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THE MOBILITIES OF IONS IN THEIR PARENT GASES

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CONTENTS

The available experimental data on the mobilities at low field strengths of ions in their parent gases are analyzed on the basis of a simple theoretical description. It is shown that the maxima observed in recent measurements of charge-transfer cross-sections are difficult to reconcile with measured mobilities of atomic ions in atomic gases, and that it is not necessary to invoke charge transfer to explain the observed mobilities of diatomic and polyatomic molecular ions in atomic gases; however, charge transfer is probably operative in cases of diatomic ions in diatomic gases. Finally, a semi-empirical method is used to predict the mobilities over a wide range of temperature and the charge-transfer cross-sections over a wide range of impact energies of the ions of atomic hydrogen and deuterium, the inert gases, mercury and atomic oxygen, and an estimate is given of the mobility of N_2^+ ions in N_2.

1. Introduction

The original theoretical work of Massey & Mohr (1934) showed that the mobility of an atomic ion in its parent atomic gas is determined largely by the corresponding probability of charge transfer. It is possible therefore to assess the accuracy of measurements of charge-transfer cross-sections using measurements of ion mobilities but it is only recently that data on ions of definite identification have become available.

2. Theory

Throughout this paper we shall use the same notations as in paper I, preceding (Dalgarno, McDowell & Williams 1958).

2·1. Because of the identity of the nuclear fields there are two possible modes of interaction between an atomic ion and its parent atom, one $V^+(R)$ symmetric in the nuclei, the other $V^-(R)$ antisymmetric. The quantal method of taking this into account in the description of transport phenomena has been described by Massey & Mohr (1934) who showed that different expressions result for the transport cross-sections according to the statistics obeyed by the nuclei. If η_l^+ is the lth-order phase shift associated with elastic scattering by $V^+(R)$ and η_l^- that associated with $V^-(R)$ and s is the nuclear spin, then in the case of Bose–Einstein statistics the diffusion cross-section is given by

$$Q_d = \frac{s+1}{2s+1}Q^+ + \frac{s}{2s+1}Q^- \qquad (1)$$

and in the case of Fermi–Dirac statistics by

$$Q_d = \frac{s+1}{2s+1}Q^- + \frac{s}{2s+1}Q^+, \tag{2}$$

where $$Q^+ = \frac{4\pi}{k^2}\sum_{l=0}^{\infty}(l+1)\sin^2(\eta_l - \eta_{l+1}), \tag{3}$$

with $\eta_{2r} = \eta_{2r}^+$ and $\eta_{2r+1} = \eta_{2r+1}^-$ and Q^- is an exactly similar expression with $\eta_{2r} = \eta_{2r}^-$ and $\eta_{2r+1} = \eta_{2r+1}^+$.

2·2. Although no strictly classical analogue of (3) exists, we may develop a classical approximation to it by following the procedure used in § 3·1 of paper I to demonstrate the limiting equivalence of classical and quantum diffusion cross-sections for unlike particles. This amounts to writing $\eta_l^{\pm} - \eta_{l+1}^{\mp} = \zeta^{\pm}(p)$, replacing the summation over l by an integration over p so that Q^+ and Q^- become identical to each other and to Q_d and are given by

$$Q_d = 2\pi\int_0^{\infty} p\{\sin^2\zeta^+(p) + \sin^2\zeta^-(p)\}\,\mathrm{d}p \tag{4}$$

and using Jeffreys's approximation to calculate $\zeta^{\pm}(p)$. If now p^* can be so chosen that the Massey–Mohr approximation can be used for all $p > p^*$, then

$$Q_d = \pi p^{*2} + 2\pi\int_{p^*}^{\infty} p\{\sin^2\zeta^+(p) + \sin^2\zeta^-(p)\}\,\mathrm{d}p, \tag{5}$$

where $$\zeta^{\pm}(p) = \mp\frac{k}{2\mathscr{E}}\int_p^{\infty}\frac{V^{\pm}(R) - V^{\mp}(R)}{\{1 - p^2/R^2\}^{\frac{1}{2}}}\,\mathrm{d}R + \frac{1}{2\mathscr{E}}\frac{\partial}{\partial p}\int_p^{\infty}\frac{V^{\mp}(R)}{\{1 - p^2/R^2\}^{\frac{1}{2}}}\,\mathrm{d}R \tag{6}$$

and p^* is such that $\sin\zeta^{\pm}(p)$ is a rapidly oscillating function of p for $p < p^*$.

It follows that at high temperatures

$$\zeta^{\pm}(p) = \pm(\eta_l^+ - \eta_l^-) = \pm\Gamma(p), \quad \text{say}, \tag{7}$$

and consequently $$Q_d = 4\pi\int_0^{\infty} p\sin^2\Gamma(p)\,\mathrm{d}p. \tag{8}$$

Massey & Smith (1933) (see also Bates, Massey & Stewart 1953) have shown that the cross-section for the charge-transfer process

$$X^+ + X \rightarrow X + X^+, \tag{9}$$

X being an atomic system, is given by

$$Q_t = 2\pi\int_0^{\infty} p\sin^2\Gamma(p)\,\mathrm{d}p \tag{10}$$

provided the impact energy E is not so low that the discreteness of p need be taken into account but not so high that transfer of electron momentum is significant (cf. Bates & Dalgarno 1951; Dalgarno & Yadav 1952). Comparing (10) with (8) we have

$$Q_d = 2Q_t, \tag{11}$$

a result which is probably valid in most cases for temperatures greater than 400 °K. It is worth noting that at high temperatures in contrast to the case of unlike particles for which given the interaction Q_d depends only upon the particle energy, Q_d for like particles depends only upon the particle velocity.

