

Mobilities and reactions of diatomic rare-gas ions in their parent gases, helium, neon, argon and krypton

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Abstract. The mobilities of He_2^+ , Ne_2^+ , Ar_2^+ and Kr_2^+ have been measured in their parent gases as a function of E/N at 293 K (for He), 77 K (for Ne and Ar) and 295 K (for Kr). Mobility data are also presented for Ne_3^+ in Ne, Ar^+ in Ne and Ar, and Ar_3^+ in Ar; in each of these cases the gas is at 77 K. The reduced zero-field mobilities were obtained by extrapolation for all these ions and are compared with previous measurements where they are available. The clustering reaction for the formation of Ar_3^+ has been investigated and it is demonstrated that the dissociation energy for Ar_3^+ is greater than that for He_3^+ . The magnitudes of the mobilities of the diatomic inert-gas ions in their parent gases and the variation of the mobility with E/N are discussed.

1. Introduction

A number of investigations of the mobility of diatomic ions in their parent gases have been made (for a survey see Massey 1971) but the data are fragmentary and in some cases doubtful due to the lack of ion identification. The present work was undertaken to obtain more complete and accurate data for the rare-gas dimer ions in their parent gases, helium, neon, argon and krypton. The reaction equilibrium of dimer and trimer ions in neon and argon at low energies has also been investigated. The work presented here is an extension of two recent studies into the behaviour of molecular rare-gas ions in helium and xenon (Helm 1976a,b).

2. Experimental details

The ionic mobilities were measured by the Bradbury–Nielsen technique using two experimental systems. A static-gas 10 cm drift tube (Elford 1972) (tube A) and a drift tube with mass spectrometer (Helm and Elford 1977) (tube B) were used. The technique of the measurement and the error analysis have been subject to extensive investigations and are not repeated in detail here. The gases used were Matheson Research Grade obtained from stainless-steel cylinders. No further purification was carried out. The mobility values quoted have all been normalised to standard gas

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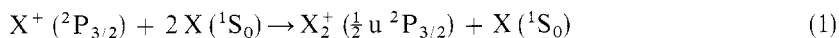
number density and are referred to as reduced mobilities. The reduced mobility κ is obtained from the ionic drift velocity, W , by the relation

$$\kappa = W(E/N)^{-1} N_s^{-1}$$

where N_s is the standard gas number density. All mobility values quoted are in units of $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and all values of E/N are in townsend (1 Td = 10^{-17}V cm^2).

3. Production and state of dimer ions

The dimer ions were produced in a radioactive source (Crompton and Elford 1973) in associative ionisation events or via three-body reactions from atomic ions. Due to spin-orbit coupling, the rare-gas ions X^+ (where X is a rare gas other than helium) exist in either of the two spin states $^2P_{1/2}$ or $^2P_{3/2}$ and Mulliken's (1970) analysis shows that the spin state of the ion has a significant effect on molecular ion formation. The interaction of a ground-state atomic ion X^+ ($^2P_{3/2}$) with a ground-state atom $X(^1S_0)$ can give rise to a molecular ion X_2^+ ($\frac{1}{2} u \ ^2P_{3/2}$) which is strongly bound with a binding energy greater than approximately 1 eV. It is the ion in this state, the $\frac{1}{2} u \ ^2P_{3/2}$, which is normally referred to in discussing homonuclear diatomic rare-gas ions. The X_2^+ ($\frac{1}{2} u \ ^2P_{3/2}$) ion is formed either by a three-body reaction



or the associative ionisation of a short-lived highly excited atom X^* (Hornbeck-Molnar process):



where the condition is that the ionisation potential of X^* is less than or equal to the dissociation energy of X_2^+ in its ground vibrational state.

