quoted error, no significant effect is apparent due to errors in $\Delta\nu$.

The effects of spin-exchange frequency shifts were experimentally treated by using both senses of circular polarization in all combinations for both Cs and Rb species, and in addition, by extrapolation of the results to zero-light intensities. Furthermore, an attempt was made to observe the frequency shift at high light intensities under the

various combinations of senses of circular polarization for the two lamps. Any possible frequency shifts were <0.1 Hz [16] at high light intensities. Since the polarizations of the species approach zero as light intensities are reduced to zero, and since the shifts are expected to be zero at zero polarization, the results extrapolated to zero-light intensity should not be significantly influenced by spin-exchange frequency shifts.

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Longitudinal-Diffusion Coefficient for Potassium Ions in Nitrogen at 293 K

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The Bradbury-Nielsen time-of-flight technique has been used to measure the longitudinal-diffusion coefficient D_L for potassium ions in nitrogen in the E/N range $2.83 \leqslant E/N$ (Td) $\leqslant 28.3$, where E is the electric field strength and N the gas number density. The results are consistent with the value predicted by the Nernst-Townsend (or Einstein) relation to within the claimed experimental error of 3%. The variation of D_L with E/N has been compared with the predictions of Wannier, based on a Maxwellian model.

I. INTRODUCTION

There are several parameters or transport coefficients which may be used to describe the motion of ions drifting under the influence of an electric field $\vec{E}$ in a gas of neutral particles of density N, but until recent years the majority of investigators have concentrated on measuring one particular coefficient, the reduced mobility κ. This quantity is defined as the mobility $K(=W/E)$ in a gas at standard number density N_s (i.e., that of a gas at

273.16 K and 760 Torr). Thus

$$\kappa = W/(760E/p_{273.16}) \,,$$

where W is the drift velocity. The reduced pressure $p_{273.16}$ is given by

$$p_{273.16} = p_T \times 273.16/T \text{ Torr},$$

where p_T is the pressure in Torr measured at an absolute gas temperature T. In practice, the parameter E/N rather than $E/p_{273.16}$ is used to enable convenient comparison of data to be made. [1] The

reduced mobility is then defined as

$$\kappa = \left(W \, \frac{1}{E/N} \right) \times 3.7215 \times 10^{-3} \ \mathrm{cm^2 \, V^{-1} \, sec^{-1}} \ ,$$

where E/N is in townsends [1 townsend (Td) = 10^{-17} V cm^2].

The diffusion coefficients are equally valuable in describing the behavior of ion swarms and, as in the case of the mobilities, they may be used to determine interaction potentials. The theoretical understanding of the diffusion of ions was developed largely by Wannier,[2] who pointed out that, in general, the coefficient of diffusion D_L in the direction of the electric field (longitudinal direction) is different from the diffusion coefficient D_T in the direction transverse to the field direction. Thus to describe fully the macroscopic diffusion processes in a drift tube, one requires both of these parameters. In the limiting case when the magnitude of the electric field tends to zero these coefficients are indistinguishable and can be calculated from the Nernst–Townsend relation

$$D_L = D_T = K_0 \, \frac{kT}{e} = \frac{N_s}{N} \, \kappa_0 \, \frac{kT}{e} \ , \tag{1}$$

where k is Boltzmann's constant, e is the ionic charge and K_0 and κ_0 are the mobility and reduced mobility, respectively, obtained by extrapolation to zero field strength. Thus the diffusion coefficient for ions in thermal equilibrium with the gas can be calculated once the zero field mobility has been determined.

Although there have been several determinations of D_L reported in the literature, the values of the coefficient extrapolated to zero field strength have been found to disagree by as much as 25% with the predictions of the Nernst–Townsend relation. Even considering the experimental scatter of the measurements, it is apparent that the values for positive ions are in general higher than the values predicted theoretically,[3–6] while those for negative ions are lower than the predicted values.[5] The purpose of the present work was to investigate the variation of D_L at low values of E/N and to see if the values obtained were consistent with the Nernst–Townsend relation. Such consistency is strong evidence for the reliability of experimental values of D_L.