2·3. The value of p^* corresponding to (6) will usually be so large that for $R > p^*$, $V^+(R) = V^-(R) = C/R^4$ so that (6) can be written

$$\zeta^{\pm}(p) = \pm\Gamma(p) + \beta(p), \tag{12}$$

where

$$\beta(p) = 3\pi C/8p^4\mathscr{E}. \tag{13}$$

Because $\Delta E(R) = V^+(R) - V^-(R)$ decreases exponentially a reasonable estimate of Q_d valid at lower temperatures than (11) is (Dalgarno & McDowell 1956)

$$Q_d = 2(Q_t + Q_p), \tag{14}$$

where

$$Q_p = 2\pi \int_{p^*}^{\infty} p \sin^2 \beta(p)\, \mathrm{d}p \tag{15}$$

and has been plotted in paper I. The accuracy of (14) has been investigated recently for the case of He^+ in He by Lynn & Moiseiwitsch (1957), who showed it to be very satisfactory.

2·4. At low temperatures (12) becomes identical to $\beta(p)$, the phase difference obtained in paper I. Thus in the limit of low temperatures, the classical approximation to Q_d is

$$Q_d = 2{\cdot}210(-C/\mathscr{E})^{\frac{1}{2}} \tag{16}$$

just as for unlike particles.

2·5. The expression

$$\Gamma(p) = -\frac{k}{2\mathscr{E}} \int_p^{\infty} \frac{V^+(R) - V^-(R)}{\{1 - p^2/R^2\}^{\frac{1}{2}}}\, \mathrm{d}R \tag{17}$$

has been evaluated by Dalgarno & McDowell (1956) for the case when

$$\Delta E(R) = \mathrm{A} \exp(-\gamma R),$$

A and γ being constants, and they give the result

$$\Gamma(p) = -kApK_1(\gamma p)/2\mathscr{E}. \tag{18}$$

If now p^* is chosen as the largest value of p for which $|\Gamma(p)| = \frac{1}{4}\pi$, $\sin^2\Gamma(p)$ is replaced by $\{\Gamma(p)\}^2$ for $p \geqslant p^*$ and γp^* is assumed large, then (10) and (11) give

$$Q_d = \pi p^{*2} + \pi^3 p^*/8\gamma = 2Q_t, \tag{19}$$

where

$$p^* \exp(-2\gamma p^*) = \pi\gamma\mathscr{E}^2/2A^2k^2. \tag{20}$$

The expression (19) is similar to an approximation,

$$Q_d = \pi p^{*2} + \pi p^*/\gamma, \tag{21}$$

obtained by Holstein (1952) who based his analysis on time-dependent perturbation theory.

Although Holstein develops his approximation assuming that $\Delta E(R)$ has the form $A \exp(-\gamma R)$ he shows that a better representation is $AR \exp(-\gamma R)$ and it is an advantage of the formulation presented here that it can easily be generalized to this case. By simply differentiating (18) with respect to γ we obtain

$$\Gamma(p) = -kAp\{pK_0(\gamma p) + K_1(\gamma p)/\gamma\}/2\mathscr{E}. \tag{22}$$

Then making the same approximations that led to (19) and (20) we find that Q_d is still given by (19) but with p^* determined by

$$p^{*3} \exp(-2\gamma p^*) = \pi\gamma\mathscr{E}^2/2A^2k^2. \tag{23}$$

2·6. The approximate expression (19) for Q_t, taken with either (20) or (23), increases monotonically with decreasing energy, the limiting form being given by

$$Q_t \sim (a \ln v - b)^2, \tag{24}$$

where a and b are constants depending upon $\Delta E(R)$ and v is the relative velocity (Dalgarno 1957). This variation is identical in form to that deduced earlier by Demkov (1952) using different methods. It provides a useful method of extrapolating measured values to lower energies.

2·7. To a similar accuracy the modification of (19) and (23) to take account of the long-range polarization forces is

$$Q_d = \pi p^{*2} + \frac{\pi^2 k^2 A^2}{4\mathscr{E}^2 \gamma^2} p^{*4} \exp(-2\gamma p^*) + \frac{3\pi^3 C^2}{32\mathscr{E}^2} \frac{1\cdot279}{p^{*6}}, \tag{25}$$

where in place of (23), p^* is such that

$$\frac{k^2 A^2}{\mathscr{E}^2 \gamma} p^{*3} \exp(-2\gamma p^*) + \frac{9\pi C^2}{8\mathscr{E}^2 p^{*6}} = \frac{\pi}{2} \tag{26}$$

and the factor 1·279 has been arbitrarily inserted to ensure that (25) tends to the correct numerical limit (16) as the temperature tends to zero. The modification of (19) and (20) suggested by Holstein involves only a change in the definition (20) of p^*, the expression (19) being retained. The resulting formula does not behave correctly in the limit of vanishing temperature, but it does provide a rapid indication of the temperature below which polarization forces are becoming significant.

