only the \( Li^+ \) isotopes but also \( Li^+.H_2 \) clusters were observed. The measured abundance of the clusters increased linearly with pressure and was about 0.6% at 1 torr. Thus if the \( Li^+.H_2 \) clusters were formed in the drift region they would be expected to have an abundance of about 25% at the highest pressure used and this would in all probability give rise
to a significant pressure dependence of the reduced mobility. Thus there is
strong evidence to suggest that the Li⁺.H₂ clusters and also some of the
K⁺-inert gas clusters observed by Thomson et al. (1972) were formed in the
jet of isentropically cooled gas escaping from the drift region. Similar
discrepancies were also found in the results of experiments with Li⁺ ions
in Ar. In this case the abundance of the Li⁺.Ar cluster, measured with the
quadrupole mass spectrometer, was found to increase linearly with pressure
but in a time-of-flight experiment under the same E/N and p conditions it
was conclusively shown that the forward and backward clustering reactions
were not in equilibrium.

It will be assumed in the discussions to follow that the detection
system consists of three separate sections, the exit hole of the drift
tube, the skimmer and the quadrupole mass spectrometer. This is probably
an oversimplification as the flow of gas from the drift tube and hence
the exit hole conditions must be affected by the conical skimmer. This
skimmer also affects the focusing conditions at the entry to the quadrupole
rods. However, the advantage of this division is that it is possible,
at least to first order, to isolate the sources of mass discrimination and
investigate each one separately.

The mass discrimination at the exit hole depends critically on
the nature of the gas flow. When the mean free path between neutral-
neutral collisions is very much greater than the hole diameter the flow
is "molecular" and the conductance of the neutral particles, Q \propto M⁻¹²
but at much higher pressures when the inequality is reversed and the flow
becomes "viscous", Q \propto M⁻¹⁸. In the range of experiments reported here the
flow was in the transitional range and it is difficult to estimate the
magnitude of the mass discrimination. In the case of ions the situation
is obviously more complicated and the only treatment seems to be that of
Parkes (1971) who considered the mass discrimination effects at the high
pressure side of the aperture.

10.1.1 Theory

The mass discrimination was studied by comparing the measured
current distribution across the exit plate of the drift tube with the
distribution predicted theoretically.
If it is assumed that the boundary conditions at the exit plate are the same as those for a metal surface then the ratio, $R$, of the current passing through the exit aperture to the total current is given by the expression used to describe the lateral motion of charged particles in a Townsend-Huxley experiment (see section 3.4.1),

$$R = 1 - \frac{h}{d} \exp\left(-\frac{(d-h)}{W/(2D_T)}\right),$$

where $h$ is the drift distance and $(d^2-h^2)^{1/2} = b$, the radius of the exit aperture. It follows that as $W/(2D_T)$ was always less than 150 cm$^{-1}$ and $(d-h)$ was always less than 0.00004 cm, $R$ was accurately given by

$$R = \frac{(d-h)}{W/(2D_T)}.$$

Under all the experimental conditions used in this investigation $R$ should increase linearly from the origin with increasing pressure for a constant $E/p$.

10.1.2 Experimental details

Fig. 10.1 shows the region of the apparatus under study in this investigation. The only modification made to System A for this investigation was to remove the three Bradbury-Nielsen shutters. This was carried out to ensure that the lateral motion of the ions in the drift tube was not affected by charged layers on the shutter wires. Thus the drift section was treated purely as an ion source. At various stages Li$^+$, K$^+$ and Cs$^+$ ions were used but most of the mass discrimination investigation was carried out with K$^+$ and Cs$^+$ ions as these ions do not react significantly at room temperature with the lighter inert gases or with H$_2$. The value of $E/p$ was kept constant at 5 V cm$^{-1}$ torr$^{-1}$. This is a convenient value as the ion energies are not greatly in excess of thermal and because relatively high ion currents can be used without serious space charge effects. It was established experimentally that the errors in $R$ due to space charge repulsion between the ions in the drift section were always less than 5% if currents of less than $1.5 \times 10^{-11}$ A were used.
10.1.3 Experimental results

A typical set of results is shown in Fig. 10.1 where $R_p$, a measure of the fraction of the drift tube current transmitted through the exit aperture and collected by the particle multiplier, is plotted as a function of the pressure in the drift section for Li⁺, K⁺ and Cs⁺ ions in Ar. It can clearly be seen that the results are in serious disagreement with theory which predicts a linear increase in $R_p$ with pressure. It was concluded that the discrepancy could only be resolved by careful investigation of the sampling region in a strong function of pressure. A number of additional experiments were carried out to determine whether the errors were being introduced at the inlet to the ion beam, or whether the quadrupole mass spectrometer could detect any such errors caused by incorrect operation of the mass spectrometer. There was evidence that indicates that an incorrect operation caused by insufficient knowledge of the operating conditions was produced before the ion beam was introduced to the mass spectrometer.

Fig. 10.1.
10.1.3 Experimental results

A typical set of results is shown in Fig. 10.2 where $R_m$, a measure of the fraction of the drift tube current transmitted through the exit aperture and collected by the particle multiplier, is plotted as a function of the pressure in the drift section for $\text{Li}^+$, $\text{K}^+$ and $\text{Cs}^+$ ions in Ar. It can clearly be seen that the results are in severe disagreement with theory which predicts a linear increase in $R_m$ with pressure. It can also be deduced from the data in this figure that the mass discrimination in the sampling region is a strong function of pressure. A number of additional experiments were carried out to determine where the errors were being introduced and if it was possible to reduce them and the conclusions from these experiments are given below.

(1) It was concluded that the anomalous transmission characteristics, as shown in Fig. 10.2, were not due to the focussing action of the quadrupole since the variation of $R_m$ with pressure did not depend on whether the quadrupole mass spectrometer was adjusted to measure the resolved peak of the ion being used or whether the rods were earthed. There was evidence that large mass discrimination errors could be caused by incorrect adjustment of the quadrupole power supply, but no evidence that this error was pressure dependent. It was concluded from these experiments that the pressure dependent mass discrimination effects are introduced before the ions enter the rods of the mass spectrometer.

(2) It was possible to distinguish between the mass discrimination errors introduced at the exit aperture of the drift tube and those introduced at the conical skimmer. This was done by moving the analyser horizontally about 2 mm from the position for maximum transmission and collecting the total current transmitted through the exit hole with the conical skimmer. The sampling errors introduced by the exit plate and skimmer are shown in Fig. 10.3 where the mass discrimination factor, defined to be the ratio of $R$ for $\text{Cs}^+$ ions to $R$ for $\text{K}^+$ ions is plotted as a function of pressure in the drift tube. Both curves have been normalized to one at zero pressure. It can be seen that the errors introduced at the exit plate are considerably smaller than the errors introduced at the skimmer.
Fig. 10.2.

Li$^+$ in Ar

K$^+$ in Ar

Cs$^+$ in Ar

0.19 mm dia.

Pressure (torr)
These experiments were carried out with an 0.1 in hole 1.0 cm diameter. Unfortunately when two smaller holes were used the currents to the skimmer were too small to be accurately measured.

(3) There was better agreement between theory and experiment if a small exit hole was used. This can be seen in Fig. 10.4 where the variation of $I_{h}$ with pressure for $K^+$ ions in argon is plotted for various exit hole sizes. A small exit hole was used in argon.

(4) There was better agreement between theory and experiment if the ratio $m/N$ was large (m is the mass of the ion and N the mass of the gas molecule). The variation of $I_{h}$ for $Li^+$ ions in He and Ar is shown in Fig. 10.5 and the variation of $I_{h}$ for $La^+$ and $Ca^+$ ions in Ar has already been shown in Fig. 10.2. It can also be deduced from the data in these figures that the mass discrimination factor $D$ is independent of the ratio of the specific heats of the gas and the mean free path of the ions in the gas.

(5) The variation of $I_{h}$ with pressure in the drift region did not depend on the electric field strength in the region between the skimmer and the exit plate, although the electric field did increase the magnitude of the transmission. Thus, it was also found that the measured abundance of $Li^+$ ions, although dependent on the magnitude of the electric field, was independent of the skimmer-exit plate separation.

(6) When the two larger exit apertures (0.05 in and 1.00 cm) were used the variation of $I_{h}$ with pressure for $K^+$ and $Ca^+$ ions in Ar depended on the distance between the skimmer and the exit plate, the disagreement between theory and experiment decreasing as this distance was increased. From the discussion in (4) above it would seem unlikely that this effect is due to changes in the electric field strength in this region and may therefore be due to changes in the flow of the neutral gas from the drift tube. This is discussed more fully in Section 10.1.4. When an exit hole of 0.19 in diameter was used it was found that the variation of $I_{h}$ with pressure was independent of the skimmer-exit plate separation.