II. THEORY

The method used to determine D_L was based on the time-of-flight technique developed by Bradbury and Nielsen,[7] a technique that has been extensively used to measure both ion and electron drift velocities.[8,9]

The time taken for a swarm of ions to drift a known distance h between two electrical shutters S_1 and S_2 (Fig. 1) is measured in terms of the fre-quency of an alternating potential difference. Each shutter consists of a coplanar set of parallel wires with alternate wires connected together. Thus ions are transmitted only when the voltage difference between the two sets of wires is small. In the present experiment sine-wave gating was used, the phase difference between the signal applied to the two sets of wires in one shutter being π. If the transit time t of an ion corresponds to an integral number of half-cylces of the gating signal, the ion will be transmitted by the second shutter S_2 and collected. Thus the transit time is related to the frequency of the gating signal by $t = m/2f$, where m is the integral number of half-cycles. The determination of D_L consists in measuring the spread of arrival times at a plane which is at a fixed distance from the source.

The continuity equation which describes the time rate of change of the ionic number density $n(x, y, z, t)$ at all points in space other than the source is[10]

$$\frac{\partial n}{\partial t} = D_T \left(\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} \right) + D_L \, \frac{\partial^2 n}{\partial z^2} - W \, \frac{\partial n}{\partial z} \ , \tag{2}$$

where the electric field is in the z direction. It is pointed out later that since the results for ND_L show no observable variation with pressure, the effect of ion-molecule reactions can be ignored. If both the radial boundaries and the source of the drift tube are assumed to be of infinite extent, the continuity equation can be reduced to a one-dimensional form. Equation (2) then has the solution[11]

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

where it is assumed that $n = 0$ at the source electrode (first shutter) except at $t = 0$, and that N_0' ions per unit area escape from the source. It is an important experimental requirement that the pulse transmitted by the first shutter is a close approximation to a δ function in time.

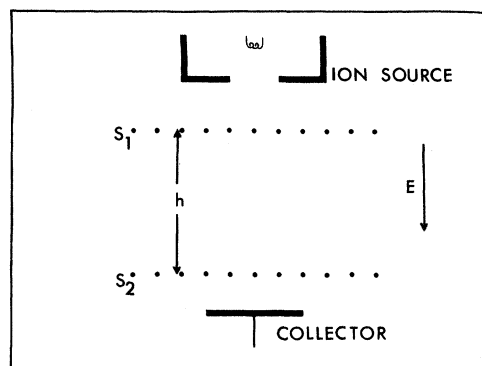In order to satisfy the boundary condition $n = 0$ at

FIG. 1. Schematic diagram of the Bradbury–Nielsen shutter method.

the second shutter while maintaining the boundary condition at the first shutter, an infinite series of terms is added to the solution given above, which results in the following expression for $n(z, t)$ [11]:

$$n(z, t) = \frac{N_0 2t}{(4\pi D_L t)^{1/2}} \frac{1}{Wt} \left\{ z \exp\left[-\left(\frac{(z - Wt)^2}{4D_L t} \right) \right] \right.$$

$$\left. + (z - 2h) e^{hW/D_L} \exp\left[-\left(\frac{(z - 2h - Wt)^2}{4D_L t} \right) \right] + \cdots \right\},$$

where h is the drift distance. This can be truncated after two terms without appreciable error. [11] In the series expansion for $n(z, t)$ it is assumed that the number transmitted by a shutter in a single pulse depends on the open time of that shutter and thus, for a given gating-signal amplitude, is inversely proportional to the signal frequency. The expression for N_0' has therefore been replaced by

$$N_0'(f) = N_0/f = 2t N_0 ,$$

where it is assumed that the peak corresponding to $m = 1$ is being monitored. 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 frequency is canceled by the direct dependence on the number of pulses transmitted per unit time. The quantity measured experimentally is the flux Φ of ions to a metal plate of area A situated beyond the second shutter. With the boundary condition $n = 0$ at the second shutter (except when the shutter opens momentarily), the instantaneous flux transmitted by the shutter and incident on the metal plate is

$$\Phi = -A D_L \left(\frac{\partial n}{\partial z} \right)_{z=h}$$

$$= (\text{const}) \, t^{-1/2} \left(\frac{h^2}{4D_L t} - 2 \right) \exp\left[-\left(\frac{(h - Wt)^2}{4D_L t} \right) \right].$$

$$(3)$$

Under the present experimental conditions, $h^2/4D_L t \gg 2$ and thus Eq. (3) can be written

$$\Phi = (\text{const}) \, t^{-3/2} \exp\left\{ -[(h - Wt)^2/4D_L t] \right\} . \qquad (4)$$