3. Analysis of experimental data on atomic ions

3·1. The energies of interaction between atomic ions and their parent atoms are known accurately for no cases other than protons and deuterons in atomic hydrogen and deuterium. Holstein (1952) has suggested an approximation which is applicable generally (a comparison with the exact values of Bates, Ledsham & Stewart (1953) reveals considerable discrepancies, however) and several sets of approximate values are available for He$^+$ in He, the most recently calculated being those of Moiseiwitsch (1956). In view of the uncertainties in these calculated values it seems more realistic for the purposes of this paper to select interactions which reproduce experimental data on charge-transfer cross-sections and use them to predict mobilities.

3·2. Unfortunately, there are serious discrepancies, especially at low energies, amongst the observations of Q_t by different workers. For the process

$$\mathrm{He}^+ + \mathrm{He} \rightarrow \mathrm{He} + \mathrm{He}^+, \tag{27}$$

the measurements of Hasted (1951) (see also Hasted & Stedeford 1955), and of Potter (1954), are in essentially perfect agreement at all energies (25 to 250 eV) common to both experiments, but are smaller at low energies than those of Dillon, Sheridan, Edwards & Ghosh (1955), who calibrated their apparatus by requiring that the value of Q_t measured at 450 eV for the process

$$A^+ + A \rightarrow A + A^+ \tag{28}$$

equalled that obtained by Hasted (1951). The most recent measurements (Gilbody & Hasted 1957) on (28) yield a much higher value of Q_t at 450 eV so that all the values reported by Dillon *et al.* (1955) must presumably be modified. The measurements of Gilbody & Hasted on (27) also are somewhat different from Hasted's earlier values. They are in reasonable agreement with the modified results of Dillon *et al.* and with the recent theoretical calculations of Moiseiwitsch (1956), but the earlier harmony with Potter is lost. Below 150 eV there is an increasing numerical discrepancy, the Q_t-E curve obtained by Gilbody & Hasted tending apparently to a finite value at zero energy (the smallest energy at which measurements were made is 10 eV) in contrast to that obtained by Dillon *et al.* which is tending to increase more rapidly. Dillon *et al.* made measurements only for $E > 50$ eV, whilst the ultimate shape of the curve obtained by Gilbody & Hasted only becomes apparent at 25 eV, so that there may in fact be no qualitative discrepancy.

However, in reaction (28) and

$$\mathrm{Ne^+ + Ne \rightarrow Ne + Ne^+} \tag{29}$$

there are definite discrepancies in shape for, in agreement with the early work of Rostagni (1935), Gilbody & Hasted find that each of the Q_t-E curves passes through a maximum which is located in the range of the measurements of Dillon *et al.* who observe no such behaviour. At lower energies Gilbody & Hasted obtain minima (at $E \sim 25$ eV) followed by slight but steady increases to the limit $E = 10$ eV of the measurements. Marked alterations of slope must occur for $E < 10$ eV if the curves are to pass through the values measured at the single energies of 1 eV for (28) and 0·8 eV for (29) by Ziegler (1953).

To explain the occurrence of the maxima, which are not expected theoretically (cf. § 2·6), Gilbody & Hasted point out that the positive ions of both Ne and A have a spin multiplicity so that their measurements include also the non-resonance charge-transfer reactions

$$\mathrm{A^+(^2P_{\frac{1}{2}}) + A \rightarrow A + A^+(^2P_{\frac{3}{2}})}, \tag{30}$$

$$\mathrm{A^+(^2P_{\frac{3}{2}}) + A \rightarrow A + A^+(^2P_{\frac{1}{2}})} \tag{31}$$

for A, and similarly for Ne. Although there is some evidence (Lochte-Holtgreven 1928), that reactions similar to the direct reaction

$$\mathrm{A^+(^2P_{\frac{1}{2}}) + A \rightarrow A^+(^2P_{\frac{3}{2}}) + A} \tag{32}$$

and its inverse may be very efficient, no unambiguous information is available on processes similar to (30) and (31) (cf. Massey & Burhop 1952).

It seems improbable that the cross-sections of (30) and (31) are large enough to explain the observations, but the possibility cannot be excluded; as Gilbody & Hasted note, the locations of the maxima are in conformity with the semi-adiabatic hypothesis (Massey 1949) for the reactions concerned. However, quite apart from the experimental discrepancies, there is a serious objection to accepting the proposed interpretation (which does not in any event explain the curious variation observed for He⁺ in He).

This objection will be developed in the following section, where it will be shown that good agreement with experimental data on the mobilities of $\mathrm{He^+}$, $\mathrm{Ne^+}$ and $\mathrm{A^+}$ in their parent gases is obtained, provided it is assumed that the limiting form of Q_t is in accordance with the theoretical prediction (24). Evidence in support of the objection is already available in the work of Lynn & Moiseiwitsch (1957). Using an approximate interaction (Moiseiwitsch

1956) but without further approximation other than the use of Jeffreys's approximation for the phase shifts (cf. Mott & Massey 1949), these authors calculated the mobility of He^+ in He at various temperatures. They obtained results in good agreement with the experimental data of Biondi & Chanin (1957), but their values of Q_t agree in form with (24) and differ considerably from that measured at low impact energies.

