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THE MOBILITIES OF IONS IN UNLIKE GASES

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CONTENTS

The available experimental data on the mobilities at low field strengths of ions in unlike gases are analyzed on the basis of a simple theoretical description. Some of the earlier conclusions are modified and the current discrepancies between theory and experiment are emphasized. It is shown that most of the measurements can be explained by classical theory on the assumption that the interaction between an ion and a gas particle is due to the polarization of the gas particle, but that there appears to be a consistent discrepancy of about 8 % between theoretical predictions and the series of measurements by the Bristol group. For gases of low polarizability or at high temperatures, the contribution of the repulsive forces must be considered and the case of Li^+ in He is investigated in detail, an interaction being derived from which the observed variation of mobility with temperature may be reproduced.

1. Introduction

The energy of interaction between an ion and a gas particle may be derived from measurements of the variation with temperature of the mobility at low field strengths of the ion in the gas. This has been done in the past using either the Langevin or the Lennard-Jones model, both of which are somewhat unrealistic. A simple yet accurate theoretical description can be given which allows the use of a more suitable interaction, but it is desirable first to assess systematically the accuracy of the available data.

2. Theory

2·1. The mobility at low field strengths of an ion of mass M_1 moving in a gas composed of particles of mass M_2 is given in terms of the diffusion coefficient D by

$$\mathrm{K} = eD/\boldsymbol{k}T, \tag{1}$$

where e is the charge of the ion, $\boldsymbol{k}$ is Boltzmann's constant and T is the absolute temperature (cf. Massey & Burhop 1952). According to the Chapman–Enskog formula (cf. Chapman & Cowling 1939; Kihara 1953), if n_1 and n_2 are respectively the ion and gas number densities

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and μ is the reduced mass $M_1M_2/(M_1+M_2)$, D may be expressed in terms of the diffusion cross-section Q_d as

$$D = \frac{3\pi^{\frac{1}{2}}}{16(n_1+n_2)}\left(\frac{2\boldsymbol{k}T}{\mu}\right)^{\frac{1}{2}}\frac{1+\epsilon_0}{P}, \tag{2}$$

where ϵ_0 is a small correction factor, which is never greater than 0·13 and

$$P = \frac{1}{2}\int_0^\infty x^2Q_d(x)\exp(-x)\,\mathrm{d}x, \tag{3}$$

x being related to the energy $\mathscr{E}$ of relative motion of an ion and a gas particle by

$$x = \frac{\mathscr{E}}{\boldsymbol{k}T} = \frac{1}{2}\frac{\mu v^2}{\boldsymbol{k}T}, \tag{4}$$

and v being the relative velocity. Normally $n_1 \ll n_2$ and ϵ_0 may be ignored in which case (2) simplifies to

$$D = \frac{3\pi^{\frac{1}{2}}}{16n_2}\left(\frac{2\boldsymbol{k}T}{\mu}\right)^{\frac{1}{2}}\frac{1}{P}. \tag{5}$$

We shall use (5) throughout this paper. The error introduced by ignoring ϵ_0 will be discussed by one of us (A. W) in a later communication.

2·2. The diffusion cross-section is given by

$$Q_d = 2\pi\int_0^\pi I(\theta)\,(1-\cos\theta)\sin\theta\,\mathrm{d}\theta, \tag{6}$$

where $I(\theta)$ is the differential cross-section for elastic scattering through an angle θ (cf. Mott & Massey 1949) by the interaction potential $V(R)$ of the ion and gas atom, R being their separation. At high temperatures the collision of unlike particles can be described classically except at very small scattering angles, which however do not contribute greatly to Q_d. The classical formula for Q_d is

$$Q_d = 4\pi\int_0^\infty \cos^2\alpha\, p\,\mathrm{d}p, \tag{7}$$

where p is the impact parameter and α is defined according to

$$\alpha = \int_{R_0}^\infty \frac{\mathrm{d}R}{R\phi(R)}, \tag{8}$$

with

$$\phi(R) = \left\{\frac{R^2}{p^2} - 1 - \frac{R^2}{p^2}\frac{V(R)}{\mathscr{E}}\right\}^{\frac{1}{2}}, \tag{9}$$

R_0 being the outermost zero of $\phi(R)$.

2·3. At low temperatures the quantal description must be used in which case the usual partial wave analysis (cf. Mott & Massey 1949) leads to the formula

$$Q_d = \frac{4\pi}{k^2}\sum_{l=0}^\infty (l+1)\sin^2(\eta_l - \eta_{l+1}), \tag{10}$$

where $k = \mu v/\hbar$ is the wave number of the relative motion and the lth-order phase shift η_l is defined by the condition that the regular solution of the equation

$$g_l''(R) + \left\{k^2 - \frac{2\mu V(R)}{\hbar^2} - \frac{l(l+1)}{R^2}\right\}g_l(R) = 0 \tag{11}$$

behaves asymptotically as

$$g_l(R) \sim k^{-1}\sin(kr - \tfrac{1}{2}l\pi + \eta_l). \tag{12}$$

3. Approximate formulae for phase shifts

3·1. It will usually be sufficiently accurate to evaluate the phase shifts using Jeffreys's approximation with Langer's modification (1937)

$$\eta_l = \int_{R_0}^{\infty} \left\{k^2 - \frac{2\mu V}{\hbar^2} - \frac{(l+\frac{1}{2})^2}{R^2}\right\}^{\frac{1}{2}} \mathrm{d}R - \int_{R_0'}^{\infty} \left\{k^2 - \frac{(l+\frac{1}{2})^2}{R^2}\right\}^{\frac{1}{2}} \mathrm{d}R, \tag{13}$$

the lower limits being the outermost zeros of the respective integrands. When l is large, η_l can be regarded as a function $\eta(l)$ of a continuous variable and the difference in phase shifts can be written

$$\beta(l) = \eta(l) - \eta(l+1) = -\partial\eta/\partial l, \tag{14}$$

which on transforming to the variable $p = (l+\frac{1}{2})/k$ becomes

$$\beta(p) = -k^{-1}\partial\eta/\partial p. \tag{15}$$

By substituting (13) into (15) it is easily shown (cf. Mott & Massey 1949; Bird & de Boer 1951, 1954) that $\beta = \alpha - \frac{1}{2}\pi$, so that if the summation (10) over l is replaced by an integration over p it becomes identical to the classical formula (7).

