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Phil. Trans. R. Soc. Lond. A 1982 **304**, 447-497
doi: 10.1098/rsta.1982.0018

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Phil. Trans. R. Soc. Lond. A **304**, 447–497 (1982) [447]
Printed in Great Britain

THEORY OF ION–ION RECOMBINATION

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(*Communicated by Sir David Bates, F.R.S. – Received* 11 *March* 1981)

CONTENTS

A new and basic theory of ion–ion recombination as a function of gas density N is developed from basic microscopic principles. A key equation for the distribution in phase space of ion pairs is derived together with an expression for the resulting rate α

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of recombination. Further development of the theory leads to interesting insights into the full variation with N of α, which is shown to yield the correct limits at low and high N. The recombination rate α is determined by the limiting step of the rate α_{rn} for ion reaction and of the rate α_{tr} for ion transport to the reaction zone. An analytical solution of the time-dependent Debye–Smoluchowski equation, which is a natural consequence of this theory, is provided for transport–reaction under a general interaction V, for an instantaneous reaction ($\alpha_{\text{rn}} \gg \alpha_{\text{tr}}$) and for a finite rate ($\alpha_{\text{rn}} \approx \alpha_{\text{tr}}$) of reaction within a kinetic sink rendered compressible by variation of gas density. Expressions for the transient recombination rates $\alpha(t)$ are then derived, and are illustrated. The exhibited time dependence lends itself to eventual experimental verification at high N.

A theory that investigates the variation of α with ion density $N^{\pm}$ is also developed. Here the ion–ion interaction V can no longer be assumed *ab initio* to be pure coulomb but is solved self-consistently with the recombination. Recombination rates for various systems are illustrated as a function of N by a simplified method for the reaction rate. Finally, two theoretical procedures are proposed for the solution of the general phase-space ion distributions.

1. INTRODUCTION

Ever since the pioneering developments by Langevin (1903) of ion–ion recombination at high gas densities N, and by Thomson (1924) of the low density limit, theorists have sought a basic theory to link the linear three-body (Thomson) region to the nonlinear gas density region with the aim of eventual connection to the high density (Langevin) region in which the combined macroscopic effects of mobility (Langevin 1903) and of diffusion (Harper 1932, 1935) control events. Natanson (1959), by generalization of a method of Fuks (1958) on evaporation of water droplets in a gaseous medium, provided some insight to this link, although his approach remains phenomenological in the spirit of the approaches of both Langevin and Thomson. The concept of a trapping radius was invoked in all three studies and was so chosen by Thomson and Natanson that a single strong ion–neutral collision for ion pairs with separations within this radius produced recombination. Mechanisms resulting in mobility or diffusion, or both, were treated (if at all) as macroscopic.

These phenomenological approaches masked the essential theoretical problem, which is complex and difficult in that the macroscopic effects and recombination sinks require address in language of their basic microscopic origins. Any simplifications introduced through concepts of mobility, diffusion and trapping radii for description of macroscopic phenomena without recourse to their microscopic origin are inherently theoretically unsound, unless the full and detailed phase-space history of an ion pair has first been established, with all macroscopic characteristics being the effect of, rather than the cause of, such microscopic behaviour.

Suffice it to note this history has, in general, not been established, except in the low-density limit when diffusion–mobility effects are sufficiently fast to support equilibrium such that recombination is limited by reaction alone, as opposed to transport. Bates & Moffett (1966) and Bates & Flannery (1968) succeeded in developing the first rigorous theoretical account of recombination–reaction based on microscopic energy-change principles; they then established by quasi-equilibrium kinetics the essential development in internal energy E of ion pairs recombining solely by reaction. Bates & Mendaš (1978*a*), by distinguishing between expanding and contracting ion pairs, have proposed an interesting extension of the quasi-equilibrium method into the nonlinear region and have shown a variation of the recombination coefficient α with gas density N, consistent with the initial nonlinear ascent with N as given in the phenomenological

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treatment of Thomson (1924). However, at pressures greater than 1 atm† (at 0 °C), the Thomson model predicts saturation in α, and fails. Coupling with the macroscopic effect of mobility, i.e. the diminishing effect of accelerations produced between collisions by the mutual ion–ion electrostatic field, is absent in both treatments. As will be shown here, the Thomson model is a model for the reaction rate and neglects the rate of ion transport, an assumption valid only at low N. Bates (1975) generalized the Harper–Langevin result by including (macroscopically) both diffusion and drift in the ion-transport rate which in the limit of high N is the rate of recombination since reaction proceeds infinitely fast.

The above references reflect the key pivotal theoretical developments, until now, that have contributed to the basic understanding of ion–ion recombination in a gas.

Since the overall theoretical problem is so complex and difficult, resort in the meantime has been made to procedures (Flannery 1978, Flannery & Yang 1978*a*, *b*, Wadehra & Bardsley 1978, Flannery 1976) that are all essentially modifications of Natanson's expression (based on the strong collision concept) or else to Monte-Carlo computer simulations (Bates 1980*a*, *b*; Bates & Mendaš 1978*b*, Bardsley & Wadehra 1980, Morgan *et al.* 1980) which, although they produce numerical coefficients α, do not deepen theoretical understanding of the basic issues involved. However, the Monte-Carlo results may exhibit special characteristics requiring further theoretical explanation (as in Bates 1980*c*). The renewed activity in recombination has been largely prompted by continuing interest in the overall problem, and in some measure by the key role (cf. Flannery 1979) of ion–ion recombination in populating the upper molecular states of rare gas–halide lasers which operate not only at high gas pressures ($\frac{1}{2}$–10 atm) but also at high ion-densities $10^{12} \lesssim N^{\pm} \lesssim 10^{14}\,\mathrm{cm}^{-3}$. This is a region for which laboratory experiments of benchmark quality are as yet not forthcoming because of severe problems (even at low $N^{\pm}$, but especially at intermediate and high N).

The aim of this paper is to present the first basic theoretical account of a classical problem, i.e. the determination of the recombination rate α of

$$X^{+} + Y^{-} + Z \rightarrow [XY] + Z \tag{1.1}$$

as a function both of gas density and of ion density. The first account of the explicit variation of $\alpha(t)$ with time will also be provided. To provide some insight, it is worthwhile to review the essential underlying phenomenological features of ion–ion recombination within a modern perspective.

1.1. *Physical concepts*

At high gas densities N, the relative velocity $\boldsymbol{v}$ of the positive and negative ions X^{+} and Y^{-}, labelled 1 and 2, respectively, is governed by $\boldsymbol{v}_{\mathrm{d}}$, the drift velocity $(K_1 + K_2)\boldsymbol{E}$ acquired from the 1–2 mutual electrostatic field of intensity $\boldsymbol{E}$ by the ions with mobilities $K_{1,\,2}$ in the neutral gas Z, labelled 3. The ion–neutral collision frequency (v/λ_i) in terms of the mean free path λ_i of either ion i is very high and $\boldsymbol{v}_{\mathrm{d}}$ is therefore in equilibrium with the field. The constant steady-state $\boldsymbol{v}_{\mathrm{d}}$ is achieved as the balance between accelerations in the field direction *between* i–3 collisions, and decelerations *during* i–3 collisions. The net (inward) flux $\mathrm{F}_{\mathrm{in}}^{-+}$ $(\mathrm{cm}^{-3}\,\mathrm{s}^{-1})$ of negative ions crossing spheres of radii R_{X} centred at each positive ion, distributed with frequency $N^{+}\,\mathrm{cm}^{-3}$, is about $4\pi R_{\mathrm{X}}^{2} v_{\mathrm{d}} N^{+} N^{-}$ so that, under the assumption that all ion pairs with separations R less than R_{X}^{-}

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† atm = 101 325 Pa.

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are assured of eventual recombination, the recombination rate at high gas densities N is equal to the rate of (drift) transport:

$$\alpha_{\mathrm{h}} = -\frac{1}{N^{+}N^{-}}\frac{\mathrm{d}N^{\pm}}{\mathrm{d}t} = \frac{F_{\mathrm{in}}^{-+}}{N^{+}N^{-}} = 4\pi e(K_1+K_2), \tag{1.2}$$

This is the Langevin result, which decreases as N^{-1}. The rate (1.2) is the rate α_{tr} of ionic transport in the absence of diffusion, which is appropriate only at asymptotic R, and is valid when the rate α_{rn} of reaction (by three-body collisions within R_{X}) is much faster than α_{tr}, as at high N where the large number of third bodies ensures instant deactivation of the ion pairs. The above method (fortuitously) provides the correct result only for a pure Coulomb attraction; for a general interaction, the full diffusional-drift equation (§ 2.4) must be solved.

At low gas densities N, ion–neutral collision frequencies are vanishingly small, so the relative 1–2 approach velocity $\boldsymbol{v}$ becomes much higher than the thermal velocity, and a large fraction of the close ion–ion 1, 2 encounters (within R_{X}) do not result in mutual neutralization by electron transfer. Of the velocity-changing i–3 collisions, the ones effective for recombination are those that occur for 1–2 separations $R \leqslant R_{\mathrm{T}}$ where the electrostatic field is sufficiently strong for trapping. Since no angular momentum barrier at positive energies exists for pure coulomb attraction, trapping involves only those ion pairs with internal energy rendered negative by i–3 collisions. If it is assumed that recombination results from a single strong i–3 collision ($i = 1, 2$) within R_{T} centred at the other ion, then for low N, α increases linearly with N as

$$\alpha_{\mathrm{lo}} = K_{\mathrm{eq}}(R_{\mathrm{T}})\,(\langle v\rangle/\lambda_1 + \langle v\rangle/\lambda_2) \equiv \tfrac{4}{3}\pi R_{\mathrm{T}}^{3}\,N\sigma_{\mathrm{d}}\,\langle v\rangle, \tag{1.3}$$

in terms of some averaged collision frequency $\langle v\rangle/\lambda_i$ and of K_{eq}, the equilibrium constant ($\frac{4}{3}\pi R_{\mathrm{T}}^{3}$) averaged over all energies for formation of R-ion pairs with internal separations $R \leqslant R_{\mathrm{T}}$. The sum of the diffusion cross sections for each i–3 encounter is σ_{d}. For a suitable choice of the trapping radius R_{T}, (1.3) agrees with the low density limit of Thomson's result.

As N is raised, the ion–sink strength represented by α_{lo} increases to such an extent that its effect on the number density $N_{\mathrm{i}}(R)$ of R-ion pairs becomes important and must be coupled to the solution of N_{i} though the diffusion–drift equation thereby resulting in an overall increase with N less than linear (see § 2.3) and in eventual decrease, i.e. the rate of reaction increases, becomes comparable with, and eventually becomes much faster than the transport rate as N is increased. In contrast, however, Thomson assumed that as N is raised the probability $P_3(R_{\mathrm{T}}/\lambda_i)$ of *effective*† ion–neutral collisions, for ion pairs with $R \leqslant R_{\mathrm{T}}$, eventually increased to unity as

$$P_3(X) = W(X_1) + W(X_2) - W(X_1)\,W(X_2), \quad X_i = R_{\mathrm{T}}/\lambda_i, \tag{1.4}$$

where the individual ion–neutral collision probability is (Loeb 1955)

$$W(X) = 1-(1/2X^2)\,[1-\exp(-2X)\,(1+2X)] \rightarrow \begin{cases} \frac{4}{3}X(1-\frac{3}{4}X+\frac{2}{5}X^2-\frac{1}{6}X^3+\ldots), & \text{low } N, \\ 1, \quad \text{high } N, \end{cases} \tag{1.5}$$

which yields (1.3) for N low, but which leads to a defective result at high N (although Thomson's survival-diffusion concept is essentially correct). The extension by Bates & Mendaš (1978*a*) into the nonlinear region is consistent with the initial nonlinear N-variation of (1.5). The Thomson rate is only the reaction rate, while Bates & Mendaš introduced the additional transport mechanism of diffusion.

The failure of the Thomson model at high N is due both to the neglect within R_{T} of the decreasing effect of accelerations produced by the ion–ion field between frequent ion–neutral

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† In the sense of promoting the reaction phase of the recombination.

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collisions, a mobility effect required for thermodynamic equilibrium in the absence of sources and sinks within R_T, and to the explicit neglect of ion transport by both diffusion and drift under V outside the reaction R_T-sphere. Both neglected effects, which originate with the transport of ions in phase space under a field, are a natural consequence of the basic theory (§ 2). Thus the Thomson rate is essentially the rate of reaction α_{rn} within an incompressible field-free sink S of ions brought to S not by ion transport (which is ignored) but by their thermal energy. Within the P_3-factor of (1.4), diffusion is acknowledged only within the field-free sink through the decrease in survival rate of the ions towards increasingly effective collisions with an increasingly dense gas. The survival–collision probability P_3 remains therefore limited to unity at sufficiently high N (infinitely large collision probability for ions with infinitesimal survival probability).

It will subsequently become apparent that recombination occurs by reaction, at rate α_{rn}, of ion pairs (via three-body effective collisions) brought together by ion net transport at a rate α_{tr} such that the rate α of recombination is determined by the rate-limiting step, i.e. by

$$\alpha = \alpha_{rn}\alpha_{tr}/(\alpha_{rn}+\alpha_{tr}) \tag{1.6a}$$

where

$$\alpha_{rn} \sim (\pi R_T^2)\, P_3(X) \exp[-V(R_T)/kT]\, \langle v_{12}\rangle \tag{1.6b}$$

is the rate of reaction within R_T, and

$$\alpha_{tr} = 4\pi D \Big/ \int_{R_T}^{\infty} \exp(KV/De)\, R^{-2}\, dR = 4\pi Ke[1-\exp(-e^2/R_T kT)]^{-1} \tag{1.6c}$$

is the transport rate in terms of the coefficients $D \equiv K(kT/e)$ and K for relative diffusion and mobility respectively and of the integral which is related to the probability for diffusional escape in the presence of an instantaneous sink at R_T and an attractive interaction V which is taken as Coulomb. In this sense, Langevin and Thomson focused on each of the essential components (transport and reaction, respectively) required for a complete theory of recombination. Each component provides the correct limit: i.e. at high N when the reaction is instantaneous in comparison with transport ($\alpha_{rn} \gg \alpha_{tr}$), the overall rate α from (1.6a) reduces to (1.6c) while at low N, when the ionic transport is faster than the reaction ($\alpha_{tr} \gg \alpha_{rn}$), (1.6a) reduces to (1.6b).

The reaction rate α_{rn} is the recombination rate that would pertain (§ 2) provided a Boltzmann distribution of ions were maintained, a situation that results in no net diffusional drift.

Bates & Flannery (1969) have already noted that Natanson's expression, designed to cover all N, could essentially be written as (1.6a). By analogy with the behaviour of a steady current through an electrical network of two capacitances in series, Bates (1974) expressed a 'series' rate such as (1.6a) in terms of a theorem. It will subsequently become apparent that the full microscopic theory of ion–ion recombination places (1.6a) on a firm theoretical foundation and yields remarkable analogies to many macroscopic areas of physics (fluid dynamics, evaporation theory, coagulation of colloids, diffusion in a field, chemical reactions in dense gases, fluorescence quenching, electrostatics (cf. Appendix A), etc.) and that therein lies partly its fascination.

1.2. *Physical concepts in the present theory*

The present theory allows for the full evolution of the density of ion pairs in phase space by effective and ineffective† microscopic collisions, by inward and outward diffusion due respectively to the presence of the recombination sink (at small and intermediate R) and to the diffusional escape reaction to the effect of inward drift (at larger R), and by the accelerations

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† In the sense that these collisions promote thermodynamic equilibrium by ion transport.