4. MOBILITIES AND CHARGE-TRANSFER CROSS-SECTIONS OF ATOMIC IONS

4·1. *Mobility formula*

The appropriate formulae for the mobility have been given in paper I from which it may easily be established that if the reduced mass μ is measured in units of the proton mass and the average cross-section P in units of πa_0^2 ($\pi a_0^2 = 8\cdot8 \times 10^{-17}\,\text{cm}^2$) then the reduced mobility $\mathscr{K}$ is given by

$$\mathscr{K} = \frac{2\cdot10 \times 10^4}{P\sqrt{(\mu T)}}\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}. \tag{33}$$

4·2. H^+ *in* H

The energies of interaction of protons and hydrogen atoms in the ground state have been calculated exactly by Bates *et al.* (1953). A satisfactory fit to their values of $\Delta E(R)$ at large R can readily be made with the form $AR \exp(-\gamma R)$ and Q_d (and hence P) calculated by means of (25) and (26). A check on the accuracy of the method is obtained by comparing values of Q_t derived from (19) and (23) with the more accurate calculations of Dalgarno & Yadav (1953). The values of $\mathscr{K}$ so derived are given for temperatures below 400 °K in table 1. For temperatures above 400 °K the effect of the polarization forces is insignificant and the values $\mathscr{K}$ obtained by Boyd & Dalgarno (1958) are reproduced. The results of these authors, who, whilst ignoring polarization forces, made essentially no further approximations other than the use of (17), should be more accurate at these temperatures.

TABLE 1.† MOBILITIES OF ATOMIC IONS IN THEIR PARENT ATOMIC GASES

$\mathscr{K}$ ($\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$)

T (°K) \ gas	H	D	Kr	Xe	Hg	O
0	26·3	18·6	1·4	0·86	0·61	2·0
100	16·7	10·6	1·3	0·84	0·34	1·9
200	13·6	8·2	1·0	0·68	0·26	1·7
300	12·4	7·2	0·90	0·60	0·23	1·6
400	11·0	6·4	0·80	0·53	0·21	$1\cdot4_5$
500	10·2	5·9	0·72	0·48	0·19	1·3
1000	7·4	4·5	0·53	0·35	0·14	1·0
2000	5·7	3·4	0·39	0·26	0·10	0·75
5000	4·0	2·4	0·26	0·17	0·07	0·52

† The values given here have all been computed using the semi-empirical method described in the text. Those for Hg and O are very uncertain.

4·3. D^+ *in* D

The calculation of the mobility of deuterons in deuterium gas proceeds in an exactly similar way, $\Delta E(R)$ being the same as for H^+ in H. The influence of the long-range forces at any given temperature is smaller than for H^+ in H due to the velocity dependence of Q_t noted in § 2·2. The results are given in table 1, those for temperatures greater than 400 °K being again reproduced from the work of Boyd & Dalgarno (1958). Values of the mobilities of

H^+ in D and of D^+ in H could be calculated similarly, if required, but results sufficiently accurate for most conceivable purposes can be obtained by linear interpolation of $\mathscr{K}\sqrt{\mu}$ between the results for H^+ in H and D^+ in D and will not be given here.

4·4. He^+ *in* He

Although disagreeing at lower energies, the data on Q_t for (27) of Gilbody & Hasted (1957) are in harmony within the limits of experimental accuracy with the modified data of Dillon *et al.* (1955) for energies greater than 200 eV. To a similar accuracy their values are reproduced by the expressions (19) and (23) when the interaction $\Delta E(R)$ is represented by

$$\Delta E(R) = 9{\cdot}84 R \exp(-1{\cdot}40 R)\ \mathrm{Ry}, \tag{34}$$

and these values of A and γ taken with the known value of the polarizability of He yield when used in (25), (26) and (33) a value of $10{\cdot}4\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ for $\mathscr{K}$ at 300 °K. The experimental value (Hornbeck 1951; Biondi & Chanin 1954, 1957) of either 10·5 or $10{\cdot}8\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$ lies well within the probable theoretical error. Whilst the values of Q_t derived from (34) differ considerably in the experimentally difficult low energy region from those measured by Gilbody & Hasted, which seem therefore to be in contradiction to the experimental mobility, the accuracy of the theoretical mobility supports both their high-energy measurements and those of Dillon *et al.*

TABLE 2.† MOBILITIES OF He^+ IN He, Ne^+ IN Ne AND A^+ IN A

$\mathscr{K}$ ($\mathrm{cm^2\,V^{-1}\,s^{-1}}$)

T (°K)	(*a*)	(*b*)	(*c*)	(*d*)	(*a*)	(*b*)	(*c*)	(*a*)	(*b*)	(*c*)
0	21·5	—	—	—	6·9	—	—	2·4	—	—
100	14·0	16·4	13·4	13·9	5·1	5·4	5·1	2·2	2·2	2·1
200	11·5	13·7	12·0	11·4	4·4	4·6	4·5	1·8	1·85	2·0
300	10·4	12·2	10·8	10·2	4·0	4·1	4·2	1·6	1·65	1·6
400	9·4	11·1	—	9·3	3·6	3·8	—	1·4	1·5	—
500	8·6	10·3	—	8·7	3·3	3·5	—	1·3	1·4	—
1000	6·5	8·0	—	6·8	2·5	2·7	—	0·95	1·1	—
2000	4·9	—	—	—	1·9	—	—	0·71	—	—
5000	3·4	—	—	—	1·3	—	—	0·47	—	—

† (*a*) This paper, semi-empirical; (*b*) Biondi & Chanin (1957), theoretical; (*c*) Biondi & Chanin (1957), experimental; (*d*) Lynn & Moiseiwitsch (1957), theoretical.