The formation of molecular ions from the upper level of the lowest ionic state, X^+ ($^2P_{1/2}$) is less clear. The two modes of adiabatic interaction resulting from a collision of X^+ ($^2P_{1/2}$) with $X (^1S_0)$ have strongly repulsive potential curves at internuclear distances where the stable molecule formed in reactions (1) and (2) exists. At those distances, however, corresponding roughly to the position of the Van der Waals minimum of the neutral dimer, the interaction X^+ ($^2P_{1/2}$) + X is considered to have a shallow minimum as a result of a balance of exchange and dispersion forces (Mulliken 1970). Direct evidence for these minima has now been forthcoming with the experiments of Jones *et al* (1974) and Dehmer and Dehmer (1977). In xenon minima of the order of a few hundred meV were found. If this information is combined with the experimental observation that the molecular ions formed from the atomic ions X^+ ($^2P_{3/2}$) and X^+ ($^2P_{1/2}$) are indistinguishable in their mobilities and their ability to form trimer ions (Helm 1976b,c, Liu and Conway 1974) we may draw the conclusion that the end product of a reaction of X^+ ($^2P_{1/2}$) with X is identical with that of reaction (1) but involves as an intermediate step optical transitions of the weakly bound X^+ ($^2P_{1/2}$) $X (^1S_0)$ complexes to the X_2^+ ($\frac{1}{2} u \ ^2P_{3/2}$) state (Helm and Varney 1978).

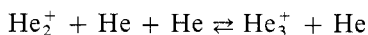
It should be noted that uncertainty exists as to the degree of vibrational excitation of the molecular ions under study. In the light of recent photodissociation studies (Miller *et al* 1976) it is assumed that due to the high-pressure environment in our

experiment most molecular rare-gas dimer ions have thermalised to the ground vibrational state before entering the drift space.

4. Results

4.1. Helium

Measurements of the mobility of the molecular helium ion in helium were performed at 293 K in tube A in the pressure range from 0.3 to 8 kPa. No mass-spectrometric mobility determination has been undertaken as the identity of this ion He_2^+ has been established previously beyond doubt (Beaty and Patterson 1964, McFarland *et al* 1973). No pressure dependence of the measured mobility was found, as was expected, since the equilibrium of the reaction



has shifted entirely to the left at the ion energies and in the pressure range investigated here (see also Helm 1976a). The data are shown in figure 1 together with some of the previous data. The current data are considered to be in error by less than 1% and therefore agreement exists between all the data sets presented in figure 1.

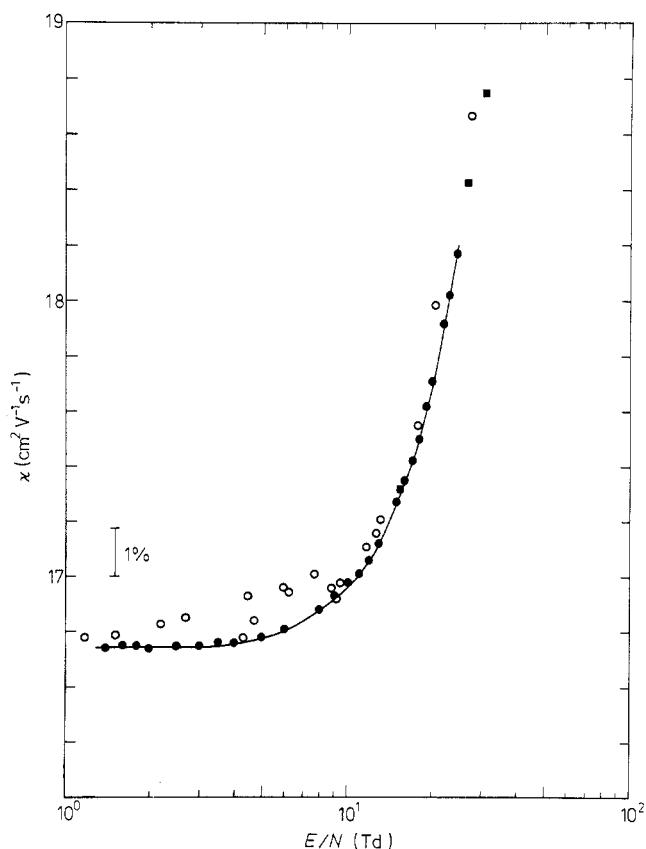


Figure 1. Reduced mobility of He_2^+ in He at 293 K measured in tube A as a function of E/N (full circles). Two sets of previous data are shown for comparison: open circles, Beaty and Patterson (1964); full squares, McFarland *et al* (1973).