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produced by mutual electrostatic ion–ion fields between ion–neutral collisions in an increasingly dense medium. In so doing, the macroscopic effects of diffusion and mobility are properly traced from their microscopic origins which in turn are responsible for the recombination sink, so that various physical mechanisms are not twice included (unwittingly) through some particular graft of macroscopic phenomena and microscopic mechanisms. In low density treatments (Bates & Moffett 1966, Bates & Flannery 1968), the acceleration due to the ion–ion interaction is included correctly; but as the gas density is raised, the diminishing effect of this acceleration due to increased collision frequencies must be properly acknowledged. Thermal equilibrium at high gas densities, without the effect of sinks, sources or chemical reactions, is achieved as a balance between the accelerations so produced by the field between collisions (or by macroscopic inward mobility) and the outward diffusion of ions due to the R-inhomogeneity produced by the ion–ion interaction. Presence of a sink naturally implies additional inward diffusion, which becomes effective at smaller and intermediate R.

1.3. *Notation*

The equation in the text in which the symbol is first precisely defined is given in parentheses.

α	recombination rate ($\mathrm{cm^3\,s^{-1}}$), (2.51)
$\alpha_{\mathrm{rn}}, \alpha_{\mathrm{lo}}$	reaction rate ($\mathrm{cm^3\,s^{-1}}$) or recombination rate appropriate to a Boltzmann distribution of ions, recombination rate at low gas densities, (2.61)
α_3	$\alpha_{\mathrm{rn}} \exp[V(R)/kT]$, (2.44), such that $\alpha_3(R)\,n^-(R)$ is frequency of reaction within R-sphere.
α_{h}	Langevin rate ($4\pi Ke$), (1.2)
$\alpha_{\mathrm{tr}}(R)$	transport rate $\left[\alpha_{\mathrm{h}}\left\{R_e \int_R^\infty \exp(V/kT)\,R^{-2}\,\mathrm{d}R\right\}^{-1}\right]$, (2.63)
α_{hi}	$\alpha_{\mathrm{tr}}(R_E)$; recombination rate at high gas density, (2.63)
$\Gamma_3(R)$, $\Gamma(R)$	speed of reaction of R-ion pairs, (2.82)
C	all states of ion pairs in the energy continuum, (2.5)
$\boldsymbol{D}$	diffusion tensor, (2.37)
D	relative diffusion coefficient ($\mathrm{cm^2\,s^{-1}}$) of positive and negative ions, (2.43)
D_S	diffusion coefficient in the presence of a sink, (5.49)
$\mathscr{D}$	diffusion drift operator, (2.46*a*)
δ	collision parameter, (4.15)
$\mathbf{E}$	electric field intensity, (2.3)
$-E$	energy of arbitrary bound level ($-$E) of ion pair, (2.47*a*)
$E_{-\mathrm{S}}$, $E_{-\mathrm{V}}$, $E_{-\mathrm{M}}$	energy of bound levels $-$S, $-$V, and $-$M of ion pair such that $E_{-\mathrm{M}} = \max[E_{-\mathrm{V}}, E_{-\mathrm{S}}]$, (2.49)
E_{i}	internal energy of the ion pair in state i
e	electronic charge (4.80324×10^{-10} e.s.u)
F	inward flux (negative ions $\mathrm{s^{-1}}$) across a sphere centred at a positive ion, (2.69)
$F_0(v_{\mathrm{i}})\,\mathrm{d}v_{\mathrm{i}}$	Maxwellian distribution of speeds, (2.13)
g, $\boldsymbol{g}_{\mathrm{i}}$	ion–neutral relative speed, and velocity, (2.4)
$j(R, t)$	current (negative ions $\mathrm{cm^{-2}\,s^{-1}}$) across an R-sphere centred at a positive ion, (2.45*b*)
k	Boltzmann constant ($1.38066 \times 10^{-23}\,\mathrm{J\,K^{-1}}$)
K	relative mobility ($\mathrm{cm^2\,Stat\,V^{-1}\,s^{-1}}$) of positive and negative ions, (2.38), (2.43)

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$k_{\mathrm{if}}(R)$, $k_{\mathrm{if}}(E_{\mathrm{i}}, E_{\mathrm{f}}, R)$	collisional rate coefficient ($\mathrm{cm^3\,s^{-1}}$) for conversion of R_{i}-ion pairs (with internal separation R and internal energy E_{i}) to R_{f}-ion pairs by collision with a third body (gas atom), (2.6)
$L(v_{\mathrm{i}})$	peculiar path length of ions with speed v_{i} in absence of recombination sink, (5.34, 5.35)
$l_{\mathrm{i}}(R, E_{\mathrm{i}})$	peculiar path length of ions in recombination process, (5.31)
λ_i	mean free path averaged over all speeds of ions in equilibrium, (1.3)
$-\mathrm{M}$	bound level of energy $E_{-\mathrm{M}}$ such that $E_{-\mathrm{M}} = \max[E_{-\mathrm{V}}(R), E_{-\mathrm{S}}]$, (2.11)
N	gas bulk density ($\mathrm{cm^{-3}}$), (1.3)
N_{L}	gas density ($2.69 \times 10^{19}\,\mathrm{cm^{-3}}$) at s.t.p. (Loschmidt's number), after (2.128)
$N^{\pm}$	ion bulk density ($\mathrm{cm^{-3}}$), (1.2)
$N_0(\boldsymbol{R}, \boldsymbol{v}_0, t)$	phase-space gas density ($\mathrm{cm^{-3}/(cm\,s^{-1})^3}$), i.e. gas density per unit $\mathrm{d}\boldsymbol{v}_0$-interval, (2.4)
$N(\boldsymbol{R}, t)$	configuration-space gas density ($\mathrm{cm^{-3}}$) $\int N_0(\boldsymbol{R}, \boldsymbol{v}_0, t)\,\mathrm{d}\boldsymbol{v}_0$, (2.34)
$n_{\mathrm{i}}(\boldsymbol{R}, \boldsymbol{v}_{\mathrm{i}}, t)$	phase-space density of negative ions, (2.2), (2.3)
$\left.\begin{matrix} n_{\mathrm{i}}(\boldsymbol{R}, v_{\mathrm{i}}, t) \\ n_{\mathrm{i}}(\boldsymbol{R}, E_{\mathrm{i}}, t) \end{matrix}\right\}$	$4\pi v_{\mathrm{i}}^2 n_{\mathrm{i}}(\boldsymbol{R}, \boldsymbol{v}_{\mathrm{i}}, t)$ ($\mathrm{cm^{-3}/(cm\,s^{-1})}$), density of negative ions per unit speed-interval about v_{i}, (2.8)
$n_0(R, v_{\mathrm{i}})$	Maxwell–Boltzmann ion density per unit $\mathrm{d}v_{\mathrm{i}}$-interval, (2.13)
$\left.\begin{matrix} n(\boldsymbol{R}, t) \\ n(R, t) \\ n^{-}(R, t) \end{matrix}\right\}$	configuration-space negative ion density ($\mathrm{cm^{-3}}$) $\int n_{\mathrm{i}}(\boldsymbol{R}, \boldsymbol{v}_{\mathrm{i}}, t)\,\mathrm{d}\boldsymbol{v}_{\mathrm{i}}$, (2.26)
$N_{\mathrm{i}}^{*}(R, E_{\mathrm{i}}, t)$	configuration density of R_{i}-ion pairs per unit $\mathrm{d}R$-interval, $4\pi R^2 n(R, E_{\mathrm{i}}, t)\,N^{+}$ ($\mathrm{cm^{-4}}$) with internal energy $E_{\mathrm{i}} < 0$, or per unit $\mathrm{d}R\,\mathrm{d}v_{\mathrm{i}}$-interval for $E_{\mathrm{i}} > 0$, (2.10)
$N_{\mathrm{i}}^{*}(R, E_{\mathrm{i}}, \hat{\boldsymbol{v}}_{\mathrm{i}}, t)$	phase-space density of R_{i}-ion pairs, i.e. configuration density per unit $\mathrm{d}\boldsymbol{v}_{\mathrm{i}}$-interval, (2.2)
$N_0(R, E_{\mathrm{i}})$	Maxwell–Boltzmann ion pair density per unit $\mathrm{d}R\,\mathrm{d}E_{\mathrm{i}}$-interval, (2.14)
P_3	probability of an ion-pair–neutral collision, (1.4)
$P_{\mathrm{d}}(R)$, $P(R)$	$R_e \int_R^{\infty} \exp(V/kT)\,R^{-2}\,\mathrm{d}R$, (2.56), which is such that $P(R_0)/P(R_E)$ is the probability $\mathscr{P}^{\mathrm{c}}$ that an R_0-ion-pair contracts by diffusional drift in the presence of an instantaneous sink at R_E, (2.77)
$\mathscr{P}^{\mathrm{c}}(R, R_E)$	(2.77 *a*) for instantaneous sink and (2.77 *b*) for finite-rate sink.
$\mathscr{P}^{\mathrm{e}}(R, R_E)$	probability that an R-ion pair expands by diffusion to infinite internal separation against attractive force, (2.78)
$Q^{\mathrm{E,X}}$	integral cross section for ion–neutral elastic (E) or charge-transfer (X) collisions, (2.7), Appendix B.
R_e	natural unit of length (e^2/kT or e^2K/De) appropriate to coulomb attraction, (2.57) $\approx$ 55.7 nm at 300 K.
R_E, $R(E)$	outermost turning point associated with bound-level of energy $-E$, (2.17), (2.51); maximum radius of three-body collision sink
R_{i}	Internal separation of ion pairs with internal energy E_{i}, before (2.3)
R_i	trapping radius appropriate to ion species i as a function of gas density, (4.17), (4.21)
R_{s}	screening length, (4.7)
R_{T}	Thomson trapping radius ($2e^2/3kT$) $\approx$ 37 nm at 300 K, (4.17)
S	radius of strong-collision sink, compressible with increasing N, (2.70, 2.82)

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$\sigma(g, \psi)$	differential cross section for ion–neutral scattering in the centre-of-mass frame
T	gas temperature (K)
τ_i	time-interval between collisions, (5.20), (5.34)
$V(R)$	ion–ion interaction potential
$-\mathrm{V}$	bound level given by intersection of R and $V(R)$, (2.5)
$\boldsymbol{v}_0$, $\boldsymbol{v}_i$	velocities of gas atom and ion before collision, (2.4)
$\boldsymbol{v}_0'$, $\boldsymbol{v}_f$	velocities of gas atom and ion after collision, (2.4)
W	probability for an ion–neutral collision, (1.5)
X_i	internal kinetic energy of relative motion of an ion pair, normalized to kT, (5.36)

2. THEORY OF ION–ION RECOMBINATION AS A FUNCTION OF NEUTRAL GAS DENSITY

In this section is presented the development of the basic equations to be solved for determination of the phase-space densities of ion pairs (§ 2.1), and the development (§ 2.2) of the basic expression for the rate α of recombination. An exact expression for the steady-state α is provided (§ 2.3) in terms of the rates for ionic transport and reaction, and similarities with a density-dependent reaction sink are explored in § 2.4. Finally, in § 2.5 is presented an analytical time-dependent solution of the Debye–Smoluchowski equation associated with a general spherical field for time-dependent ion densities and recombination rates $\alpha(t)$, a macroscopic equation which follows quite naturally from the present microscopic theory.

2.1. *Basic equation for ion-pair phase density*

Consider the drift of negative ions of density $n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)$ and velocity $\boldsymbol{v}_i$ at time t under interaction $V(R)$ across spheres of radius R centred on each positive ion, which are distributed with density $N^+\,\mathrm{cm}^{-3}$, so that the number density $N_i^*(R, E_i, t)$ of ion pairs with reduced mass M_{12}, within the R-shells of thickness $\mathrm{d}R$, with internal energy

$$E_i = \tfrac{1}{2}\mathrm{M}_{12} v_i^2 + V(R), \tag{2.1}$$

and with internal motion directed along $\hat{\boldsymbol{v}}_i$, is

$$N_i^*(R, E_i, \hat{\boldsymbol{v}}_i, t)\,\mathrm{d}R = 4\pi R^2\,\mathrm{d}R\, n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)\, N^+. \tag{2.2}$$

Two approaches with similar effect can be adopted. The fate of an ion pair may be established by considering its previous history of *elastic and inelastic* collisions with the neutral gas. Here the mutual interaction $V(R)$ between the positive and negative ions is internal to the ion-pair system. The other approach, which we adopt here, is based on the motion of a given species of ion (negative ions, say) moving under a field of intensity $\boldsymbol{E} \equiv -\nabla V/e$ (which is conservative and now external to the negative ion) and undergoing *elastic* ion–neutral gas collisions. Expressions (2.1) and (2.2) link the basic quantities associated with each approach.

The present development is based on the Boltzmann equation (cf. Chapman & Cowling 1970), which (in this instance) equates the complete time rate of change of the phase-space distribution of ions with the appropriate ion–neutral collision rate integrated over the velocity distribution of the neutral gas species. The basic assumptions inherent in the derivation of the Boltzmann equation from the fully general Liouville equation (or from the B.B.G.K.Y.† hierarchy of

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† After Bogoliubov, Born and Green, Kirkwood and Yvon who independently derived the equations between 1935 and 1949 (cf. Ferziger & Kaper 1972).

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equations) for the phase-space distribution of all ionic and gas particles are (*a*) that only binary collisions occur via (*b*) interactions $V_i(R)$ of short range R outside which (*c*) the *precollision* velocities are distributed randomly with no correlation (molecular chaos), and (*d*) that the distribution functions do not vary appreciably during an encounter. These approximations are fully justified for percussive collisions between spherical particles. For van der Waals neutral–neutral and polarization ion–neutral attractions for which $V_i \sim R^{-6}$, and $V_i \sim R^{-4}$ respectively, long-range collisions do not, however, furnish the significant contribution to the collision integral, and so for ions moving in a gas, the Boltzmann equation remains valid.

The phase density $n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)$ of negative ions (to be called R_i-ions which form R_i-ion pairs) of mass m ($\equiv \mathrm{M}_{12}$ the reduced mass of an ion pair) in a conservative external field of intensity $\boldsymbol{E}$ satisfies the Boltzmann equation (cf. Chapman & Cowling 1970, Ferziger & Kaper 1972, Holt & Haskell 1965)

$$\frac{\partial n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)}{\partial t} + \boldsymbol{v}_i \cdot [\nabla_{\boldsymbol{R}} n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)] + \left(\frac{e\boldsymbol{E}}{m}\right) \cdot \nabla_{\boldsymbol{v}_i} n_i(\boldsymbol{R}, \boldsymbol{v}_i, t) = \left(\frac{\partial n_i}{\partial t}\right)_{\mathrm{el}} - \left(\frac{\partial n_i}{\partial t}\right)_S, \qquad (2.3)$$

in which the explicit time rate of change $(\partial n_i/\partial t)$ results from the following four mechanisms.

(*a*) The continuous transport (diffusion) of R_i-ions across the R-sphere due to the $\boldsymbol{R}$-inhomogeneity in n_i.

(*b*) The continuous drift in velocity space due to $\boldsymbol{E}$ which produces an acceleration $e\boldsymbol{E}/m$ in each of the $n_i \Delta \boldsymbol{R}$ ions initially with velocity points $\boldsymbol{v}_i$ within the phase element $\Delta \boldsymbol{v}_i \Delta \boldsymbol{R}$, i.e. the R_i-ions drift in velocity space at the common rate $e\boldsymbol{E}/m$ and are therefore lost from the initial elementary region.