Theoretical values of $\mathscr{K}$ for temperatures up to 5000 °K are given in table 2 together with some values (interpolated where necessary) measured at low temperatures by Biondi & Chanin (1957). These authors have also computed $\mathscr{K}$ using Holstein's approximate formulae for $\Delta E(R)$ and Q_d (cf. §§ 2·5 and 2·7), and their results and those of Lynn & Moiseiwitsch (1957), described earlier (§ 3·2) are also given in table 2. The agreement is satisfactory, the values obtained here being in closest harmony with experimental data. However, this is partly fortuitous and the small differences between the three sets of theoretical results provide a measure of the absolute accuracy which can be claimed. Biondi & Chanin have suggested that the increasing discrepancy between their experimental and theoretical results with decreasing temperature is due to some additional interaction which becomes significant at lower temperatures and this may be the case; because of the velocity dependence of Q_t the higher terms of the series representation of the long-range forces (cf. (39) of paper I), will be more important for He^+ in He than for heavier ions; however, the possibility of cluster formation cannot be excluded (cf. § 5·4).

4·5. Ne^+ *in* Ne

The data on Q_t for (29) of Gilbody & Hasted do not agree well at any energy with those of Dillon *et al.*, and A and γ have been determined by a trial-and-error procedure so that the values of Q_t computed from (19) and (23) are in agreement with an average of the two sets of experimental data at high energies and so that the mobility at 300 °K computed from (25) and (26) agrees with the experimental mobility (Biondi & Chanin 1954, 1957). As in the case of He the theoretical values of Q_t differ markedly at low energies from those observed.

The theoretical values of $\mathscr{K}$ for temperatures up to 5000 °K are listed in table 2. Where comparison is possible they are in excellent agreement with the theoretical and experimental values of Biondi & Chanin (1957) also given in table 2.

4·6. A^+ *in* A

The procedure adopted was similar to that followed for Ne and the results obtained are given in table 2 together with the comparison data of Biondi & Chanin (1954, 1957) which agree at 300 °K with the earlier value $1{\cdot}63\,cm^2\,V^{-1}\,s^{-1}$ measured by Hornbeck (1951), but disagree with the value $1{\cdot}38\,cm^2\,V^{-1}\,s^{-1}$ measured by Beaty (1956). The theoretical values obtained here do not in themselves support either 1·6 or 1·4, since they are so arranged that they reproduce Biondi & Chanin's value at 300 °K. The agreement between the theoretical and experimental values of Biondi & Chanin is more significant, but it should be noted that their theoretical value for Q_t (assuming that $Q_d = 2Q_t$) at an impact energy of 200 eV is much smaller than that observed. There are, however, experimental reasons for preferring the 1·6 measurement though the problem of identifying the ion of mobility $1{\cdot}4\,cm^2\,V^{-1}\,s^{-1}$ still remains (cf. § 5·4). The only other information on $\mathscr{K}$ is a value $1{\cdot}4\,cm^2\,V^{-1}\,s^{-1}$ obtained by Redfield & Holt (1951) from data on ambipolar diffusion, no temperature being specified. This 1·4 value should be reliable (but see Frost 1957) and can be reconciled with Biondi & Chanin's data by attributing to the Redfield–Holt experiment a positive ion temperature of about 400 °K.

The harmony at other temperatures of the two sets of theoretical results is sufficiently close to cast doubt on the accuracy of Biondi & Chanin's measurement near 200 °K, which appears to be too large by about 10 %.

4·7. Kr^+ *in* Kr *and* Xe^+ *in* Xe

The mobilities of Kr^+ in Kr and of Xe^+ in Xe were first measured by Munson & Tyndall (1940), the uncertainty about the nature of the ion having been resolved by the more definite measurements of Varney (1952) and of Biondi & Chanin (1954). At 300 °K their values are respectively 0·90 and $0{\cdot}58\,cm^2\,V^{-1}\,s^{-1}$ (Biondi & Chanin 1954), but the only information on the variation with temperature is due to Beaty (1956) who gives the ratio of the mobilities of Kr^+ at 90 and 300 °K to be somewhat larger than 1·2. The only measurements of Q_t for Kr^+ in Kr and for Xe^+ in Xe over a range of energies are by Dillon *et al.* (1955), though Ziegler (1953) has reported a value for Xe^+ in Xe at the single energy 1·2 eV.

The values of $\mathscr{K}$, computed as before so that the measurements of $\mathscr{K}$ at 300 °K are reproduced exactly and so that the measurements of Q_t over the range of experimental energies are reproduced as closely as possible, are given in table 1 up to 5000 °K. Previous theoretical values of 1·0 and 0·66 cm² V⁻¹ s⁻¹ for Kr^+ and Xe^+ respectively, at 300 °K have been computed by Bernstein (cf. Biondi & Chanin 1954).

The ratio measured by Beaty (1956) is in harmony with that calculated, but further experimental comparison data at temperatures other than 300 °K are desirable, those for Xe^+ being of particular interest, since they should provide a check on the correctness of the predicted form in the limit of vanishing temperature.