Fig. 10.3.
These experiments were carried out with an exit hole 1.0 mm diameter. Unfortunately when two smaller holes were used the currents to the skimmer were too small to be accurately measured.

3) There was better agreement between theory and experiment if a small exit hole were used. This can be seen in Fig. 10.4 where the variation of $R_m$ with pressure for $K^+$ ions in argon is plotted for various exit hole sizes. A similar dependence on hole size was observed for $Cs^+$ ions in argon.

4) There was better agreement between theory and experiment if the ratio $m/M$ was large ($m$ is the ionic mass and $M$ the mass of the gas molecule). The variation of $R_m$ for $K^+$ ions in $H_2$, $He$ and $Ar$ is shown in Fig. 10.5 and the variation of $R_m$ for $Li^+$, $K^+$ and $Cs^+$ ions in $Ar$ has already been shown in Fig. 10.2. It can also be deduced from the data in these figures that the agreement between theory and experiment was not connected in a straightforward way to the ratio of the specific heats of the gases or the mean free path of the ions in the gases.

5) The variation of $R_m$ with pressure in the drift section did not depend on the electric field strength in the region between the skimmer and the exit plate, although increasing this field did increase the magnitude of the transmitted current. It was also found that the measured abundance of $Li^+.H_2$ was independent of the magnitude of the electric field in this region and also of the energy with which the ions travelled down the quadrupole rods.

6) When the two larger exit apertures (0.5 mm and 1.00 mm) were used the variation of $R_m$ with pressure for $K^+$ and $Cs^+$ ions in $Ar$ depended on the distance between the skimmer and the exit plate, the disagreement between theory and experiment decreasing as this distance was increased. From the discussion in (4) above it would seem unlikely that this effect is due to changes in the electric field strength in this region and may therefore be due to changes in the flow of the neutral gas from the drift tube. This is discussed more fully in Section 10.1.4. When an exit hole of 0.19 mm diameter was used it was found that the variation of $R_m$ with pressure was independent of the skimmer-exit plate separation.
Fig. 10.4.
Fig. 10.5.

K$^+$ in H$_2$

0.19 mm dia.

K$^+$ in He

0.19 mm dia.

K$^+$ in Ar

0.19 mm dia.
The measured ratio of the abundance of the \( \text{Li}^+ \cdot \text{H}_2 \) clusters to the abundance of the \( \text{Li}^+ \) ions was found to be independent of the skimmer-exit plate separation.

10.1.4 Discussion

It has been shown that in the present apparatus mass discrimination errors were introduced at the exit hole of the drift tube and at the conical skimmer situated between the drift tube and the quadrupole mass spectrometer. Although these are certainly not the only sources of mass discrimination it was concluded that they account for the observed dependence of the mass discrimination on pressure.

The results of the experiments described above indicate that the sampling errors at the exit aperture could be reduced by decreasing the hole size. It is estimated that an aperture of 0.07 mm diameter would still give adequate signal levels for accurate measurement.

It seems likely that the errors introduced by the conical skimmer were caused by the formation of shock fronts. An explanation in these terms is consistent with many of the experimental results discussed in section 10.1.3. For example shock fronts are more likely to be formed in argon than in helium or hydrogen (R.J. Stalker, private communication). The most effective way of overcoming the problems associated with the skimmer would be to remove it altogether and use a smaller exit hole to avoid the risk of breakdown in the particle multiplier. The use of a smaller exit hole would therefore seem to be an obvious modification. If the skimmer were removed it would probably be advisable to insert a lens system between the exit plate and the quadrupole rods to increase the transmission.

The problem of the formation of clusters in the expanding jet of neutral gas is more difficult and may impose a fundamental limitation on the current ratio and curve fitting methods unless molecular flow conditions are used.

10.2 THE FORMATION OF \( \text{K}^+ \cdot \text{N}_2 \) CLUSTERS

One of the largest uncertainties in atomic collision experiments at pressures beneath about 1 torr is the determination of the gas pressure. McDaniel and Martin (1971) suggested that this problem could be largely overcome by using the value of the reduced zero field mobility of \( \text{K}^+ \) ions...
in N₂ (as determined from measurements at gas pressures of several torr where pressure measurement is not a major source of error) to calibrate gauges at lower pressures. This proposal, which was based on the assumptions that the zero field reduced mobility of K⁺ ions in N₂ is independent of pressure and is accurately (± 0.5%) known, was briefly discussed by Elford (1971) who concluded that the calibration procedure was questionable in view of his observed pressure dependence of the reduced mobility. At about the same time Beyer and Keller (1971) reported the first observation of the K⁺N₂ cluster, which had not been observed by either Moseley, Gatland et al. (1969) or by Elford (1971). This was an important observation because if the K⁺N₂ clusters were formed in the drift section, the clustering reactions would not only partly explain Elford's observed pressure dependence for this case but would also render McDaniel's suggestion invalid. McDaniel (1972) has disputed this latter point.

The present work was undertaken in an attempt to clarify the situation. The motion of K⁺ ions in N₂ was investigated by using System B to measure the reduced mobility over a wider range of pressures and System A to study the formation of product ions. These investigations will now be described in more detail.

10.2.1 The pressure dependence of the reduced mobility of K⁺ ions in N₂

The results of Elford (1971) for the reduced mobility of K⁺ ions in N₂ extend from 1.44 to 18.8 torr and it can be seen from these results that the form of the pressure dependence in this case is significantly different from the form of the pressure dependence observed in He, Ne, Ar and H₂. However, no conclusions were reached about the reason for this difference. The present measurements, which extend from 5.11 to 190 torr, have already been discussed in section 5.6.1 and are listed in Table D.4. At pressures greater than about 50 torr there was some evidence of the presence of more than one ion in the current-frequency spectrum but as the magnitude of the subsidiary peak increased slowly with time it was concluded that this peak was due to a cluster ion formed by the K⁺ ions combining with impurity molecules - probably water. As the measured mobility of the major ion species did not change by more than ± 0.1% in a period of hours it was concluded that the results in Table D.4 were not significantly affected by impurities.
At each pressure the reduced zero field mobility was estimated in the manner described in section 6.3 and the estimated variation of the reduced zero field mobility with pressure is shown in Fig. 10.6. In the case of K\(^+\) ions in N\(_2\), the errors involved in estimating the reduced zero field mobility are smaller than in the cases considered in Chapter 6 as the intrinsic variation of \(\kappa\) with E/N at values of E/N < 15 Td is insignificant. For this reason it is estimated that the relative errors in the measurements are less than \(\pm 0.2\%\) at all pressures and these errors are shown in Fig. 10.6. It follows that as the total systematic error on each data point is \(\pm 0.8\%\) (see section 5.6.1) the total error on the data in Fig. 10.6 is \(\pm 1\%). It can be seen that the variation of \(\kappa_0\) with pressure is 4.1\% between 5 and 190 torr, about 4 times larger than that observed with K\(^+\) ions in Ar and 20 times larger than the random error in the measurements.

If a clustering reaction of the form

\[
K^+ + N_2 + N_2 \rightarrow K^+.N_2 + N_2
\]

was taking place, then as the peaks in the current-frequency spectrum not associated with impurities were symmetrical an equilibrium must have been established between the clustered and unclustered ions before the ions reached the first shutter and the identity of any single ion must have changed several times in its drift between the shutters. Under these conditions the measured reduced mobility, \(\kappa_m\), is the weighted mean of the mobilities of the clustered and unclustered ions and is given by (Voshall et al. 1965)

\[
\kappa_m = \frac{\kappa_1 [K^+] + \kappa_2 [K^+.N_2]}{[K^+] + [K^+.N_2]}, \quad 10.2.1
\]

where the square brackets denote ion densities and \(\kappa_1\) and \(\kappa_2\) are the reduced mobilities of the unclustered and clustered ions respectively. The ratios of the ion densities can be expressed in terms of the equilibrium constant \(K = [K^+.N_2]/(N[K^+])\) and hence the measured reduced mobility can be written
It is possible to fit the pressure dependence of the reduced zero field mobility of $K^+$ ions in $N_2$ with a relation of the form given by equation 10.3.1. The curve of best fit, as shown by the continuous curve in Fig. 10.6, was obtained with the following parameters:

$\kappa = 2.39 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

Although the value of $K$ is in good agreement with the experimental value of $10^{-13}$ cm$^2$V$^{-1}$s$^{-1}$ quoted by Beyer and Keller (1971), it is not possible to fit the data accurately with this existing procedure and thus the agreement may be fortuitous. On the other hand, it is shown by some recent work that an adequate fit can be obtained. The value of $2.50 \pm 0.05$ cm$^2$V$^{-1}$s$^{-1}$ obtained by Beyer and Keller (1971) from the data of Crompton and Ittel (1959) (1.54 $\pm 0.02$ cm$^2$V$^{-1}$s$^{-1}$ at 6.2 torr) and of Crompton and Ittel (1959) (0.39 $\pm 0.07$ cm$^2$V$^{-1}$s$^{-1}$ at 6.2 torr) using the Bradbury-Nielson method and the experimental results which were accurately evaluated in this work (Crompton and Ittel, private communication) it seems likely that a systematic error caused the earlier results from this group to be about 25 high.