(*c*) The quasidiscontinuous change $(\partial n_i/\partial t)_{\mathrm{el}}$ of ions with velocities within $\Delta \boldsymbol{v}_i$ upon elastic ion–neutral collisions which therefore remove ions from one velocity element $\Delta \boldsymbol{v}_i$ to another. Replenishment to $\Delta \boldsymbol{v}_i$ is due to similar displacements from other elements of velocity space. Hence,

$$\left[\frac{\partial n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)}{\partial t}\right]_{\mathrm{el}} = \int_{\boldsymbol{v}_0} \int_{\Omega'} \{[n_f(\boldsymbol{R}, \boldsymbol{v}_f, t)\, N_0(\boldsymbol{R}, \boldsymbol{v}_0', t) - n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)\, N_0(\boldsymbol{R}, \boldsymbol{v}_0, t)][g\sigma(g, \psi)\, \mathrm{d}\Omega]\}\, \mathrm{d}\boldsymbol{v}_0, \qquad (2.4)$$

where $N_0(\boldsymbol{R}, \boldsymbol{v}_0, t)$ is the phase-space density of neutral gas species, and where the ion–neutral differential cross section at relative velocity $\boldsymbol{g}_i(= \boldsymbol{v}_i - \boldsymbol{v}_0)$ for elastic scattering by angle ψ into solid angle $\mathrm{d}\Omega$ is $\sigma\,\mathrm{d}\Omega$. The Ω-integration is over that scattering region Ω' made accessible for the production of speeds associated with final ion and neutral velocities $\boldsymbol{v}_f(\boldsymbol{v}_i, \boldsymbol{v}_0, \Omega)$ and $\boldsymbol{v}_0'(\boldsymbol{v}_i, \boldsymbol{v}_0, \Omega)$, respectively consistent with initial fixed $\boldsymbol{v}_i$ and $\boldsymbol{v}_0$. Note, however, that these elastic scattering terms produce energy changes (inelastic effects) to the internal energy E_i of an ion-pair system.

(*d*) The loss of ions $(\partial n_i/\partial t)_S$ due to the recombination sink tends to cause a redistribution in internal energies E_i of an ion pair with fixed internal separation $\boldsymbol{R}$ and represents, in this sense, a transition probability. We seek to develop a theoretical expression for the microscopic and overall effect of this term.

Because of their continuous development in phase space, (*a*) and (*b*) provide the 'streaming' or transport terms. We note that the ion density $N^{\pm}$ must be sufficiently low (less than about $10^{16}\,\mathrm{cm}^{-3}$) compared with the gas density N_0 so that the effect of ion–ion direct collisions can be neglected in comparison with ion–neutral collisions which are only included in (2.4). Hence N_0 in (2.4) can be taken as the Maxwell–Boltzmann distribution such that (2.3) with (2.4) is then the 'linear' Boltzmann equation.

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As already mentioned, (2.4) produces *inelastic* transitions ($E_{\mathrm{i}} \rightarrow E_{\mathrm{f}}$) in an R_{i}-ion pair and on integrating over $v_{\mathrm{i}}^2\,\mathrm{d}\hat{\boldsymbol{v}}_{\mathrm{i}}$, an equivalent expression for (2.4) can, on replacing v_{i} by (2.1), therefore be written as,

$$\left[\frac{\partial n_{\mathrm{i}}(R, E_{\mathrm{i}}, t)}{\partial t}\right]_{\mathrm{el}} = N\left[\sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} n_{\mathrm{f}}(R, E_{\mathrm{f}}, t)\, k_{\mathrm{fi}}(R) - n_{\mathrm{i}}(R, E_{\mathrm{i}}, t) \sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} k_{\mathrm{if}}(R)\right], \tag{2.5}$$

where N is the number density of gas atoms (or molecules) Z, and $Nk_{\mathrm{if}}(R)$ is the frequency at which an R_{i}-ion pair is converted into an R_{f}-ion pair by *elastic* collision of either ion with Z, i.e.

$$\mathrm{N}\sum_{\mathrm{f}}^{\mathrm{f}+\Delta\mathrm{f}} k_{\mathrm{if}}(R) \equiv Nk'_{\mathrm{if}}(E_{\mathrm{i}}, E_{\mathrm{f}}, R)\,\mathrm{d}E_{\mathrm{f}} = \int_{v_{\min}}^{v_{\max}} 4\pi N_0(\boldsymbol{v}_0)\left[\iint_{\Omega'} g\sigma(g,\psi)\,\mathrm{d}(\cos\psi)\,\mathrm{d}\phi\right] v_0^2\,\mathrm{d}v_0\,\tfrac{1}{2}\mathrm{d}(\cos\theta_{\mathrm{i}});$$

$$\cos\theta_{\mathrm{i}} = \hat{\boldsymbol{v}}_0\cdot\hat{\boldsymbol{v}}_{\mathrm{i}}, \tag{2.6}$$

where $v_{\min}$, $v_{\max}$ and Ω' are such that a final speed v_{f} of ion–ion relative motion is obtained from a given v_{i} and g and where $\Delta\mathrm{f}$ is the number of states in the energy interval $\mathrm{d}E_{\mathrm{f}}$ about E_{f}. For example, for symmetrical resonance charge-transfer ion–neutral collisions, with cross section Q^{X} independent of relative collision speed, we have (Flannery 1980, Bates & Moffett 1966)

$$\sum_{\mathrm{f}} k_{\mathrm{if}}(E_{\mathrm{i}}, E_{\mathrm{f}}, R) \equiv \int k'_{\mathrm{if}}\,\mathrm{d}E_{\mathrm{f}} = \left(\frac{1+c}{c}\right)^{\frac{3}{2}} \frac{Q^{\mathrm{X}}}{2\mathrm{M}_1 v_{\mathrm{i}}} \int \mathrm{d}E_{\mathrm{f}} \int_{v_{\min}}^{v_{\max}} \frac{F_0(v_0)\,\mathrm{d}v_0}{v_0}\,[v_0^2 - (v_{\mathrm{i}}^2 + 2\varDelta/\mathrm{M}_1)]^{\frac{1}{2}}, \tag{2.7}$$

where F_0 is the Maxwellian distribution in speed v_0 of the neutral gas, c is the ratio of the mass M_1 of the colliding ion to the mass of the spectator ion, and $\varDelta = T_{\mathrm{f}} - T_{\mathrm{i}}$, the change in initial and final kinetic energies $\frac{1}{2}\mathrm{M}_1(1+c)\,v_{\mathrm{i,f}}^2$ of relative motion of the positive and negative ions. The f-summation, over all final bound and continuum states of the ion pair, can be replaced by an integral when a quasicontinuous spectrum of internal energies is assumed. Detailed expressions for the rates k_{if} associated with elastic ion–neutral collisions have been provided (Bates & Flannery 1968, Flannery 1981 *a*). The sum or integration is taken over all final states f of the ion pairs, from the continuum C down to a level $-\mathrm{V}$, the lowest accessible at R appropriate to interaction energy $V(R)$. Summation of (2.5), the elastic collision integral, over all initial levels E_{i} (or integration over all ion speeds v_{i}) is null, in accord with the fact that the number density of all ions is conserved in elastic collisions. Implicit in the rate (2.5) are the following assumptions.

(*a*) The gas is in thermal equilibrium so that its density distribution $N_0(\boldsymbol{v}_0)$ in gas velocities is isotropic, is independent of both time t and position $\boldsymbol{R}$ and depends only on the speed v_0.

(*b*) The number densities $N^{\pm}$ of ions are much less than N_0 so momentum and energy imparted to the ions by their mutual field of intensity $\boldsymbol{E}$ and transferred subsequently by collision with the gas Z have a completely negligible effect on $N_0(\boldsymbol{v}_0)$. When such thermal gradients do exist, they cause thermal diffusion in mixtures. The centre of mass of the ion pair is therefore assumed to be in thermodynamic equilibrium with the gas Z.

(*c*) There are spherical symmetric $\boldsymbol{R}$- and $\boldsymbol{v}$-distributions of negative ions about each central positive ion so that the ion densities in (2.4) and (2.5) are related at fixed R by

$$n_{\mathrm{i}}(R, v_{\mathrm{i}}, t) = 4\pi v_{\mathrm{i}}^2 n_{\mathrm{i}}(R, \boldsymbol{v}_{\mathrm{i}}, t) \equiv n_{\mathrm{i}}(R, E_{\mathrm{i}}, t), \tag{2.8}$$

$$\sum_{\mathrm{i}=-\mathrm{V}}^{\mathrm{C}} n_{\mathrm{i}}(R, E_{\mathrm{i}}, t) \equiv 4\pi\int_0^{\infty} n_{\mathrm{i}}(R, \boldsymbol{v}_{\mathrm{i}}, t)\, v_{\mathrm{i}}^2\, dv_{\mathrm{i}} = \int_0^{\infty} n_{\mathrm{i}}(R, v_{\mathrm{i}}, t)\,\mathrm{d}v_{\mathrm{i}}. \tag{2.9}$$

Also the density N_{i}^* of ion pairs in the R-shell of thickness $\mathrm{d}R$ is related to the negative-ion density n_{i} by

$$N_{\mathrm{i}}^*(R, v_{\mathrm{i}}, t)\,\mathrm{d}R = (4\pi R^2\,\mathrm{d}R)\, n_{\mathrm{i}}(R, v_{\mathrm{i}}, t)\, N^+ \equiv N_{\mathrm{i}}^*(R, E_{\mathrm{i}}, t)\,\mathrm{d}R. \tag{2.10}$$

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(*d*) The interaction V between the ions is switched off during the ion–neutral collision to be consistent with the left-hand side of (2.5), in which the field is *external* to each negative ion, i.e. the field cannot be included on both sides of the Boltzmann equation (2.3).

The sink term in (2.3) can be written as,

$$\left[\frac{\partial n_\mathrm{i}(R,E_\mathrm{i},t)}{\partial t}\right]_S = N \sum_{\mathrm{f}=-\mathrm{V}(R)}^{-\mathrm{M}(R)} n_\mathrm{f}(R,E_\mathrm{f},t)\,k_\mathrm{fi}(R) = \frac{N}{4\pi R^2 N^+} \sum_{\mathrm{f}=-\mathrm{V}(R)}^{-\mathrm{M}(R)} N_\mathrm{f}^*(R,E_\mathrm{f},t)\,k_\mathrm{fi}(R) \qquad (2.11)$$

where the energy of the bound level $-\mathrm{M}$ is $E_{-\mathrm{M}} = \max[E_{-\mathrm{V}}(R), E_{-\mathrm{S}}]$ in which $E_{-\mathrm{S}}$ is the negative energy of the bound level $-\mathrm{S}$ below which recombination is assumed stabilized against any upward collisional transitions in energy. If the level $-\mathrm{V}(R)$ of energy $E_{-\mathrm{V}}(R)$ at R is above $-E_\mathrm{S}$, then the sink term is ineffective. The sink term (2.11) in effect ensures that upward transitions, in internal energy, due to elastic ion–neutral collisions, from levels between $-\mathrm{V}$ and $-\mathrm{M}$ are not included in the right-hand side of the Boltzmann equation (2.3), and compensates for their oversubscription in (2.5). With the assumption of R-spherical symmetry in n_i, (2.3), with the aid of (2.4)–(2.11), yields

$$\frac{\partial n_\mathrm{i}(R,v_\mathrm{i},t)}{\partial t} + v_\mathrm{i}\left\{\frac{\partial n_\mathrm{i}(R,v_\mathrm{i},t)}{\partial R} - \frac{4\pi v_\mathrm{i}^2}{m v_\mathrm{i}}\frac{\partial}{\partial v_\mathrm{i}}\left[\frac{n_\mathrm{i}(R,v_\mathrm{i},t)}{4\pi v_\mathrm{i}^2}\right]\left(\frac{\partial V}{\partial R}\right)\right\}$$

$$= \int\!\!\int_{\Omega'} [n_\mathrm{f}(R,v_\mathrm{f},t)\,N_0(\boldsymbol{v}_0') - n_\mathrm{i}(R,v_\mathrm{i},t)\,N_0(\boldsymbol{v}_0)][g\sigma(g,\psi)\,d\Omega]\,\mathrm{d}\boldsymbol{v}_0$$

$$\equiv N\left[\sum_{\mathrm{f}=-\mathrm{M}(R)}^{\mathrm{C}} n_\mathrm{f}(R,v_\mathrm{f},t)\,k_\mathrm{fi}(R) - n_\mathrm{i}(R,v_\mathrm{i},t)\sum_{\mathrm{f}=-\mathrm{V}(R)}^{\mathrm{C}} k_\mathrm{if}(R)\right], \qquad (2.12)$$

as the basic equation for the solution of the phase-space densities of negative ions. The corresponding equation for phase-space densities $N_\mathrm{i}^*(R,E_\mathrm{i},t)$ of ion pairs follows directly from (2.12) with the aid of (2.10) and of $\partial/\partial v_\mathrm{i} \equiv m v_\mathrm{i}\,\partial/\partial E_\mathrm{i}$ at fixed R.

When thermodynamic equilibrium prevails, i.e. in the absence of the sink term (2.11), the steady-state solution to (2.12) is a product of two independent functions, one of position R and the other of speed v_i and is such that both sides of (2.12) simultaneously vanish. The equilibrium number density of negative ions is found (after a not too trivial exercise) to be

$$n_0(R,v_\mathrm{i})\,\mathrm{d}v_\mathrm{i} = N^-\exp[-V(R)/kT]\,F_0(v_\mathrm{i})\,\mathrm{d}v_\mathrm{i} \qquad (2.13a)$$

$$\equiv N^-\exp[-V(R)/kT]\,[4\pi v_\mathrm{i}^2(m/2\pi kT)^{\frac{3}{2}}\exp(-\tfrac{1}{2}m v_\mathrm{i}^2/kT)\,dv_\mathrm{i}], \qquad (2.13b)$$

where $F_0(v_\mathrm{i})\,\mathrm{d}v_\mathrm{i}$ is the Maxwell distribution in ion speeds v_i at temperature T. The equilibrium number density of R_i-ion pairs in the R-shell of thickness $\mathrm{d}R$ and with internal energy in the interval $\mathrm{d}E_\mathrm{i}$ about E_i is, therefore, with (2.1) and (2.2),

$$N_0(R,E_\mathrm{i})\,\mathrm{d}R\,\mathrm{d}E_\mathrm{i} = 4\pi R^2\,\mathrm{d}R\left[\frac{2}{\pi^{\frac{1}{2}}}\frac{1}{(kT)^{\frac{3}{2}}}[E_\mathrm{i}-V(R)]^{\frac{1}{2}}\exp(-E_\mathrm{i}/kT)\,\mathrm{d}E_\mathrm{i}\right]N^+N^-, \qquad (2.14)$$

of which one half move inward and one half move outward across the R-sphere, respectively. Also the rates k_if satisfy the detailed balance relation (Flannery 1981 *a*)

$$N_0(R,E_\mathrm{i})\,k_\mathrm{if}(R) = N_0(R,E_\mathrm{f})\,k_\mathrm{fi}(R) \qquad (2.15)$$

as expected. The equilibrium number density of all ion pairs in all permitted internal-energy states within the R-shell is

$$N_0(R)\,\mathrm{d}R = \mathrm{d}R\int_{E_\mathrm{i}=-V(R)}^{\infty} N_0(R,E_\mathrm{i})\,\mathrm{d}E_\mathrm{i} = 4\pi R^2\,\mathrm{d}R\exp[-V(R)/kT]\,N^+N^-. \qquad (2.16)$$

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The equilibrium number density of ion pairs bound with negative energy in the interval $\mathrm{d}E$ about E is

$$N_0(E)\,\mathrm{d}E = \mathrm{d}E\int_0^{R_E(E)} N_0(R,E)\,\mathrm{d}R = \frac{8\pi^{\frac{1}{2}}}{kT}[C(E)\exp(-E/kT)\,\mathrm{d}E]\,N^+N^-, \tag{2.17}$$

where $R_E(E)$ is the outermost turning point obtained from $E = V(R_E)$, and where for a pure coulomb attraction

$$C(E) = \int_0^{e^2/|E|} (e^2/R - |E|)^{\frac{1}{2}}\,R^2\,\mathrm{d}R = \tfrac{1}{6}\pi e^6\,|E|^{\frac{5}{2}}, \tag{2.18}$$

as obtained (Bates & Flannery 1968) for the equilibrium energy distribution of bound X$^+$–Y$^-$ ion pairs in the absence of the gas Z.