3·2. It is in general impossible to evaluate (13) analytically. However, Massey & Mohr (1934) have shown that for large values of l, (13) can be approximated by

$$\eta_l = -\frac{\mu}{\hbar^2} \int_{R_0'}^{\infty} \frac{V(R)}{\left\{k^2 - \dfrac{(l+\frac{1}{2})^2}{R^2}\right\}^{\frac{1}{2}}} \mathrm{d}R, \tag{16}$$

which is equivalent to

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

and (17) can be evaluated analytically for most forms of $V(R)$ encountered in practice. We shall require $\eta(p)$ when $V(R) = CR^{-n}$, C being a constant and n a positive integer, for which (17) gives

$$\eta(p) = -\frac{kC}{2\mathscr{E}} \frac{1}{p^{n-1}} f(n), \tag{18}$$

where

$$f(2) = \tfrac{1}{2}\pi, \quad f(3) = 1$$

and

$$\begin{aligned} f(n) &= \frac{(n-3)\,(n-5)\,\ldots\,\pi}{(n-2)\,(n-4)\,\ldots\,2} \quad (n>2 \text{ and even}) \\ &= \frac{(n-3)\,(n-5)\,\ldots\,2}{(n-2)\,(n-4)\,\ldots\,3} \quad (n>3 \text{ and odd}) \end{aligned} \tag{19}$$

(Massey & Mohr 1934), and when $V = C\exp(-\zeta R)$, ζ being another constant, for which (17) gives

$$\eta(p) = -\frac{kC}{2\mathscr{E}} p K_1(\zeta p) \tag{20}$$

(Dalgarno & McDowell 1956), where K_1 is the first-order modified Bessel function of the second kind.

3·3. It is of interest to compare (18) and (20) with the Born approximation to the phase shift

$$\eta_l = -\frac{\pi k^2}{2\mathscr{E}} \int_{0}^{\infty} RV(R)\,[J_{l+\frac{1}{2}}(kR)]^2\,\mathrm{d}R, \tag{21}$$

where $J_{l+\frac{1}{2}}$ is the $(l+\frac{1}{2})$th order Bessel function of the first kind, for it is generally supposed that Born's approximation is accurate when the phase shift is small whereas Jeffreys's approximation is likely to be more accurate when the phase shift is large (cf. McMillen 1939; Mott & Massey 1949).

If $V(R) = CR^{-n}$, (21) is easily evaluated (cf. Watson 1952; Geltman 1953) as

$$\eta_l = -\frac{kC\pi}{2\mathscr{E}}\left(\frac{k}{2}\right)^{n-1}\frac{\Gamma(n-1)\,\Gamma(l-\frac{1}{2}n+\frac{3}{2})}{[\Gamma(\frac{1}{2}n)]^2\,\Gamma(l+\frac{1}{2}n+\frac{1}{2})}, \tag{22}$$

which is identical to (19) in the limit of infinite l for all values of k, and if $V(R) = C\exp(-\zeta R)$, (21) gives

$$\eta_l = \frac{k}{2\mathscr{E}}\frac{\partial}{\partial \xi}Q_l(1+\zeta^2/2k^2) \tag{23}$$

(cf. Watson 1952), where Q_l is the lth order Legendre polynomial of the second kind. Provided $\zeta/k \ll 1$, the limit of $Q_l(1+\zeta^2/2k^2)$ as l becomes large can be written

$$Q_l(1+\zeta^2/2k^2) \sim \left(\frac{\pi}{l}\right)^{\frac{1}{2}}\exp\left[-(l+\tfrac{1}{2})\,\zeta/k\right]\left(\frac{2k}{\zeta}\right)^{\frac{1}{2}} \tag{24}$$

(Hobson 1931) so that the limiting value of (23) is

$$\eta(p) = -\frac{k}{2\mathscr{E}}\sqrt{\left(\frac{\pi}{2p\zeta}\right)}\,p\exp(-p\zeta), \tag{25}$$

which is identical to the limiting value of (20).

This equivalence of Jeffreys's and Born's approximation for large l suggests that Jeffreys's approximation is suitable for all values of l. Some quantitative comparisons are given in the following section for the case when $V(R) = CR^{-4}$.