4·8. Hg^+ *in* Hg

Biondi (1953) has measured the diffusion coefficient of Hg^+ in Hg at 350 °K to be approximately $1\cdot8\times10^{17}/n_2\,\mathrm{cm^2\,s^{-1}}$, n_2 being the gas number density, and he also reports an unpublished theoretical prediction by Bernstein & Holstein of $1\cdot9\,\mathrm{cm^{-1}\,s^{-1}}$, no details of which are given. The corresponding mobilities, 0·22 and 0·23 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, respectively (cf. (1) of paper I) agree quite well with the earlier value of 0·29 measured by Mierdel (1943), but are difficult to reconcile with the measured values of Q_t (Dillon *et al.* 1955), a rough extrapolation of which leads to a mobility at 350 °K of not less than $0\cdot5\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. The measured values Q_t which are of the order of $50\pi a_0^2$ seem on general grounds to be very small and we assume that they are incorrect.

We proceed by arbitrarily taking the parameter γ to be 1·40, a choice dictated largely by computational simplicity. The parameter A may then be determined by a trial-and-error method so that (25) and (26) reproduce the observed value of $\mathscr{K}$ at 350 °K, and (25) and (26) may then be used to predict $\mathscr{K}$ at other temperatures. Results are given in table 1 but their accuracy, especially at higher temperatures, may be much less than that of previous cases. No comparison data are available.

4·9. O^+ *in* O

The mobility of O^+ in O is an important quantity in discussions of the stability of the F_2 layer (Ferraro 1945; Cowling 1945; Ratcliffe, Schmerling, Setty & Thomas 1956) but no experimental information is available either on Q_t or on $\mathscr{K}$ so that it is not possible to derive either of the parameters A or γ directly. However, by fixing γ to be 1·4 and reanalyzing all the previous data on ions with outer p-shells it was found that the values of A so derived could be roughly correlated with the ionization potentials of the neutral atoms. This correlation allowed a value of A corresponding to O^+ in O to be deduced and hence $\mathscr{K}$ to be computed, an approximate formula suggested by Dalgarno & Lewis (1957) being used to estimate the polarizability of O. The values are given in table 1; they are probably correct to within a factor of 2. Their application to the F_2 layer will be given elsewhere.

4·10. *Charge-transfer cross-sections*

All the theoretical values of Q_t obtained in this paper are collected in table 3. Values at intermediate energies may be obtained by fitting those given with a function of the form (24). No great accuracy can be claimed for the high-energy values, but those for E equal to 0·1 and 1 eV should be reliable, except for Hg and O where the data that have been used are very uncertain.

At energies between 10 and 200 eV the predicted values consistently disagree in shape from those measured by Gilbody & Hasted (1957) and only for Xe^+ in Xe is agreement obtained with the measurements at 1 eV by Ziegler (1953). At higher energies they are in fair harmony with the values obtained by Dillon *et al.* (1955), by Gilbody & Hasted (1957) and by De Heer, Huizenga & Kistemaker (1957), except for Hg^+ in Hg for which they are about three times larger. For this case the theoretical values are uncertain. Further experimental work is necessary.

After the completion of this work a paper by Ghosh & Sheridan (1957) appeared, in which further values of Q_t are reported. They are in slightly poorer agreement with those obtained here than are their earlier measurements (Dillon *et al.* 1955) modified as indicated in the text.

TABLE 3.† CHARGE-TRANSFER CROSS-SECTIONS

$Q_t(\pi a_0^2)$

gas \ $\log_{10} E$ (eV)	−1	0	1	2	3
H	68	54	41	29	19
D	79	62	47	35	25
He	41	33	25	19	13
Ne	47	38	30	23	17
A	84	73	62	52	43
Kr	104	91	80	69	58
Xe	124	111	98	86	74
Hg	256	228	202	179	156
O	114	100	89	77	66

† All values are theoretical, those for Hg and O being very uncertain. At low energies they differ markedly from the experimental values.

5. MOBILITIES OF DIATOMIC AND POLYATOMIC IONS IN THEIR PARENT GASES

5·1. Much of the difficulty in explaining the measurements of $\mathscr{K}$ for ions in their parent gases arises from the uncertain identification of the ion concerned. Thus, the old discrepancy between the measurements of Tyndall & Powell (1932) and Tyndall & Pearce (1935) of the mobilities of ions in helium gas and the theoretical calculation of $\mathscr{K}$ for He^+ in He by Massey & Mohr (1934) (which was in quite close agreement with an earlier measurement of Tyndall & Powell (1930)) was not finally resolved until recently (Biondi & Brown 1949; Boyd 1950; Hornbeck 1951; Phelps & Brown 1952) when it was established (cf. Loeb 1955) that the later measurements referred to He^+ as Meyerott (1944) suggested, whilst the 1930 experiment referred to He^+. The experiments of Munson & Tyndall (1941) on Ne and A similarly refer to Ne_2^+ and A_2^+, respectively (however, see § 5·3) but their experiments on Kr and Xe refer to the atomic ions, the molecular ions being less readily formed for these two gases (Hornbeck & Molnar 1951).