The right-hand side of (2.12) can be replaced by $N_i^*\nu_i$ where ν_i is some averaged collision frequency. The characteristic time for substantial variation in the $\partial/\partial t$-term in (2.12) is much longer than the mean time ν_i^{-1} between collisions so that the explicit time derivative in (2.12) is negligible with respect to the right-hand side. Hence, by setting

$$N_i^*(R,E_i,t) = N_i^*(R,E_i)\exp[-A(E_i)\,t], \tag{2.19}$$

in (2.12) and by ignoring the small decay frequency $A(E_i)$ of level i in comparison with ν_i, as in a steady-state solution, we have

$$v_i\left[\!\!\left[\int_0^R 4\pi R^2\frac{\partial}{\partial R}\left[\frac{N_i^*(R,v_i)}{4\pi R^2}\right]\mathrm{d}R - \frac{4\pi v_i^2}{mv_i}\frac{\partial}{\partial v_i}\left\{\frac{1}{4\pi v_i^2}\left[\int_0^R N_i^*(R,v_i)\frac{\partial V}{\partial R}\,\mathrm{d}R\right]\right\}\right]\!\!\right]$$

$$= \iint_{\Omega'}[N_f^*(R,v_f)\,N_0(\boldsymbol{v}_0') - N_i^*(R,v_i)\,N_0(\boldsymbol{v}_0)]\,(g\sigma\,\mathrm{d}\Omega)\,\mathrm{d}\boldsymbol{v}_0 \tag{2.20a}$$

$$\equiv N\left[\int_0^R \mathrm{d}R\sum_{f=-M(R)}^{C} N_f^*(R,E_f)\,k_{fi}(R) - N_i^*(R,E_i)\sum_{f=-V(R)}^{C} k_{if}(R)\right] \tag{2.20b}$$

as the basic set of coupled integro-differential equations to be solved in general for the steady-state (R,E_i)-distributions of the ion-pair number densities $N_i^*(R,E_i)$. This set is solved subject to the boundary conditions that

$$N_i^*(R,v_i) = N_i^*(R,E_i) = \begin{cases} N_0(R,E_i), & E_i > 0, \quad R\to\infty,\\ N_0(R,E_i), & E_i\to\infty, \quad \text{all accessible } R,\\ 0, & E_i < -E_S, \quad R < R_c(E_S),\end{cases} \tag{2.21}$$

appropriate to the continuous generation of ion pairs with infinite separation.

Note that when the R-integration in (2.20) is taken over the full range of internal separations occupied by an ion pair of energy E_i, i.e. between the turning points R_c of $E_i = V(R)$, where $v_i(R_c,E_i)$ vanishes, then upon assuming that the left-hand side of (2.20) vanishes everywhere in this range we have

$$N_i^*(E_i)\sum_{f=-V}^{C}\langle k_{if}\rangle = \sum_{f=-S}^{C} N_f^*(E_i)\,\langle k_{fi}\rangle \tag{2.22}$$

where $-$V is the lowest bound energy level, the averaged rate is

$$\langle k_{if}(E_i,E_f)\rangle = \frac{1}{N_i^*(E_i)}\int_0^{R_M} N_i^*(R,E_i)\,k_{if}(E_i,E_f,R)\,\mathrm{d}R, \quad R_M = \min[R(E_i),R(E_f)], \tag{2.23}$$

and the physical density of ion pairs with energy E_i is,

$$N_i^*(E_i) = \int_0^{R(E_i)} N_i^*(R,E_i)\,\mathrm{d}R. \tag{2.24}$$

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Results (2.22)–(2.24) apply when the left-hand side of (2.20) is assumed negligible at all R (rather than at the turning points alone), and correspond to the quasi-equilibrium result originally introduced by Bates & Moffett (1966) and by Bates & Flannery (1968) in their treatment of ion–ion recombination in the low gas-density limit, when the diffusional-drift streaming terms balance in a Maxwell–Boltzmann quasi-equilibrium. In general, however, the full set of basic equations (2.20) require solution subject to (2.21) as the gas density is increased.

2.2. *Recombination coefficient α from derived equations of continuity, momentum and flux*

To develop an expression for the recombination coefficient α in terms of ion-pair number densities $N_i^*(R, E_i)$, we proceed by constructing the appropriate flux or momentum equation from the Boltzmann equation (2.3) as follows. Returning again to $(\boldsymbol{R}, \boldsymbol{v}_i)$-phase space occupied by the incoming negative ions of density $n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)$, we write the $\boldsymbol{v}_i$-averaged value of some physical quantity $P_i(\boldsymbol{R}, \boldsymbol{v}_i, t)$ as

$$P(\boldsymbol{R}, t) = \langle P_i \rangle = \frac{1}{n(\boldsymbol{R}, t)} \int n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)\, P_i(\boldsymbol{R}, \boldsymbol{v}_i, t)\, \mathrm{d}\boldsymbol{v}_i, \tag{2.25}$$

where the configuration-space density is

$$n(\boldsymbol{R}, t) = \int n_i(\boldsymbol{R}, \boldsymbol{v}_i, t)\, \mathrm{d}\boldsymbol{v}_i. \tag{2.26}$$

On multiplying the Boltzmann equation (2.3) by P_i and integrating over $\boldsymbol{v}_i$, we have

$$\begin{aligned} \frac{\partial n \langle P_i \rangle}{\partial t} - n \left\langle \frac{\partial P_i}{\partial t} \right\rangle + \nabla_{\boldsymbol{R}} \cdot [n \langle P_i \boldsymbol{v}_i \rangle] - n \langle \boldsymbol{v}_i \cdot \nabla_{\boldsymbol{R}} P_i \rangle - n \left(\frac{e\boldsymbol{E}}{m} \right) \cdot \langle \nabla_{\boldsymbol{v}_i} P_i \rangle \\ = \int_{\boldsymbol{v}_i} P_i(\boldsymbol{R}, \boldsymbol{v}_i, t) \left(\frac{\partial n_i}{\partial t} \right)_{\mathrm{el}} \mathrm{d}\boldsymbol{v}_i - \int_{\boldsymbol{v}_i} P_i(\boldsymbol{R}, \boldsymbol{v}_i, t) \left(\frac{\partial n_i}{\partial t} \right)_{S} \mathrm{d}\boldsymbol{v}_i. \end{aligned} \tag{2.27}$$

However, microreversibility between the direct and corresponding reverse encounters applies and

$$\int_{\boldsymbol{v}_i} \int_{\boldsymbol{v}_0} \int_{\Omega} P_i n_f N_0' [g_i \sigma(g_i, \psi)]\, \mathrm{d}\Omega\, \mathrm{d}\boldsymbol{v}_i\, \mathrm{d}\boldsymbol{v}_0 = \int_{\boldsymbol{v}_f} \int_{\boldsymbol{v}_0'} \int_{\Omega} P_f n_i N_0 [g_f \sigma(g_f, \psi)]\, \mathrm{d}\Omega\, \mathrm{d}\boldsymbol{v}_f\, \mathrm{d}\boldsymbol{v}_0', \tag{2.28}$$

since the collision is elastic ($g_i = g_f$), and since $d\boldsymbol{v}_i \mathrm{d}\boldsymbol{v}_0 = d\boldsymbol{v}_f \mathrm{d}\boldsymbol{v}_0'$, so that, with the aid of (2.4),

$$\int_{\boldsymbol{v}_i} P_i \left(\frac{\partial n_i}{\partial t} \right)_{\mathrm{el}} \mathrm{d}\boldsymbol{v}_i = \int_{\boldsymbol{v}_i} \int_{\boldsymbol{v}_0} \int_{\Omega'} [P_f(\boldsymbol{R}, \boldsymbol{v}_f, t) - P_i(\boldsymbol{R}, \boldsymbol{v}_i, t)]\, n_i N_0 [g \sigma(g, \psi)\, \mathrm{d}\Omega]\, \mathrm{d}\boldsymbol{v}_i\, \mathrm{d}\boldsymbol{v}_0. \tag{2.29}$$

When P_i is set to unity the effect of elastic collisions is null (conservation of ions with all speeds) and (2.27) reduces to

$$\frac{\partial n(\boldsymbol{R}, t)}{\partial t} + \nabla_{\boldsymbol{R}} \cdot n(\boldsymbol{R}, t)\, \langle \boldsymbol{v}_i \rangle = -\int_{\boldsymbol{v}_i} \left(\frac{\partial n_i}{\partial t} \right)_S \mathrm{d}\boldsymbol{v}_i, \tag{2.30}$$

the equation of continuity in the presence of the sink S. When P_i is taken as the vector $m\boldsymbol{v}_i$, since $m(\boldsymbol{v}_f - \boldsymbol{v}_i) = \mu(\boldsymbol{g}_f - \boldsymbol{g}_i)$, where μ is the ion–neutral reduced mass, we can show, after some analysis, that

$$\int_{\boldsymbol{v}_i} m\boldsymbol{v}_i \left(\frac{\partial n_i}{\partial t} \right)_{\mathrm{el}} \mathrm{d}\boldsymbol{v}_i = -\mu \int \boldsymbol{g}_i R_D(g_i)\, n_i(R, \boldsymbol{v}_i, t)\, N_0(\boldsymbol{R}, \boldsymbol{v}_0, t)\, \mathrm{d}\boldsymbol{v}_i\, \mathrm{d}\boldsymbol{v}_0, \tag{2.31}$$

where

$$R_D(g_i) = \int g_i (1 - \cos\psi)\, \sigma(g_i, \psi)\, \mathrm{d}\Omega \tag{2.32}$$

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is the momentum-transfer rate (cm^3 s^{-1}) which, for an ion–neutral pure polarization attraction, is independent of g_i, the relative speed $|(\boldsymbol{v}_i - \boldsymbol{v}_0)|$. Since the gas is, on average, considered at rest (with respect to the centre of mass of the ion pair), $\langle \boldsymbol{v}_0 \rangle$ is zero such that

$$\int_{\boldsymbol{v}_i} \boldsymbol{v}_i \left(\frac{\partial n_i}{\partial t}\right)_{\text{el}} \mathrm{d}\boldsymbol{v}_i = -n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \rangle \left[\frac{\mu}{m} R_D\, N(\boldsymbol{R},t)\right] \equiv -n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \rangle\,\nu, \tag{2.33}$$

where the configuration-space density of neutrals is

$$N(\boldsymbol{R},t) = \int N_0(\boldsymbol{R},\boldsymbol{v}_0,t)\,\mathrm{d}\boldsymbol{v}_0, \tag{2.34}$$

and the term in square brackets, the frequency ν of ion–neutral collisions, is only approximately a constant for ion–neutral interactions that depart from the pure polarization form. This frequency can also be derived from (2.5) with the result that

$$n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \rangle \nu = N \sum_{i=-V}^{C} v_i \sum_{f=-V}^{C} [n_f(R,E_f,t)\,k_{fi}(R) - n_i(R,E_i,t)\,k_{if}], \tag{2.35}$$

where v_i can be expressed in terms of E_i by (2.1). Hence with (2.33), (2.27) yields *the momentum equation*

$$\frac{\partial[n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \rangle]}{\partial t} + \nabla_{\boldsymbol{R}} \cdot [n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle] - \frac{e\boldsymbol{E}}{m} n(\boldsymbol{R},t) = -n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \rangle\,\nu + \int_{\boldsymbol{v}_i} \boldsymbol{v}_i \left(\frac{\partial n_i}{\partial t}\right)_S \mathrm{d}\boldsymbol{v}_i, \tag{2.36}$$

where the jk-element of the direct product $\langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle$ tensor is $v_i^{(j)} v_i^{(k)}$, the product of cartesian components $\{v_i^{(j)}, j = x, y, z\}$ of the velocity $\boldsymbol{v}_i$.

In ion–ion recombination: (*a*) the recombination–sink rate is many orders of magnitude less than the collisional rate so that the sink term in (2.36) can be neglected in comparison with $n\,\langle v_i \rangle\,\nu$; (*b*) the characteristic time for substantial variation of $n(\boldsymbol{R},t)\,\langle v_i \rangle$ is much longer than the mean time ν^{-1} between collisions so the time derivative in (2.36) is also negligible with respect to $n\,\langle v_i \rangle\,\nu$. Macroscopic diffusion is characterized by a flux vector $\boldsymbol{D} \cdot \nabla_{\boldsymbol{R}} n(\boldsymbol{R},t)$ both in equilibrium (Maxwellian) and in non-equilibrium situations, where the diffusion (symmetric) tensor is

$$\boldsymbol{D} = \langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle / \nu \quad (\text{cm}^2\,\text{s}^{-1}) \tag{2.37}$$

in terms of the averaged kinetic energy and collision frequency given in (2.33) or (2.35), while macroscopic drift is characterized by a flux vector $K\boldsymbol{E}\,n(\boldsymbol{R},t)$ where the mobility is

$$K = e/m\nu \quad (\text{cm}^2\,\text{Stat}\,\text{V}^{-1}\,\text{s}^{-1}). \tag{2.38}$$

The ion–neutral collision frequency ν is central to both quantities. In thermal equilibrium, i.e in the low E/N region where the thermal energy dominates the drift energy, $m\langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle = (kT)\,\mathbf{1}$, where $\mathbf{1}$ is the unit tensor. When departures from spatial isotropy are dominated by the electric field $\boldsymbol{E}$, the diffusion tensor $\boldsymbol{D}$ is diagonal with elements (D_L, D_T, D_T), longitudinal L and transverse T to the field direction $\hat{\boldsymbol{E}}$. In thermal equilibrium these elements are equal so that the Einstein relation $(De = KkT)$ holds.