Table 1. Mobilities measured in this work. The values given are mean values, measured at various pressures as indicated in the text. The mobilities at room temperature vary by less than $\pm 0.15\%$ over the range of pressures used, and at 77 K by less than $\pm 0.3\%$.

Ion	He ₂ ⁺	Ne ₂ ⁺	Ar ⁺	Ar ⁺	Ar ₂ ⁺	Kr ₂ ⁺
Gas	He	Ne	Ne	Ar	Ar	Kr
T(K)	293	77	77	77	77	295
<i>E/N</i> (Td) =	2	16.74				
	4	16.76				
	6	16.81				0.994
	8	16.88				0.994
	10	16.97	5.40	6.39		0.994
	12	17.06		6.40		
	14	17.20		6.46		
	16	17.35	5.40	6.51	1.99	0.995
	18	17.50		6.55	1.98	
	20	17.68	5.52	6.59		0.996
	22	17.92				
	24	18.12				
	30		6.00		1.90	0.998
	35		6.25		1.85	0.999
	40		6.47		1.81	1.000
	43	19.56				
	45		6.60		1.78	1.002
	50		6.66			1.003
	55		6.67			1.005
	60				1.70	1.006
	65				1.67	1.006
	70				1.64	1.010
	80				1.59	1.013
	90				1.54	1.019
	100				1.90	1.022
	110					1.026
	120					1.027
	130					1.029
	140					1.027
	150					1.023
	160					1.018
	170					1.011

The data are given in tabulated form in table 1. It was not possible to take data between 24 and 40 Td as in this *E/N* range the mobility of He₂⁺ is approximately twice that of He⁺ and therefore arrival-time spectra for different ions of different order overlap. Mobility values for the molecular ion could not be obtained above 45 Td due to lack of ion current and electrical breakdown problems.

4.2. Neon

Mobilities of ions in neon were measured at 77 K in tube A and tube B in the range 0.07 to 0.1 kPa[†]. The results are shown together with those reported earlier for the atomic ions Ne⁺ (²P_{3/2}) and Ne⁺ (²P_{1/2}) (Helm and Elford 1977) in figure

[†] Higher pressures could not be investigated in tube A in neon due to the overlap of arrival time spectra of molecular and atomic ions at low values of *E/N*.

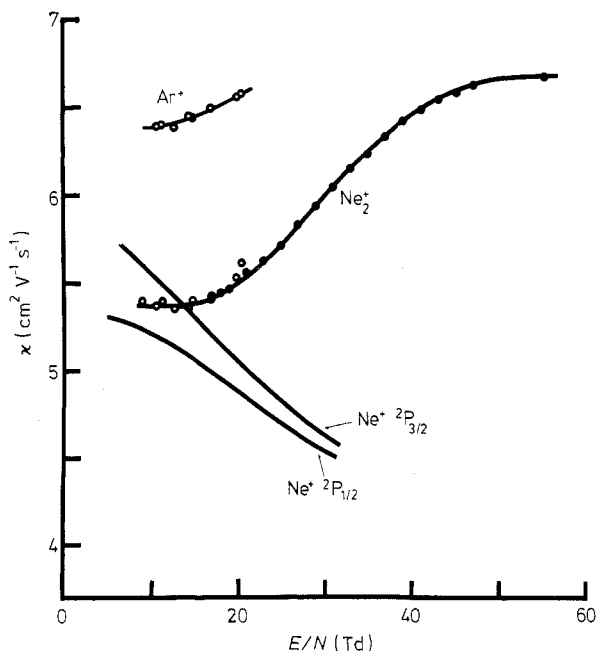


Figure 2. Reduced mobilities of ions in neon at 77 K measured in tube A (full circles) and tube B (open circles) as a function of E/N .

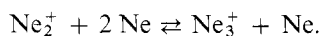
2. The full circles refer to measurements in tube A, the open circles to measurements in tube B. The data are to be found in table 1.

Three important points should be noted with respect to figure 2.

