

Mobilities of Potassium and Nitrogen Ions in Nitrogen

P. G. Davies, J. Dutton and F. Llewellyn Jones

Phil. Trans. R. Soc. Lond. A 1966 259, 321-330

doi: 10.1098/rsta.1966.0017

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click here

To subscribe to Phil. Trans. R. Soc. Lond. A go to: http://rsta.royalsocietypublishing.org/subscriptions

[321]

MOBILITIES OF POTASSIUM AND NITROGEN IONS IN NITROGEN

By P. G. DAVIES, J. DUTTON AND F. LLEWELLYN JONES

1. Introduction

It was shown in part I that there is a need for further experimental data on the drift velocity W of ions in gases such as nitrogen and argon where there are still unresolved problems. In addition, measurements of quantities such as the diffusion coefficient D and mean energy e are required for ions in most gases since published data on these quantities are scanty.

In principle, it is possible to determine these quantities by measuring both the drift velocity W and the ratio W/D for selected groups of ions in an apparatus combining a time of drift electrode system, similar to that used by Tyndall et al. (1928) and Tyndall (1938), with a lateral diffusion system similar to that used by Townsend (1925) for the measurement of the ratio W/D for electrons. The advantages of using a time of drift selector for the ions rather than, say, a mass spectrometer are first, that there is no pressure gradient between the selector and the diffusion apparatus, so that no differential pumping is necessary, and secondly, that not only are the ions selected but their mobility is measured at the same time.

With the first practical construction of this arrangement, tests showed that while reliable measurements of W could be made, it was not possible for the reasons discussed in $\S 2(d)$, to determine W/D. Later, the apparatus was redesigned and successful measurements of W/D obtained; the present part of this paper is, however, concerned with measurements of the drift velocity of ions in nitrogen with the original apparatus. Thus, this apparatus, together with techniques common to all the present investigations are described in the next section.

2. Description of apparatus and experimental techniques

(a) The electrode system

A diagrammatic section of the apparatus is shown in figure 1, where electrodes A to Jform the time of drift section and electrodes J to O are the diffusion section.

The electrodes were pressed from oxygen-free high conductivity copper 1 mm thick and were polished with coarse and fine alumina. Uniformity of the electric field was ensured by means of guard rings, D, E, H, K, and L which were annular with an internal radius of 1.5 cm and an external radius of 2.25 cm. The shutter electrodes B, C, F and G were circular of radius 2.25 cm and had a central pattern consisting of forty-nine 1mm diameter holes drilled in a square of side 13 mm. Electrode A had a central pattern of thirty-six holes of 1 mm diameter drilled in a square of side 11 mm in such a way that the holes were out of line with those in electrodes B, C, F and G. This arrangement minimized the liberation of photoelectrons from the collecting electrodes M, N and O by light from the glow discharge in the source.

Ions, which had been selected in the drift section, entered the diffusion region through an orifice in the electrode J which was a composite electrode made up of two disks 1 mm thick riveted together. One of these disks had a hole 2 mm diameter at its centre while the other disk had a central sliding section in which three holes 0.5, 0.75 and 1 mm diameter were drilled 3 mm apart. This central sliding section was operated externally by means of a screw thread and bellows so arranged that the entrance to the diffusion chamber could be completely closed or that any one of these holes could be selected to admit ions to the diffusion chamber. This facility enabled the choice of an entrance hole which most nearly met the theoretical boundary conditions of a point source of ions, but at the same time gave a measurable current ($\gtrsim 10^{-14} \,\mathrm{A}$) to the collecting electrodes in the conditions of the experiment.