We now assume (*c*) that $\langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle$ is R-independent, as in quasi-equilibrium when the phase-space distribution n_i separates into a product $n_1(\boldsymbol{R})\,n_2(\boldsymbol{v}_i)$ of separate functions of $\boldsymbol{R}$ and $\boldsymbol{v}_i$ as in the Maxwell–Boltzmann distribution (2.13*a*). Under assumptions (*a*)–(*c*), (2.36) provides the current

$$\boldsymbol{J}(\boldsymbol{R},t) = n(\boldsymbol{R},t)\,\langle \boldsymbol{v}_i \rangle = -\boldsymbol{D} \cdot \nabla_{\boldsymbol{R}} n(\boldsymbol{R},t) + K\boldsymbol{E}\,n(\boldsymbol{R},t), \tag{2.39}$$

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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

which together with the equation of continuity (2.30) implies

$$\frac{\partial n(\boldsymbol{R},t)}{\partial t}+\nabla_{\boldsymbol{R}}\cdot[-\boldsymbol{D}\cdot\nabla_{\boldsymbol{R}}\,n(\boldsymbol{R},t)+K\boldsymbol{E}\,n(\boldsymbol{R},t)] = -\int_{\boldsymbol{v}_{\mathrm{i}}}\left[\frac{\partial n_{\mathrm{i}}(\boldsymbol{R},\boldsymbol{v}_{\mathrm{i}},t)}{\partial t}\right]_S \mathrm{d}\boldsymbol{v}_{\mathrm{i}}$$

$$\equiv -\sum_{\mathrm{i}=-\mathrm{V}(R)}^{\mathrm{C}}\left[\frac{\partial n_{\mathrm{i}}(\boldsymbol{R},E_{\mathrm{i}},t)}{\partial t}\right]_S, \tag{2.40}$$

in which the summation or integration over all states i between $-\mathrm{V}(R)$ and C is equivalent to the $\boldsymbol{v}_{\mathrm{i}}$-integration for spherical R-symmetry. On introduction of the null collision quantity,

$$\sum_{\mathrm{i}=-\mathrm{A}}^{\mathrm{C}}\left\{N_{\mathrm{i}}^*(\boldsymbol{R},E_{\mathrm{i}},t)\sum_{\mathrm{f}=-\mathrm{A}}^{\mathrm{C}}k_{\mathrm{if}}(R)-\sum_{\mathrm{f}=-\mathrm{A}}^{\mathrm{C}}N_{\mathrm{f}}^*(\boldsymbol{R},E_{\mathrm{f}},t)\,k_{\mathrm{fi}}(R)\right\} = 0, \tag{2.41}$$

where $-\mathrm{A}$ is an arbitrary bound level, the sink term in (2.40) and given by (2.11) may be written as

$$\sum_{\mathrm{i}=-\mathrm{V}(R)}^{\mathrm{C}}\left[\frac{\partial n_{\mathrm{i}}}{\partial t}\right]_S = N\left[\sum_{\mathrm{i}=-\mathrm{V}(R)}^{\mathrm{C}}N_{\mathrm{i}}^*(\boldsymbol{R},E_{\mathrm{i}},t)\sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}}k_{\mathrm{if}}(R)-\sum_{\mathrm{i}=-\mathrm{V}}^{\mathrm{C}}\sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}}N_{\mathrm{f}}^*(\boldsymbol{R},E_{\mathrm{f}},t)\,k_{\mathrm{fi}}(R)\right](4\pi R^2N^+)^{-1}. \tag{2.42}$$

On integration of (2.40) over $\boldsymbol{R}$ and with the aid of Gauss's theorem, of spherical symmetry and of (2.2), we have, on replacing $\boldsymbol{E}$ by $-(\nabla V)/e$, *the appropriate flux equation*

$$\frac{\partial}{\partial t}\left[\int_0^R N^*(R,t)\,\mathrm{d}R\right]-4\pi R^2\left[D\frac{\partial n(R,t)}{\partial R}+n(R,t)\frac{K}{e}\frac{\partial V}{\partial R}\right]N^+ = -\alpha_3(R)\,n(R,t)\,N^+ \tag{2.43}$$

in terms of the net depletion (recombination) rate (cm^{-3} s^{-1})

$$\alpha_3(R)\,n(R,t)\,N^+ = N\int_0^R \mathrm{d}R\left\{\sum_{\mathrm{i}=-\mathrm{V}}^{\mathrm{C}}\left[N_{\mathrm{i}}^*(R,E_{\mathrm{i}},t)\sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}}k_{\mathrm{if}}(R)-\sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}}N_{\mathrm{f}}^*(R,E_{\mathrm{f}},t)\,k_{\mathrm{fi}}(R)\right]\right\}, \tag{2.44}$$

appropriate to the local (rather than asymptotic) density $n(R,t)$ of negative ions.

Subdivide the spectrum of internal energy into three regions: I, from C to some arbitrary bound level $-\mathrm{E}$; II, from $-\mathrm{E}$ to $-\mathrm{M}$; and III, from $-\mathrm{M}$ to $-\mathrm{V}$. Regions I and II are interconnected by upward and downward collisional transitions and are inaccessible from region III which is therefore connected with I and II only through downward transitions. Introduce the inward diffusion-drift operator

$$\hat{\mathscr{J}}_{\mathrm{i}} = D\nabla+(K/e)\,\nabla V\equiv D\exp(-V/kT)\,\nabla\exp(V/kT), \tag{2.45}$$

such that the inward current j (cm^{-2} s^{-1}) is $\hat{\mathscr{J}}_{\mathrm{i}}n(R,t)$, and the flux operator $\mathscr{D}$ which is such that the flux across the spheres each of radius R and surface area $\mathscr{S}$ is

$$\mathscr{D}[4\pi R^2N^+n(R,t)]\equiv -N^+\int_{\mathscr{S}}\boldsymbol{J}\cdot\mathrm{d}\boldsymbol{S}\equiv 4\pi R^2N^+j(R,t). \tag{2.46}$$

Einstein's relation $De = KkT$ has been used in (2.45) since the ions are in quasi-equilibrium with the field.

The contribution from region I to the left-hand side of (2.43) is therefore

$$-\frac{\partial}{\partial t}\left[\int_0^R N_{\mathrm{I}}^*(R,t)\,\mathrm{d}R\right]+\mathscr{D}N_{\mathrm{I}}^*(R,t) = N\int_0^R \mathrm{d}R\sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}}\left(N_{\mathrm{i}}^*\sum_{\mathrm{f}=-\mathrm{V}}^{-\mathrm{E}}k_{\mathrm{if}}-\sum_{\mathrm{f}=-\mathrm{M}}^{-\mathrm{E}}N_{\mathrm{f}}^*k_{\mathrm{fi}}\right), \tag{2.47a}$$

on making use of the null collision relation (2.41) with $-\mathrm{A}$ taken as $-\mathrm{E}$, and where explicit dependences in the right-hand side are omitted. The right-hand side of (2.47*a*) is constant for $R\geqslant R_E$, the outermost turning point associated with $-\mathrm{E}$, i.e. $V(R_E) = -E$. For region II,

$$-\frac{\partial}{\partial t}\left[\int_0^R \mathrm{N}_{\mathrm{II}}^*(R,t)\,\mathrm{d}R\right]+\mathscr{D}N_{\mathrm{II}}^*(R,t) = N\int_0^R \mathrm{d}R\sum_{\mathrm{i}=-\mathrm{M}}^{-\mathrm{E}}\left(N_{\mathrm{i}}^*\sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}}k_{\mathrm{if}}-\sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}}N_{\mathrm{f}}^*k_{\mathrm{fi}}\right), \tag{2.47b}$$

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while for region III,

$$-\frac{\partial}{\partial t}\left[\int_0^R N^*_{\mathrm{III}}(R,t)\,\mathrm{d}R\right]+\mathscr{D}N^*_{\mathrm{III}}(R,t) = -N\int_0^R \mathrm{d}R \sum_{\mathrm{i}=-\mathrm{V}}^{-\mathrm{M}} \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} N^*_{\mathrm{f}}\, k_{\mathrm{fi}}. \tag{2.47c}$$

For all three regions the number densities $N_{\mathrm{i}}^*(R, E_{\mathrm{i}}, t)$ on the right-hand side of (2.47) are solutions of the time-independent set (2.20) of coupled integro-differential equations. As previously noted, the left-hand side of (2.20) vanishes as R tends to the turning points $R(E_{\mathrm{i}})$ associated with bounded motion for a state of (negative) energy E_{i}. For the spectrum of bound levels in region II, it follows that the left-hand side of (2.20) does not depart appreciably from zero, particularly for levels $-$E and $-$M sufficiently close and deep, so that the radial extent of the associated bound orbits is minimal. Hence for region II, we have

$$N^*_{\mathrm{i}}(R,E_{\mathrm{i}},t) \sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} k_{\mathrm{if}}(R) \approx \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} N^*_{\mathrm{f}}(R,E_{\mathrm{f}},t)\, k_{\mathrm{fi}}(R);\ -E \geqslant E_{\mathrm{i}} \geqslant E_{-\mathrm{M}}, \tag{2.48}$$

as for quasi-equilibrium at each R. Thus the right-hand side of (2.47 *b*) vanishes in this approximation, in contrast to that for region I which includes the unbounded continuum and highly excited vibrational levels with large amplitudes of radial motion. Since all ion pairs with energy below $-E_{\mathrm{M}}$ have recombined and are irretrievably lost to the recombination in progress, $N^*_{\mathrm{i}}(R, (E_{-\mathrm{M}} \rightarrow E_{-\mathrm{V}}))$ vanishes, so that (2.48) implies, in the above approximation, that

$$\sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} N^*_{\mathrm{f}}(R,E_{\mathrm{f}},t)\, k_{\mathrm{fi}}(R) \approx 0, \quad E_{-\mathrm{M}} \geqslant E_{\mathrm{i}} \geqslant E_{-\mathrm{V}}, \tag{2.49}$$

which makes the right-hand side of (2.47 *c*) vanish. This effectively zero rate is not difficult to establish since the collision rates k_{if} are relatively large only between neighbouring levels, which in this case are in a range surrounding $-$M at which the number densities N^*_{f} of active ion pairs have already become much reduced from their equilibrium values (2.14) by the recombination process. Hence upon addition of 2.47 (*a*)–(*c*) over the three regions, the overall number density $N^*(R,t)$ satisfies

$$-\frac{\partial}{\partial t}\left[\int_0^R N^*(R,t)\,\mathrm{d}R\right] - N^+\int_{\mathscr{S}} \boldsymbol{J}\cdot\mathrm{d}\boldsymbol{S} = N\int_0^R \mathrm{d}R \sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}} \left(N^*_{\mathrm{i}} \sum_{\mathrm{f}=-\mathrm{V}}^{-\mathrm{E}} k_{\mathrm{if}} - \sum_{\mathrm{f}=-\mathrm{M}}^{-\mathrm{E}} N^*_{\mathrm{f}}\, k_{\mathrm{fi}}\right)$$

$$\equiv \alpha_3(R)\, n(R,t)\, N^+. \tag{2.50}$$

Steady-state conditions can be maintained by continuous generation of ion pairs with infinite separation at an inward flux rate

$$F_\infty = -N^+\int_{\mathscr{S}\rightarrow\infty} \boldsymbol{J}\cdot\mathrm{d}\boldsymbol{S}$$

so that

$$-\mathrm{d}(N^{\pm})/\mathrm{d}t + F_\infty = \alpha_3(R_E, t)\, n(R_E)\, N^+ = \alpha N^+N^-, \tag{2.51}$$

where R_E is the maximum radius associated with collisional transitions across the energy level $-$E, i.e. $V(R_E) = -E$. Hence the steady-state recombination coefficient is,

$$\begin{aligned}\alpha &= \alpha_3(R_E)\, n(R_E)/N^- \\ &= \left(\frac{N}{N^+N^-}\right)\int_0^{R_E} \mathrm{d}R \sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}} \left[N^*_{\mathrm{i}}(R,E_{\mathrm{i}}) \sum_{\mathrm{f}=-\mathrm{V}}^{-\mathrm{E}} k_{\mathrm{if}}(R) - \sum_{\mathrm{f}=-\mathrm{M}}^{-\mathrm{E}} N^*_{\mathrm{f}}(R,E_{\mathrm{f}})\, k_{\mathrm{fi}}(R)\right],\end{aligned} \tag{2.52}$$

where the number densities $N^*_{\mathrm{i}}(R, E_{\mathrm{i}})$ are determined by appropriate solution of (2.20) subject to the boundary conditions (2.21). The solutions will, in general, depend on gas density N, and α

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is then a general function of N. We note that (2.51) equates the steady-state inward flux αN^- or $4\pi R^2 \hat{\mathscr{J}}_{\mathrm{i}} n$ with $\alpha_3(R_{\mathrm{E}})\, n(R_{\mathrm{E}})$ which is the net rate of reaction within R_{E}. Thus (2.51) and (2.52) manifest quite clearly a partially absorbing boundary condition at R_{E} around which the ion density is continuous.

In summary we have obtained in this section the necessary equation (2.20) for solution of $N_{\mathrm{i}}^*(R, E_{\mathrm{i}}, t)$, and the appropriate equation (2.50) or equivalent expression (2.52) for the recombination coefficient α from the appropriate flux equation (2.43), a combination of a derived momentum equation (2.36) and the equation of continuity (2.30).

2.3. *Steady-state solution*

As $R \to R_E$ and beyond, $N^+ F_{\mathrm{c}}(R)$, the right-hand side of the flux (2.50) becomes constant. Let the ion-density $N^*(R, t)$ decay as $N^*(R) \exp(-At)$ so that (2.50) reduces, with the aid of (2.51), to

$$N^+ F_{\mathrm{c}}(R_E) = AN^+ \int_0^R 4\pi R^2 n^-(R)\, \mathrm{d}R + 4\pi R^2 N^+ D \exp(-V/kT) \frac{\partial}{\partial R}[n^-(R, t) \exp(V/kT)]$$
$$= \alpha_3(R)\, n^-(R)\, N^+ = \alpha N^+ N^-, \quad R \geqslant R_E. \tag{2.53}$$

where $n^-(R)$ denotes the density of negative ions.

The steady-state solution of (2.50) involves neglect in (2.53) of the A-term which depends on $n^-(R)$ within R_E. This neglect implies

$$\int_0^{R_E} 4\pi R^2\, n^-(R)\, \mathrm{d}R \ll 1 \tag{2.54a}$$

since $A \sim \alpha N^-$, such that
$$N^- \ll (\tfrac{4}{3}\pi R_E^3)^{-1}, \tag{2.54b}$$

i.e. few unreacted ions must be present in the ‘recombination volume’ as measured by the R_E-sphere in order that the frequency decay constant A may be neglected. Given $R_E \sim e^2/kT$ for example, appropriate to a bound level at kT below the dissociation limit, $N^\pm \ll 10^{16}\,\mathrm{cm}^{-3}$ for validity, while smaller R_E (as at high N) will extend the limits to higher $N^\pm$. Integration of (2.53) under the steady-state condition then yields

$$N^- - n^-(R) \exp(V/kT_{\mathrm{eff}}) = [F_{\mathrm{c}}(R_E)/\alpha_{\mathrm{h}}]\, P(R), \quad R \geqslant R_E, \tag{2.55}$$

where $\alpha_{\mathrm{h}} = 4\pi D R_e$, the high density Langevin limit (1.2);

$$P(R) = R_e \int_R^\infty \exp(V/kT_{\mathrm{eff}})\, \mathrm{d}R/R^2, \tag{2.56}$$

is an important function related to the probability (§2.4) that the R-ion pair expands by diffusional drift to infinite separation; and

$$R_e = e^2/(De/K) \equiv e^2/kT_{\mathrm{eff}}, \tag{2.57}$$

is the natural unit of length. At low E/N when the thermal energy dominates the drift energy, thermal equilibrium at temperature T is obtained, and the Einstein relation $De = KkT$ or, equivalently, $DR_e = Ke$, holds such that T_{eff} in (2.55) and (2.56) is simply T. The steady-state negative-ion density outside R_E can, with the aid of (2.53) be written in two equivalent forms:

$$n^-(R) = N^- \exp(-V/kT)\left[1 - \frac{\alpha}{\alpha_{\mathrm{h}}} P(R)\right] = \frac{N^- \exp[-V(R)/kT]\,[\alpha_{\mathrm{h}}/P(R)]}{\alpha_3(R) \exp[-V(R)/kT] + \alpha_{\mathrm{h}}/P(R)}, \quad R \geqslant R_E, \tag{2.58a}$$

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

in which T_{eff} is denoted here by T for brevity;

$$n^-(R) = N^-\exp(-V/kT)\exp\left[-\frac{R_e}{\alpha_\text{h}}\int_R^\infty \alpha_3(R)\,R^{-2}\,\mathrm{d}R\right]. \tag{2.58b}$$

Hence the overall recombination coefficient α from (2.53) is

$$\alpha = \alpha_3(R_E)\,n^-(R_E)/N^- = \frac{\alpha_3(R_E)\exp[-V(R_E)/kT]\,[\alpha_\text{h}/P(R_E)]}{\alpha_3(R_E)\exp[-V(R_E)/kT]+\alpha_\text{h}/P(R_E)} = \text{const.} \tag{2.59}$$

in terms of α_h which is known, and of $\alpha_3(R_E)$ which is yet to be determined. Since α_3 is internally dependent on the phase densities, $N_\text{i}^*(R, E_\text{i})$, through (2.44), we note that α, with this required knowledge of N_i^*, may, of course, be determined directly from (2.52) rather than from (2.59). However, not only does (2.59) promote further physical and basic understanding of recombination, but it is also very effective when alternative means are used to deduce $\alpha_3(R_E)$, as, for example, in § 4.2. Steady-state conditions are also achieved at $R > R_E$ effectively instantaneously for low N, and after time lapse $t \gg R_E^2/D$ for high N (see § 2.5), and are independent of condition (2.54b).