5·2. The significance of charge transfer for the mobilities of an atomic ion in its parent atomic gas arises essentially from the identity of the nuclear fields in which the transferred electron moves. It is to be expected, therefore, that a diatomic or polyatomic ion in its parent atomic gas can be treated as an ion in an unlike gas, so that provided the orientation-dependent interaction can be replaced by an effective spherically symmetric interaction, the results of paper I can be applied. Thus, in the limit of vanishing temperature, $\mathscr{K}$ should equal $35{\cdot}9/\surd(\alpha\mu)$ cm^2 V^{-1} s^{-1} and the general shape of the $\mathscr{K}'$-T curve should be similar to, say, that for Cs^+ in He (figure 2 of paper I), in marked contrast to that for, say He^+ in He (table 2). The variation of $\mathscr{K}$ with T may be decisive in identifying the ion; as Dalgarno (1957) has remarked, the variation observed by Tyndall & Pearce (1935) shows clearly that the ion was not He^+.

Although charge transfer has no fundamental significance for the motion of diatomic ions in atomic gases it may affect the observations by changing the identity of the ions during the period of the measurement. Thus the charge-transfer process

$$X_2^+ + X \rightarrow (X+X) + X^+ \tag{35}$$

may occur. It is unlikely to be efficient at thermal energies but the ion-atom interchange process (Bates 1955)

$$X_2^+ + X \rightarrow X^+ + (X+X), \tag{36}$$

which has the same end products as (35), may be quite rapid.

5·3. The available experimental data at 300 °K for the inert gases (Tyndall & Powell 1930; Tyndall & Pearce 1935; Munson & Tyndall 1941; Hornbeck 1951; Lauer 1952; Varney 1952; Biondi & Chanin 1954, 1957; Beaty 1956), but excluding the atomic ions, are collected in table 4. It is to be expected that they will all be somewhat larger (cf. paper I) than the values predicted for zero temperature, also given in table 4, and this is the case except for A for which only the measurements of Biondi & Chanin are larger, and except for Beaty's measurement for Kr. An analysis of the measurements by Geltman using the rigid sphere model (quoted by Biondi & Chanin 1957) strongly supports the belief that the 2·7 value refers to A_2^+, but there can in any event be little doubt that the 1·9 value does not. Biondi & Chanin (1954), suggest that it arises from an impurity, but it seems more probable that it is due to a complex ion such as A_3^+ or A_4^+. The predicted mobility of A_4^+ in A at 300 °K is about 1·9 to 2·1 cm^2 V^{-1} s^{-1} and it is noteworthy that the gas pressure was much lower in the experiments of Biondi & Chanin than in those of other workers. The position regarding Beaty's measurement in Kr is less certain but a similar explanation may be correct.

TABLE 4. MOBILITIES OF DIATOMIC IONS IN ATOMIC GASES

$\mathscr{K}$ (cm^2 V^{-1} s^{-1})

T (°K) \ gas	He	Ne	A	Kr	Xe
0	18·6	5·98	2·10	1·18	0·74
22	17·0	—	—	—	—
77	18·0	6·7	2·7	—	—
195	21·7	7·3	2·9	—	—
300	20·3	6·5	2·7 1·95	1·21 1·00	0·79 —

The values at zero temperature are theoretical, the value for He at 22 °K is due to Tyndall & Pearce (1935), the 1·95 value for A at 300 °K to Munson & Tyndall (1941), Hornbeck (1951), Lauer (1952) and Beatty (1956), the 1·00 value for Kr at 300 °K to Beatty (1956), and all others to Biondi & Chanin (1954, 1957), whose results are in harmony with those of Varney (1952).

5·4. The observed variations of $\mathscr{K}$ with temperature for He_2^+ in He, Ne_2^+ in Ne and A_2^+ in A (Tyndall & Pearce 1935; Biondi & Chanin 1957) are given in table 4. In general accord with theoretical expectations $\mathscr{K}$ passes through a maximum as T decreases and appears to tend to a finite limit at zero temperature. For each of Ne and A the $\mathscr{K}'$-T curve falls smoothly towards the predicted limiting value but for He it falls below it. A similar behaviour was indicated for He$^+$ in He (cf. § 4·4) and Biondi & Chanin (1957) suggested that it might be due to an additional interaction. However, Geltman (1953) has computed $\mathscr{K}$ for He_2^+ in He using an averaged spherically symmetric interaction which includes an attractive R^{-6} term but does not obtain any minimum. On the basis of some calculations using the

the statistical clustering theory of Bloom & Margenau (1952), Geltman put forward the tentative suggestion that the decrease observed by Tyndall & Pearce (1935) is due to clustering. The theory is open to criticism in that it ignores steric exclusion, but it seems at present to offer the most plausible explanation. The success of any attempt to explain the data by invoking reactions such as (35) and (36) seems to be precluded by the observation by Biondi & Chanin (1957) of two different and distinct mobilities, one attributable to He^+ and the other to He_2^+, during the same run.

The only other difficulty in understanding the inert gas data arises from the observation by Beaty (1956) of an ion in A at 300 °K with a mobility equal to $1{\cdot}4\,cm^2\,V^{-1}\,s^{-1}$. Beaty also measured $\mathscr{K}$ at 77 °K obtaining a ratio for $\mathscr{K}$ at 300 °K to $\mathscr{K}$ at 77 °K which equalled that obtained by Biondi & Chanin (1957). Unless the two measurements refer to different ions, such a variation can only occur for A^+, the mobility of a diatomic or a polyatomic ion in A being unlikely to *decrease* between 77 and 300° K (unless the ion is a very large cluster). It seems most probable that the discrepancy with Biondi & Chanin arises simply from the lengthy extrapolation required to obtain a zero-field mobility from Beaty's measurements.