The results of Davies et al. (1966) exhibit an anomalous dependence of $\kappa$ on $R$/$N$ and should probably be treated with caution. For these and other reasons outlined in this section it is clear that little confidence can be placed in the error quoted by Bhatia and Nair.

### Direct Identification of the Cluster Ion $K_3^+$

The cluster ion $K_3^+$ was observed with the mass identification

$$P_{273.2} \text{ (torr)}$$

Fig. 10.6.
It is possible to fit the pressure dependence of the reduced zero field mobility of K⁺ ions in N₂ with a relation of the form given by equation 10.2.2. The curve of best fit, as shown by the continuous curve in Fig. 10.6, was obtained with the following parameters,

\[
\kappa_1 = 2.508 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}
\]

\[
\kappa_2 = 2.330 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}
\]

\[
K = 1.67 \times 10^{-19} \text{ cm}^3
\]

Although the value of K is in good agreement with the experimental value of \(2 \times 10^{-19} \text{ cm}^3\) quoted by Beyer and Keller (1971), it is not possible to determine either \(K_1\) or \(K_2\) accurately with this fitting procedure and thus the agreement may be fortuitous. On the other hand if \(\kappa_1\) is varied by more than ± 0.2% an adequate fit cannot be obtained. The value of \(2.508 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\), obtained for \(\kappa_1\) is 1.3% lower than the "standard value" of \(2.54 \pm 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) estimated by McDaniel and Martin (1971) from the results of Crompton and Elford (1959) (2.54 ± 0.01 cm²V⁻¹s⁻¹ at 6.2 torr), Fleming et al. (1969b) (2.53 ± 0.02 cm²V⁻¹s⁻¹) and Davies et al. (1966) (2.55 ± 0.07 cm²V⁻¹s⁻¹). However as Crompton and Elford used the Bradbury-Nielsen method and as each experimental parameter was more accurately measured in this work (Crompton and Elford, private communication) it seems likely that a systematic error caused the earlier results from this group to be about 2% high. The results of Davies et al. (1966) exhibit an anomalous dependence of \(K\) on E/N and should probably be treated with caution. For these and the other reasons outlined in this section it would appear that little confidence can be placed in the error limits quoted by McDaniel and Martin.

10.2.2 Direct identification of the cluster ion \(K^+_N\)

The cluster ion \(K^+_N\) was observed with the mass identification facilities in System A. The measured equilibrium constant of \(3 \times 10^{-20} \text{ cm}^3\) at low E/N values is only in fair agreement with Beyer and Keller's value of \(2 \times 10^{-19} \text{ cm}^3\) but in view of the discussion in section 10.1 disagreement of this order would not be unexpected.
As in the case of the cluster ion \( \text{Li}^+ \cdot \text{H}_2 \) it was not possible to determine to what extent the measurements were affected by the formation and break-up of clusters in the analyser section.

In previous work with this apparatus Creaser (1969) and Elford (1971) failed to observe \( \text{K}^+ \cdot \text{N}_2 \) clusters. This was almost certainly due to either incorrect adjustment of the mass spectrometer power supply or to the different skimmer design.

10.2.3 Discussion

This investigation has shown that under certain circumstances more information can be gained about clustering reaction by using an electrical shutter technique and no mass identification than can be gained by using direct mass identification facilities. The advantages of using an electrical shutter technique without mass identification facilities are that a much larger range of pressures can be used and that there are, at least to first order, no mass discrimination errors. The disadvantage, apart from the obvious difficulty of ion identification, associated with shutter techniques is the same as that for any time-of-flight method, namely insensitivity when the mobilities of the parent and product species are similar. Probably the best solution would be to use both techniques, but for many ion-molecule systems this will not be possible for quantitative measurements until the problems associated with ion sampling from drift tubes have been overcome.
The derivation of Robson's expression for deviations from Blanc's Law.

It has been shown in Chapter 2 that under spatially uniform, steady state conditions, and with the assumption that ion-ion interactions can be neglected, the equations which represent the balances between the momentum and energy gained from the field and the momentum and energy lost in collisions with neutral particles may be written in the following approximate forms,

\[ eE = N\mu W \nu_m (\langle \varepsilon \rangle) \]  

\[ eE_W = \frac{Nu}{m+M} \left( m \langle c^2 \rangle - 3kT \right) \nu_m (\langle \varepsilon \rangle). \]

It is also possible to express the mean relative energy of an ion in a convenient form. Since \( \langle C \rangle = 0 \) we have

\[ \langle \varepsilon \rangle = \frac{1}{2} \mu \langle g^2 \rangle = \frac{1}{2} \mu \left( \langle c^2 \rangle + 3kT/M \right). \]

By combining A.1 and A.2 the mean ion energy can be written,

\[ m \langle c^2 \rangle = (m+M) W^2 + 3kT, \]

and on substitution of A.4 into A.3 we have

\[ \langle \varepsilon \rangle = \frac{1}{2} \left[ M W^2 + 3kT \right]. \]

Equation A.5 is the well known Wannier expression for the mean ion energy in a constant mean free time situation.

Suppose now that there are several species of neutral gas present with densities \( N_i (i = 1, 2, ...) \) and concentrations

\[ x_i = \frac{N_i}{N}, \]

where

\[ N = \sum_i N_i. \]

The generalization of equations A.1 and A.2 to gas mixtures is
\[ eE = W_{\text{mix}} \sum_i N_i \frac{\nu_i \nu_{\text{mi}} \langle \varepsilon_i^{\text{mix}} \rangle}{\langle \varepsilon_i^{\text{mix}} \rangle} \]  
\[ A.6 \]

\[ eE \frac{W_{\text{mix}}}{W_i} = \left[ m <c_2^{\text{mix}} - 3kT \right] \sum_i N_i \frac{\nu_i \nu_{\text{mi}} \langle \varepsilon_i^{\text{mix}} \rangle/(m+M_i)}{\langle \varepsilon_i^{\text{mix}} \rangle} \]  
\[ A.7 \]

where

\[ \langle \varepsilon_i^{\text{mix}} \rangle = \frac{1}{2} \frac{\nu_i}{W_i} \left( <c_2^{\text{mix}} + 3kT/M_i \right). \]  
\[ A.8 \]

Equations A.6 and A.7 constitute two coupled equations in the two unknowns, \( W_{\text{mix}} \) and \( <c_2^{\text{mix}} \), and can in principle be solved if the \( \nu_{\text{mi}} \) are given functions of energy. Clearly, however, the complexity of the problem is greater than for a pure gas.

If only one neutral species (say the \( i^{th} \)) is present then \( x_i = 1 \) (\( x_j = 0 \), \( j \neq i \)) and we regain equations A.1, A.2, A.4 and A.5 with the appropriate quantities now labelled by the index \( i \).

\[ eE = N \frac{\nu_i}{W_i} \langle \varepsilon_i \rangle \]  
\[ A.9 \]

\[ eE \frac{W_i}{W_{\text{mix}}} = N \frac{\nu_i}{m+M_i} \langle \varepsilon_i \rangle \]  
\[ A.10 \]

\[ m<c_2^{\text{i}} = (m+M_i) W_i^2 + 3kT \]  
\[ A.11 \]

\[ \langle \varepsilon_i \rangle = \frac{1}{2} (M_i W_i^2 + 3kT). \]  
\[ A.12 \]

Elimination of \( \nu_i/eE \) between A.6, A.7 and A.9 gives

\[ \frac{1}{W_{\text{mix}}} = \sum_i x_i \frac{\nu_i \nu_{\text{mi}} \langle \varepsilon_i^{\text{mix}} \rangle}{\langle \varepsilon_i^{\text{mix}} \rangle} \]  
\[ A.13 \]

\[ W_{\text{mix}} = \left[ m<c_2^{\text{mix}} - 3kT \right] \sum_i x_i \frac{\nu_i \nu_{\text{mi}} \langle \varepsilon_i^{\text{mix}} \rangle/(m+M_i)}{\langle \varepsilon_i \rangle}. \]  
\[ A.14 \]

Equation A.13 predicts that Blanc's Law will be obeyed exactly if and only if
Such a condition holds

(a) for a Maxwell (constant mean free time) model,

\[ \nu_{mi}(\langle \varepsilon \rangle_{\text{mix}}) = \nu_{mi}(\langle \varepsilon \rangle) . \]  

A.15

\( \langle \varepsilon \rangle_{\text{mix}} = \langle \varepsilon \rangle = \frac{3}{2} kT . \)  

In general, however, A.15 is not satisfied although, as was discussed in Chapter 2, the \( \nu_{mi} \) and the mobilities are sometimes only slowly varying functions. When this is the case deviations from Blanc's Law can be expected to be small although dependent to a large extent upon the types and concentrations of the gases comprising the mixture as well as the magnitude of \( E/N \).