3·4. We consider the more general interaction

$$\begin{aligned} V(R) &= \infty \quad \text{for} \quad R<\rho \\ &= CR^{-4} \quad \text{for} \quad R>\rho, \end{aligned} \tag{26}$$

corresponding to the rigid sphere model with a long-range polarization force (Langevin 1905). Then (13) can be obtained in terms of the incomplete elliptic integrals $E(x,\phi)$ and $K(x,\phi)$ of the first and second kinds respectively of which adequate tables are available (Byrd & Friedman 1954). The result follows after integration by parts and for $C<0$ is

$$\eta_l = kq\{F(x,\phi)-2E(x,\phi)\}-(l+\tfrac{1}{2})^2\frac{1}{2kq}F(x,\phi)+(l+\tfrac{1}{2})\,\tfrac{1}{2}\pi, \tag{27}$$

where
$$q^4 = -C/\mathscr{E},$$

$$x = \frac{2q^2+(l+\frac{1}{2})^2/k^2}{4q^2}$$

and
$$\phi = \cos^{-1}[(\rho^2-q^2)/(\rho^2+q^2)]$$

for l such that $(l+\frac{1}{2})^2 < 2k^2q^2$ and is

$$\eta(l) = K(x')\,\{2ka-(l+\tfrac{1}{2})^2/ka\}-2kaE(x')+(l+\tfrac{1}{2})\,\tfrac{1}{2}\pi, \tag{28}$$

where $E(x')$ and $K(x')$ are complete elliptic integrals,

$$x'^2 = b^2/a^2,$$

$$2a^2 = p^2 + (p^4 - 4q^4)^{\frac{1}{2}}$$

and
$$2b^2 = p^2 - (p^4 - 4q^4)^{\frac{1}{2}},$$

for $(l+\frac{1}{2})^2 > 2k^2q^2$ (that is, for a real) unless $\rho > a$ in which case (27) still applies.

There is a sharp discontinuity in the phase shift at $(l+\frac{1}{2})^2 = 2k^2q^2$ corresponding to the (classical) occurrence of spiralling orbits (cf. Bird, Hirschfelder & Spotz 1948; Eliason, Stogryn & Hirschfelder 1956). The corresponding impact parameter is $p_c = q\surd 2$ and Wannier (1953) has suggested that the associated 'capture' cross-section

$$Q_c = \pi p_c^2 = 2\pi(-C/\mathscr{E})^{\frac{1}{2}} \tag{29}$$

is a good approximation to Q_d. This relation ignores contributions to Q_d arising from $p > p_c$ (cf. § 4·2).

3·5. It is easily demonstrated that for large l

$$\eta(l) = \frac{\pi q^4 k}{8p^3}\left(1 + \frac{15q^4}{16p^4}\right), \tag{30}$$

whereas (18) becomes for $n = 4$
$$\eta(l) = \pi q^4 k/8p^3, \tag{31}$$

which is the leading term of (30). The Massey–Mohr approximation is therefore an accurate representation of (28) for impact parameters p large compared to q. This is equivalent to the condition that $V(R)/\mathscr{E}$ be small compared to unity for all values of R greater than p.

The Born approximation (22) becomes for $n = 4$

$$\eta(l) = \pi q^4 k^4/8(l+1)\, l(l-1), \tag{32}$$

and numerical comparisons of (28), (31) and (32) for $ka_0 = 1$ ($a_0 = 5{\cdot}29 \times 10^{-9}$ cm) are given in Table 1 for the long-range interaction of Li^+ with He and with Xe, the former having a small and the latter a large polarizability. The three approximations are in reasonable harmony.

TABLE 1. PHASE SHIFTS η_l FOR $ka_0 = 1$

	Li⁺ in He				Li⁺ in Xe		
l	Jeffreys	Massey–Mohr	Born	l	Jeffreys	Massey–Mohr	Born
13	1·335	1·026	1·032	43	1·708	1·549	1·605
16	0·617	0·562	0·564	48	1·187	1·118	1·153
19	0·355	0·341	0·342	53	0·867	0·833	0·858
22	0·226	0·222	0·222	58	0·655	0·637	0·654
25	0·154	0·152	0·152	63	0·508	0·498	0·510
28	0·109	0·109	0·109	68	0·403	0·397	0·405

4. CALCULATION OF CROSS-SECTIONS

4·1. The integral (7) for Q_d may be evaluated by dividing the region of integration into parts at $p = p^*$, where p^* is so chosen that for $p < p^*$, $\sin^2\beta(p)$ oscillates rapidly and may be replaced by its average value of $\frac{1}{2}$, a procedure which can usually be followed except when $V(R)$ is a slowly varying repulsive interaction. Thus

$$Q_d = 4\pi\left\{\int_0^{p^*} \tfrac{1}{2}p\,\mathrm{d}p + \int_{p^*}^{\infty} p\sin^2\beta(p)\,\mathrm{d}p\right\}. \tag{33}$$

Assuming that p^* is also such that the Massey–Mohr approximation (17) may be employed, it follows that for $V = CR^{-4}$,

$$Q_d = \pi p^{*2} + 4\pi \int_{p^*}^{\infty} p \sin^2 \left\{ \frac{3\pi q^4}{8p^4} \right\} \mathrm{d}p. \tag{34}$$

This can be evaluated in terms of the Fresnel integral

$$\mathscr{S}(x) = \int_0^x \sin\left(\frac{\pi t^2}{2}\right) \mathrm{d}t$$

and is given by

$$Q_d = \pi p^{*2} \cos\left(\frac{3\pi q^4}{4p^{*4}}\right) + \pi^2 q^2 \sqrt{\tfrac{3}{2}}\, \mathscr{S}\left(q^2 \sqrt{\tfrac{3}{2}}/p^{*2}\right). \tag{35}$$

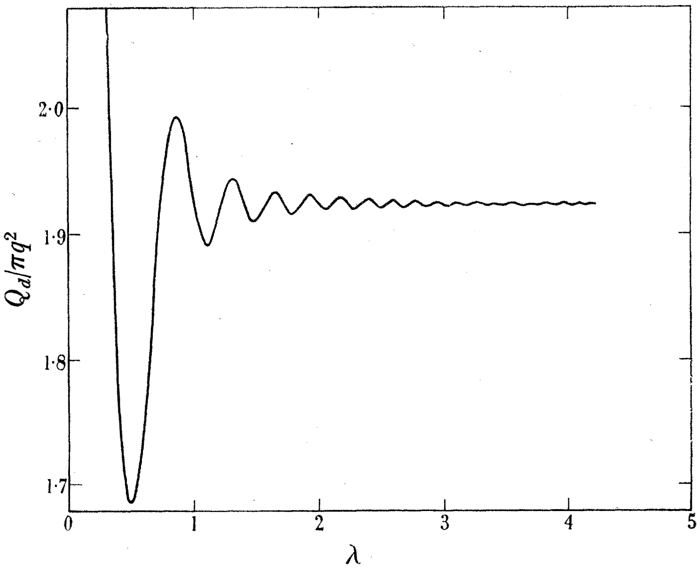

FIGURE 1. $Q_d(\lambda)$ for a pure R^{-4} interaction according to the Massey–Mohr approximation.