In practice the quantity measured is the resolving power $\mathfrak{R}$, which is defined as the ratio of the frequency at which the maximum current occurs divided by the frequency 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 Eq. (4), that is, the current peak is described by

$$\Phi = (\text{const}) \exp\left\{ -[(h - Wt)^2/4D_L t] \right\} . \qquad (5)$$

Table I shows the magnitude of the error incurred in making this assumption for a typical set of experimental conditions. Values of Φ are given

for the two solutions (4) and (5), both normalized to equal intensity Φ_{max} at the measured peak maximum. It can be seen that the two peaks are displaced from each other but that the difference in the resolving power of each peak is only 0.2%.

Following Lowke[12] the time difference at half the maximum current is $t'' - t'$ where t'' and t' are the roots of

$$(\text{const}) \exp\left\{ -[(h - Wt)^2/4D_L t] \right\} = \tfrac{1}{2} \Phi_{max} .$$

The resolving power can then be written[13]

$$\mathfrak{R} = \frac{t_0}{t'' - t'} = \frac{1}{4} \left(\frac{hW}{D_L \ln 2} \right)^{1/2} ,$$

where t_0 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., ND_L, and thus the resolving power is written in the form

$$\mathfrak{R} = \frac{1}{4} \left(\frac{hE}{\ln 2 \, D_L \, N/N_s \, \kappa} \right)^{1/2}$$

or

$$ND_L = \frac{hN_s}{16 \ln 2} \frac{E\kappa}{\mathfrak{R}^2} .$$

III. EXPERIMENTAL DETAILS

A. Apparatus

The drift tube was initially constructed with the aim of measuring ionic drift velocities by the Brad-

TABLE I. Comparison of the peak spectra predicted by Eqs. (4) and (5). The following conditions were used to generate the spectra: $E/N = 5.66$ Td, $N = 1.800 \times 10^{17}$ cm^{-3}, drift distance $= 3.395$ cm, $\kappa = 2.502$ cm$^2 V^{-1}$ sec^{-1}. It can be seen that $t'' - t'$ from Eq. (4) $= 0.0826$ msec and $t'' - t'$ from Eq. (5) $= 0.0828$ msec. This results in a difference in resolving power of 0.2%.

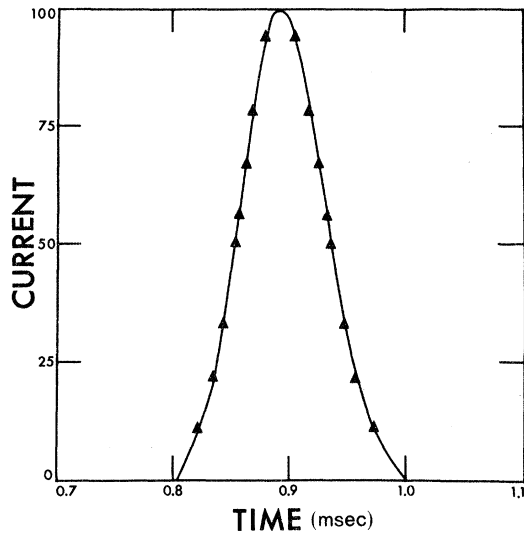| Drift time (msec)	Φ from Eq. (4)	Φ from Eq. (5)
0.820	15.1	13.4
0.8449	50.0	
0.8468		50.0
0.855	67.6	63.9
0.870	90.5	87.8
0.887	100.0	100.0
0.901	90.8	92.9
0.917	66.6	70.1
0.9275	50.0	
0.9296		50.0
0.952	18.2	20.2

FIG. 2. Arrival-time spectrum for potassium ions in nitrogen, taken at $E/N = 5.66$ Td, $N = 1.800 \times 10^{17}$ cm^{-3}. The measured values for ND_L and κ are given in Table II.

bury–Nielsen method[7] and in this mode it has been used and described by Elford[9] (System C). The drift distance was 3.395 cm in this investigation.