(a) The mobility of the molecular ion Ne_2^+ in Ne falls below that of the atomic ground-state ion Ne^+ in Ne at values of E/N less than 16 Td. This corresponds to a mean ion energy in the centre-of-mass (CM) frame[†] of about 15 meV. This is the *first* time that an inversion of the almost 'classical' principle that the atomic ion—though lighter—moves more slowly than the molecular ion has been observed.

(b) Residual traces of argon in one of the neon samples and deliberate doping with argon produced enough Ar^+ for its mobility to be determined with direct ion identification. It may be seen from figure 2 that the mobility of Ar^+ in neon is about 20% higher than that of the ion of equal mass Ne_2^+ in neon at low values of E/N (see also table 1).

(c) At values of $E/N \lesssim 20$ Td the triatomic ion Ne_3^+ was detected in the mass spectrometer with an apparent mobility *identical* to that of Ne_2^+ . The two ions are considered to come into equilibrium in the drift space at values of $E/N < 20$ Td through the reaction



The lack of a measurable pressure dependence of the measured mobility indicates that the mobilities of the two molecular neon ions are similar. This latter observation is in strong contrast to the observation made in helium (Helm 1976a) where the triatomic ion was found to move *considerably faster* than the diatomic ion.

It may be noted that higher-order clusters such as Ne_4^+ , ArNe^+ and ArNe_2^+ were observed though their mobilities could not be determined accurately. The only

[†] Calculated with Wannier's formula (see §5).

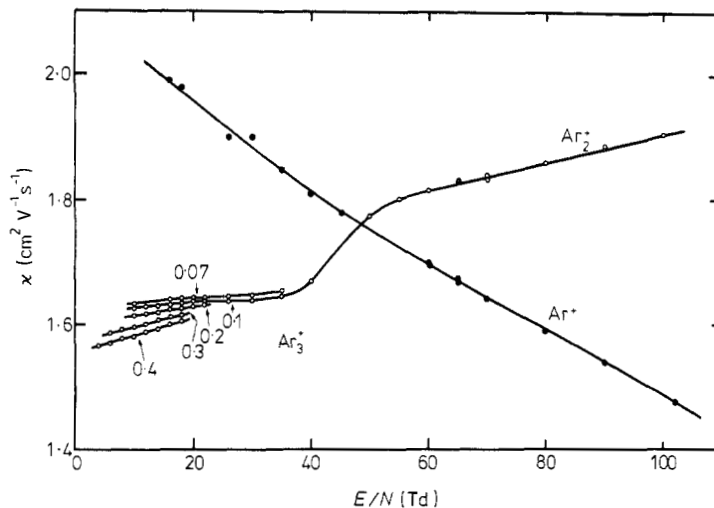


Figure 3. Reduced mobilities of ions in argon at 77 K measured in tube A as a function of E/N . The parameter is the gas pressure (p_{77} in units of kPa).

previous data for molecular ions in neon at 77 K are those of Chanin and Biondi (1957). These data are in serious disagreement with those reported here.

4.3. Argon

Mobilities of ions in argon were measured at 77 K in tube A and tube B in the pressure range 0.03 to 2.7 kPa and 0.03 to 0.13 kPa respectively. Figure 3 shows a sample of the data obtained in tube A. Measurements in tube B were limited

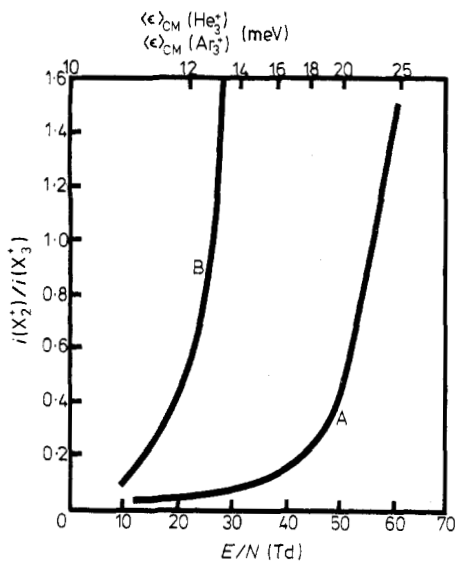
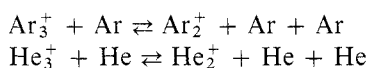