If \( \nu_{mi}(\langle \varepsilon \rangle_{\text{mix}}) \) is a slowly varying function of energy over the range of \( E/N \) considered, the expansion

\[ \nu_{mi}(\langle \varepsilon \rangle_{\text{mix}}) = \nu_{mi}(\langle \varepsilon \rangle) + \delta < \varepsilon > \nu_{mi}'(\langle \varepsilon \rangle) + \ldots . \]  

A.16

will converge rapidly, no matter what the value of the energy difference

\[ \delta < \varepsilon > \equiv < \varepsilon >_{\text{mix}} - < \varepsilon > . \]  

A.17

In A.16, \( \nu_{mi}'(\varepsilon) \) denotes the derivative, \( d\nu_{mi}/d\varepsilon \).

Substituting A.16 into A.13 and retaining only first order derivatives of \( \nu_{mi}' \), we obtain

\[ \frac{1}{W_{\text{mix}}} = \frac{1}{W_{B}} + \sum_{i} \frac{x_{i}}{W_{i}} \delta < \varepsilon > \frac{\nu_{mi}'(< \varepsilon >)}{\nu_{mi}(< \varepsilon >)} , \]  

A.18

where

\[ \frac{1}{W_{\text{mix}}} = \frac{x_{i}}{W_{i}}, \]  

A.19
is the prediction from Blanc's Law for drift velocity in the mixture. The deviation from Blanc's Law (the second term on the RHS of A.18) will now be expressed entirely in terms of drift velocities (or mobilities) of the ions in the pure gases.

Differentiating A.9 w.r.t. \( E/N \), and making use of A.12, we find that

\[
\frac{\nu'_{mi}(\langle \epsilon_i \rangle)}{\nu_{mi}(\langle \epsilon_i \rangle)} = \frac{1}{M_i W_i} \left\{ \frac{\partial \ln W_i}{\partial \ln E/N} \right\}_{-1}^{1}. 
\]

In calculating \( \delta \langle \epsilon_i \rangle \), we neglect terms in \( \nu'_i(\langle \epsilon_i \rangle) \), as these will provide only second order corrections to A.18. In this approximation, we find from A.8, A.11, A.14 and A.17 that

\[
\delta \langle \epsilon_i \rangle = \frac{1}{2} \frac{M_i}{m+M_i} \left\{ \sum \frac{x_i}{W_j} \right\}_{-1}^{1} \left\{ \sum \frac{x_k}{W_k (m+M_k)} \right\}_{-1}^{1} - \left( m+M_i \right) W_i^2 \]

\( (+ \text{ terms in } \nu'_{mi}) \).

Substitution of A.20 and A.21 into A.18 thus gives for the deviation from Blanc's Law,

\[
\Delta \frac{1}{W_{\text{mix}}} = \frac{1}{W_{\text{B}}} - \frac{1}{W_{\text{mix}}} = - \frac{1}{2} \sum \frac{x_i}{W_i} \left\{ \frac{\partial \ln W_i}{\partial \ln E/N} \right\}_{-1}^{1}
\]

\[
\times \left\{ \left( m+M_i \right) W_i^2 \sum \frac{x_j}{W_j} \sum \frac{x_k}{W_k (m+M_k)} \right\}_{-1}^{1} .
\]

In terms of the reduced mobilities we have,

\[
\left[ \frac{\partial \ln W_i}{\partial \ln E/N} \right]^{1-1} = - \frac{\partial \ln \kappa_i}{\partial \ln E/N} + \frac{\partial \ln \kappa_i}{\partial \ln E/N}.
\]

\[
\Delta = - \frac{\partial \ln \kappa_i}{\partial \ln E/N}.
\]
Thus the deviations from Blanc's Law can be written,

\[
\Delta \frac{1}{\kappa_{\text{mix}}} = \frac{1}{\kappa_{\text{mix}}} - \frac{1}{\kappa_{\text{B}}} \cdot \frac{X}{a_{n} \kappa_{i} E/N} \left\{ \left[ (m+M_{i}) \kappa_{i} \right]^{2} - \frac{X_{i}}{\kappa_{i}} \sum_{j} \sum_{k} \frac{X_{j} X_{k}}{\kappa_{j} \kappa_{k} (m+M_{k})} \right\}^{-1} \right. \]

A.24
APPENDIX B

THE COMPUTER CONTROL OF THE QUADRUPOLE MASS SPECTROMETER

The quadrupole mass spectrometer in System A was controlled by using a P.D.P.8/E digital computer. A schematic diagram of the control circuit is shown in Fig. B.1 and the individual components are described below. In Fig. B.1 all terminals which either receive or transmit pulses from ground to level one are denoted with an open circle; if a terminal is unmarked it receives or transmits pulses from level one to ground.

Device Selectors.

These modules provide the links between the computer and the circuitry. When suitable combinations of pulses from the computer are applied to the input side, predetermined output gates are opened and pulses transmitted. Each flip chip module consists of three parallel circuits which can be used independently or in certain combinations. For example, it is possible to pulse each output on any module consecutively by means of only one computer command. Each of the three circuits on any module can transmit pulses to earth or to level one.

Counter.

The counter has a maximum capacity of $2^{12} = 4096$ counts. When this number is exceeded an overflow pulse is generated and the counter cleared and restarted automatically. The overflow pulse could be fed to another identical counter, but, in this work, an overflow was a relatively infrequent occurrence (the maximum count rates were of the order of $10^5 \text{s}^{-1}$) and there was ample time to use the computer itself as the auxiliary counter. At the end of each counting period data was strobed into the input/output register, or accumulator, of the computer and processed.

D.A.C.

The twelve bit digital to analogue converter normally has an output range of from 0 to 10 volts. Since the quadrupole requires negative going voltages the zero of the D.A.C. was offset by -10v and the input signal was complemented. The D.A.C. has a settling down time of 50 µs for a full scale change in voltage.

Buffer.

The output of the D.A.C. is determined at all times by the state of the input lines. Thus it is necessary to hold the input constant and isolated from the computer during the timing delay. This is done by means of a buffer. The output lines of the buffer are only connected to the input lines when a pulse is applied to the input gate. At other times the output lines are held at the value determined at the previous gating pulse.
Fig. B.1
Delays.

Two delays were used.

Delay 1: this was used to allow first the D.A.C. and then the quadrupole to adjust to the change in the input signal before the counter was started. A nominal delay time of 10 ms. was used, but since this time was at least an order of magnitude larger than that required, fluctuations in the delay time of several percent were unimportant.

Delay 2: this delay controlled the counting time. The stability requirements were therefore severe. The delay time was either 0.5s or 1.0s and could be varied by simple programming procedures. Usually the 0.5s delay was used. The delay times were accurate to better than one cycle of the clock time, namely 1 µs.

Flag Module.

When, for example, the counter overflow pulse is generated, the computer cannot distinguish this signal from other possible signals from this and other experiments. Flag modules allow one to programme the computer to determine from which device the signal came. Instead of connecting the counter overflow line directly to the computer, it is connected to a switch or flag on this module. When this flag is set, a flag in the computer is also set by a signal shown as "interrupt" in Fig. B.1. The computer services the interrupt when it has finished executing the instruction or non-visible series of instructions it was engaged in when the interrupt flag was set. To do this, it determines, by means of the device selectors and the "test" lines which flag has been set. The computer then resets the flag and executes the instructions required. There are three independent flag circuits on each flip chip module, but all flags can be reset by means of the "clear all flags" facility.

A typical sequence of events for the operation of these logic circuits is as follows:

1. Clear all flags.
   Load the binary number corresponding to the beginning of the first mass number into the accumulator of the computer.