B. Method

To measure the resolving power it is necessary to measure the frequency of the peak maximum and the frequencies at which the measured current is one-half the maximum current. It is then neces- sary to ensure that the basic assumption in the the- ory is valid, that is, that the initial pulse closely approximates a δ function. This was checked by varying the amplitude of the gating signal to the shutters and by measuring the resolving power of more than one peak in the current-frequency spec- trum. In both these tests the effective open time of the shutters is varied. It was found that errors from this cause could be reduced to less than the experimental scatter. Usually the second peak in the current-frequency spectrum was used, with typical shutter-signal amplitudes of 10 V peak to peak at $E/N = 5.66$ Td and 38 V peak to peak at $E/N = 28.3$ Td.

It is also necessary to ensure that the peaks are not anomalously broadened by space-charge ef- fects. The procedure used was to measure the re- solving power at a particular tube current and then to double the current and remeasure the resolving power. It was found that when tube currents of less than 10^{-12} A were used there was no detectable space-charge broadening.

A further experimental check which was carried out was to investigate the arrival-time spectrum of the ions. A typical spectrum is shown in Fig. 2, in which the experimental points are shown together

with the spectrum predicted from Eq. (4) using the measured values of D_L and W. It can be seen that the agreement between experiment and theory is very satisfactory.

C. Results

The values of ND_L as a function of E/N are listed in Table II together with the reduced mobilities. Two gas pressures were used, $p_{273.2} = 5.09$ Torr, corresponding to a gas number density of 1.80 $\times 10^{17}$ cm^{-3} and $p_{273.2} = 9.82$ Torr, corresponding to a gas number density of 3.47×10^{17} cm^{-3}. The data taken at $p_{273.2} = 9.82$ Torr are enclosed in brackets in Table II. The temperature, measured by a thermometer placed in the water jacket surround- ing the drift tube, was 292.7 K. A correction of $3D_L/hW$ was applied to all the mobility data to ac- count for diffusive effects.[14] It can be seen from Table II that the reduced mobility is pressure de- pendent, an effect which is possibly due to an ion- molecule reaction. The pressure dependence causes a 0.3% difference between the two values of ND_L predicted by the Nernst–Townsend relation; this pressure dependence has been ignored because it is small compared with the other errors in the measurement of D_L. The lack of an observable pressure dependence in the values of ND_L also in- dicates that the measurements were not falsified by end effects as the errors due to end effects scale inversely with the pressure at a given value of E/N.

D. Errors

The two major errors are considered to be the temperature gradient between the water jacket and the drift tube and the difficulty in measuring the resolving power of the current peak. The maxi- mum error due to the temperature measurement is estimated to be ± 1 K and in the resolving-power measurement the error is considered to be ap-

TABLE II. ND_L and κ for K^+ ions in N_2 at 293 K.

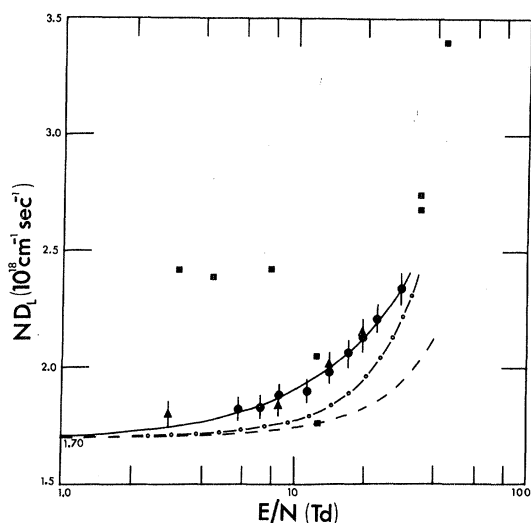| E/N (Td)	ND_L (10^{18} cm^{-1} sec^{-1})	κ (cm^2 V^{-1} sec^{-1})
2.83	(1.80)	(2.496)
5.66	1.82	2.503
7.07	1.83	2.503
8.49	1.88 (1.84)	2.504 (2.494)
11.3	1.90	2.502
14.1	1.98 (2.02)	2.502 (2.494)
17.0	2.06	2.502
19.8	2.13 (2.15)	2.503 (2.495)
22.6	2.21	2.503
28.3	2.34	2.506