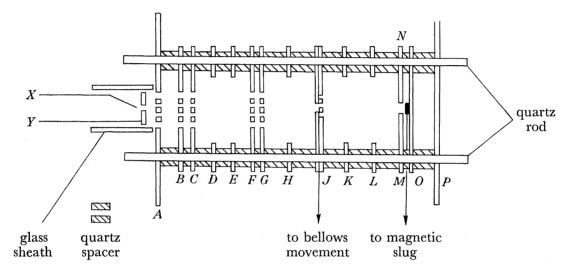


FIGURE 1. The electrode system

Adjustment of this central sliding section also allowed the hole to be positioned centrally with respect to the electrodes so that a symmetrical beam of ions fell on the co-planar electrodes M and N. The collecting electrodes in the diffusion chamber consisted of two D-shaped copper plates M and N separated by a parallel sided gap (ca. 3 mm wide), and a third copper disk O mounted 2 mm behind M and N. In order to confirm that the current registered on electrode O was in fact due to positive ions which had passed through the gap between M and N, a copper foil strip, loosely attached to one of the D-shaped electrodes and operated by an externally applied magnet, was used to mask off this gap.

The whole electrode assembly was supported on four quartz rods 4 mm in diameter which passed through the electrodes. The electrodes were maintained parallel to each other by means of accurately ground quartz spacers which fitted over the quartz rods. The complete assembly was rigidly secured with spring-loaded clamps attached at the ends of the quartz rods. Electrodes A and P, which had a larger radius (3.75 cm) than the other electrodes, held the main assembly away from the walls of the borosilicate glass envelope.

Connexions to the electrodes were made using copper foil strips which were riveted into the edges of the electrodes and taken out radially through the side walls of the envelope by means of tungsten-glass seals. This arrangement ensured minimum distortion of the field between the electrodes by the electrical leads. At one end, the envelope was drawn down

and welded to a socket into which a cone carrying electrodes for a potassium ion source or a glow discharge ion source could be placed. The potassium ion source was a Kunsman source similar to that used by Munson & Tyndall (1939).

To produce ions of the parent gas a glow discharge source was used. The glow discharge could be struck between the electrodes X and Y or between the perforated electrode Y and electrode A (see figure 1). In order to confine the glow region and to prevent ions diffusing towards the glass envelope, a glass sheath was placed around the discharge electrodes. A similar sheath was used to prevent potassium ions diffusing outwards laterally to the walls.

(b) The current measuring and gas systems

The current measuring system incorporating a double tetrode electrometer valve was designed to measure currents in the range 10⁻⁹ to 10⁻¹³ A (see Crompton & Sutton 1952).

A conventional vacuum and gas system which could be evacuated to a residual pressure less than 10^{-5} mmHg was used. Incorporated into the gas system was a mass spectrometer unit which enabled samples of gas drawn from the drift tube to be analysed.

(c) Operation of the electrical shutters

The steady d.c. potentials on the various electrodes were obtained by connecting them to the appropriate points on an $8.4 \,\mathrm{M}\Omega$ resistor chain across which a potential of ca. 300 V was applied from dry batteries. In this way a uniform unidirectional electric field was maintained between all the electrodes except in the regions BC and FG where reverse fields could be applied (see Davies, Dutton & Llewellyn Jones 1961).

Two methods of pulsing the shutter electrodes were used in the investigation. These are known as the 'out of phase' and 'in phase' methods of pulsing.

(i) The out of phase method of pulsing

Most of the measurements were obtained by the out of phase method in which pulses from an Advance signal generator were applied to the outer electrodes B and G of the electrical shutters. This method is called 'out of phase' since advancing phases open the first gate BC while retarding phases open the second gate FG. This method has the advantage that for the greater part of their travel the ions move under the influence of a steady uniform electric field. The amplitude of the pulses applied to the electrodes B and G was sufficient to overcome the reverse fields normally maintained in the regions BC and FG and produced a field in the same direction and of approximately the same magnitude as the main electric field. Precautions were taken to ensure that the pulses did not affect the steady d.c. potentials of the other electrodes, and this was done by incorporating pulse integration circuits and decoupling condensers.

For these out of phase measurements the frequency f for peak currents to the collecting electrode J is given by t=(2n+1)/2f,

where n is an integer and t is the ion transit time between electrodes B and F.