The choice of p^* is to some extent arbitrary and it is clear that for the method to be useful, (35) must be largely independent of p^* for values of p^* in the oscillating region of the integrand. Defining λ by $p^* = (3/8\lambda^2)^{\frac{1}{4}} q$, or equivalently by $\beta(p^*) = \lambda^2\pi$ and making use of the tables $\mathscr{S}(x)$ prepared by Mayall (1897) and by Jahnke & Emde (1945), (35) is illustrated in figure 1 as a function of λ, the units of Q_d being πq^2. The figure demonstrates that the method of evaluating (7) is indeed accurate. If an error of 15 % can be accepted, p^* can be taken as large as $\frac{3}{2}q$, in which case provided $a(p^*) > p$ the Massey–Mohr approximation can be used for all values of p for which phase shifts are required. Any value of p^* less than $0{\cdot}9q$ yields an accuracy of 98 %, and though the Massey–Mohr approximation is becoming very inaccurate for p as small as $0{\cdot}9q$, the error caused in (7) by its use must nevertheless be small.

4·2. Expression (35) can be written as

$$Q_d = \pi p^{*2} + \pi^2 q^2 \sqrt{\tfrac{3}{2}}\, \mathscr{S}\left(q^2 \sqrt{\tfrac{3}{2}}/p^{*2}\right) - 2\pi p^{*2} \sin^2\left(3\pi q^4/8p^{*4}\right) \tag{36}$$

and the last two terms are, therefore, the contribution to Q_d of impact parameters $p > p^*$. Taking $p^* = p_c = q\sqrt{2}$ (36) gives

$$Q_d = 2{\cdot}120\pi q^2, \tag{37}$$

which represents an improvement of Wannier's suggestion, noted in § 3·4, that $Q_d \sim Q_c$ since (37) takes account of $p > p_c$ whereas (29) does not.

4·3. The classical formula (7) for Q_d has been evaluated numerically by Langevin (1905) and by Hasse (1926). Because of § 3·1, their result

$$Q_d = 2{\cdot}210\pi q^2 \tag{38}$$

is the correct value of (33). Thus, (37) is correct to within an error of 5 % and although this may be partly fortuitous, it demonstrates that the approximations leading to (37) are satisfactory.

4·4. The value of p_c is such that (28) can be used for all the phases required in the evaluation of Q_d provided $a(p_c) = q > \rho$. The parameter ρ is a measure of the short-range repulsive forces so that (35) and (37) demonstrate that the diffusion cross-sections (and hence the mobility) will be independent of the repulsive forces provided these forces are negligible at separations R greater than q. Since $q = (-C/\mathscr{E})^{\frac{1}{4}}$, this will be the case for gases of high polarizability at low temperatures. For sufficiently low temperatures, however, the classical description is invalid and (10) must be evaluated by summation of the individual terms.

4·5. The long-range interaction between an atomic ion and a gas atom is not simply proportional to R^{-4}, but has the more general form (cf. Margenau 1939)

$$V(R) = -\left(\frac{a}{R^4}+\frac{b}{R^6}+\frac{c}{R^7}+\dots\right). \tag{39}$$

Simple dimensional considerations show that when $V(R) = CR^{-n}$ the energy dependence of the classical diffusion cross-section is given by

$$Q_d = \text{constant} \times (-C/\mathscr{E})^{2/n}, \tag{40}$$

this result holding for both positive and negative values of n. The higher terms of the series (39) should manifest themselves therefore in a modification of the $\mathscr{E}^{-\frac{1}{2}}$ dependence at low temperatures which is predicted for a pure R^{-4} interaction.

Their importance can be investigated without undue labour by a consideration of the 'capture' cross-section $Q_c = \pi p_c^2$, where p_c is the smallest value of p for which

$$\Phi(R) = \{R^2 - p^2 - R^2 V(R)/\mathscr{E}\} \tag{41}$$

has a real root. It will suffice to consider the case in which terms greater than the sixth power of R^{-1} may be ignored. Then provided the ratio b/a is small compared to p_c^2, a single iteration shows that

$$p_c^2 \sim 2\sqrt{\frac{a}{\mathscr{E}}}+\frac{b}{a}. \tag{42}$$

Expresssion (42) is very useful in indicating whether or not it is necessary to take account of the higher-order terms in (39). Values of a and b have been estimated by Margenau (1941) for a large number of cases, and substitution of them in (42) demonstrates that in general the correction factor differs little from unity at any temperature for which it is permissible to assume that (39) is an adequate representation of the interaction.

4·6. At low temperatures the approximations (13) and (33) are no longer valid and in consequence the dependence on mass and the variation with energy are modified, Q_d becoming sensitive to the precise nature of the repulsive forces. Although Jeffreys's approximation, (13), is inadequate when k is small and when k is such that (classical) orbiting occurs, some general conclusions can nevertheless be drawn without carrying out the laborious computations involved in solving the partial wave equations (11) numerically, which in view of our uncertain knowledge of the short-range forces seems hardly worth while.

