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Mobilities of Ions in Argon

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III. MOBILITIES OF IONS IN ARGON

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1. Potassium ions in argon

The calibration of the apparatus for potassium ions in nitrogen was described in part II. Since the same source, giving potassium ions only, was available, measurements of the mobility of potassium ions in argon were also made. All the measurements were obtained pulsing the electrodes *B* and *G* out of phase with sine waves and with a reverse field in the regions *BC* and *FG* equal to half the main field. The mobility calculated from second order current maxima was found to remain constant (see figure 5), independent of E/p_0 for $9\cdot5 < E/p_0 < 26$ V cm^{-1} mmHg^{-1} and for pressures in the range 1·0 to 1·8 mmHg.

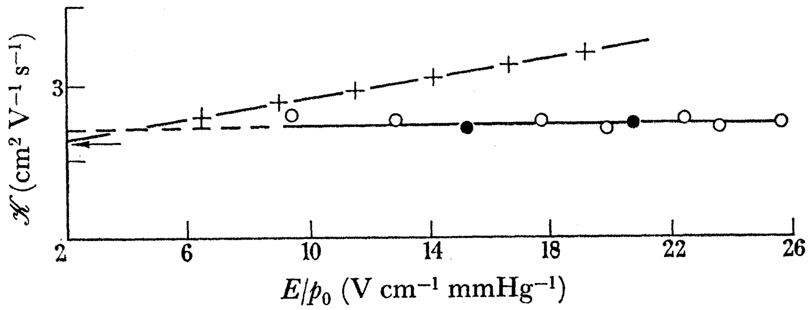

Figure 5. Mobility of potassium ions in argon. Experimental points (present paper, part III); ○, p_0 = 1·76 mmHg; ●, p_0 = 1·1 mmHg. +, Hershey (1939). ←—, Munson & Tyndall (1939); Hoselitz (1941).

Table 9. Experimental and theoretical zero-field mobilities for potassium ions in argon

	investigator	zero-field mobilities (cm^2 V^{-1} s^{-1})	range of E/p_0 (V cm^{-1} mmHg^{-1})	range of pressure (mmHg)
experimental	present paper (part III)	2·75 ± 0·05	9·5 to 26	1 to 2
	Munson & Tyndall (1939)	2·64	not given	not given
	Hershey (1939)	2·65	5 to 110	0·3 to 0·7
	Hoselitz (1941)	2·64	not given	not given
theoretical	Langevin equation (4) (part I)	2·79	—	—
	Langevin equation (6) (part I)	2·45	—	—

Also shown in figure 5 are the measurements of Munson & Tyndall (1939) and of Hershey (1939) whose results were obtained at the pressures 0·3 and 0·7 mmHg. Hershey found that the mobility continually increased over the range of E/p_0 from 0 to 35 V cm^{-1} mmHg^{-1}, but neither Munson & Tyndall nor Hoselitz (1941), who measured the variation of mobility with temperature for potassium ions in argon, gave any indication of the form of variation with E/p_0.

Table 9 shows the agreement between the theoretical and experimental values for the zero-field mobility. The experimental values lie intermediate between the theoretical values calculated from the Langevin equation (4) part I and the Langevin polarization equation (6) part I. In the present case, the experimental value of $2{\cdot}75 \pm 0{\cdot}05\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ is 4 % larger than the values found by Munson & Tyndall and Hershey and lies close to the theoretical Langevin value of 2·79.

2. Ions from a glow discharge source in argon

In argon, three separate sets of measurements of the drift velocity and mobility of ions produced in a glow discharge were taken with different gas samples and in different gas handling systems. In all cases the argon was obtained spectroscopically pure from the British Oxygen Company.

(a) *First set*

These measurements were taken with pressures in the range $3{\cdot}3 < p_0 < 8{\cdot}1$ mmHg and with E/p_0 in the range $3 < E/p_0 < 22\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$. The sample of gas was left to stand over well out-gassed uranium for a period of about 24 h. The uranium acts as a getter for hydrogen (Dieke & Crosswhite 1952). Positive ions were drawn from a glow discharge run at approximately 0·3 mA. The electrodes *B* and *G* were pulsed out of phase with sine waves, and in the regions *BC* and *FG* reverse electric fields of magnitude equal to half the main field were maintained.