Figure 4. Ratio of dimer to trimer ion currents measured at 77 K in tube B at $p_{77} = 130$ Pa. The E/N scale refers to the argon data. The mean centre-of-mass energy scale at the top refers to both the argon (A) and helium (B) results.

to values of E/N below 60 Td due to breakdown problems. Tube B data were identical with those taken in tube A. As in neon, the mobility of the molecular ion falls below that of the atomic ion at low values of E/N (corresponding to mean CM energies below about 20 meV). A remarkable change in the apparent mobility of the diatomic and triatomic ion is observed in the range between 40 and 60 Td and is accompanied by a dramatic change in the relative abundance of Ar_2^+ and Ar_3^+ ions. Figure 4 gives the variation of the ion current ratio $i(\text{Ar}_2^+)/i(\text{Ar}_3^+)$ as a function of E/N at 130 Pa and 77 K as measured in tube B. In the investigation of helium (Helm 1976a) a similar variation of $i(\text{He}_2^+)/i(\text{He}_3^+)$ with E/N was found. The scale at the top of figure 4 refers to the mean ion energy in the CM frame for Ar_3^+ in Ar. The variation of $i(\text{He}_2^+)/i(\text{He}_3^+)$ with the mean CM energy of He_3^+ is plotted on the same scale. The steep variation of the ion current ratios with E/N corresponds to a dramatic switch in the equilibrium of the reactions



from the left- to the right-hand side as E/N is raised. The observed fact (figure 4) that the break-up of Ar_3^+ into $\text{Ar}_2^+ + \text{Ar}$ sets in at higher values of ion energy than does the break-up of He_3^+ into $\text{He}_2^+ + \text{He}$ may be taken as an indication that the dissociation energy $D(\text{Ar}_2^+ + \text{Ar})$ is greater than $D(\text{He}_2^+ + \text{He})$.

The pressure dependence and the drastic variation of the apparent mobility of molecular argon ions for $E/N \lesssim 60$ Td can be explained in terms of an equilibrium between Ar_2^+ , Ar_3^+ and higher-order cluster ions of argon. A necessary condition for a mobility measurement in such a situation is that the reaction rates in both directions of



are fast enough for the ions to switch from Ar_n^+ to Ar_{n+1}^+ a number of times while they traverse the drift tube. Then the arrival time spectra of Ar_n^+ ($n \geq 2$)† measured separately in the mass spectrometer are identical and symmetric with respect to the peak maximum. This is indeed observed in our experiment. The arrival time spectra then refer to an apparent mobility κ_m , which is given by (Helm 1976a)

$$\kappa_m = \frac{\kappa_n(K_e/N) + \kappa_{n+1}}{(K_e/N) + 1} \quad (4)$$

where κ_n and κ_{n+1} are mobilities of Ar_n^+ and Ar_{n+1}^+ respectively, and K_e is the equilibrium constant for reaction (3) given by

$$K_e = [\text{Ar}_n^+]N/[\text{Ar}_{n+1}^+] \quad (5)$$

with the values in square brackets denoting the ionic concentrations. It must be noted that K_e is strongly dependent on E/N as the reduced electric field strength controls the ion energies and hence the rate of break-up and formation of the cluster ions.

The variation of the measured ion current ratio with E/N (see figure 4) is a relative measure‡ of the variation of the equilibrium constant with E/N . Equation

† The switching reaction (3) for $n = 1$ is not observed for ions with near-thermal energy since the binding energy of Ar_2^+ is too high (1.33 eV, Moseley *et al* 1977).

‡ Relative since the measured current ratio is affected by unknown mass-dependent sampling efficiencies.

(4) predicts that as, at a given pressure, K_e increases from very small values to large values, κ_m changes from κ_{n+1} to κ_n . Hence the decrease in the apparent mobility between 60 and 40 Td indicates that above 60 Td where K_e is large, e.g. Ar_2^+ dominates the molecular ion spectrum, the apparent mobility is close to that of pure Ar_2^+ (see equation (4)) while below around 40 Td where K_e is small and Ar_3^+ is the dominant ion, the apparent mobility is close to that of pure Ar_3^+ .