Orbiting, which occurs classically at impact parameters equal to $q\sqrt{2}$ when $q\sqrt{2} > \rho$, introduces discontinuities into Q_d when the discrete summation (10) is used. By examining the limits of (27) and (28) when kq approaches $(l+\frac{1}{2})/\sqrt{2}$, l being a positive integer, it is easily shown that the order of magnitude of any discontinuity is $4\pi q\sqrt{2}/k$. The quantal 'tunnel' process will exert a smoothing effect on these discontinuities, transforming them into oscillations about the classical value $2{\cdot}210\pi q^2$. The frequency of the oscillations will be unaltered and is such that $kq\sqrt{2}$ changes by unity in one oscillation but the amplitude is presumably much reduced. This has been shown explicitly for the 'capture' cross-section by Vogt & Wannier (1954) who treated the origin of co-ordinates as a sink. Even in the most favourable case, that of protons in helium, it seems that the oscillations would be detectable only at temperatures well below 20 °K. A comparison at higher temperatures with the case of deuterons in helium might, however, be revealing for both the frequency and the amplitude of the oscillations are mass dependent. Measurements on isotopes in the same gas are particularly valuable since the short-range forces manifest themselves at very low temperatures largely in a masking of the orbiting effect.

5. CALCULATION OF MOBILITIES

5·1. Having obtained Q_d as a function of energy, the mobility is easily calculated from (1) and (5). The coefficient of the R^{-4} term in the interaction between an atomic ion and a gas atom is given by

$$C = -\tfrac{1}{2}\alpha e^2, \tag{43}$$

where α is the polarizability of the gas atom, so that the mobility corresponding to (38) is given by

$$\mathrm{K} = 35{\cdot}9/\sqrt{\alpha\mu}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}, \tag{44}$$

where α is measured in atomic units (a_0^3), μ is measured in units of the proton mass and K is referred to a (constant) gas density of $2{\cdot}69\times10^{19}\,\mathrm{cm^{-3}}$. The linear dependence of K on $1/\sqrt{\mu}$ is predicted by classical theory for *all* interactions but its constancy with temperature is true only for a pure R^{-4} effective interaction. Since α is a property of the gas alone, it also follows from (44) that $\mathrm{K}\sqrt{\mu}$ is independent of the nature of the ion.† This is extremely useful in testing the accuracy of experimental data on atomic ions in atomic gases, for the independence of $\mathrm{K}\sqrt{\mu}$ on the particular ion must be accompanied by its constancy with temperature and conversely. Because of § 4·4 and (42), (44) should hold for gases with small polarizabilities provided sufficiently low temperatures can be reached before quantum modifications become important.

5·2. Corresponding to (40),

$$\mathrm{K}\sqrt{\mu} = \text{constant}\times T^{2/n}/\sqrt{T}, \tag{45}$$

so that similarly to Q_d the higher terms of (39) should manifest themselves at low temperatures in a modification of the temperature independence of (44). Corresponding to (42),

$$\mathrm{K}\sqrt{\mu} = \text{constant}\times\left(1+\frac{2b}{3a}\sqrt{\frac{\mathbf{k}T}{a\pi}}\right)^{-1}, \tag{46}$$

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† The formula also demonstrates that for a pure R^{-4} interaction, the mobility is independent of the charge state of the ion.

and the denominator is in general very little different from unity at the temperatures for which (42) is valid. Nevertheless, measurements of the variation of K with temperature could yield valuable information on the coefficients in (39), but their precision would have to be much greater than that of the experimental data presently available.

5·3. As the temperature increases, q becomes small and $a(p_c)$ becomes less than ρ (of § 4·4) and the diffusion cross-section and mobility then depend upon the specific nature of the repulsive forces. Initially there occurs cancellation between the short-range and attractive long-range forces and the mobility therefore increases, but ultimately the mobility is entirely determined by the short-range forces and decreases steadily with increasing temperature, the rate of fall depending sensitively on the form of the short-range forces.

Corresponding to the interaction (26), putting n infinite in (45) shows that K decreases as $T^{-\frac{1}{2}}$ in agreement with the exact classical calculations of Langevin (1905) and Hassé (1926), and corresponding to

$$V(R) = \frac{A}{R^8} - \frac{B}{R^4} \tag{47}$$

putting $n = 8$ in (45) shows that K decreases as $T^{-\frac{1}{4}}$ in agreement with the exact classical calculations of Hassé & Cook (1929, 1931). Thus the observed rate of fall at high temperatures leads directly to the functional form of the repulsive forces. Unfortunately, no measurements have been carried out at temperatures sufficiently high that long-range forces can be completely ignored.

The shape and location of the predicted maximum are sensitive to the cancellation effects between the short- and long-range forces at intermediate separations. Some quantitative comparisons are made with observations in § 6·2.

5·4. At very low temperatures quantum modifications become important and cause the mobility to oscillate with decreasing temperature much as Q_d oscillates, though the velocity distributions will damp the oscillations to some extent (cf. Buckingham & Halpern 1955). There are no experimental data at temperatures in the quantum region. Considerable interest would be attached to measurements of the mobilities of H^+ and D^+ in He, since these are the most likely to exhibit quantum effects.

6. Comparison with experimental data

A considerable collection of data is available on the mobilities of positive ions in gases (cf. Tyndall 1938; Massey & Burhop 1952; Loeb 1955; von Engel 1955) and many comparisons have been made in individual papers of experimental data and theoretical predictions based upon the Langevin interaction (26) or upon the Lennard-Jones interaction (47). Owing largely to an unrealistic choice of the parameters ρ and A, the erroneous impression has been given that much of the data can only be explained by a very complicated form of interaction. In some cases, however, the agreement is less good than has been implied, insufficient attention having been paid to the variation with temperature. In addition, some confusion has arisen from the lack of consistency in the choice of n_2 in (5) and indeed in many of the earlier papers it is not easy to decide what choice has been made.