(ii) The in phase method of pulsing

In some experiments, an E.T.C. pulse generator, model 104A, was used to pulse the electrodes B and F of the electrical shutters with square waves of positive polarity.

Vol. 259. A.

323

This method is known as the in phase method since both gates are simultaneously opened by the same positive pulse. The steady potentials were applied so that the regions BC and FG were field free when the pulses were not applied. The amplitude of the pulses was adjusted so that the ions in the regions BC and FG travelled in the same electric field as the main field when the shutters were open.

This method of pulsing had the advantage that with the pulse generator available the width of the applied pulses could be adjusted to control the number of ions allowed through the shutters and so give improved resolution. Ions admitted through the first gate during one pulse and through the second gate during the successive pulse crossed the drift space in a uniform electric field. However, when conditions were such that ions admitted through the first gate during one pulse passed through the second gate two or more pulses later, the ions travelled in a reduced field for part of the time. For this method of pulsing, the transit time of the ions across the drift space was given by

$$t = n/f$$

where n is an integer and f the frequency at the current maximum.

The frequencies of both the Advance signal generator and the E.T.C. pulse generator were calibrated to better than 1 % by means of a scalar counting unit. The Advance generator had a sinusoidal output over the frequency range 15 to 50 000 c/s or alternatively an approximately 50:50 square wave output, over the frequency range 15 to 20000 c/s while the E.T.C. pulse generator gave square waves of a variable duration over the range 15 to 100000 c/s.

(d) Operation of the apparatus

The drift section of the apparatus was tested by measuring the drift velocity of potassium ions in nitrogen. A typical example of the curve of the current ($\sim 10^{-12} A$) to electrode J as a function of frequency was given in a preliminary report of this work (Davies et al. 1961) which showed that the maximum of the ion current occurred at frequencies very nearly in the ratio 1:3:5 when the shutters were pulsed out of phase. This showed that the drift section of the apparatus was operating satisfactorily.

Preliminary experiments with the diffusion section of the apparatus, on the other hand, showed that the ion currents to the collecting electrodes M, N and O were ca. 10^{-14} A when the alkali ion source was used and these currents were too small to be measured with the existing electrometer system. Further tests, using glow discharges in hydrogen and argon to produce the ions, showed that there were appreciable currents to the collecting electrodes, but it was found that the currents to M, N and O were not greatly affected when the entrance hole in electrode J was open or closed. Moreover, the current to electrode O was not greatly altered by placing the mask in position between M and N. It was concluded that the currents to the collecting electrodes were due either to leakage of charge along the quartz rods supporting the electrodes, or to ions moving through the gas to the collecting electrodes outside the electrode system. It was, therefore, not possible to obtain measurements of the ratio W/D with the apparatus as originally constructed.

The apparatus was then redesigned and a second electrode system constructed. With this, the spurious currents previously experienced were eliminated, and measurements of the ratio W/D are reported in part IV. While the redesigned apparatus was being constructed

advantage was taken of the fact that the drift section of the apparatus described above was operating satisfactorily. Measurements of drift velocities of potassium and nitrogen ions in nitrogen were made and these results are described in the next section. Further investigation of the drift velocities of ions in argon using this apparatus are discussed in Part III.

3. Results for potassium ions in nitrogen

In order to calibrate the apparatus and to ascertain whether the end effects due to the varying electric field in the region of the shutters were important, the drift velocity of potassium ions in nitrogen was first measured. This combination of ion and gas was chosen as the most suitable for calibration purposes because there is agreement between the values of the zero-field mobility published by several previous observers (Mitchell & Ridler 1934; Hershey 1939; Crompton & Elford 1959), and furthermore potassium ions can be readily produced without any doubt about the identity of the ions.