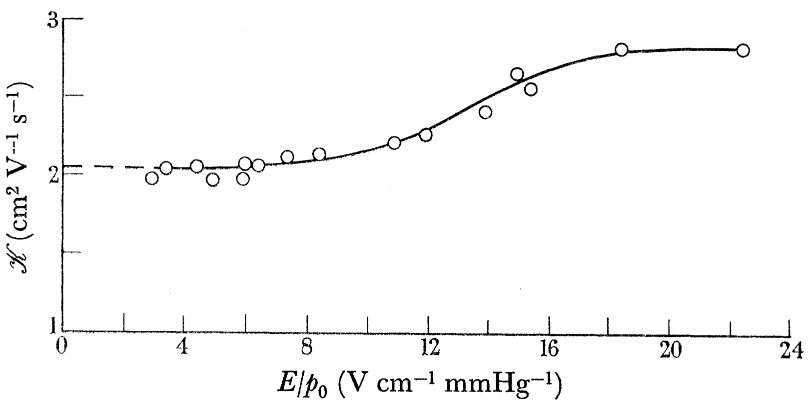

Figure 6. Mobility of ions in argon. First set of results (see text).

Values for the mobility of the ions were calculated from the second order current maxima of the current-frequency curves and are shown as a function of E/p_0 in figure 6. The variation of mobility with E/p_0 seemed to indicate the possibility that measurements were being made on two different species of ion having mobilities 2·9 and $2{\cdot}1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. However, the current-frequency curves indicated that only one species of ion was involved.

At this stage of the investigation the system was not connected to a mass spectrometer and hence no analysis of this gas sample was made.

(b) *Second set*

To investigate further the shape of the mobility curve shown in figure 6 a second set of measurements was taken in a different sample of gas which had not been standing over uranium. The electrodes *B* and *G* were pulsed out of phase with sine waves and the reverse fields in the regions *BC* and *FG* were set equal to half the main field.

Results were obtained for $1{\cdot}6 < p_0 < 6{\cdot}1$ mmHg, for $4 < E/p_0 < 23$ V cm^{-1} mmHg^{-1} and with glow currents in the range 0·3 to 1·0 mA. The current-frequency curves indicated that one ion of mobility $2{\cdot}9 \pm 0{\cdot}1$ cm^2 V^{-1} s^{-1} was predominant, but careful scrutiny of the curves obtained at the pressures 4·03 and 6·09 mmHg revealed a small perturbation of the left hand side of the third order current peaks (see figure 7), showing that at these two pressures a second slower group of ions was also present.

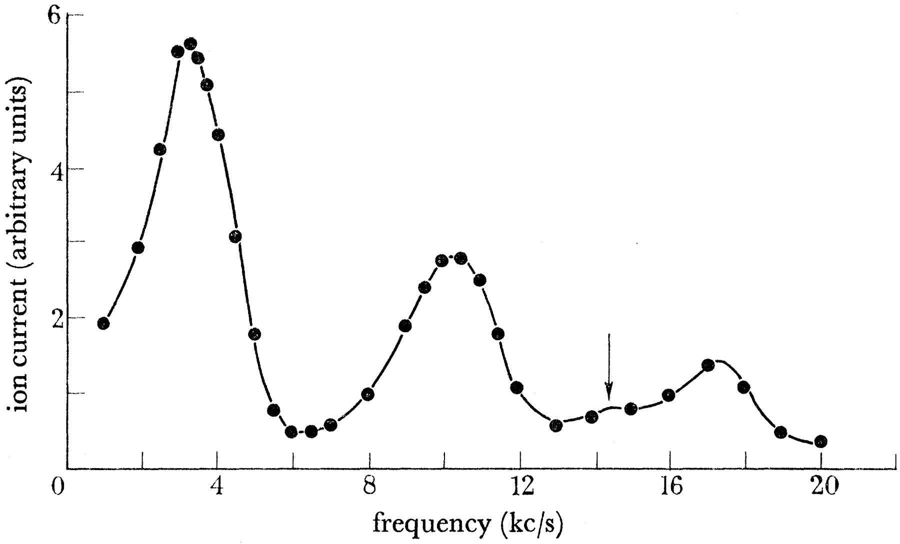

FIGURE 7. Ion current–frequency curve. The arrowed perturbation indicates the presence of a second species.