2. Strobe this number into the D.A.C., start the settling time delay and clear the counter.
   When this short delay is over the timing delay and the counter are automatically started. If during the timing delay the counter overflows the sequence of events is:-

3. Overflow flag set.

4. Test overflow flag, find flag set, adjust count.
(5) reset overflow flag.
Now assume the timing delay ends before the counter overflows again.
(6) timing delay ends, counter stops and timing flag set.
(7) test for timing flag, find flag set.
(8) strobe count into accumulator and then transfer into memory.
(9) reset timing flag.
Continue programme.
APPENDIX C

The reduced mobility of Li$^+$ ions in He, Ne, Ar, H$_2$ and N$_2$. 
### TABLE C.1

Reduced Mobility of Li\(^+\) ions in Helium at 294K

<table>
<thead>
<tr>
<th>(E/p_{273.2}) (\text{V/cm} \times \text{torr}^{-1})</th>
<th>(E/N) (\text{Td})</th>
<th>(\kappa) (\text{cm}^2 \text{V}^{-1} \text{s}^{-1}) at (p_{273.2}) (torr) of</th>
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Data taken using System A: 9 cms drift distance.
Table C.2
Reduced Mobility of Li\(^+\) ions in Neon at 294K

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<th>E/p(_{273.2}) (V cm(^{-1}) torr(^{-1}))</th>
<th>E/N (Td)</th>
<th>(\kappa) (cm(^2) V(^{-1}) s(^{-1})) at p(_{273.2}) (torr) of</th>
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Data taken using System A: 9 cms drift distance.
### TABLE C.3

Reduced Mobility of Li\(^+\) ions in Argon at 293K

| $E/p_{273.2}$ (V cm\(^{-1}\) torr\(^{-1}\)) | $E/N$ (Td) | $\kappa$ (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) at $p_{273.2}$ (torr) of |  
|---------------------------------|---------|-------------------------------------------------|---|
| 4.0                             | 11.3    | 4.645                                           | 4.628|
| 6.0                             | 17.0    | 4.644                                           | 4.626|
| 8.0                             | 22.6    | 4.657                                           | 4.640|
| 10.0                            | 28.3    | 4.699                                           |      |

Data taken using System A: 3 cms drift distance.
TABLE C.4

Reduced Mobility of Li\(^+\) ions in Hydrogen at 294K

| E/P\(_{273.2}\) (V cm\(^{-1}\) torr\(^{-1}\)) | E/N (Td) | \(\kappa\) (cm\(^2\) V\(^{-1}\) s\(^{-1}\)) at P\(_{273.2}\) (torr) of |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 0.75 | 2.12 | .817 | 2.39 | 5.06 | 9.68 | 19.1 | 37.9 |
| 1.0 | 2.83 | | | | | |  |
| 2.0 | 5.66 | | | | | |  |
| 4.0 | 11.3 | | | | | |  |
| 6.0 | 17.0 | | 12.26 | 12.26 | 12.26 | 12.25 | 12.22 |
| 8.0 | 22.6 | | 12.26 | 12.26 | 12.26 | 12.25 |  |
| 10.0 | 28.3 | | 12.26 | 12.26 | 12.26 | 12.25 |  |
| 12.0 | 33.9 | | 12.26 | 12.26 | 12.26 | 12.25 |  |
| 14.0 | 39.6 | | 12.26 | 12.26 | 12.26 | 12.25 |  |
| 18.0 | 50.9 | | 12.26 | 12.26 | 12.26 | 12.25 |  |

Data taken using System A: 9 cms drift distance.
## TABLE C.5

Reduced Mobility of Li\(^{+}\) ions in Nitrogen at 293K

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<th>$\frac{E}{P_{273.2}}$ (V cm(^{-1}) torr(^{-1}))</th>
<th>$\frac{E}{N}$ (Td)</th>
<th>$\kappa$ (cm(^2) V(^{-1}) s(^{-1})) at $P_{273.2}$ (torr) of 100</th>
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Data taken using System A: 3 cms drift distance.
APPENDIX D

The reduced mobility of K\(^+\) ions in He, Ar, H\(_2\), N\(_2\) and O\(_2\)
<table>
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<th>E/p_{273.2} (V cm^{-1} torr^{-1})</th>
<th>E/N (Td)</th>
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Data taken using System B.
### TABLE D.2

Reduced Mobility of $K^+$ ions in Argon at 291K

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<th>$E/p_{273.2}$ (V cm$^{-1}$ torr$^{-1}$)</th>
<th>E/N ($T_d$)</th>
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Data taken using System B except those in italic figures which were taken using System C.
### TABLE D.4

Reduced Mobility of $\text{K}^+$ ions in Nitrogen at 293K

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<th>$E/p_{273.2}$ \ (V cm$^{-1}$ torr$^{-1}$)</th>
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Data taken using System B.
### TABLE D.5

**Reduced Mobility of $K^+$ ions in Oxygen at 292K**

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<th>$E/p_{273.2}$ (V cm$^{-1}$ torr$^{-1}$)</th>
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*Data taken using System B.*
APPENDIX E

The reduced mobility of Cs\(^+\) ions in He and Ne
## TABLE E.1

Reduced Mobility of Cs\(^+\) ions in Helium at 293K

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Data taken using System A except those in italic figures which were taken using System B.
APPENDIX F

The reduced mobility of $K^+$ ions in He-Ne, Ne-Ar and $H_2-N_2$ mixtures
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<th>0</th>
<th>25</th>
<th>50</th>
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Data taken using System B.
APPENDIX G

The longitudinal diffusion coefficient of K$^+$ ions in He, Ne and Ar
### Table G.1

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<th>$E/N$ (Td)</th>
<th>$P_{273.2}$ (torr)</th>
<th>$D_{L}/K$ (mV)</th>
<th>$N_{DL}$ ($\times 10^{18}$ cm$^{-1}$ s$^{-1}$)</th>
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Data taken using System B.
TABLE G.2

ND_L and D_L/K for K⁺ ions in Ar at 292K

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<th>E/N</th>
<th>P_{273.2}</th>
<th>D_L/K</th>
<th>ND_L</th>
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<td>(V cm⁻¹ torr⁻¹)</td>
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<td>(torr)</td>
<td>(mV)</td>
<td>(× 10¹⁸ cm⁻¹ s⁻¹)</td>
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Data taken using System B.
TABLE G.3

NDL and DL/K for K⁺ ions in N₂ at 293K

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<th>E/N (Td)</th>
<th>P_{273.2} (torr)</th>
<th>D_L/K (mV)</th>
<th>NDL (× 10¹⁸ cm⁻¹ s⁻¹)</th>
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Data taken using System B.
APPENDIX H

An investigation into the effects of bombarding low energy electrons and $K^+$ ions onto various metal surfaces

In an attempt to understand the phenomenon of upcurving, which is described in Chapter 6, a study was made of the effects of collecting electrons and $K^+$ ions on various metal surfaces. The only previous study of a similar nature appears to be that of Petit-Clerc and Carette (1968) who investigated the effects of bombarding low energy electrons and positive gaseous ions onto aluminium and stainless steel surfaces. There appear to be no previous studies of the effects of alkali ions on metal surfaces. The technique used by Petit-Clerc and Carette and also used in this work was to compare the contact potential difference between a metal probe and the surface before and after the surface had been bombarded.

The method usually used to measure contact potential differences involves positioning a metal probe a small distance (typically 1mm) above the surface under investigation and then moving the probe quickly to a new position further from the surface. If a potential difference exists between the probe and the metal surface the change in capacitance between the probe and the surface when the probe is moved will induce a transient current to flow in the external circuit. This current is easily measured with an electrometer. The contact potential difference is then measured by adjusting the potential of, in this case, the metal surface until no current flows in the external circuit when the probe is moved.

The apparatus used in this work is shown in Fig. H.1 and has previously been described by Crompton et al. (1965). The surface to be examined is supported by insulating glass blocks on a table that can be rotated by a shaft passing through the baseplate. The probe can be raised and lowered by means of a sliding rod and can also be moved in the horizontal plane. By the movement of the probe and turntable any area 0.6 cm in diameter (the diameter of the probe) on a surface 10 cm in diameter can be examined. For this work the apparatus was modified to include a filament assembly situated about 1 cm from the metal surface under investigation and an additional electrode (repeller plate) situated above the filament. The repeller plate ensured that only a small area of the surface
was bombarded. Base pressures of approximately $10^{-4}$ torr were achieved with a trapped $5/4$ torr pump. The surfaces were carefully cleaned before they were placed in the vacuum system. In particular the surfaces were cleaned with metal polishes, detergents, alcohol and cleaned in a vapour degreasing bath. It was found that if the vapour degreasing bath was not used the effects did not change by a significant amount. It was also found that the effects did not depend on whether a sheet of polished metal was used or whether the surfaces were formed by vacuum deposition of a thin film onto an unlike substrate.

Experimental results.

A. x$^+$ ions.

The results of the experiments with x$^+$ ions have been reported in Chapter 4.

b. Electron bombardment.