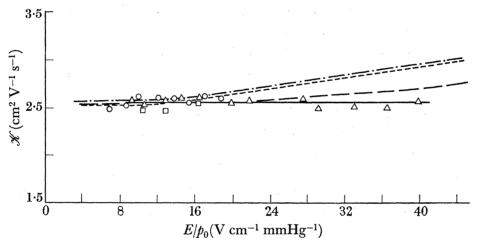


FIGURE 2. Mobility of potassium ions in nitrogen. Comparison of the present out of phase results with those of other investigators. — —, Crompton & Elford (1959); ----, Mitchell & Ridler (1934); ———, Hershey (1939).

experimental points (present paper, part II) P_0 (mmHg) 1.15 (sine) Δ 1.15 (square) 1.25 (sine) 0

Crompton & Elford have suggested that end effects in the apparatus used by Mitchell & Ridler might account for the discrepancy concerning the form of the variation of mobility with E/p_0 for potassium ions in nitrogen (see figure 2). There are at least two ways to investigate the influence of end affects (a) by using an apparatus with a movable shutter such as that used by Tyndall and Powell (1932) for helium ions in helium, or (b) applying pulses of different shapes and by pulsing the shutters both in phase and out of phase.

In the present work method (b) was the most suitable and it will be shown that no appreciable end corrections were involved. The variation of drift velocity and mobility was studied for pressures in the range 1 to 3 mmHg and for $7 < E/p_0 < 40 \,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$.

Measurements were obtained by pulsing the electrodes B and G out of phase with both sine and square waves from the Advance signal generator and by pulsing the electrodes B and F in phase with square waves from the E.T.C. pulse generator. When the apparatus is operated in these two ways, however, the following points must be considered if the best values for mobility are to be obtained.

First, for the out of phase measurements, values of mobility computed from the first order maxima are the least accurate because in the first order the resolution of the apparatus is not as high as in higher orders. The reason for this is that a much wider band of ions is allowed through the shutters in the first order; in particular, for 50:50 square waves the band of ions extends across the whole of the drift region. Secondly, when the electrodes B and F are pulsed in phase with square waves the values obtained for the mobility should be higher the lower the order of the peak considered. As previously explained the reason for this is that for maxima other than the first order the ions travel in a reduced field for part of the time. For these reasons, therefore, it is considered that the values of mobility calculated from the higher order peaks when pulsing out of phase and from the first order peaks when pulsing in phase are the most reliable.

In order to compare the present data with the previous experimental and theoretical data, all the values of mobility obtained have been reduced to the same standard gas density (see Part I, $\S 4(a)$).

Figure 2 shows the experimental results for mobility (calculated from the second order current maxima) when the electrodes B and G were pulsed out of phase with both sine and square waves from the Advanced signal generator and with a reverse field in the regions BC and FG equal to half the main field. Also shown are the previous measurements of Mitchell & Ridler, of Hershey, and of Crompton & Elford. It will be seen that at the lower values of E/p_0 all the results agree and the zero-field values are shown in table 6.

Table 6. Values of zero-field mobility of potassium ions in nitrogen at standard gas density

	investigator	zero-field mobility (cm ² V ⁻¹ s ⁻¹)	range of E/p_0 (V cm $^{-1}$ mmHg $^{-1}$)	range of pressure (mmHg)
experimental	(present work, part II) Hershey (1939) Crompton & Elford (1959) Mitchell & Ridler (1934)	$ 2.55 \pm 0.07 2.5 2.54 2.53 $	7 to 50 5 to 150 3 to 48 2 to 24	1 to 3 0·3 to 0·7 1 to 6 not given
theoretical	Langevin equation (6) part I	2.53	and residence.	

The zero-field value of $2\cdot55\pm0\cdot07$ cm² V⁻¹ s⁻¹ found in the present work is also in agreement with the theoretical Langevin value.

To test the apparatus further, values of mobility were computed from the first, second and third order maxima. The third order values were in good agreement with the second order values of mobility which have already been described (figure 2). For values of $E/p_0 < 20 \,\mathrm{V}$ cm⁻¹ mmHg⁻¹ the values of mobility computed from the first order maxima were lower (on the average about 8 %) than those calculated from the second and third order maxima. The difference between the first and second order values increased as E/p_0 decreased.