5·5. The remaining available data on ions in their parent gases refer to N_2, O_2, CO and H_2. Varney (1953) has reported measurements on the first three gases over a wide range of electric field strengths and has analyzed them on the basis of Wannier's theory (1951, 1952). For N_2 and CO he obtains evidence for changes in the nature of the ion as the field strength is decreased. At low field strengths his measurements in N_2 fit smoothly on to those of Mitchell & Ridler (1934) and are in harmony with those of Bradbury (1932) and Huber (1955). Largely on the basis of some observations by Luhr (1933) with a mass spectrometer, Varney identifies the ion at low field strengths as N_4^+. The predicted value of $\mathscr{K}$ for N_4^+ in N_2 at zero temperature can be derived from table 4 of paper I and is $2{\cdot}36\,cm^2\,V^{-1}\,s^{-1}$, which is, as would be expected, somewhat smaller than the observed value of 2·5 (cf. table 4). With the identification of the low field strength ion as N_4^+ it seems that the ion in the strong field must be N_2^+ and Varney has suggested reactions which can account for these changes with field strength.

Since the rates of these reactions are presumably controlled by the velocities of the colliding particles, similar measurements at other temperatures would be of interest. The available rather sparse data (Tyndall & Pearce 1935) on the variation of $\mathscr{K}$ with T show indications of clustering below at least 170 °K, but above 290 °K agree qualitatively with the shape predicted for ions in unlike gases.

5·6. For O_2 Varney observes a single ion whose low field strength mobility, $2{\cdot}25\,cm^2\,V^{-1}\,s^{-1}$, agrees with the value $2{\cdot}2 \pm 0{\cdot}1$ measured by Huber (1955), but disagrees with the value 1·6 measured by Bradbury (1932), which, however, almost certainly refers to an impurity (cf. Loeb 1939). The evidence in support of Varney's identification of the ion as O_2^+ is strong. O_3^+ and O_4^+ are excluded both by Luhr's failure (1933) to detect them under similar conditions and by the observation of only a single mobility, whilst O^+ is excluded since its predicted value is somewhat greater than 3·3. For O_2^+ in O_2 charge transfer is presumably operative so that a discrepancy between 2·25 and the value of about 2·9 calculated on the basis of an ion in an unlike gas is to be anticipated. Measurements of the variation with temperature could provide decisive confirmation.

By applying Wannier's analysis (cf. Hornbeck & Wannier 1951), Varney deduces from his high field measurements so-called molecular cross-sections for O_2^+ in O_2 and N_2^+ in N_2. Their absolute values are rather small compared to the measured values of $2Q_t$ (Dillon *et al.* 1955), which may, however, include reactions which are not energetically possible under Varney's conditions, but the ratios for the two gases are in reasonable harmony. A value of $1{\cdot}5\,cm^2\,V^{-1}\,s^{-1}$ therefore seems plausible for the mobility of N_2^+ in N_2; because of the transformation of N_2^+ to N_4^+ at low field strengths, Varney is unable to measure this quantity, which is important in other connexions.

Very recently Burch & Geballe (1957) have observed ions in O_2 with mobilities of 3·4, 2·6 and 1·9 $cm^2\,V^{-1}\,s^{-1}$, the first two of which they ascribe to O^- and O_3^-, respectively, and the last of which to both O_2^+ and O_2^-. The predicted zero-temperature values of O^- and O_3^- of respectively about 3·3 and 2·5 are in harmony with the measurements, but the suggestion that O_2^+ and O_2^- have the same mobility is acceptable only if charge transfer is not operative, in which case a value of about 2·9 would be expected. If the role of charge transfer is similar to that obtaining for atoms, then because of the diffuse structure of O_2^-, $1{\cdot}0\,cm^2\,V^{-1}\,s^{-1}$ would seem to be an upper bound for its mobility at ordinary temperatures, a value as small as $0{\cdot}2\,cm^2\,V^{-1}\,s^{-1}$ being not unreasonable.

5·7. For CO as for N_2, Varney finds evidence indicating that the nature of the ion changes with field strength and suggests that at one stage or another his measurements involve CO^+, C^+ and CO_2^+. The low field strength mobility, $1{\cdot}6\,cm^2\,V^{-1}\,s^{-1}$, probably refers to CO^+ for the ratio of the corresponding molecular cross-section to that for N_2^+ in N_2 is in harmony with the ratio of Q_t measured by Dillon *et al.* (1955) for CO^+ in CO and N_2^+ in N_2.

5·8. For H_2, Mitchell (quoted by Tyndall 1938), Bradbury (1932) and Lauer (1953) all report a mobility of about $13{\cdot}4\,cm^2\,V^{-1}\,s^{-1}$. The ion is probably H_3^+, but it is difficult to identify it with certainty without additional information. Measurements of the temperature variation or on ions in D_2 would be very helpful.

5·9. In the discussions of this paper and of paper I the influence of the parameter ϵ_0 in equation (2) of paper I has been ignored. It is investigated in a later paper (Williams 1958).

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