Since $\alpha_\text{h} \sim N^{-1}$, from (2.58), at low gas densities N,

$$n^-(R) \approx N^-\exp[-V(R)/kT], \quad R \geqslant R_E, \tag{2.60}$$

the Boltzmann distribution, such that (2.59) tends at low N to

$$\alpha_{\text{lo}} = \alpha_3(R_E)\exp[-V(R_E)/kT] \equiv \alpha_{\text{rn}}(R_E), \tag{2.61}$$

which is from (2.53) the recombination coefficient that would pertain provided the Boltzmann ion-distribution were maintained (as at low N), i.e. α_{rn} in the absence of net ionic transport (as in a Boltzmann distribution) measures the rate of reaction within R_E. Thus, (2.59) reads,

$$\alpha = \alpha_{\text{rn}}\alpha_{\text{tr}}/(\alpha_{\text{rn}}+\alpha_{\text{tr}}), \tag{2.62}$$

where the recombination coefficient α_{hi} at high gas densities is,

$$\alpha_{\text{hi}} = 4\pi D\Big/\int_{R_E}^\infty \exp(KV/De)R^{-2}\,\mathrm{d}R = [\alpha_\text{h}/P(R_E)] \equiv \alpha_{\text{tr}} \tag{2.63}$$

the rate of ion transport by diffusional-drift. Hence, the ion number density (2.58) is

$$n^-(R) = N^-\exp(-V/kT)\left[1-\frac{\alpha}{\alpha_{\text{tr}}}\frac{P(R)}{P(R_E)}\right], \quad R \geqslant R_E. \tag{2.64}$$

At high N, therefore, $n^-(R)$ from (2.64) departs significantly from the Boltzmann distribution at $R \approx R_E$, where the reactivity of the ion pairs is strong; and at low N, n^- is approximately Boltzmann where the reactivity is weak. As N is increased, the reactivity of the ion pairs (resulting from 'effective' collisions in the increasingly dense gas) becomes so great compared with the rates of ionic transport that continued reaction causes significant depletion in the ionic concentration in a localized region, and the ion R-distribution from (2.64) is far from Boltzmann. This feature is, in general, responsible for the failure of the use of equilibrium kinetics (partition functions, etc.) or of equilibrium concentrations of reactants for rates of chemical reactions in a dense medium, in contrast to that evident for low density gases (see (2.60)). It is also this feature that invalidates the *ab initio* use of the Debye–Hückel interaction, appropriate only for equilibrium situations at asymptotic R, so as to acknowledge possible plasma sheathing effects when the ion densities $N^\pm$ are raised from $10^8\,\text{cm}^{-3}$ to about $10^{14}\,\text{cm}^{-3}$. Use of an interaction, self-consistent with the ionic distribution and recombination sink, is the correct procedure (see § 4).

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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

We note that α_3 and hence α_{lo} contain, in general, a complicated dependence on N through (2.44) and (2.20). The overall recombination rate (2.59) is, therefore, controlled by the rate-limiting step of the rate of ionic transport, as measured by α_{tr}, and of the rate of ion–ion reaction (by effective three-body collisions), as measured by α_{rn}. Thus, the full theoretical development of the relation (2.62) has provided basic insight into a relation previously suspected (Bates & Flannery 1969), of one that is useful when the rate α_{rn} of reaction can be deduced without explicit knowledge of the phase densities $N_{\text{i}}^*(R, E_{\text{i}})$, as in § 4.2.

The physical significance of $P(R)$ in (2.63) and in (2.64) where it provides the R-variation of the departure of $n^-(R)$ from pure Boltzmann is made apparent in the following subsection; further study is also made of the separation of recombination into its transport-rate and reaction-rate components.

2.4. *Partially absorbing and fully absorbing sinks: transport and reaction rates*

The time-dependent continuity equation (2.40) is

$$\frac{\partial n^-(R,t)}{\partial t} + \nabla_{\boldsymbol{R}} \cdot \boldsymbol{J} = -\sum_{\text{i}=-\text{V}(R)}^{\text{C}} \left[\frac{\partial n_{\text{i}}(\boldsymbol{R}, E_{\text{i}}, t)}{\partial t}\right]_S, \tag{2.65}$$

where the current vector (number of ions per second crossing unit area of an R-sphere)

$$\boldsymbol{J} = -D[\nabla n^-(\boldsymbol{R},t) + n^-(\boldsymbol{R},t)\, \nabla(V/kT)] \equiv -D \exp(-V/kT)\{\mathrm{d}[n^- \exp(V/kT)]/\mathrm{d}R\}\, \hat{\boldsymbol{R}}, \tag{2.66}$$

arises from diffusional drift of the ions with relative diffusion coefficient D in the gas Z under an external spherically symmetric field of potential $V(R)$. The sink term (2.11) has been shown to be,

$$\alpha_3(R,t)\, n^-(R,t)\, N^+ = N \int_0^R \mathrm{d}R \left\{ \sum_{\text{i}=-\text{E}}^{\text{C}} \left[N_{\text{i}}^*(R, E_{\text{i}}, t) \sum_{\text{f}=-\text{V}}^{-\text{E}} k_{\text{if}}(R) - \sum_{\text{f}=-\text{M}}^{-\text{E}} N_{\text{f}}^*(R, E_{\text{f}}, t)\, k_{\text{fi}}(R) \right] \right\}. \tag{2.67}$$

which equates the frequency of production of R-ion pairs by diffusional drift to the frequency of ion reaction within R.

Although the phase-space densities $n_{\text{i}}(R, E_{\text{i}}, t)$ are in principle solutions of the appropriate time-dependent Boltzmann equation (2.12), important progress can be achieved upon assumption of either an instantaneous reactive sink or a partially absorbing sink that operates for ion pairs with internal separations $R \leqslant S$. Also, the physical meaning of P in (2.63) becomes apparent. Thus (2.65) is equivalent, with $\boldsymbol{j} \equiv -\boldsymbol{J}$, to,

$$\frac{\partial n^-}{\partial t} - \frac{1}{R^2}\frac{\partial(R^2 j)}{\partial R} = 0, \tag{2.68}$$

solved subject to prescribed boundary conditions that characterize the sink under different gas densities.

The steady-state solutions at R_1 and R_2 therefore satisfy

$$[n^-(R) \exp(V/kT)]_{R_1}^{R_2} = (F/4\pi \mathrm{D})\, [P(R_1) - P(R_2)], \tag{2.69}$$

where $P(R)$ is given by (2.56) and F is the steady-state constant inward flux $4\pi R^2 j$. For ion pairs that react (neutralize) instantaneously within the sink S, as at high N,

$$\left.\begin{aligned} n^-(R,t) &= 0, & R &\leqslant S, \\ n^-(R,t) &= N^-, & R &\to \infty \end{aligned}\right\} \tag{2.70}$$

such that (2.68) yields,

$$\alpha_{\text{tr}} = \alpha_{\text{hi}} = F/N^- = 4\pi D \bigg/ \int_S^\infty \exp(V/kT)\, \mathrm{d}R/R^2, \tag{2.71}$$

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the transport rate, which at high N is equivalent to the recombination rate. This reduces to

$$\alpha_{\mathrm{d}} = 4\pi DS \tag{2.72}$$

when the interaction V between the ions is neglected, and to

$$\alpha_{\mathrm{hi}} = 4\pi DR_e/[1-\exp(-R_e/S)], \tag{2.73}$$

for pure coulomb attraction

$$V/kT = -Z_1Z_2e^2/RkT \equiv -(R_e/R) \tag{2.74}$$

between ions of charge Z_1e and $-Z_2e$.

For recombination in a gas, (2.72) and (2.73) are the diffusion and diffusional-drift results of Harper (1932) and of Bates (1975) respectively. For coagulation of colloid suspensions in a liquid of permittivity ϵ, analogous expressions (with $R_e = Z_1Z_2e^2/\epsilon kT$) have been obtained by Smoluchowski (1917) and by Debye (1942). For this reason the full time-dependent equation (2.68) for a spherical field is frequently referenced as the Debye–Smoluchowski equation, derived originally by Smoluchowski (1916, 1917) from a stochastic random-walk picture of the process. The interesting feature is that it is a natural consequence of the basic microscopic treatment, which therefore provides its full generalization (2.65) and (2.67) to an arbitrary compressible sink based on detailed collisional kinetics which in turn depend on the phase-space densities $n_{\mathrm{i}}(R, E_{\mathrm{i}}, t)$. However, with this knowledge of n_{i}, the steady-state α can be obtained directly from (2.52), rather than from the solution of (2.65).

It is interesting to note from comparison of (2.72) and (2.73) that proper account of the interaction field is acknowledged simply by replacing S in the field-free case (2.72) by $R_e/P(S)$; and that (2.72) alone is incorrect if realistic $S \propto (R_e/N)^{\frac{1}{2}}$ (see § 4.2) are adopted. As N is increased, it is obvious that the three-body reaction zone must decrease and cannot be arbitrarily held at R_e to ensure identity between (2.72) and the correct limit (2.73). This note helps resolve previous confusion that existed (see Flannery 1976, p. 423) between treatments based either on pure diffusion (Harper 1932) or on pure mobility (Langevin 1903). Neither treatment is rigorously correct: mobility and diffusion effects must be coupled as in (2.71), although *only* for pure Coulomb attraction any error in Langevin's derivation disappears in the high-N limit unlike that involved with (2.72). This coupling also ensures thermodynamic equilibrium between effects of mobility and diffusion and is very important to the general determination of the phase-space densities (§ 5.2) at intermediate and high N.

A correlation can be established between two problems differing only in the generation boundary condition, i.e. between the recombination rate α for the homogeneous case where the process is driven by the boundary condition (2.70) for $n(R \rightarrow \infty)$ and the probability $\mathscr{P}^{\mathrm{c}}(R_0, R_E)$ for the diffusional-drift contraction of ions generated at R_0. Between R_0 and an instantaneous sink at $R_E < R_0$, (2.69) then yields

$$n^{-}(R)\exp(V/kT) = (F_{\mathrm{c}}/4\pi D)\,[P(R_E)-P(R)], \quad R_E \leqslant R \leqslant R_0, \tag{2.75}$$

where F_{c} is the net inward flux at R. In the presence of a sink at infinity,

$$n^{-}(R)\exp(V/kT) = (F_{\mathrm{e}}/4\pi D)\,P(R), \quad R_0 \leqslant R \leqslant \infty, \tag{2.76}$$

where F_{e} is the net outward flux at R. The probability that an isolated R_0-ion pair contracts by diffusional-drift is

$$\mathscr{P}^{\mathrm{c}}_{(\mathrm{s})}(R_0, R_E) = F_{\mathrm{c}}(R_0)/[F_{\mathrm{e}}(R_0)+F_{\mathrm{c}}(R_0)] = P(R_0)/P(R_E), \tag{2.77a}$$

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where the subscript (s) denotes that this $\mathscr{P}^{\rm c}$ pertains only to the case of spontaneous reaction. The probability that it expands (by diffusion against the force of attraction enhanced by the presence of the sink) to infinite internal separation is

$$\mathscr{P}^{\rm e}_{(\rm s)}(R_0, R_E) = F_{\rm e}(R_0)/[F_{\rm e}(R_0)+F_{\rm c}(R_0)] = 1-P(R_0)/P(R_E). \qquad (2.78\,a)$$

Thus, in the homogeneous case the negative ion density (2.58) can be rewritten as

$$n^-(R) = N^-\exp(-V/kT)\,[1-(\alpha/\alpha_{\rm tr})\,\mathscr{P}^{\rm c}_{(\rm s)}(R,R_E)] \xrightarrow{N\to\infty} N^-\exp(-V/kT)\,\mathscr{P}^{\rm e}_{(\rm s)}(R,R_E), \quad (2.79\,a)$$

where $\mathscr{P}^{\rm e}_{(\rm s)}$ is interpreted as the probability of diffusional escape of an R-ion to infinity in the presence of an instantaneous sink at R_E, and yields the fractional departure of $n^-(R)$ from pure Boltzmann at high N.

Hence the recombination rate at high N is the transport rate

$$\alpha_{\rm tr} = 4\pi R_E^2 D\exp(-V/kT)\,[\partial\mathscr{P}^{\rm c}_{(\rm s)}(R,R_E)/\partial R]_{R_E} = \alpha_{\rm h}/P(R_E), \qquad (2.80\,a)$$

where $\alpha_{\rm h}$ is the Langevin rate $4\pi DR_e$ and $\mathscr{P}^{\rm c}_{(\rm s)}$ is the probability of contraction from R to R_E against diffusional escape. Thus, the physical origin of P in the transport rate (2.63), which is identical to the recombination rate at high N, is now apparent. For pure coulomb attraction at high N when the sink radius $R_E \ll R_e$, the escape and recombination probabilities reduce to

$$\mathscr{P}^{\rm e}_{(\rm s)}(R) \sim \exp(-R_e/R), \qquad (2.81\,a)$$

and

$$\mathscr{P}^{\rm c}_{(\rm s)}(R) \sim 1-\exp(-R_e/R) \qquad (2.81\,b)$$

in agreement with Onsager (1938), and $n^-(R) \approx N^-\exp(-V/kT)\exp(-R_e/R)$.

Extension of the rate (2.73), valid only for instantaneous reaction after ion approach by mobility–diffusion, to lower gas densities N can be achieved by solving (2.68) subject to the more accurate boundary condition

$$j(R,t) = \Gamma_3 n^-(R,t), \quad R = S, \qquad (2.82)$$

where $\Gamma_3(R)$ is the speed of reaction of R-ion pairs. This (radiation or partial absorption) condition acknowledges the finite rate of reaction (by three-body effective collisions) after ion approach and implies a probability for subsequent diffusional-drift expansion of the unreacted ion pairs; if Γ_3 is infinitely fast as at high N then (2.70) is recovered. The diffusion–drift equation (2.68) governs ion transport up to S from which the ion departs inward with an effective finite speed $\Gamma_3(S)$ towards certain recombination within S, the radius that characterized the transition from transport (i.e. ineffective collisions) alone to reaction (i.e. effective collisions). Since

$$F = 4\pi R^2 j = (4\pi R^2\Gamma_3)\,n^-(R,t) = \alpha(t)\,N^-, \qquad (2.83)$$

then, provided Boltzmann equilibrium conditions for the ions are maintained, the recombination coefficient (F/N^-) would be

$$\alpha_{\rm rn} = (4\pi R^2\Gamma_3)\exp(-V/kT) \equiv \alpha_3(R)\exp(-V/kT), \qquad (2.84)$$

where we are reminded of the role of the finite rate of three-body energy-change collision (the reaction rate) by attaching 3 as a subscript to both α and Γ.