327

However, for values of $E/p_0 > 20$ the difference between values computed from the first and second order was within the experimental error. The reason for this discrepancy at the lower values of E/p_0 is not clear.

Further measurements of mobility were obtained by pulsing the electrodes B and F in phase with square waves of variable duration. In the range of E/p_0 studied (6 < E/p_0 < 20 V cm⁻¹ mmHg⁻¹) the mobility remained constant, giving a zero-field value of 2.55 in agreement with the value obtained by the out of phase method.

The present results therefore show that it makes no significant difference to the values of mobility obtained whether the electrodes are pulsed in phase or out of phase. Furthermore, the use of sine or square waves has negligible influence on the value of the mobility obtained. In fact, throughout the range of E/p_0 studied the mobility remained constant independent of E/p_0 . This result is contrary to those of other investigators, who observed an increase of mobility at the higher values of E/p_0 . Since the value obtained for the zerofield mobility was the same for both methods of pulsing, was independent of the shape of the applied pulse and was in agreement with the values found by other investigators, it was concluded that the apparatus was functioning correctly and that it was not necessary to apply any correction for end effects at the shutters.

4. Results for nitrogen ions in nitrogen

(a) Present results

The drift velocity and mobility of ions issuing from a glow discharge source in nitrogen were studied for $4 < E/p_0 < 40 \,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ and for pressures in the range

$$0.8 < p_0 < 7.6 \,\mathrm{mmHg}.$$

It has already been shown that the values obtained for mobility were independent of the type of voltage pulses (either sinusoidal or square wave) applied to the shutters. For nitrogen ions it was convenient to pulse the electrodes B and G out of phase with sine waves from the Advance signal generator. The reverse field in the regions BC and FG was set equal to half the main field.

The drift velocity was found to depend linearly upon E/p_0 and could be expressed by the empirical relation, $W = 1.93 \times 10^3 E/p_0$.

The mobility (see figure 3) was thus constant in the range of E/p_0 studied and most of the experimental points can be seen to lie in the range 2.5 ± 0.12 cm² V⁻¹ s⁻¹.

At low values of E/p_0 , however, a few of the experimental values lie above this range. It is interesting to note that these high values of mobility at low values of E/p_0 were always obtained when high values of the glow current in the ion source were used; the two measurements at a pressure of 7.57 mmHg, for example, were taken with glow currents $\simeq 20$ mA. At a pressure of 1.98 mmHg values of mobility for various values of the glow current were obtained, and it was found that using low glow currents (less than 0.5 mA) the values of mobility were within the range 2.5 ± 0.12 cm² V⁻¹ s⁻¹, whereas when the glow current was increased to 1.0 mA. at the same gas pressure, two measurements of mobility taken at $E/p_0 = 4.3$ and $5.4 \,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ gave a higher value of $2.78 \,\mathrm{cm^2\,V^{-1}\,s^{-1}}$.

A similar effect when the glow current was increased was also observed at a pressure of $3.62 \,\mathrm{mmHg}$ for values of E/p_0 of 7.4 and $9.3 \,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$. Careful examination of

the third order current maxima of the current-frequency curves for these two measurements indicated that two species of ions were present. The second species of ion was present in such small numbers, however, that it was not resolved in the first and second order maxima but distorted the first and second order peaks sufficiently to lead to a high value for the mobility. The value for the mobility of the second faster group of ions obtained from the third order peaks of the curves in which it was resolved was found to be about 2.9 cm² V⁻¹ s⁻¹.