In the tables all values refer to the reduced mobility

$$\mathscr{K} = \frac{n_2 \mathrm{K}}{2{\cdot}69 \times 10^{19}}, \tag{48}$$

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where n_2 is the number density at atmospheric pressure at the temperature at which the measurements were made. Since classical theory shows that the mobility depends inversely on the square root of the reduced mass, it is convenient for comparison purposes to introduce the mass independent quantity

$$\mathscr{K}' = \mathscr{K}\sqrt{\mu}. \tag{49}$$

6·1. *Atomic ions in atomic gases*

All the available data at temperatures between 290 and 293 °K on the mobilities of atomic ions in unlike atomic gases are collected in table 2, $\mathscr{K}'$ being measured in $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$. Except where otherwise indicated the data used were taken from Tyndall (1938). His table agrees with the earlier data of the Bristol group (Tyndall & Powell 1932; Brata & Powell 1932; Brata 1933; Pearce 1936) except for Na^+ in He, but occasionally less well with the more recent results of Hershey (1939), Hoselitz (1941) and Biondi (1951, 1953).

TABLE 2. VALUES OF $\mathscr{K}'$ MEASURED AT TEMPERATURES BETWEEN 290 AND 293 °K ($\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$)

ion \ gas	He	Ne	A	Kr	Xe
Li	38·6	30·4†	11·4	9·4	7·3
	—	25·2	—	—	—
Na	41·9	26·8	11·5	9·3	7·5
K	41·0	27·4	11·7	9·6	7·4
Rb	39·3	27·2	11·7	9·5	7·4
Cs	36·3	25·5	11·5	9·5	7·4‡
A	39·9§	—	—	—	7·7‡
In	*40·5*‖	*27·5*	*10·9*	—	—
Tl	*37·6*	*26·7*	*11·1*	—	—
Hg	26·5	—	—	—	—
	37·0¶	—	—	—	—
$35{\cdot}9/\sqrt{\alpha}$	30·5	21·9	10·8	8·9	6·9
$38{\cdot}4/\sqrt{\alpha}$	32·8	23·5	11·6	9·6	7·4

† Brata & Powell (1932); ‡ Hoselitz (1941); § Biondi (1951); ‖ italicized values are given by Tyndall (1938) as doubtful; ¶ Biondi (1953).

TABLE 3. VALUES OF $\mathscr{K}'$ MEASURED AT VARIOUS TEMPERATURES

T (°K)	Li^+ in He†	Cs^+ in He‡	Na^+ in He‡	K^+ in A†	Rb^+ in Kr†	Cs^+ in Xe†
20	29·$_9$	—	—	—	—	—
78	32·$_6$	—	—	5·$_4$	—	—
79	—	32·$_3$	—	—	—	—
90	33·$_2$	—	—	6·$_3$	6·$_9$	—
92	—	33·$_3$	32·$_1$	—	—	—
195	35·$_7$	35·$_5$	36·$_2$	9·$_7$	9·$_5$	7·$_7$
290	—	—	39·$_5$	—	—	—
291	38·$_6$	35·$_0$	—	11·$_6$	9·$_5$	7·$_6$
389	41·$_6$	—	—	—	9·$_6$	—
392	—	33·$_5$	—	—	—	7·$_7$
405	—	—	41·$_6$	12·$_7$	—	—
477	—	—	42·$_6$	12·$_0$	9·$_9$	7·$_8$
483	43·$_7$	—	—	—	—	—
492	—	32·$_2$	—	—	—	—

† Hoselitz (1941); ‡ Pearce (1936).

In the case of Xe, the gas of highest polarizability, $\mathscr{K}'$ is seen to be constant within the probable experimental error of 2 % in accordance with theoretical predictions based upon a pure R^{-4} interaction. This interaction also gives rise to a mobility independent of temperature and table 3, which reproduces the measurements of Hoselitz (1941), shows that this is well satisfied. In an analysis of his data on Cs^+ in Xe on the basis of the Lennard-Jones interaction (47), Hoselitz concluded that a more complicated form of interaction was required and that in particular the long-range contribution was greatly *underestimated*. Some support for his contention was supplied by Margenau's calculations (1941) who showed that at a separation equal to the sum of the atomic radii listed by Goldschmidt (1929) the R^{-6} term in (39) was nearly half as large as the R^{-4} term. The significant comparison is, however, at the separation $R = p_c$, as was demonstrated in § 4·3, and at the experimental temperatures the R^{-4} term provides the major contribution to $V(R)$ at $R = p_c$. Hoselitz actually *overestimated* the importance of the repulsive forces. The observed minimum in $\mathscr{K}$ may, however, be real and would then be due to a small contribution from the higher terms of (39) (cf. (46)). As Margenau's work demonstrates, these terms are more important for this case than for less easily polarized ions.

There is a small numerical discrepancy and, in order to obtain exact agreement with experiment, formula (5) must be multiplied by 1·08. The theoretical predictions so modified are given in the last row of table 2. This discrepancy cannot be attributed to the correction ϵ_0 occurring in (2) for it vanishes for a pure R^{-4} interaction and may possibly be due to a systematic error in the Bristol data, it being unlikely that Langevin and Hassé made the *same* computational error.

The agreement between theory and experiment is also essentially perfect for Kr, both as regards magnitude and temperature variation. The mobility of Rb^+ in Kr at various temperatures (Hoselitz 1941) is shown in table 3 and, if the measurement at 90 °K is ignored, it is seen to be constant. The low value at 90 °K is almost certainly due to clustering effects.