FIG. 3. The product ND_L for potassium ions in nitro-
gen at 293 K. The experimental points in this investiga-
tion, taken at 5.09 Torr are denoted by solid circles and
the values at 9.82 Torr by solid triangles. The points of
McDaniel *et al.* are denoted by solid squares. The dashed
line is the line of best fit to the values of Fleming *et al.*
for ND_T. The values of ND_L predicted by Wannier's ex-
pression, based on a constant-mean-free-time model,
are denoted by the dashed dotted line. The figure 1.70
on the ordinate is the value predicted by the Nernst–
Townsend relation using the measured reduced mobility.

proximately $\pm 1\%$. Thus error bars of $\pm 3\%$ have
been put on the values of ND_L. Because of the esti-
mated uncertainty of $\pm 1\%$ in the value of the re-
duced zero field mobility, there is a corresponding
error in the value of ND_L predicted from the
Nernst–Townsend relation. The error in the de-
termination of E/N is insignificant compared with
this.

IV. DISCUSSION

A plot of the product ND_L as a function of E/N is
shown in Fig. 3. It can be seen that a curve can
be drawn through the points that has zero initial
slope and that is consistent with the Nernst–Town-
send relation at zero E/N to within the estimated
experimental errors. Although the curve as drawn
may not provide the optimum fit to the present data,
an extrapolation, based on the general theoretical
prediction that ND_L is proportional to $(E/N)^2$ at
low values of E/N,[15] yields an intercept of 1.77,
which is only 4% higher than the Nernst–Townsend
value of 1.70. Also shown in Fig. 3 are the only
other experimental data available for this case,
those of Moseley *et al.*[3,4] for ND_L. It is noticeable
from the figure that the data of Moseley *et al.* are
systematically higher than the present values.
However, even though all the effects discussed in
Sec. III lead to an apparent increase in D_L, it

seems unlikely that any of them contribute signifi-
cantly to the error incurred by Moseley *et al.*,
since the results of these workers do not appear to
be a function of drift distance. The values pub-
lished by Fleming *et al.*[16] for the transverse-diffu-
sion coefficient are included for the sake of com-
parison in Fig. 3. McDaniel and Moseley[17] have
also compared the results of Moseley *et al.* with
Wannier's theory.

Since the data of Moseley *et al.*[3,4] were pub-
lished, Beyer and Keller have found that potassium
ions can cluster to nitrogen molecules.[18] Thus at
high enough pressures this effect will influence the
measurement of the transport coefficients. How-
ever, in the present work, the lack of variation of
ND_L with pressure eliminates clustering as a sig-
nificant source of error.

In general the solution of the Boltzmann equation
to predict diffusion coefficients involves several
mathematical difficulties. However Wannier[2] has
derived analytical expressions for D_L for three
scattering models. Two of the models assume that
the only contribution to the ion-molecule interac-
tion arises from the polarization force (i. e., Max-
wellian model). With this assumption D_L can be
written

$$D_L = \frac{M+m}{Mm} (0.905 \, \tau_s) kT$$

$$+ \frac{1}{3} \frac{(M+m)^3 (M+3.72m)}{M^2 m (M+1.908m)} \left(\frac{Ee}{m}\right)^2 (0.905 \, \tau_s)^3 , \quad (6)$$

where M is the mass of the molecule, m is the
mass of the ion, and τ_s is the mean free time for
spiraling collisions. From the expression for the
zero field diffusion coefficient D_t, that is,

$$D_t = \frac{M+m}{Mm} (0.905 \, \tau_s) kT ,$$

an estimate of τ_s can be obtained and the variation
of ND_L calculated as a function of E. The predic-
tions of Eq. (6) are shown in Fig. 3. Over the
range of E/N covered by this investigation, there
is a maximum difference of 11% between the results
of the present experiment and the predictions of
Wannier. Two possible reasons for the extent of
disagreement are the neglect of inelastic scatter-
ing in the theory and the simplicity of the model
assumed. However, since the reduced mobility is
constant this tends to confirm that a constant-
mean-free-time model is a good approximation at
low values of E/N and thus the larger source of er-
ror may be due to the neglect of inelastic scatter-
ing.

A better test of the theory would be the mea-
surement of D_L for potassium ions in argon but

no data for this particular case are available at present.

V. CONCLUSION

The longitudinal-diffusion coefficient D_L for potassium ions in nitrogen has been measured as a function of E/N in the range $2.83 \leq E/N$ (Td) ≤ 28.3. The disagreement between the present results and the theory of Wannier based on a constant-mean-free-time model is as large as 11% over the E/N range used.

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