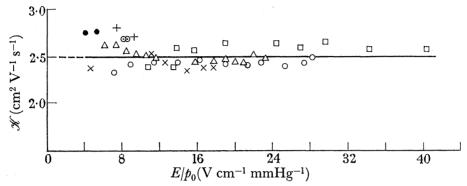


Figure 3. Observed variation of mobility with E/p_0 for nitrogen ions in nitrogen. The mobility was calculated from the second order current maxima when the electrodes B and G were pulsed out of phase with sine waves.

experimental		approx. glow
points	$p_0(\mathrm{mmHg})$	current (mA)
0	1.65	0.4 to 1.5
	0.78	0·1 to 0·2
· 🛆	1.98	0.3 to 0.5
•	1.98	1.0
×	$3 \cdot 62$	2·3 to 4
+	$3 \cdot 62$	$5 \cdot 0$
•	7.57	20.0

A mass spectrometer analysis was made of the same sample of gas which was used in the drift experiment. With a glow discharge current of about 3 mA (which was the lowest value at which a measurable positive ion current could be obtained at the collector of the mass spectrometer), the ions N^+ , N_2^+ and a small number of N_3^+ , together with several types of impurity ions such as H₂⁺ and NH₃⁺ or H₂O⁺, were identified. No N₄⁺ ions were observed.

(b) Comparison of the present measurements with the results of previous investigators

The results of the present investigation are compared with those of previous investigators in table 7, which gives the values of zero-field mobilities, together with a summary of the experimental conditions, and in figure 4, which shows the variation of mobility with E/p_0 . From table 7 it can be seen that zero-field mobility of 2.5 cm² V⁻¹ s⁻¹ for the main species of ion in the present work is in agreement with that obtained by Tyndall & Pearce (1935), Mitchell & Ridler (1934), Vogel (1957), Huber (1955) and with the value for the ion species identified as N⁺ in the work of Keller et al. (1965)*. The results of the present investigation taken with those of Vogel and of Keller et al. indicate that there is an ion species having a mobility which is constant and independent of E/p_0 over the range of E/p_0 from 4 to 70 V cm⁻¹ mmHg⁻¹ (see figure 4). The results of Mitchell & Ridler, on the other hand, show a

^{*} See also Saporoschenko (1965c).

329

sharp increase in the mobility at values of $E/p_0 \gtrsim 24 \,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$. It seems likely that this sharp break is instrumental in origin, since such an increase is a general feature of the mobility curves of the Bristol school. Sharp increases of this type have not been found in the present investigation for any combination of ion and gas studied.

Table 7. Experimental values of zero-field mobility of nitrogen ions IN NITROGEN AT STANDARD GAS DENSITY

experimenter	zero-field mobility $(cm^2 V^{-1}$ $s^{-1})$	cange of E/p_0 (V cm ⁻¹ mmHg ⁻¹)	range of p_0 (mmHg)	source of ions	deduction concerning nature of ion
Tyndall & Powell (1930)	1.86	not given	62 to 390	α -particle ionization	no prediction
Tyndall & Pearce (1935)	2.50	not given	not given	glow discharge	N_2^+
Bradbury (1932)	1.85	not given	not given	X-ray ionization	no prediction
Mitchell & Ridler (1934)	2.50	8 to 40	4 to 9	glow discharge	N_2^+
Varney (1953)	*	38 to 860	not given	Townsend avalanche	N_4^+ at low E/p_0 N_2^+ at high E/p_0
Kovar <i>et al</i> . (1957)	*	40 to 1000	0·1 to 32	Townsend avalanche	N_4^+ at low E/p_0 N_2^+ at high E/p_0
Vogel (1957)	2.5	40 to 70	not given	Townsend avalanche	N_4^+
Huber (1955)	2.36	non-uniform field	25 to 600	α-particle ionization	N_4^+
Dahlquist (1963)	1.6	20 to 800	0·16 to 5	glow discharge	N_2^+
	$3\cdot 2$	6 to 300			$\begin{matrix} \mathbf{N_2^+} \\ \mathbf{N_3^+} \end{matrix}$
McAfee & Edelson	† *	190 to 550	up to 10	Townsend	N^+
(1963)	*	190 to 300		avalanche	$N_3^+ \ N_3^+ \ N_2^+ \ N_4^+$
	*	65 to 900			N_2^+
	1.9	5 to 20 and			N_4^+
		100 to 300			
Woo (1965)	$3 \cdot 4$	8 to 100	0·4 to 1·5	ionization by	N^+
	2.9	9 to 45		accelerated	N_3^+
	*	50 to 200		electrons	$egin{array}{c} \mathbf{N_3^+} \ \mathbf{N_2^+} \end{array}$
Keller† et al.	$2 \cdot 47$	7 to 70	0.05 to 0.20	ionization by	N^+
(1965)	1.44	8 to 100		accelerated	N_2^+
	*	8 to 45		electrons	$N_3^{ ilde{+}}$
	1.84	5 to 70			$egin{array}{c} \mathbf{N_3^{\mp}} \ \mathbf{N_4^{+}} \end{array}$
this paper (part II)	2.5 ± 0.12 ~ 2.9	4 to 40 (see text)	0.8 to 7.6	glow discharge	N ⁺