This situation is basically similar to the observations in helium (Helm 1976a). However, in the present case the pressure dependence of the apparent mobility could not be studied *in extenso* in this E/N range (40–60 Td) as was possible in helium where K_e (E/N) could be deduced from the pressure dependence of the apparent mobility. Reasons for this are intrinsic experimental limitations, namely lack of ion current at too low pressure and breakdown problems at too high pressures.

The observation that the triatomic ion in argon moves more slowly than the diatomic ion (see figure 3) is opposite to that found for the corresponding case in helium (Helm 1976a). At values of $E/N > 60$ Td, Ar_2^+ is the dominant ion and no pressure dependence of its apparent mobility was observed for $0.03 \leq p \leq 0.11$ kPa. At values of E/N less than 20 Td the abundance of Ar_2^+ is less than 5% of Ar_3^+ at the pressures used here and therefore Ar_2^+ can clearly not be the cause of the strong pressure dependence of the apparent mobility of Ar_3^+ . The strong pressure dependence is attributed to the formation of higher-order clusters such as Ar_n^+ ($n > 4$). It was found that the apparent mobility dropped steadily to values below a mobility of 1.4 as the pressure was raised to above 2 kPa.

Table 1 lists the mobility data for Ar^+ , and those for Ar_2^+ in the E/N range where they were found to be independent of pressure. The only previous data at 77 K are again those of Chanin and Biondi (1957). While there is agreement with the present data to within about 10% for Ar^+ , the molecular ion data of Chanin and Biondi (1957) are in strong disagreement with our values.

4.4. Krypton

The mobility of Kr_2^+ in Kr was measured at 295 K in the range 0.07 to 2 kPa in tube A. The identification of this ion relies on a mass-identified mobility value obtained in tube B (Helm 1976c) at 48 Td. Our mobility values are shown in figure 5 together with previous measurements. While there is reasonable agreement between the data of Varney (1952) and Beaty (1956) and ours, the data of Biondi and Chanin (1954) lie about 20% above our data at values of E/N below 140 Td. Our actual data points are displayed in figure 6 on an enlarged scale. These data have been measured at ten different pressures. The mean values are given as a function of E/N in table 1. A high E/N limit to these measurements was set by the initiation of electron avalanches at the shutter grid wires resulting in distortions of the arrival-time spectra of primary ions (Helm 1978). At pressures greater than 2 kPa and values of E/N less than 6 Td the apparent mobility of Kr_2^+ was found to decrease slowly with increasing pressure. No detailed investigation of this pressure dependence was carried out, however.

4.5. Zero-field mobilities

The reduced zero-field mobilities, κ_0 , were obtained by graphical extrapolation of the experimental data and are listed in table 2. The error bars given represent the

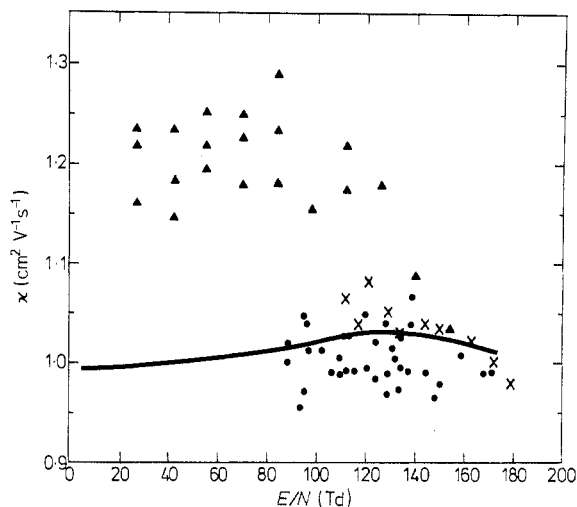


Figure 5. Reduced mobilities of ions in krypton as a function of E/N around room temperature. All current values of the mobility of Kr_2^+ in Kr at 295 K fall within the thickness of the full curve. The crosses are the measurements of Varney (1952), the full triangles are the results of Biondi and Chanin (1954) and the full circles are the data of Beatty (1956).

sum of the extrapolation error and the experimental errors. When no error bars are given the extrapolation is too uncertain to assign a specific uncertainty. The value obtained, however, is considered to be in error by less than 10%. The present results may be compared with previous data which are listed.