When surfaces of gold, platinum and copper were bombarded with low energy electrons (< 15 V) it was found that the potential of the surface close to the filament increased positively. The potential of the surface was then found to decay to a new equilibrium value above that of the filament. The surface behaviour with positive potentials could not be distinguished from the behaviour exhibited after bombardment with positive potentials on a non-potential or stainless-steel surface. The potential of the surface increased positively. The surface then returned to its former value in a few hours. Fig. H.1 shows the variation of the surface potential with time for a selection of materials and potentials. An attempt was made to determine the electron bombardment damage on the gold plate in a vapour deposition bath for a period of time. The plate was then bombarded with 2 cm of gold and no damage was observed. This result was repeated with a gold plate in a vapour deposition bath for a period of time. The plate was then bombarded with 2 cm of gold and no damage was observed. This result was repeated with a gold plate in a vapour deposition bath for a period of time.
was bombarded. Base pressures of approximately $10^{-5}$ torr were achieved with a trapped 8 l/s ion pump. The surfaces were carefully cleaned before they were placed in the vacuum system. In particular the surfaces were cleaned with metal polishes, detergent and hexane and then placed in a vapour degreasing bath. It was found that if the vapour degreasing bath was not used the effects did not change by a significant amount. It was also found that the effects did not depend on whether a sheet of pure metal was used or whether the surfaces were formed by vacuum deposition of a thin film onto an unlike substrate.

**Experimental results**

**A. $K^+$ ions.**

The results of the experiments with $K^+$ ions have been reported in Chapter 6.

**B. Electrons.**

When surfaces of gold, platinum and copper were bombarded with low energy electrons ($< 13$ V) it was found that the potential of the surface close to the filament increased positively. The potentials of the surface was then found to decrease with time and come to a new equilibrium value above that of the initial level. The surface behaviour with these metals could not be distinguished from the behaviour exhibited after bombardment with positive potassium ions. On the other hand when aluminium and stainless steel surfaces were used the potential of the irradiated portion of the surface increased negatively. The surface then returned to its former value in a few hours. Fig. H.2 shows the variation of the surface potential with time for samples of gold and aluminium.

An attempt was made to correlate the anomalous results of the electron bombardment experiments on gold, platinum and copper with the presence of contaminants in the vacuum system. The most likely contaminants were hydrocarbons, water, nitrogen and carbon monoxide. Part of a gold surface was smeared with Apiezon N grease, the grease used in the vacuum seals, and some of the grease was then removed by placing the metal plate in a vapour degreasing bath for a short time. When the plate was placed in the vacuum system the film of grease was thick enough to make it visible to the naked eye. After the system had been pumped down to about $10^{-5}$ torr electrons were bombarded onto part of the surface covered
Consider first a clean metal surface covered with a few layers of hydrocarbon molecules. It is assumed that there is no interdiffusion of the hydrocarbon molecules on the metal surface. If electrons with a few electron volts energy strike this surface they may ionize some of the hydrocarbon molecules. The electrons formed in this process and the incident electrons would be attracted to the metal surface by diffusion through the hydrocarbon molecules which it is assumed cannot be quickly neutralized because the molecules cannot be scattered by the high retarding potentials of the incident electrons. Thus the incident electrons are not deviated and the potential of the bombarded surface does not rise unreasonably. In the case of metals like aluminium and stainless steel which are covered with insulating oxide layers the situation is similar. The oxide layer is essentially the same as in the case of electrodes, the charge arising at the surface is stored because of the insulating layer. In the case of...
with grease. This resulted in the potential of the bombarded area increasing negatively by 2 volts, a change opposite in sign and about an order of magnitude greater than that observed with nominally grease free surfaces under similar conditions.

**DISCUSSION**

Both the effects observed with $K^+$ ions and the effects with electrons on aluminium and stainless steel are consistent with the gaseous ion and electron work of Petit-Clerc and Carette but as far as is known there are no reports of electrons charging surfaces positively (apart from the Malter effect (Malter 1936)). The apparent build-up of charge on a metal surface will now be discussed in more detail.

Consider first a clean metal surface covered with a few layers of hydrocarbon molecules. It is assumed that there is no insulating oxide film on the metal surface. If electrons with a few electron volts energy hit this surface they may ionize some of the hydrocarbon molecules. The electrons formed in this process and the incident electrons would be able to move to the metal surface both by diffusion through the hydrocarbon layers and by drift motion under the action of the electric field. This process would leave the surface layers with a net positive charge, as is observed in the electron experiments with gold, platinum and copper. This charge cannot be quickly neutralized because electrons cannot be easily ejected out of the metal surface as the work function for most metals is a few electron volts. Thus the long time constants observed for the decay of the potential of the bombarded patches do not seem unreasonable.

If the surface layers of hydrocarbons are very thick (by atomic standards) the oil will act as an insulator and even if some ionization takes place the resultant electrons will be unable to move quickly to the metal surface. The surface will therefore charge negatively if bombarded with electrons. This was observed when the gold surface was smeared with grease. The same situation will arise in the case of metals like aluminium and stainless steel which are covered with insulating oxide layers.

Bombardment by positive ions resulted in a net positive charge on each surface. In the case of aluminium and stainless steel the action is essentially the same as in the case of electrons; the charge arriving at the surface is stored because of the insulating layer. In the cases of
gold and copper which are assumed to have only a thin layer of insulation material on top of the pure metal surface, it is postulated that the transmission of the $K^+$ ions by diffusion processes is very poor and even a few monolayers of hydrocarbons act as a considerable impedance to the passage of ions. Also, as before, it is unlikely that an electron will escape from the metal to neutralize the ion.
A Gas Analyzer for Trace Impurity Analysis

M. T. Elford and H. B. Milloy

Ion Diffusion Unit, Research School of Physical Sciences, Australian National University, Canberra, Australia

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A commercial residual gas analyzer has been modified by the addition of a directed gas jet to enable impurity concentrations to be measured in the low parts per million range. Particular attention has been paid to the abundance of N2 in Ne and Ar. The errors in the abundance measurements are estimated to be less than 0.2 ppm at 0.2 ppm of N2 in Ne and 0.6 ppm at 5 ppm of N2 in Ar. The choice of operating parameters, sources of error and advantages of this type of analyzer are discussed.

Introduction

In a number of laboratories where ultra-pure gases are used it is common for a residual gas analyzer to be employed to monitor the behaviour of ultrahigh vacuum systems. It has been found that with the simple addition of a gas jet and a careful choice of operating parameters the residual gas analyzer can be converted to measure trace impurities in gas samples in the low parts per million range. The major experimental problem in abundance measurements at this level is the necessity of ensuring that the current peak due to the impurity is much larger than either the noise of the detection system or the current due to the residual gas background. The usual approach to this problem is to use high inlet gas pressures, but with enclosed ion sources memory effects may become significant. To avoid this problem a number of workers have used a beam of gas and a very open (or skeletal) ion source structure. The gas beam is arranged so that it intersects the electron beam but does not significantly impinge on the electrodes of the ion source. This is the technique used in the present work. One other alternative method of gas analysis using a gas beam is that of Olander and Waddell in which a gas beam is modulated and a phase sensitive detector is used. This method is both complex and expensive and not readily adapted for routine analysis.

I. Apparatus

The gas analyzer is shown schematically in Fig. 1. A jet of gas formed by a stainless steel tube (0.2 mm diam, 13 mm in length) passes through the ion source of a commercial residual gas analyzer (EAI Quad 150A) in a direction normal to both the electron beam and the axis of the quadrupole rod system. The degree of collimation obtained with this tube was found to be sufficient for the present purposes and it was therefore unnecessary to use high inlet gas pressures as a means of increasing the signal to noise ratio.

Figure 1. Schematic diagram of gas analyzer.

the bundles of very fine tubes which are frequently used to produce well-collimated gas beams. The inlet tube was vacuum-brazed into a stainless steel tube which was welded into a vacuum flange, thus avoiding the necessity of supporting the inlet tube from the ion source. The electrode system of the commercial instrument could therefore be used without any modification. The ion source conditions were as follows: electron emission current ratios were calculated from the currents to the electrode system of the commercial instrument could be used without any modification. The ion currents were detected by a 14-stage Be-Cu particle multiplier operated with the first dynode at a potential of 3 kV. The ion currents were measured with a quartz spiral manometer (Texas Instruments Ltd.). The gas inlet system with the exception of the leak valve, the line between the leak valve and the gas cylinder, and the connections to the pressure gauge were baked to 150°C at the same time as the analyzer was heated. The sections of the inlet system not baked were either subject to very high gas pressures (the section between the gas bottle and the leak valve) or were small in surface area (connections to the pressure regulator was used in order to avoid contamination from elastomers commonly found in these devices. The pressure in the inlet lines varied between 1–20 Torr and was measured with a quartz spiral manometer.