No extrapolation to zero-field possible in these cases.

It is interesting to note that the ion observed in small numbers for high currents (> 1mA) in the glow discharge source in the present work has a mobility in agreement with that obtained for a species of ions studied by Woo, and close to the value of 3.2 cm² V⁻¹ s⁻¹ obtained by Dahlquist.

(c) Discussion

In the present work, the mass spectrometer analysis, previously referred to, showed that N+, N2+, a small number of N3+ and some impurity ions were issuing directly from the

[†] Apparatus incorporating mass analyses.

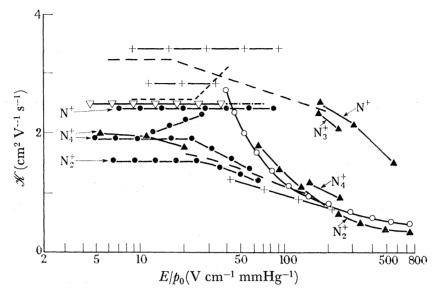


Figure 4. Available data for the mobility of nitrogen ions in nitrogen at T=300 °K. ∇ , Present paper (part II); ·, Vogel (1957); o, Varney (1953); ---, Mitchell & Ridler (1934); A, McAfee & Edelson (1963); •, Keller et al. (1965); ---, Dahlquist (1963); +, Woo (1965).

glow discharge. No N₄ ions were observed in the mass spectrometer system. However, it is possible that in the drift experiment N₄ ions could have been formed by collision between the primary ions and the gas molecules in drifting through the gas to the first shutter of the measuring apparatus. Thus, the four ions N⁺, N₂⁺, N₃⁺ and N₄⁺ must be considered in attempting to identify the species of ions on which mobility measurements were made.

From the work of Keller et al. it appears that the main ion species studied was N⁺. If this is the case, then the experimental value of 2.5 cm² V⁻¹ s⁻¹ for N⁺ lies considerably below the value of 3·42 cm² V⁻¹ s⁻¹ predicted by the Langevin polarization equation (see table 8). Indeed, from theoretical considerations, it would appear more likely that the ion

TABLE 8. THEORETICAL VALUES FOR THE ZERO-FIELD MOBILITY OF NITROGEN

IONS IN NITROGEN				
ion	N+	N_2^+	N_3^+	N_4^+
Langevin equation (6) (see part I)	3.42	2.80	2.55	2.42

was either N_3^+ or N_4^+ . The values of zero-field mobility determined by Keller et al. and also by McAfee & Edelson for N₄ ions was 1.9 cm² V⁻¹ s⁻¹, which again falls well below the theoretical value of 2·42 cm² V⁻¹ s⁻¹. For N₂⁺ ions, it is to be expected that the mobility would be lower than the value calculated using the Langevin polarization equation because of electron charge transfer. The experimental value determined by Keller et al. for the mobility of N₂⁺ ions is 1.44 cm² V⁻¹ s⁻¹; this result is in close agreement with the value of 1.5 cm² V⁻¹ s⁻¹ which Dalgarno (1958) considers to be plausible for the mobility of N_2^+ ions in nitrogen.

If the main ion species observed in the present work is N⁺, then the indications are that this species undergoes a reaction with the gas molecules the nature of which is not yet clear.