Hence, (2.82) is simply

$$\alpha_3(S)\,n^-(S,t) = 4\pi S^2 j(S,t) = \alpha N^-, \qquad (2.85)$$

which equates the *finite* collisional recombination rate within S to the flux of production of S-ion pairs. The basis of this radiation condition (2.82) or (2.85) has already been established

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theoretically by (2.52). Thus the steady-state solution of (2.68) for the ion density subject to (2.82) or (2.85) is

$$n^-(R, t \to \infty) = N^- \exp(-V/kT)\left[1 - \frac{\alpha}{\alpha_{\mathrm{tr}}}\frac{P(R)}{P(S)}\right] \tag{2.86}$$

which yields the following steady-state recombination coefficient:

$$\alpha(t \to \infty) = \frac{\alpha_3(S)\exp(-V(S)/kT)\,\alpha_{\mathrm{tr}}}{\alpha_3(S)\exp(-V(S)/kT) + \alpha_{\mathrm{tr}}} \equiv \frac{\alpha_{\mathrm{rn}}\alpha_{\mathrm{tr}}}{\alpha_{\mathrm{rn}} + \alpha_{\mathrm{tr}}} \tag{2.87a}$$

in agreement with the results (2.64) and (2.58) of the previous subsection.

For this case of finite reaction, a relation between α for the homogeneous case (with source only at infinity), and the contraction and escape probabilities $\mathscr{P}^{\mathrm{c,e}}(R, R_E)$ for the case where ion-pairs are continuously generated with internal separation R, can be obtained, as before, from (2.69) to yield

and $$\mathscr{P}^{\mathrm{c}}(R, R_E) = \frac{[n^-(R) - (\alpha/\alpha_{\mathrm{rn}})\,N^-\exp(-V/kT)]\,P(R)}{n^-(R)\,P(R_E) - (\alpha/\alpha_{\mathrm{rn}})\,N^-\exp(-V/kT)\,P(R)} \xrightarrow{\alpha_{\mathrm{rn}} \gg \alpha} \frac{P(R)}{P(R_E)} \tag{2.77b}$$

$$\mathscr{P}^{\mathrm{e}}(R, R_E) = \frac{P(R_E) - P(R)}{P(R_E) - (\alpha/\alpha_{\mathrm{rn}})\,N^-\exp(-V/kT)\,P(R)/n^-(R)} \xrightarrow{\alpha_{\mathrm{rn}} \gg \alpha} 1 - \frac{P(R)}{P(R_E)}. \tag{2.78b}$$

The number density of ion pairs generated with internal separations in the interval $\mathrm{d}R$ about R is $4\pi R^2 n^-(R)\,N^+\,\mathrm{d}R$.

When n^- is given by (2.86) with $S = R_E$ then

$$\mathscr{P}^{\mathrm{c}}(R, R_E) = \frac{\alpha}{\alpha_{\mathrm{tr}}}\frac{P(R)}{P(R_E)} \equiv 1 - \mathscr{P}^{\mathrm{e}}(R, R_E), \tag{2.77c}$$

so that $$n^-(R) = N^-\exp(-V/kT)\,\mathscr{P}^{\mathrm{e}}(R, R_E) \tag{2.79b}$$

and $$\alpha = 4\pi R_E^2\,D\exp(-V/kT)\,[\partial\mathscr{P}^{\mathrm{c}}/\partial R]_{R_E}, \tag{2.80b}$$

which are the direct generalizations of (2.79a) and (2.80a) to finite reaction. Thus $\mathscr{P}^{\mathrm{e}}$, in general, may be interpreted as the fractional departure of the ion density from Boltzmann equilibrium and is the solution of $\nabla\cdot\{\exp(-V/kT)\,\nabla\mathscr{P}^{\mathrm{e}}\} = 0$ subject to $\mathscr{P}^{\mathrm{e}}(\infty) \to 1$ and $D(\partial\mathscr{P}^{\mathrm{e}}/\partial R) = \Gamma_3\,\mathscr{P}^{\mathrm{e}}$ at R_E. Hence (2.85) and (2.87a) may be rewritten as

$$\alpha = \mathscr{P}_{\mathrm{r}}\alpha_{\mathrm{tr}} = \mathscr{P}^{\mathrm{e}}(R_E, R_E)\alpha_{\mathrm{rn}} \tag{2.87b}$$

where the probability of recombination

$$\mathscr{P}_{\mathrm{r}} = \alpha_{\mathrm{rn}}/(\alpha_{\mathrm{rn}} + \alpha_{\mathrm{tr}}) = \mathscr{P}^{\mathrm{c}}(R_E, R_E) \to \begin{cases} \alpha_{\mathrm{rn}}/\alpha_{\mathrm{tr}}, & \alpha_{\mathrm{rn}} \ll \alpha_{\mathrm{tr}}, \\ 1 & \alpha_{\mathrm{rn}} \gg \alpha_{\mathrm{tr}}, \end{cases} \tag{2.77d}$$

is simply the contraction probability for ion pairs generated with internal separations equal to the sink radius, i.e. $\mathscr{P}_{\mathrm{r}} \leqslant 1$ is the probability of intrapair (geminate) recombination.

Note that the boundary condition (2.85) is essentially identical with the exact condition (2.52) based on detailed kinetics when R_E is identified with S. This boundary condition can be suitably incorporated by rewriting the time-dependent Debye–Smoluchowski equation (2.68) as

$$-\frac{\partial n^-}{\partial t} + \nabla\cdot\boldsymbol{j} = \Gamma_3 n^-\delta(R - S) = \alpha_3 n^-\delta(\boldsymbol{R} - \boldsymbol{S}), \tag{2.88a}$$

which uniquely identifies the strength of the sink as the speed of three-body recombination; for Γ_3 large compared with the rate of ionic transport, the reactivity of the sink is effectively instantaneous, and α is given then by (2.73); while (2.87) pertains when Γ_3 is comparable with the ion transport rate. No deactivating reaction implies zero Γ_3, and hence zero rate of recombination.

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PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

The number density N_i of all ion pairs AB with internal separation $R \geqslant S$ then decays at a rate

$$-\frac{\mathrm{d}N_i}{\mathrm{d}t} = -\frac{\partial}{\partial t}\int_S^\infty 4\pi R^2 N^+ n^-(R,t)\,\mathrm{d}R = [4\pi S^2 \Gamma_3 n^-(S,t) - \{F_\infty - 4\pi S^2 j(S-\epsilon, t)\}]\,N^+$$
$$= \alpha(t)\,N^+N^- - F_\infty N^+, \qquad (2.88\,b)$$

where F_∞ is the rate (s^{-1}) of generation of negative ions at infinity, and α is the time-dependent rate ($\mathrm{cm^3\,s^{-1}}$) of recombination appropriate to asymptotic ion densities $N^\pm$. If the ion current approaching S is absorbed by reaction within S, then $\lim_{\epsilon\to 0} j(S-\epsilon, t) \to 0$. In steady state, the rate $4\pi R^2 j(R,t)$ from (2.88a) is constant for $R \geqslant S+\epsilon$ and equals both the production and absorption rates F_∞ and $4\pi S^2 \Gamma_3 n^-$, respectively, in (2.88b).

In conclusion, this subsection has emphasized the decomposition of the recombination rate α into its reaction and transport components, α_{rn} and α_{tr}, respectively, which act in series so that $\alpha = \mathscr{P}_{\mathrm{r}}\alpha_{\mathrm{tr}}$ in terms of the recombination probability $\mathscr{P}_{\mathrm{r}}$ of (2.77d), and is determined by the rate limiting step α_{rn} or α_{tr} in the limit of low N and high N respectively. Also the relation has been developed between α and $\mathscr{P}_{\mathrm{r}}$ for the homogeneous case with the escape probability $\mathscr{P}^{\mathrm{e}}$ of ions generated within the medium. Steady-state recombination can therefore be regarded as being maintained either by a continuous source in ions at infinity or by a source that generates within the medium R-ion pairs with density (2.86). In the latter picture, the recombination probability $\mathscr{P}_{\mathrm{r}}$ is simply the probability $\mathscr{P}_{\mathrm{c}}$ for contraction of those geminate R_E ion pairs so generated. Also proper contact has been established between the microscopic treatment and the generalized Debye–Smoluchowski equation (2.88a) which blends the macroscopic phenomena of diffusional-drift (which is characterized by the departure from pure classical ion–ion trajectories to a zigzag statistical pattern) and reaction between individual ion pairs. The sink in (2.88a) is compressible in the sense that its radius S is determined by collisional kinetics, which depends on the gas density N, as explicitly shown in § 4.2 where S is shown to contract from *ca.* R_e to *ca.* $(R_e \lambda_i)^{\frac{1}{2}}$ as N is increased.

2.5. *Analytical solution of the time-dependent generalized Debye–Smoluchowski equation*

Equation (2.65) is frequently called by those interested in coagulation in colloid solutions the Debye–Smoluchowski equation after the original authors who found its steady-state solution for the field-free case ($V = 0$) and a coulomb interaction respectively, appropriate to an instantaneous sink ($\mathscr{P}_{\mathrm{r}} \to 1$ or $\Gamma \to \infty$). While an exact time-dependent solution can be immediately obtained in the field-free case, there has as yet been no exact solution obtained for a general interaction V, although a large body of literature exists on various analytical approximations for the coulomb interaction. These are based on Green functions, perturbation expansions, 'prescribed' diffusion, etc. (Mozumder 1968, Abell & Mozumder 1972, Abell *et al.* 1972, Magee & Tayler 1972), and on the Mathieu equation (Hong & Noolandi 1978) via the resemblance between (2.65) for the coulomb interaction and the Schrödinger equation with an R^{-4}-potential. It may also, of course, be solved by numerical procedures (Freed & Pedersen 1976).

The generalized equation (2.88a) is of basic significance not only to ion–ion and atom–atom recombination in a gas and in dilute ionic solutions, but also to medical radiology and to diffusion- and field-controlled reactions in metabolizing systems (as enzyme–substrate reactions in a cell (Reid 1952)). It is of general importance in theoretical physics. In this section, we present an

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approximate yet accurate analytical time-dependent solution, and associated recombination rates, of the equation

$$\frac{\partial n(R,t)}{\partial t} = \frac{1}{R^2}\frac{\partial}{\partial R}(R^2 j) \tag{2.89a}$$

with a general diffusional-drift current

$$j(R,t) = D\exp(-V/kT)\,\partial[n(R,t)\exp(V/kT)]/\partial R. \tag{2.89b}$$

Our basic equation (2.50) derived from microscopic principles is, in effect, equivalent to (2.89) solved subject to certain boundary conditions.

The boundary conditions are

$$n(R\to\infty,t) = N^-\exp(-V/kT), \tag{2.90}$$

the Boltzmann distribution, for continuous generation of ions at infinity, and, either

$$n(R,t) = 0, \quad R \leqslant S, \tag{2.91a}$$

for an instantaneous sink within a sphere of radius S, or

$$\Gamma_3 n(S,t) = j(S,t), \tag{2.91b}$$

for a partially absorbing sink where Γ_3 is, as before, the speed of (three-body) reaction for ion pairs brought to internal separation S by ion transport such that

$$\alpha_3 = 4\pi S^2\Gamma_3. \tag{2.91c}$$

The initial ($t = 0$) distribution

$$n(R,t=0) = N^-\exp(-V/kT), \tag{2.92}$$

is assumed Boltzmann. Two examples follow below.

(*a*) *Field-free case*, $V = 0$. Although the exact diffusion-controlled solution ($V = 0$) is known (Reid 1952), being analogous to heat conduction through a sink, we include it here for use in the case of general $V(R)$. Introduce the dimensionless quantities

$$r = R/S-1, \quad \tau = Dt/S^2, \tag{2.93}$$

and let

$$n'(R,t) = (R/S)\,n(R,t), \tag{2.94}$$

such that (2.89) with $V = 0$ reduces to

$$\partial n'(r,\tau)/\partial\tau = \partial^2 n'(r,\tau)/\partial r^2. \tag{2.95}$$

This equation can be solved directly by the method of Laplace transformation to give

$$n_{\mathrm{d}}^{(\mathrm{s})}(R,t) = N^-\{1-(S/R)\,\mathrm{erfc}\,[(R-S)/2(Dt)^{\frac{1}{2}}]\}, \tag{2.96}$$

appropriate to diffusion (d) controlled transport and spontaneous (s) reaction for an initial random distribution N^-, where the error function (or probability integral)

$$\mathrm{erfc}\,\chi = \frac{2}{\sqrt{\pi}}\int_{\chi}^{\infty}\exp(-\chi^2)\,\mathrm{d}\chi. \tag{2.97}$$

The rate of recombination for this case ($V = 0$) is

$$\alpha_{\mathrm{d}}^{(\mathrm{s})}(t) = 4\pi S^2 j(S,t)/N^- = \alpha_{\mathrm{d}}[1+S/(\pi Dt)^{\frac{1}{2}}], \tag{2.98a}$$

where

$$\alpha_{\mathrm{d}} = 4\pi SD \tag{2.98b}$$

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is the steady-state ($t \to \infty$) solution (2.72) obtained by Smoluchowski (1917) for coagulation in colloid solutions and by Harper (1932) for ion–ion recombination in a gas. The rate of decrease in the number $\mathscr{N}_R$ of diffusing species outside S can be evaluated directly from,

$$\frac{\mathrm{d}\mathscr{N}_R}{\mathrm{d}t} = N^- \frac{\mathrm{d}}{\mathrm{d}t}\int_S^\infty 4\pi SR\, \mathrm{erfc}\,[(R-S)/2(Dt)^{\frac{1}{2}}]\,\mathrm{d}R = \alpha_\mathrm{d}^{(\mathrm{s})} N^-, \tag{2.99}$$

where the derived $\alpha_\mathrm{d}^{(\mathrm{s})}$ is identical with (2.98), as expected from (2.89*a*). Under the condition (2.91*b*) for finite (f) reaction and diffusive transport,

$$n_\mathrm{d}^{(\mathrm{f})}(R,t) = N^-\{1+(\alpha/\alpha_\mathrm{d})\,(S/R)\,[\exp\,(2\Omega\chi)\exp\chi^2\,\mathrm{erfc}\,(\chi+\Omega)-\mathrm{erfc}\,\Omega]\}, \tag{2.100}$$

where the time dependence is contained in

$$\chi(t) = (1+\alpha_3/\alpha_\mathrm{d})\,(Dt)^{\frac{1}{2}}/S \equiv (\alpha_3/\alpha)\,(Dt)^{\frac{1}{2}}/S, \tag{2.101}$$

and in

$$\Omega(t) = (R-S)/2(Dt)^{\frac{1}{2}}, \tag{2.102}$$

which vanishes at the sink, and

$$\alpha = \alpha_3\alpha_\mathrm{d}/(\alpha_3+\alpha_\mathrm{d}) \tag{2.103}$$

in terms of (2.91*c*) and (2.99). When the rate α_3 of reaction is much larger than the rate α_d of ion transport, $\chi \to \infty$, $\alpha = \alpha_\mathrm{d}$, the limiting rate, and (2.96) is recovered from (2.100). The time-dependent recombination rate from the radiation condition (2.91*b*) with (2.100) is

$$\alpha_\mathrm{d}^{(\mathrm{f})}(t) = \alpha_3 n_\mathrm{d}^{(\mathrm{f})}(S,t)/N^- = \alpha[1+(\alpha_3/\alpha_\mathrm{d})\exp\chi^2\,\mathrm{erfc}\,\chi], \tag{2.104}$$

and α is therefore the steady-state ($t \to \infty$) solution (since erfc → 0). The rate (2.104) also follows directly from $4\pi S^2 D(\mathrm{d}n_\mathrm{d}/\mathrm{d}R)_S$ as expected from (2.91*b*). At $t = 0$ the recombination rate $\alpha_\mathrm{d}^{(\mathrm{f})}(0)$ is simply the rate α_3 of reaction, as expected, since an initial ion distribution N^- has been assumed. Note that (2.98) for the instantaneous sink yields an infinite recombination rate, at $t = 0$, again as expected from the assumed infinite rate of reaction.