The pumping and gas inlet systems are shown in Fig. 2. The analyzer was pumped by a 4-in. oil diffusion pump (using Santovac 5 oil) and trapped by a 4-in. liquid nitrogen trap (Granville–Phillips). This system has a pumping speed of ~100 liter/sec at the top flange of the trap. No water baffle was used. After baking the analyzer at 200°C for 16 h an ultimate pressure of 1x10⁻¹⁰ Torr was achieved, with the analyzer filament operating, the residual gas consisting predominantly of H₂ (70%) and mass number 28 (25%). No ion current peaks corresponding to hydrocarbons were detected. The gases to be analyzed were contained in stainless steel cylinders at high pressures and were connected to the gas inlet system by a uhv leak valve. No pressure regulator was used in order to avoid contamination from elastomers commonly found in these devices. The pressure in the inlet lines varied between 1–20 Torr and was measured with a quartz spiral manometer. The gas inlet system with the exception of the leak valve, the line between the leak valve and the gas cylinder, and the connections to the pressure gauge were baked to 150°C at the same time as the analyzer was heated. The sections of the inlet system not baked were either subject to very high gas pressures (the section between the gas bottle and the leak valve) or were small in surface area (connections to the pressure gauge). Subsequent tests in which the samples were held in the inlet lines at a pressure of 1 Torr for varying intervals of time (up to 1 h) before analysis showed that the outgassing of the inlet system was sufficiently low that there was no measureable dependence of the impurity level of the gas samples on the time the sample was held in the inlet system. The advantage of using high inlet gas pressures is self evident.

The choice of pumping system is significant in low level gas analysis. One obvious possibility is the use of ion pumps due to their simplicity and freedom from oil vapors. However, the presence of the gas to be analyzed at background pressures of the order of 10⁻⁴ Torr causes large quantities of gas to be desorbed from the surfaces of the ion pump and also from the walls of the vacuum system. The gases desorbed are those pumped slowly, e.g., Ar, or those produced by reactions, i.e., CO and CH₄. These effects were most pronounced when the present analyzer was pumped by a 140-liter/sec ion pump. Before analyzing a sample of hydrogen, the ion currents corresponding to the mass numbers observed in the residual gas spectrum were recorded. Hydrogen was admitted until the background pressure rose to 10⁻⁴ Torr and the ion currents again measured. All ion currents were then expressed as a ratio R of the ion currents corresponding to hydrogen at mass number 2. Thus the values of R (>) in parts per n pattern correct are shown in F the measured and the open sample was let.

One addition their low pump necessitates usiquent loss of outgassing in the

FIGURE 2. The vacuum and gas inlet system. The letters denote the following: T, liquid nitrogen trap; TG, pressure gauge; P, pirani gauge; I, ionization gauge. V₁ and V₂ are volumes used in the preparation of gas mixtures.

FIGURE 3. An inlet was used to evacuate currents measure hatched bars indicate of the hydro

values of $R \times 10^6$ may be regarded as concentrations, in parts per million, ignoring sensitivity and cracking pattern corrections. The results of these measurements are shown in Fig. 3, where the black bars correspond to the measurements with only the residual gas present and the open bars to the increase when the hydrogen sample was let in.

It can be seen that the level of argon, for example, increased by approximately two orders of magnitude. The total impurity level indicated in this analysis is about 2000 ppm. When the ion pump was replaced by a trapped diffusion pump and the analyzer operated under identical conditions, the apparent total impurity level in the hydrogen was found to decrease from 2000 to 130 ppm. After baking the analyzer, this level dropped further to less than 5 ppm. These results suggest that ion pumps should be avoided in trace analysis.

One additional factor against the use of ion pumps is their low pumping speed for the lighter inert gases. This necessitates using low inlet gas pressures with a consequent loss of sensitivity and possible errors due to outgassing in the inlet lines.

II. Choice of Operating Parameters and Results

In order to obtain the required sensitivity and accuracy in the analysis, the operating parameters, and in particular, the inlet pressure must be chosen with care. Although the impurity level can be determined at one inlet pressure, the independence of the impurity level over a range of inlet pressures provides an important check on the operation of the analyzer. The range of inlet pressures that can be used, however, is restricted by a number of factors.

The upper limit to the pressure range is determined by the onset of space charge effects. The manner in which space charge influences the primary ion current peak can be seen by plotting the sensitivity (defined here as the ion current per unit inlet pressure) as a function of the inlet pressure. A typical plot, in this case for argon, is shown in Fig. 4. The sensitivity increases with increasing inlet pressure, reaching a maximum at a pressure of $\sim 10$ Torr and thereafter decreasing. The initial rise in sensitivity is thought to be due to the gas flow from the nozzle becoming increasingly concentrated in the forward direction. As the pressure is further increased the onset of space charge effects causes the collected ion current to saturate with a resultant decrease in sensitivity. These space charge effects may occur in either the ion source or the ion beam. If the ion current extracted from the ion source is limited by space charge, then all the ion current peaks in the spectrum will be equally affected. On the other hand, if space charge effects occur in the ion beam as it travels through the rod system, the magnitude of the effect will depend on the transmitted ion current. By measuring the abundance ratio of a suitable isotope, e.g., $^{36}$Ar (abundance ratio $0.3\%$) as a function of inlet pressure it is possible to show that space charge effects occur first in the ion beam and only at higher pressures in the ion source.

The impurity peak is subject only to the effects of space charge in the ion source since the very small impurity ion currents make space charge effects which occur during the passage of impurity ions through the rod system negligible. The impurity peak is therefore influenced by space charge effects only when very high inlet pressures are used and usually the upper pressure limit is set by the necessity of avoiding discharge occurring in the particle multiplier at high background pressures rather than by the onset of space charge in the ion source.

The lower limit to the inlet gas pressure is set by two factors. Usually the dominant factor is the necessity to have a signal, which corresponds to $\approx 0.3$ ppm, larger than the noise in the detection system. Most of this noise is generated by photons, incident on the first dynode of the multiplier.\(^7\) These photons are produced by the decay of excited atoms in the ionizer and give rise to a background current at the output of the multiplier

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**Figure 3.** An ion current spectrum obtained when an ion pump was used to evacuate the analyzer. The solid bars indicate the ion currents measured before the introduction of the sample gas. The hatched bars indicate the increase in the ion currents after introduction of the hydrogen sample to a background pressure of $1 \times 10^{-4}$ Torr.

**Figure 4.** The sensitivity of Ar$^+$ as a function of the inlet gas pressure. The sensitivity is defined here as the ion current at the first dynode of the multiplier per unit inlet gas pressure.
which can be an order of magnitude larger than the ion currents due to impurities. This background current is approximately a linear function of the pressure and the procedure used in the present work was to annul this current in the measurement circuit. Although techniques such as optical baffles or an offset multiplier have been used to eliminate the photon flux to the detector, these methods were not used here in order to avoid making any modification to the commercial residual gas analyzer used.

The other lower limit to the inlet gas pressure applies only to those cases where the impurity to be detected in the sample gas corresponds to an impurity which is prevalent in the residual gas. The ion current corresponding to the impurity in the gas sample must be significantly larger than the residual gas component if an accurate impurity level is to be determined.

The limits discussed above result in a working range of inlet gas pressures of approximately 5–20 Torr, although the precise range depends on the gas and the impurity level of the gas sample being analyzed. The analyzer background pressures range between approximately 5 × 10^{-5} and 1.5 × 10^{-4} Torr.

A typical recorder trace of an ion current peak at mass number 28 for an argon sample containing 5 ppm of N₂ is shown in Fig. 5. The trace was taken with an inlet pressure of 6.7 Torr and an electron emission current of 100 μA. The ion current due to the residual gas at mass number 28 was 6.3 × 10^{-12} A or 13% of the peak shown. In general, in analyses of argon samples containing ~5 ppm of N₂, the residual gas background contributed less than 15% of the observed ion current peak at mass number 28 for all inlet pressures greater than 5 Torr. The noise shown in this trace is almost entirely due to that associated with the large background signal arising from photons incident on the multiplier.

The procedure for measuring the impurity levels was to determine the ratio of the ion current corresponding to a particular mass number to the ion current corresponding to the primary gas component. In each case the current corresponding to the residual gas background was subtracted before the ratio was calculated. The current ratio was then plotted as a function of inlet gas pressure and typical plots, in this case for mass number 28, are shown in Fig. 6 for two different samples of argon. This particular mass number is of interest as nitrogen was the most abundant impurity present in the samples of high-purity inert gases obtained from commercial sources and is responsible for significant errors in measurement of electron transport coefficients in neon and argon.