5. Discussion and conclusion

The problems arising from the directional dependence of the ion-atom interaction and the possibility of inelastic collisions in systems where rotational and vibrational

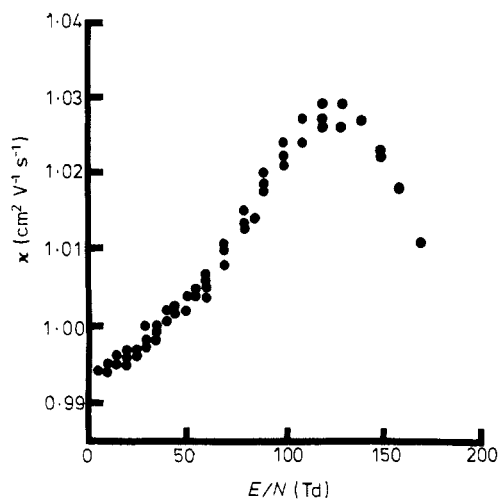


Figure 6. Current values for the reduced mobility of Kr_2^+ in Kr at 295 K measured in tube A as a function of E/N on an amplified scale.

Table 2. Reduced zero-field mobilities obtained in the current study. Previous data are given for comparison.

Ion	Gas	Temperature (K)	This work	Previous values
He ₂ ⁺	He	293	16.74 ± 0.08	16.70 ± 0.17 ^a
Ne ₂ ⁺	Ne	77	5.4 ± 0.1	6.7 ^b
Ne ₃ ⁺	Ne	77	5.4	—
Ar ⁺	Ne	77	6.4 ± 0.1	—
Ar ⁺	Ar	77	2.1 ± 0.1	2.2 ^b , 1.88 ^c
Ar ₂ ⁺	Ar	77	1.8 ± 0.1	2.7 ^b
Ar ₃ ⁺	Ar	77	1.65	—
Kr ₂ ⁺	Kr	295	0.995 ± 0.004	1.21 ^d , 1.1–1.2 ^e

^a Beaty and Patterson (1964), at 300 K; ^b Chanin and Biondi (1957); ^c Beaty (1956) (the extrapolation was made from 60 Td); ^d Biondi and Chanin (1954), at 300 K; ^e Varney (1952), at 300 K.

excitation can occur have, to our knowledge, not been taken into account in connection with the calculation of ionic mobilities. To simplify the problem the motion of diatomic rare-gas ions in their parent gases is assumed to be described adequately by theories applicable to atomic ions in an unlike gas (Dalgarno *et al* 1958). The first evidence for a strong deviation from this behaviour came from the measurements of Beaty and Patterson (1964) in the case of He₂⁺ in He. These results were interpreted by Beaty *et al* (1966) on the assumption that ion-atom interchange occurred in the collision of three like particles. The picture of ion-atom interchange and its hindering effect on the transport of ions was first applied by Varney (1960) to account for the slow motion of H₃⁺ in H₂.

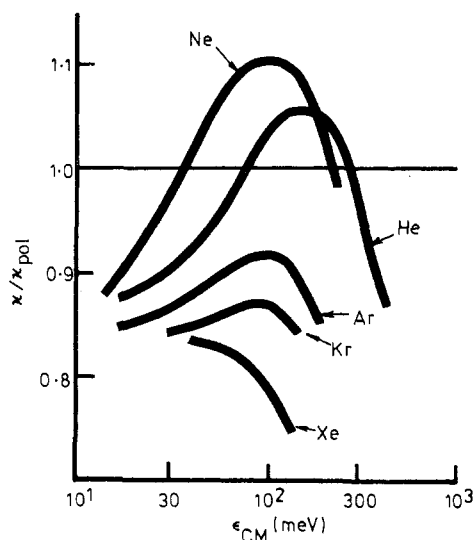


Figure 7. Mobilities of rare-gas dimer ions, normalised to the polarisation limit, as a function of the mean centre-of-mass energy. To construct this plot the experimental results of the present paper were complemented with data of McFarland *et al* (1973) for He, of Beaty and Patterson (1968) for Ne, of Beaty (1962) for Ar and Helm (1976b) for Xe.