This second slower group was resolved only in the third order maxima and was present in such small numbers that its mobility could not be accurately determined. Nevertheless, when the two groups of ion are resolved in this way the correct value is obtained for the mobility of the majority group. The lower values of mobility, sometimes found when the first and second order maxima were used, were due to the perturbation of the peaks of the majority group by the unresolved minority group. This minority group had a lower drift velocity than the other group and was seen to become more predominant as the conditions were altered so that the number of collisions between the faster ions and the gas molecules was increased.

In general, when only one species of ion was present, good agreement was obtained between the values calculated from the first, second and third order current maxima. The value calculated from the second order current maxima is shown as a function of E/p_0 in figure 8. The mobility was found to be $2{\cdot}9 \pm 0{\cdot}1$ and was generally independent of E/p_0. The figure gives, however, a few low values of mobility but these were due to distortion of the second order peaks by the group of ions with lower mobility.

The drift velocity was linearly dependent upon E/p_0 and could be expressed as

$$W = 2{\cdot}2 \times 10^3 E/p_0.$$

A mass spectrometer analysis of a sample of gas similar to that used in the investigation in a different, but similar gas system showed that ions of masses 20 ± 1 (possibly Ar^{2+}) and 40 ± 1 (Ar^+ or ArH^+) atomic units, together with H_2^+ ions were present.

In an attempt to remove the hydrogen, a sample of gas was left to stand over the uranium and the drift tube was connected directly to the mass spectrometer system. A further set of measurements of drift velocity and mobility taken at $p_0 = 2{\cdot}31$ mmHg were then made. The results were essentially the same as those described above using samples which had not been treated with uranium. One ion only with mobility $2{\cdot}9 \pm 0{\cdot}1\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ was observed. Mass spectrometer analysis of the sample of gas used in this experiment showed that hydrogen ions were still present together with a small number of ions of mass 20 ± 1 and ions of mass 40 ± 1 atomic units.

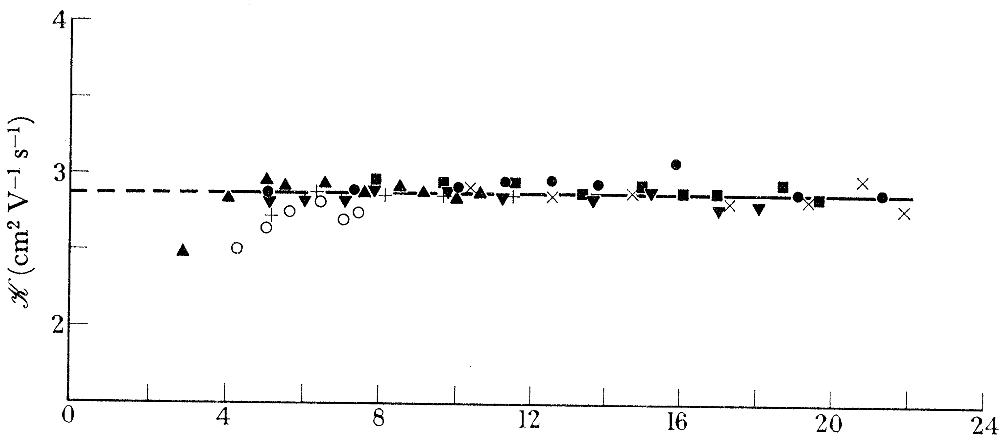

FIGURE 8. Mobility of ions in argon. Second set of results (see text).

experimental points	p_0(mmHg)	experimental points	p_0(mmHg)
●	1·64 (sine waves)	×	1·8 (sine waves)
■	2·33 (sine waves)	+	3·55 (sine and square waves)
▲	4·03 (sine waves)	▼	2·31 (sine waves in argon purified with uranium)
○	6·09 (sine waves)		

(*c*) *Third set*

At this stage the vacuum system was rebuilt in readiness for the new diffusion apparatus (see part IV) which was almost completed.