For A the numerical agreement between theory and experiment in table 2 is again perfect and indeed this case is commonly quoted in support of the mass dependence predicted by Langevin's theory (a prediction actually valid for all interactions when the classical description is used). The mobilities of K^+ in A (Hoselitz 1941), shown in table 3, are however by no means constant at different temperatures. The constancy of $\mathscr{K}'$ for different ions shown in table 2 can then only be explained by postulating that the repulsive forces between an alkali ion and A are also largely independent of the ion (for the ranges of R effective in determining the mobilities at 291 °K). Support for the approximate validity of this hypothesis in the case of He is provided by the closeness of the temperature variations of $\mathscr{K}$ for Li^+ in He (Hoselitz 1941) and for Na^+ in He (Pearce 1936) though the measurements for Cs^+ in He (Hoselitz 1941) appear to contradict it (cf. table 3). Some of the numerical values obtained for K^+ in A are, in any event, difficult to explain (unless one invokes clustering) for the effect of the repulsive forces is initially to *increase* the mobility, and there can be little doubt that the higher-order terms in (39) (which tend to decrease the mobility) play only a minor role; for temperatures at or below 195 °K the measured mobilities are nevertheless considerably *less* than the value given by table 2. The experiments are of course extremely difficult and further measurements would seem desirable.

As is expected, the values of $\mathscr{K}'$ for ions in Ne and He are not constant, the polarizabilities of Ne and He being respectively only 2·68 and 1·39, compared to the values 11·0, 16·7 and 27·1 for A, Kr and Xe (cf. Landolt & Bornstein 1950). In consequence a variation with temperature is expected and has been observed by Pearce (1936) and Hoselitz (1941), whose results are reproduced in table 3. The remainder of this section will be devoted to the derivation of interactions yielding values of $\mathscr{K}$ in harmony with these experimental data.

6·2. *Interaction energies*

The essential weakness of basing an analysis of experimental data on the interaction (47) arises because the ultimate rate of decrease of mobility with temperature is then predetermined, and no alteration of the constants A and B can affect it. A more general and theoretically preferable interaction is

$$V(R) = A\exp(-\zeta R) - \frac{B}{R^4} - \frac{C}{R^6} \tag{50}$$

and Meyerott (1944) has computed the mobility of Li^+ in He using this form with

$$A = 74{\cdot}2, \quad \zeta = 3{\cdot}12, \quad B = 1{\cdot}39, \quad C = 3{\cdot}84, \tag{51}$$

distance being in units of a_0 and energy in Rydbergs. The interaction was calculated by an approximate application of an approximate quantal method and cannot possess high accuracy. Meyerott's results, calculated using (10) for Q_d and (13) for the phases, are illustrated in figure 2, from which it might be concluded that the agreement is as good as could be hoped. It is difficult, however, to understand his results at low temperatures where only polarization forces are effective in determining the mobility, so that a constant minimum value of 19·1 is to be expected. We have therefore recomputed $\mathscr{K}$ for Li^+ in He using Meyerott's interaction (50), but with C taken as zero since its influence is slight and using the techniques of § 3·2. Corresponding to (50), $\beta(p)$ can be approximated by

$$\beta(p) = -\frac{1}{2\mathscr{E}}\{A\zeta p K_0(\zeta p) - 3\pi\beta/4p^4\} \tag{52}$$

and Q_d can be approximated by (34). In (34), p^* is chosen equal to the largest value of p for which $\sin^2\beta(p) = 1$ and the resulting value of Q_d is then multiplied by a scale factor equal to that required to correct $Q_d(p^*)$ when calculated using polarization forces only. This method removes the uncertainty normally associated with the arbitrariness of the choice of p^* and also ensures that Q_d is correct in the limit of vanishing temperature.

The resulting mobilities are illustrated in figure 2. The harmony at high temperatures between our results (based upon the Massey–Mohr approximation) and those of Meyerott (based upon the more accurate Jeffreys's approximation) is very satisfactory. The measurements of Hoselitz at 20 and at 78 °K cannot be fitted to a theoretical curve and it will be assumed that they do not refer to Li^+ but to a clustered ion. However, since the mobility-temperature plot based upon the other data tends in the limit of low temperatures to a value 1·08 times that predicted by (44), it will be further assumed that the data contain a systematic error and should be reduced by a linear factor 1/1·08. The resulting mobility-temperature plot is shown in figure 2.

By following a trial and error procedure, it is found that mobilities derived from the interaction

$$V(R) = 74{\cdot}2\exp(-2{\cdot}75R) - 1{\cdot}39/R^4\,\mathrm{Ry} \tag{53}$$

are as illustrated in figure 2, being in harmony with the modified experimental data. The dissociation energy 0·060 eV corresponding to (53) is in satisfactory agreement with the value of about 0·07 eV estimated by Hoselitz & Munson (1939) from an analysis of their clustering data.

The measurements by Pearce of $\mathscr{K}$ for Na^+ in He, reduced as for Li^+ by the factor 1/1·08, are illustrated in figure 2. They lie very near to those for Li^+ and the interaction (53) therefore explains the Na^+ data also.