It can be seen from Fig. 6 that the relative abundance is independent of the inlet pressure for both argon samples. However, when inlet pressures greater than 15 Torr were used the measured relative abundance was found to increase with inlet pressure due to space charge in the primary ion beam causing the transmitted primary ion current to saturate (see Fig. 4). In the data shown this effect does not cause the values to deviate beyond the stated error bounds but at 25 Torr this effect was found to cause the relative abundance to increase by up to 20% from the constant value found at lower pressures. The impurity levels shown in Fig. 6 have been calculated from ratios of ion currents only and have to be corrected for sensitivity variations between gases. These sensitivities are easily determined experimentally.

The systematic error in the relative abundance measurements resulting from the ion current measurements is estimated to be less than 5%. The only significant random error arises in the measurements of the current peak corresponding to the impurity. The impurity current peak is subject to short-term variations (up to 10%) in the multiplier gain from the mean value of 1 × 10^{4}. This fluctuation may be associated with the low gain figure and suggests that the dynode surfaces were in poor condition. Two other sources of error are the noise in the measurement circuit and that resulting from the photon flux to the first dynode. These three sources of random error are responsible for the deviations of the experimental points from the linear relation shown in Fig. 6. In the case of argon containing 5 ppm of N₂ it is estimated from this scatter that the abundance of mass 28 is known with a random error of ±0.3 ppm. In neon because of the much smaller photon flux to the first dynode this uncertainty is reduced to ±0.1 ppm. The gas pressure at mass number 28 was 6.3 × 10^{-12} A or 13% of the peak shown.

FIGURE 5. A recorder trace of the ion current peak at mass number 28 for an argon sample containing 5 ppm of N₂. The base level of the trace corresponds to 4.5 × 10^{-12} A which is the background current due to photons incident on the first dynode of the multiplier. The trace was taken with an inlet pressure of 6.7 Torr and an electron emission current of 100 μA.

FIGURE 6. The measured abundance of mass number 28 (in ppm) as a function of inlet gas pressure for two samples of argon.

impurity at mass number 28 in the gas samples has been assumed to be entirely due to nitrogen. This assumption is based on the conclusions of Robertson, who investigated the effect of nitrogen impurities on electron drift velocity measurements using the gas from the same cylinders used in these analyses.

An anomalous result was found when the electron emission current was varied from 50–1000 µA. It was observed that there was a dependence of the impurity level corresponding to mass number 28 on the electron emission current. An example of this variation is shown in Fig. 7 for the sample denoted Ar I. The only impurity peak which showed this effect was that corresponding to mass number 28. It has therefore been postulated that the increase in impurity level of this mass number with increasing emission current is due to the increasing production of CO at the filament surface or by electron impact at the collector surface. A correction for this effect was made by extrapolating to zero emission current. For measurements made at an emission current of 100 µA the correction was 0.2 ppm, the error incurred in this extrapolation being estimated as less than 0.1 ppm.

The N₂ impurity levels detected with the analyzer are shown in Table I together with those predicted by Robertson from an analysis of electron drift velocity data and those of a direct analysis by an independent laboratory using gas chromatography. The method of Robertson is necessarily indirect but due to the extreme sensitivity of the electron drift velocity in neon and argon to small traces of nitrogen this method has a high sensitivity. The error assigned to the impurity levels measured by the present technique was obtained by summing the random and systematic errors.

It can be seen that the present analyses are in agreement with Robertson’s predictions and the independent analysis to within the stated error limits in all cases.

Two sets of measurements were made to check the accuracy of the analyzer. In the first, 5 ppm of N₂ were added to gas from the sample Ar I (Table I) which was considered to contain 0.8 ppm of N₂. The analysis of this mixture showed a N₂ impurity level of 4.9 ppm compared with the predicted level of 5.8 ppm. The difference of 0.9 ppm is greater than the estimated measurement error of 0.6 ppm but the discrepancy is probably due to a small amount of absorption of the nitrogen impurity on the walls of the vacuum system during the preparation of the mixture and other inaccuracies in the volume sharing method used. Part of the discrepancy may also be attributed to an error in the measured value of 0.8 ppm of N₂ in the sample Ar I used for this mixture.

The second test of the accuracy of the analyzer was to analyze a sample of argon which had been purified by passage through a quartz tube containing titanium pellets heated to 850°C. No significant nitrogen level could now be detected. The minimum detectable nitrogen impurity level was estimated to be 0.3 ppm.

### III. Discussion

The experimental problems in measuring impurity levels in the low ppm range depend on the particular impurity concerned. The impurity of interest in the present work, N₂, is a particularly difficult one to measure accurately as the peak due to nitrogen at mass number 28 cannot be distinguished from that due to CO with the limited resolution of the quadrupole mass spectrometer used. At the low impurity levels considered here it is not possible to separate the CO and N₂ components of mass number 28 peak by the use of the cracking patterns since the minor peaks at mass numbers 12 and 14, respectively, are too small for accurate measurement. CO is produced at the surface of hot tungsten filaments and forms adsorbed layers on the metal surfaces of the vacuum system. To reduce the production of CO at filaments, the ionization gauge was not operated during the analysis and the filament of the ion source was operated at the lowest practicable temperature, i.e., low electron emission currents were used.

Although nitrogen was the only significant impurity observed in these analyses, there are some difficulties in determining the presence of other impurities. Because of the high gas number densities in the ion source there was a significant production of molecular ions in the neon and argon analyses and these ions can mask impurities in certain cases. For example, the production of Ne²⁺ by the reaction

\[ \text{Ne}^+ + 2\text{Ne} \rightarrow \text{Ne}_2^{2+} + \text{Ne} \]

produces a peak at mass number 40 and therefore makes it difficult to detect argon impurities in neon. Another complication is the production of doubly ionized isotopes. For example, \(^{36}\text{Ar}^{2+}\) is produced in the reaction

\[ e^+ + ^{36}\text{Ar} \rightarrow ^{36}\text{Ar}^{2+} + 2e \]

### Table I. Nitrogen impurity levels (parts per million).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Present</th>
<th>Commercial</th>
<th>Robertson</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar I</td>
<td>0.8±0.3</td>
<td>Not known</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Ar II</td>
<td>4.8±0.6</td>
<td>4.8</td>
<td>4±2</td>
</tr>
<tr>
<td>Ne I</td>
<td>0.2±0.2</td>
<td>0.4</td>
<td>b</td>
</tr>
<tr>
<td>Ne II</td>
<td>0.4±0.2</td>
<td>Not known</td>
<td>b</td>
</tr>
</tbody>
</table>

* The gas samples Ar I, Ar II, and Ne I were obtained from the Matheson Gas Company, and were of research grade. Sample Ne II was obtained from Australian Liquid Air Ltd.

** Robertson predicted that Ne I and Ne II contained equal amounts of N₂ to an accuracy of 1 ppm.
and gives a peak at mass number 18, thus interfering with the peak due to water vapor. It is possible to examine the effect of both molecular ions produced by ion–molecule reactions and doubly charged isotopes by either varying the inlet pressure in the first case or by examining the peak at mass 17 due to OH⁺ in the second. In order to determine if there was a significant memory effect deuterium was passed through the system for 1 h. Deuterium was chosen rather than hydrogen due to the negligible level of this gas in the residual gas spectrum. The system was evacuated and neon admitted. No deuterium was observed in the neon spectrum.

IV. Conclusion

The gas analyzer described is relatively inexpensive and is based on a commercial instrument which can be used without modification to the electrode system. It has been demonstrated that this analyzer is capable of measuring impurity levels of nitrogen in the inert gases neon and argon with an absolute error of less than 0.6 ppm at 5 ppm of N₂ in Ar and 0.2 ppm at 0.2 ppm of N₂ in Ne. The lower limit of detection in neon is estimated to be ~0.1 ppm and in argon 0.3 ppm. Although these errors and detection limits were adequate for the present application of this gas analyzer, both the errors and detection limits could be considerably reduced by using a multiplier of higher gain and shielded from the photon flux. The present background level of CO could be reduced by replacing the tungsten filament by one of rhenium. This study has been limited to nitrogen as the impurity but there appears to be no difficulty in extending this technique to other impurities. In particular it would be very suitable for determining the impurity level of O₂.

The major disadvantage of this analyzer is the necessity for obtaining a very low ultimate pressure by the use of ultrahigh vacuum techniques. The analyzer also has a relatively large consumption of sample gas, of the order of 5×10⁻³ Torr·liter/sec. Although this would preclude the use of this device where only small quantities of gas were available, in many experiments such as those used to study the behavior of electron swarms in gases, samples of 5×10³ Torr·liter at pressures of the order of 500 Torr are commonly available and the consumption of gas by the analyzer does not present a problem.

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APPENDIX J

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A Gas Analyzer for Trace Impurity Analysis.

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H.B. Milloy.


The Mobility of Potassium Ions in Gas Mixtures.

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