With this system the difference between the first and second sets of results was further investigated. This third set of measurements, taken with pressures in the range

$$1{\cdot}8 < p_0 < 13{\cdot}7\ \text{mmHg}$$

and with $1{\cdot}5 < E/p_0 < 24\ \text{V}\ \text{cm}^{-1}\ \text{mmHg}^{-1}$, exhibited several features similar to the first set of measurements. Glow discharges with currents in the range 0·05 to 1 mA were used to produce the ions. At low pressures and high values of E/p_0 one ion with zero-field mobility $2{\cdot}9 \pm 0{\cdot}1\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ was observed, while at high pressures and low values of E/p_0 another ion with zero-field mobility $2{\cdot}05 \pm 0{\cdot}05\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ was found. At intermediate values of pressure and E/p_0 a mixture of the two groups of ion was present.

Measurements of the drift velocity and mobility were obtained (i) by pulsing the electrodes *B* and *G* out of phase with sine waves from the Advance signal generator, and (ii) by pulsing the electrodes *B* and *F* in phase with square waves of variable duration from the E.T.C. square wave pulse generator.

By pulsing with sine waves out of phase the following effects were observed. At the pressure $p_0 = 1{\cdot}76$ mmHg, the current-frequency curves showed that for $E/p_0 > 8\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ only the ion with mobility $2{\cdot}9\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ was present. One other result taken at this pressure with $E/p_0 = 4{\cdot}8\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$, although not showing peaks for two kinds of ion, gave low values of mobility $\sim 2{\cdot}45\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ for the first and second order peaks whereas the third order peak gave a value of $2{\cdot}9\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. At the pressure $p_0 = 3{\cdot}8$ mmHg and for $5{\cdot}5 < E/p_0 < 16\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ the ion with mobility $2{\cdot}9\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ was the predominant ion with only the slightest indication that a slower group of ions was present in small numbers.

At the pressure $p_0 = 5{\cdot}56$ mmHg, the current-frequency curves showed that for

$$E/p_0 > 5\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$$

only the ion with mobility $2{\cdot}9\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ was present. However, for $3 < E/p_0 < 5\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ two groups of ion were resolved in the third order peaks, the slower group showing up as a perturbation on the left hand side of the third main peak. For $E/p_0 = 2{\cdot}2\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ only the slower species of ion with mobility $2{\cdot}1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ was observed.

A similar effect was found at the pressure $p_0 = 8{\cdot}12$ mmHg except that in the range of E/p_0 studied the faster species was always accompanied by the slower species. For $E/p_0 < 5\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ only the slower group was observed.

Finally, for $p_0 = 13{\cdot}7$ mmHg and for $1{\cdot}5 < E/p_0 < 4{\cdot}5\,\mathrm{V\,cm^{-1}\,mmHg^{-1}}$ only the slower group of ions was present.

The values of mobility calculated from the resolved third order current maxima when the electrodes B and G were pulsed out of phase with sine waves are shown as a function of E/p_0 for the two groups of ion in figure 9. The drift velocity of the faster species could be expressed as

$$W = 2{\cdot}22 \times 10^3 E/p_0,$$

in agreement with the second set of measurements. In figure 9 it can be seen that the mobility of the faster ions is independent of E/p_0, whereas the mobility of the slower ions appears to increase as E/p_0 is increased. The effect is discussed further in the next section. With square waves in phase and no reverse fields between either pair of shutter electrodes, the following results were obtained. The same effects as those just listed were also observed in this case, except that when both groups of ion were present, they were resolved for the first, second and third order peaks because of the better resolution of this arrangement. The values obtained for the zero-field mobility were $2{\cdot}9$ and $2{\cdot}1\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ as before.

The number of collisions per cm travel in the direction of the applied electric field, may be approximately expressed as $n = p_0 u/L_0 W$ where u is the agitational velocity and L_0 the mean free path at 1 mmHg pressure. Using this expression the third set of results may be summarized in the following way.

In conditions where there were less than about 1000 collisions per cm only the ion of larger mobility was observed, while in conditions when more than about 7000 collisions per cm occurred only the ion of lower mobility was observed. In conditions where the number of collisions per cm were between about 1500 and 7000 both groups of ion were present, although at the pressure $p_0 = 3{\cdot}8$ mmHg, where the faster ions made up to about 3700 collisions per cm, there were only slight indications of a slower group of ions present in small numbers.