The measurements by Hoselitz of $\mathscr{K}$ for Cs^+ in He reduced by the factor 1/1·08, are also illustrated in figure 2. The $\mathscr{K}'$-T plot has a quite different shape from that common to Li^+ and Na^+ and casts doubt on the identification of the ion as Cs^+ at all temperatures. In view of this uncertainty and the considerable labour required to derive an interaction from experimental data, the Cs^+ case has been considered only briefly. It has been found, however, that the interaction

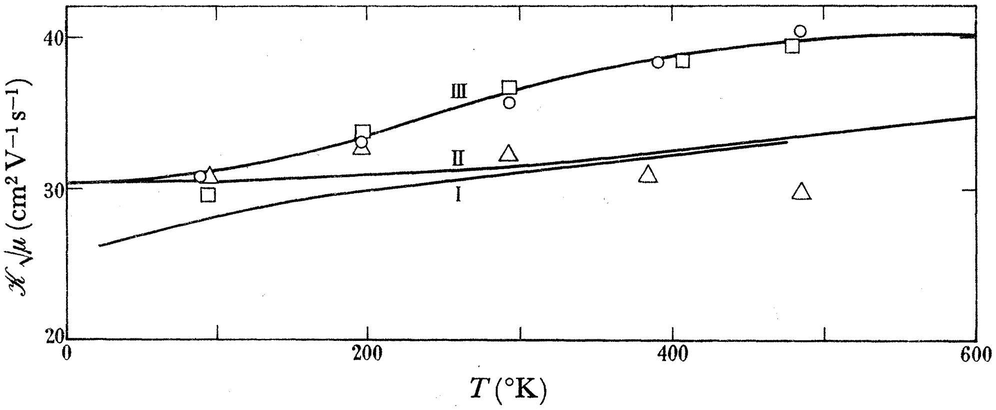

FIGURE 2. $\mathscr{K}\sqrt{\mu}$ for ions in He. Curve I, original Meyerott; curve II, modified Meyerott; curve III, corresponding to interaction (53); experimental points: ○, Li^+; □, Na^+; △, Cs^+.

$$V(R) = 90\exp(-2{\cdot}05R) - 1{\cdot}39/R^4\,\mathrm{Ry} \tag{54}$$

yields a curve of the correct shape though not in detailed agreement. Should Hoselitz's measurements be confirmed, (54) provides a reasonable initial approximation for a trial and error procedure to determine the correct $V(R)$.

This calculation is in agreement with the prediction that the larger the ion the lower the temperature at which the maximum occurs, a prediction which also follows from the Langevin theory.

6·3. *Atomic ions in molecular gases*

The theory that has been presented so far applies strictly only to spherically symmetrical interactions. However, to a first approximation the theory can still be used, provided the angular-dependent interaction between an atomic ion and a gas molecule is replaced by the spherically symmetric interaction obtained by averaging over all molecular orientations. This average long-range interaction between an ion and a diatomic homonuclear molecule will have the form $V(R) = -\frac{1}{2}\alpha e^2/R^4$, where α is some weighted mean of the parallel and perpendicular polarizabilities and so (44) still applies.

Table 4 lists the observed values of $\mathscr{K}'$, measured at 291 °K by Mitchell & Ridler (1934), for a large number of ions in N_2. The constancy of $\mathscr{K}'$ is particularly impressive for N_2, since the ions for which measurements are available have quite different electronic configurations. No definite measurements are available at other temperatures to check the predicted constancy with temperature, but it seems almost certain that the assumption of a spherically symmetric R^{-4} interaction is valid. The corresponding theoretical value of α, 11·3, is to be compared with the experimental value of 16·1 for the parallel polarizability, and 9·8 for the perpendicular polarizability (cf. Hirschfelder, Curtiss & Bird 1954). The suggestion by Johnson (1950) that the mobility of an ion in N_2 is determined primarily by the quadrupole interaction term has previously been refuted by Geltman (1954) and the harmony of the values of α given above strongly supports Geltman's contention.

TABLE 4. $\mathscr{K}'$ FOR IONS IN N_2, H_2 AND CO MEASURED AT 291 °K†

gas \ ion	Li	Na	K	Rb	Cs	Al	Ga	Kr	In	Xe	Ba	Hg	Tl
N_2	9·3	10·1	10·2	10·3	10·3	10·1	10·2	10·3	10·2	10·0	10·1	10·1	10·1
H_2	15·6	17·3	17·4	17·5	17·6	—	—	—	—	—	—	—	—
CO	5·6	8·1	8·8	8·9	8·9	—	—	—	—	—	—	—	—

† Mitchell & Ridler (1934).

The position regarding the mobility of ions in H_2 is less clear. The measured values of $\mathscr{K}'$ (Tyndall 1938; Hershey 1939), listed in table 4, are fairly constant, but the corresponding value of α of 4·3 cannot be reconciled with the measured values 6·3 and 4·8 of the parallel and perpendicular polarizabilities, respectively.

The remaining data refer to CO and H_2O. Those for H_2O will not be discussed since they almost certainly refer to clustered ions of uncertain identity (cf. Tyndall 1938), but those for CO (cf. Tyndall 1938) are reproduced in table 4. Apart from Li^+ which seems anomalous, $\mathscr{K}'$ is probably constant within the experimental error. The derived value of α is 16·3 in harmony with the parallel and perpendicular polarizabilities of 17·5 and 11·0, respectively. That the effective interaction is therefore probably purely R^{-4} is of special interest in this case, since the leading term in the interaction between an ion and a heteronuclear molecule is proportional to R^{-3}; it is orientation dependent, however, and its average vanishes if all orientations are equally probable.

7. MOLECULAR IONS IN GASES

Apart from indirect evidence from investigations of clustering, experimental data on molecular ions in unlike gases are limited. Indeed, the common procedure is to identify the ion by calculating its mass from the measured mobility using the constancy of $\mathscr{K}'$. Mitchell & Ridler (1934) identified $Na(NH_3^+)$ and NH_3^+ in N_2 in this way but the procedure requires justification, for the theoretical description must be modified (Pidduck 1926).

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