Our current study shows that the anomalous slow motion, slow compared to a theoretical value which is obtained using an interaction potential with a long-range term dominated by the polarisation interaction and elastic collisions, is characteristic of all diatomic rare-gas ions in their parent gases and particularly so at low ion energies. We have chosen figure 7 to illustrate this behaviour in detail. The ratio of the measured mobility to the polarisation limit (McDaniel and Mason 1973)

$$\kappa_{\text{pol}} = 13.876(\alpha\mu)^{-1/2}$$

is shown as a function of the mean ion energy in the CM frame as calculated from Wannier's (1953) formula

$$\langle \epsilon \rangle_{\text{CM}} = \frac{3}{2}kT + \frac{1}{2}MW^2.$$

(α is the polarisability, μ the reduced mass, k is Boltzmann's constant, T the absolute gas temperature and M the mass of the neutral gas atoms). Although basically only applicable to the case of constant collision frequency, this formula is known to be a good approximation to the true mean ion energy value (Skullerud 1973). The full curves shown in figure 7 cover normalised mobility values measured as a function of E/N at various temperatures by various authors as indicated in the caption to figure 7. As the mobility is not a function of the mean ion energy only, such a picture is of limited value but it allows the presentation of all dimer ion data in one plot and also gives a first-order approximation to the temperature dependence of the dimer ion mobilities.

Transport theories for atomic ions in an unlike gas whose interaction can be described by a $2\mathcal{N}-6-4$ potential predict that the normalised mobility should be around one at low ion energies in figure 7 (see figure 11 of Skullerud 1973). As the energy increases the mobility should rise to a maximum corresponding to partial cancellation of scattering effects by the repulsive and attractive parts of the interaction over a limited energy range (Wannier 1970). Finally, at high energies the mobility should drop off steeply to a value below one since the repulsive part of the potential curve (characterised by \mathcal{N}) causes the momentum transfer cross section to vary with the relative speed, v , as $v^{-4/\mathcal{N}}$. This in turn gives rise to a strong increase in the collision frequency with energy and therefore a drop in the mobility for the commonly assumed values of \mathcal{N} ($\mathcal{N} \geq 6$).

Quite clearly the rare-gas dimer ions deviate from such behaviour at low ion energies, the low-energy limit (from figure 7) being about 10 to 15% below the polarisation limit. While it is known that a strong attractive (r^{-6}) term in the interaction potential can cause the mobility value to drop below the polarisation limit at low energies before the hump in the mobility curve (see figure 11 of Skullerud 1973 and figure 5-3-2 of McDaniel and Mason 1973) we found it impossible to simulate the variation found experimentally by using the Kumar–Robson theory (Robson and Kumar 1973) and a $2\mathcal{N}-6-4$ potential with all parameters variable (but keeping the polarisability fixed). It is therefore concluded that the collisions of dimer ions with their parent-gas atoms are characterised by effects which are not accounted for in a simple picture of elastic collisions. There are other cases such as ArH^+ in Ar (McAfee *et al* 1967), LiAr^+ in Ar (Keller *et al* 1973) and O_4^+ in O_2 (Milloy 1975) where ion–atom interchange seems possible and an inspection of the experimental data shows that the reduced mobility data have the same general behaviour as that shown in figure 7. It may be noted here that rare-gas trimer ions, as far as

they are known today, exhibit mobilities which lie considerably below the polarisation limit.

Varney's original suggestion that ion-atom interchange is responsible for the extremely slow motion of H_3^+ would therefore appear to apply to the molecular rare-gas ion cases in their parent gases in general.

Acknowledgment

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Note added in proof. Johnsen and Biondi (1978) recently reported mobility measurements of doubly charged rare-gas ions in their parent gases. In the light of their findings it appears possible that some of the data which Biondi and Chanin (1954) attributed to molecular ions actually refer to doubly charged species.

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