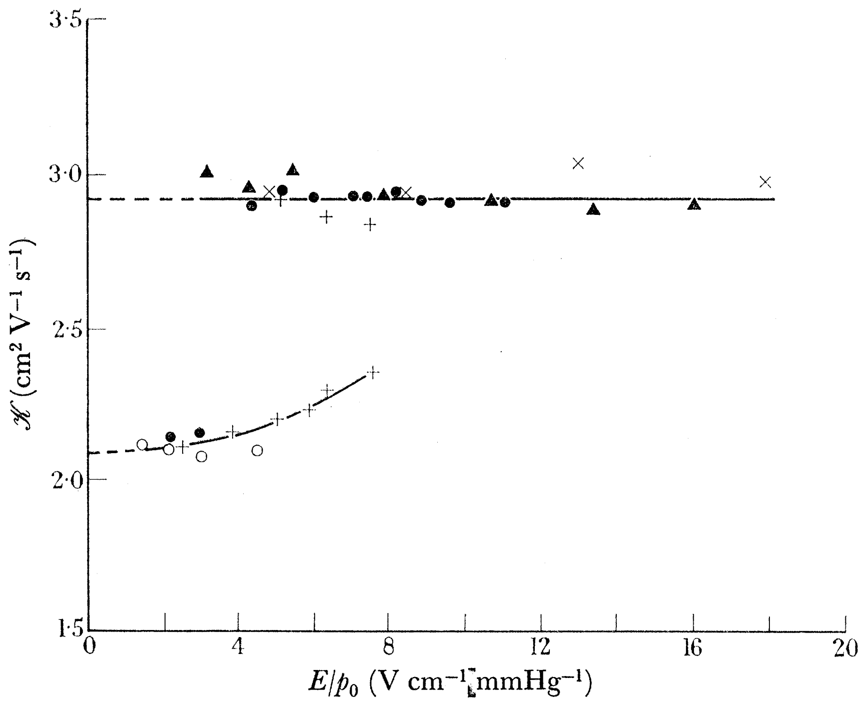

FIGURE 9. Mobility of ions in argon. Third set of results (see text).

experimental points	p_0(mmHg)	experimental points	p_0(mmHg)
×	1·76	+	8·12
▲	3·80	○	13·7
●	5·56		

3. INTERPRETATION OF PRESENT MOBILITY MEASUREMENTS IN ARGON

The results for the zero-field mobility of argon ions in argon obtained by previous investigators are given in tables 1 and 3 of part I.

It can be seen that three species of ion have been observed, the atomic ion having a mobility of about 1·6 $cm^2 V^{-1} s^{-1}$ and the molecular ions having mobilities of about 1·8 and 2·6 $cm^2 V^{-1} s^{-1}$. It is clear that the ion species with mobilities of 2·9 and 2·05 $cm^{-2} V^{-1} s^{-1}$ studied in the present investigation are different from the species on which previous measurements have been made. The reason for this probably lies in the presence of small traces of hydrogen in the argon samples used in the present work, as indicated by the mass spectrometer analysis. It is known (Pahl 1959; Pahl & Weimer 1959; Knewstubb & Tickner 1962) that, for a glow discharge in argon containing small amounts of hydrogen, the cross-section for the formation of ArH^+ ions is large. It thus seems likely that the ion species with mobility 2·9 $cm^2 V^{-1} s^{-1}$ is ArH^+, and this is in agreement with the mass spectrometer analysis which showed that the predominant ion emerging from the glow discharge had a mass of 40 ± 1. The mobility of this ion species would be expected to be considerably greater than that of Ar^+ because of the absence of charge exchange; according to the Langevin theory the mobility should lie between 2·42 $cm^2 V^{-1} s^{-1}$ using equation (6) of part I and 2·82 $cm^2 V^{-1} s^{-1}$ the maximum value using equation (4) of part I.

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There are two possibilities concerning the way in which the ion with a mobility of 2·05 was formed. Either the ion was formed in the glow discharge source or it was formed in the gas during collision of the faster ion with neutral gas molecules. The available evidence strongly supports the latter proposal, for the following reasons.

First, experiments at fixed values of glow current in the ion source showed that as the value of E/p_0 in the drift tube changed, the proportion of ions forming each group changed. As E/p_0 was decreased, i.e. as the number of collisions of ions with gas molecules increased, a larger proportion of ions with lower mobility was produced. Secondly, when the graph of mobility, calculated from the third order current maxima, was plotted as a function of E/p_0 (figure 9), the mobility of the slower ion appeared to increase with increasing values of

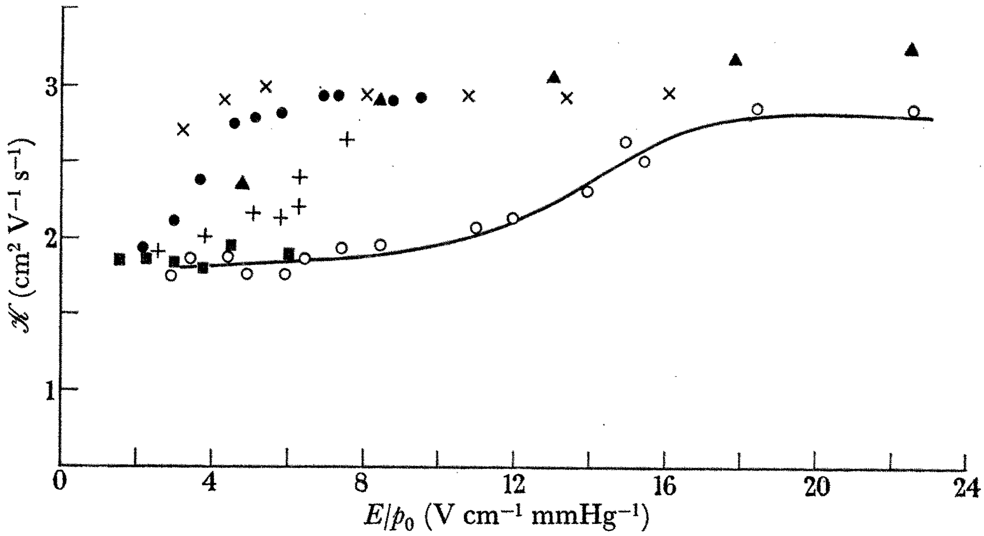

FIGURE 10. Mobility of ions in argon. Comparison of first set of results with the apparent mobility calculated from the second order unresolved peaks of the third set of results, when two ion species were known to be present.

experimental points	p_0(mmHg)	experimental points	p_0(mmHg)
▲	1·76	+	8·12
×	3·80	■	13·7
●	5·56		

○, First set of results.

E/p_0. It is very unlikely at these low values E/p_0 that the mobility genuinely increases in this way. Almost certainly the explanation lies in the fact that the slower ions were formed from the faster ions after a sufficient number of collisions with gas molecules. Depending on the region of the apparatus in which the slower ions were predominantly formed, a resultant velocity intermediate between the two ion velocities was measured.

The differences between the various sets of results can also be explained on this basis. In the third set of measurements two species of ion were resolved. It seems likely that these two species of ion were also present in the first set of experiments, but were not resolved. Indeed if the values of the apparent mobility computed from the unresolved second order peaks of the third set of results (in which it is known that two species of ions are present) are plotted as a function of E/p_0 (see figure 10), a curve similar to that obtained from the first set of experiments is obtained; it differs only in that the transition regions do not occur at the same values of E/p_0. If the values of the apparent mobility from the second set of measurements are compared with these values computed from the unresolved second order peaks of the third set of results, however, the transition regions occur at the same values of E/p_0. The reason why the transition region occurs at higher values of E/p_0 for the first set of results seems likely to have been due to differences in gas samples although this is not certain, because it was not possible to mass analyse the first sample. The three sets of results show that the proportions of the two groups of ion formed depend in a complex way upon (*a*) the composition of the gas sample, (*b*) the parameter E/p_0, and (*c*) the pressure p_0.

4. Conclusions

From the present investigation it is concluded that the ions which were formed by discharges in argon containing traces of hydrogen and which have a measured mobility of $2{\cdot}9 \pm 0{\cdot}1\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ are ArH^+ ions. The slower species of ion with a zero-field mobility of $2{\cdot}05 \pm 0{\cdot}05\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ was formed from the faster species by collision with gas atoms, but it was not possible to identify this ion.

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