(*b*) *General field V*: The following analytical solution is based on the novel transformation from R to the variable

$$\tilde{R} = \left\{\int_R^\infty \exp\,[V(R)/kT]\,\frac{\mathrm{d}R}{R^2}\right\}^{-1}; \quad \frac{\mathrm{d}\tilde{R}}{\mathrm{d}R} = \left(\frac{\tilde{R}}{R}\right)^2 \exp\,(V/kT), \tag{2.105}$$

a transformation not without its physical significance. It is related to the probability $\mathscr{P}_{(\mathrm{s})}^{\mathrm{c}}$ in (2.77*a*) that an R_0-ion pair will further contract by diffusion under V, in the presence of an *instantaneous sink* at S (or else to the diffusional expansion against V to infinite separation), i.e. (2.77*a*) is rewritten with the aid of (2.105) as

$$\mathscr{P}_{(\mathrm{s})}^{\mathrm{c}}(R_0,S) = \tilde{R}(S)/\tilde{R}(R_0) = \tilde{S}/\tilde{R}_0. \tag{2.106}$$

Let

$$n_V(R,t) = n(R,t)\exp\,(V/kT), \tag{2.107}$$

such that (2.89) becomes

$$\frac{\partial n_V(\tilde{R},t)}{\partial t} = \frac{\tilde{D}}{\tilde{R}^2}\frac{\partial}{\partial \tilde{R}}\left[\tilde{R}^2\frac{\partial n_V(\tilde{R},t)}{\partial \tilde{R}}\right], \tag{2.108}$$

where the transformed diffusion coefficient (cm² s⁻¹) is

$$\tilde{D} = D(\mathrm{d}\tilde{R}/\mathrm{d}R)^2. \tag{2.109}$$

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THE ROYAL SOCIETY A
PHILOSOPHICAL TRANSACTIONS OF

The form of this equation is, in the transformed $\tilde{R}$-representation, identical with that for the field-free case in the original R-representation. Accordingly, introduce scaled quantities (2.93) and

$$\tilde{r} = (\tilde{R}/\tilde{S})-1, \quad \tilde{\tau} = \tilde{D}t/\tilde{S}^2, \quad n' = (\tilde{R}/\tilde{S})\, n_V(\tilde{R}, t) \tag{2.110}$$

such that (2.108) reduces to

$$\frac{\partial n'(\tilde{r}, \tau)}{\partial \tau} = \left(\frac{\mathrm{d}\tilde{r}}{\mathrm{d}r}\right)^2 \frac{\partial^2 n'(\tilde{r}, \tau)}{\partial \tilde{r}^2} = \frac{\partial^2 n'}{\partial r^2} + \left\{\left(\frac{\mathrm{d}\tilde{r}}{\mathrm{d}r}\right)^2 \frac{\mathrm{d}^2 r}{\mathrm{d}\tilde{r}^2}\right\} \frac{\partial n'}{\partial r} \tag{2.111a}$$

which suggests the following two procedures for solution. Assume $(\mathrm{d}\tilde{r}/\mathrm{d}r)$ remains constant such that introduction of $\tilde{\tau}$ of (2.110) yields

$$\frac{\partial n'(\tilde{r}, \tilde{\tau})}{\partial \tilde{\tau}} = \frac{\partial^2 n'(\tilde{r}, \tilde{\tau})}{\partial \tilde{r}^2} \tag{2.111b}$$

which is the field-free diffusion equation in $\tilde{r}, \tilde{\tau}$-space. Alternatively, since

$$\left(\frac{\mathrm{d}\tilde{r}}{\mathrm{d}r}\right)^2 \frac{\mathrm{d}^2 r}{\mathrm{d}\tilde{r}^2} = -S\left[\frac{2\tilde{R}}{R^2}\exp(V/kT) - \frac{2}{R} + \frac{\partial}{\partial R}(V/kT)\right] \tag{2.112}$$

in the right-hand side of (2.111 a) vanishes to $O(R^{-3})$ for the Coulomb interaction and is negligible for $R^3 \geqslant R^3_{\min} = S(e^2/kT)^2$,

$$\frac{\partial n'(r, \tau)}{\partial \tau} = \frac{\partial^2 n'(r, \tau)}{\partial r^2}, \tag{2.111c}$$

the one-dimensional diffusion equation in r, τ-space.

The full solution of (2.89) appropriate to spontaneous reaction (2.91 a) is therefore, after some analysis, of (2.111 b),

$$n^{(\mathrm{s})}(R, t) = N^- \exp(-V/kT)\left\{1 - \frac{\tilde{S}}{\tilde{R}} \operatorname{erfc}\left[\frac{(\tilde{R}-\tilde{S})}{2(Dt)^{\frac{1}{2}}} \frac{\mathrm{d}R}{\mathrm{d}\tilde{R}}\right]\right\}. \tag{2.113}$$

The recombination rate then reduces to

$$\alpha^{(\mathrm{s})}(t) = 4\pi S^2 j(S, t)/N^- = \alpha_{\mathrm{tr}}\left\{1 + \frac{S^2 \exp[-V(S)/kT]}{\tilde{S}(\pi D t)^{\frac{1}{2}}}\right\} \tag{2.114}$$

where the steady-state transport rate

$$\alpha_{\mathrm{tr}} = 4\pi \tilde{S} D = 4\pi D R_e/P(S) \equiv \alpha_{\mathrm{hi}} \tag{2.115}$$

with

$$P(S) = R_e/\tilde{S} = R_e \int_S^\infty \exp(V/kT) \frac{\mathrm{d}R}{R^2}, \tag{2.116}$$

in terms of the natural length e^2/kT as in (2.56). Under the condition of equilibrium with the field when the Einstein relation written as $DR_e = Ke$ holds, the steady-state solution is, for a coulombic attraction

$$\alpha^{(\mathrm{s})}_{\mathrm{hi}} = 4\pi K e/[1 - \exp(-R_e/S)], \tag{2.117}$$

as previously obtained by Bates (1975) via the steady-state analysis of an instantaneous sink, leading to (2.73). The present paper represents the first time, to the author's knowledge, that the transient solutions (2.113) and (2.114) for instantaneous reaction in the presence of a general field have been obtained. Since constant $(\mathrm{d}\tilde{R}/\mathrm{d}R)$ is assumed in (2.111 b), $(\tilde{R}-\tilde{S})(\mathrm{d}R/\mathrm{d}\tilde{R})$ can be replaced by $R-S$ which yields a result also obtained via (2.111 c).

The boundary condition (2.91 b) for finite reaction under a field is

$$\Gamma_3(S)\, n^-(S, t) = D \exp[-V(S)/kT]\{\partial[n(R, t) \exp(-V/kT)]/\partial R\}, \tag{2.118}$$

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which for (2.111 b) and (2.111 c) transforms as

$$\left[\frac{\partial n'}{\partial \tilde{r}}\right]_0 = \left(\frac{\alpha_{\mathrm{rn}}}{\alpha}\right) n'(0,t) \tag{2.119a}$$

and

$$\left[\frac{\partial n'}{\partial r}\right]_0 = \left(\frac{\alpha_{\mathrm{rn}}}{\alpha}\right)\left(\frac{\mathrm{d}\tilde{r}}{\mathrm{d}r}\right)_0 n'(0,t) = \left(\frac{\alpha_{\mathrm{rn}}}{\alpha}\right)\left[\frac{\tilde{S}}{S}\exp V(S)/kT\right] n'(0,t) \tag{2.119b}$$

respectively, where

$$\alpha_{\mathrm{rn}} = 4\pi S^2\Gamma_3 \exp\left(-V(S)/kT\right), \quad \alpha = (\alpha_{\mathrm{rn}}\alpha_{\mathrm{tr}})/(\alpha_{\mathrm{rn}}+\alpha_{\mathrm{tr}}) \tag{2.120}$$

are the reaction and recombination rates, as before.

Hence, after exercising due care, we obtain for a general interaction the full time-dependent solution obtained from Laplace transformation of (2.111 b) subject to boundary conditions (2.90) and (2.119 a), and to the Boltzmann initial condition (2.92):

$$n(R,t) = N^-\exp\left(-V/kT\right)\{1+(\alpha/\alpha_{\mathrm{tr}})(\tilde{S}/\tilde{R})[\exp(2\tilde{\Omega}\tilde{\chi})\exp\tilde{\chi}^2\,\mathrm{erfc}\,(\tilde{\chi}+\tilde{\Omega})-\mathrm{erfc}\,\tilde{\Omega}]\}, \tag{2.121a}$$

where

$$\tilde{\chi}(t) = (1+\alpha_{\mathrm{rn}}/\alpha_{\mathrm{tr}})(\tilde{D}t)^{\frac{1}{2}}/\tilde{S}, \tag{2.121b}$$

$$\tilde{\Omega}(t) = (\tilde{R}-\tilde{S})/2(\tilde{D}t)^{\frac{1}{2}}, \tag{2.121c}$$

in terms of (2.105) and (2.109). Solution of (2.111 c) subject to (2.119 b) also yields (2.121 a) but with $\tilde{D}$ evaluated at S, and with $\tilde{\Omega}$ replaced by Ω of (2.102), which are essentially equivalent since constant $\mathrm{d}\tilde{R}/\mathrm{d}R$ is basic to both methods.

The full time-dependent recombination rate now follows from (2.121 a) as

$$\alpha(t) = \alpha_3 n^-(S,t)/N^- = \alpha[1+(\alpha_{\mathrm{rn}}/\alpha_{\mathrm{tr}})\exp\tilde{\chi}_S^2\,\mathrm{erfc}\,\tilde{\chi}_S], \tag{2.122a}$$

where $\tilde{\Omega}(R=S)$ in (2.121 c) vanishes, $\tilde{\chi}$ in (2.121 b) is, with the aid of (2.105), (2.109) and (2.121),

$$\tilde{\chi}_S = \left(1+\frac{\alpha_{\mathrm{rn}}}{\alpha_{\mathrm{tr}}}\right)\frac{(Dt)^{\frac{1}{2}}}{S}\exp\left[V(S)/kT\right]\left[S\int_S^{\infty}\exp\left(V/kT\right)R^{-2}\,\mathrm{d}R\right]^{-1}, \tag{2.122b}$$

at S. For the field-free case ($V=0$), (2.121) and (2.122) reduce to the diffusion-controlled results (2.100) and (2.104), respectively. Expressions (2.120) and (2.122) are the analytical time-dependent densities and rates obtained from (2.89) for an arbitrary spherical field $V(R)$ for an initial Boltzmann distribution, and are accurate where $(\mathrm{d}\tilde{r}/\mathrm{d}r)$ can be assumed constant in (2.111 a).

As t increases from zero,

$$\exp\chi^2\,\mathrm{erfc}\,\chi \rightarrow 1-(2/\sqrt{\pi})\,\chi+\chi^2-(4/3\sqrt{\pi})\,\chi^3+\ldots \tag{2.123}$$

such that

$$\alpha(t\rightarrow 0) = \alpha_{\mathrm{rn}}\left\{1-\frac{2}{\sqrt{\pi}}\frac{\alpha_{\mathrm{rn}}}{\alpha_{\mathrm{tr}}}\frac{(Dt)^{\frac{1}{2}}}{S}\exp\left[V(S)/kT\right]\left[S\int_S^{\infty}\exp\left(V/kT\right)R^{-2}\,\mathrm{d}R\right]^{-1}\right\} \tag{2.124}$$

decreases initially from the reaction rate α_{rn}. As $t\rightarrow\infty$,

$$\exp\chi^2\,\mathrm{erfc}\,\chi \rightarrow (1/\chi\sqrt{\pi})\,(1-1/2\chi^2+3/4\chi^4\ldots), \tag{2.125}$$

such that the long-time dependence is

$$\alpha(t\rightarrow\infty) = \alpha\left\{1+\frac{\alpha}{\alpha_{\mathrm{tr}}}\frac{S\exp\left[-V(S)/kT\right]}{(\pi Dt)^{\frac{1}{2}}}\left[S\int_S^{\infty}\exp\left(V/kT\right)R^{-2}\,\mathrm{d}R\right]\right\}. \tag{2.126}$$

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The transient rates (2.124) and (2.126) for short and long intervals of time are best observed at high gas densities when $\alpha_{\mathrm{rn}} \gg \alpha_{\mathrm{tr}} \approx \alpha$ respectively. The full transient densities (2.121) and rates (2.122) are of basic significance to all diffusion-drift phenomena in gases or dilute solutions, such as ion–ion, ion–atom and atom–atom recombination in dense gases, or coagulation of colloids in ionic solutions.

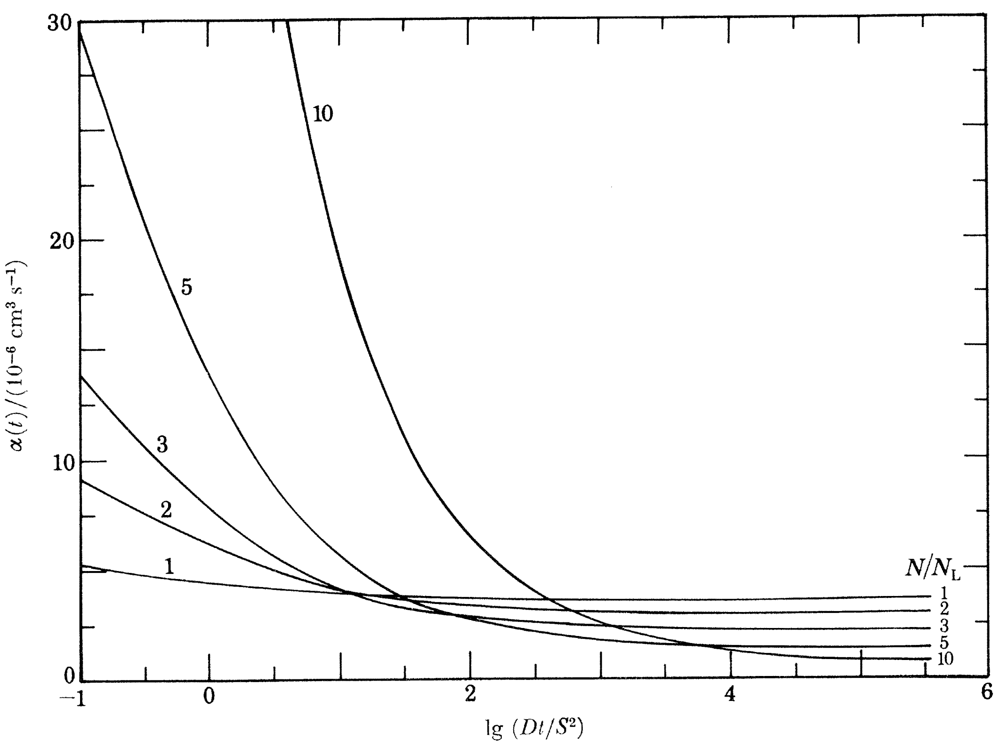

FIGURE 1. Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities N (in multiples of the Loschmidts number $N_{\mathrm{L}} = 2.69 \times 10^{19}\ \mathrm{cm}^{-3}$ at s.t.p.). Characteristic times (S^2/D) for diffusion are (16, 11, 8, 5, 3) × 10^{-12} s for $N/N_{\mathrm{L}} = 1, 2, 3, 5, 10$ respectively.

The full time dependence in (2.122*a*) for α is contained in (2.122*b*) for χ_S which, for a pure coulomb attraction, varies as

$$\tilde{\chi}_S(\tau) = (1+\alpha_{\mathrm{rn}}/\alpha_{\mathrm{tr}})\,\tau^{\frac{1}{2}}(R_e/S)\,[\exp\,(R_e/S)-1]^{-1}, \tag{2.127}$$

where the scaled time is

$$\tau = t/(S^2/D) \tag{2.128}$$

where S^2/D is the approximate time required for an ion to diffuse from the boundary to the centre of the sink.

With the aid of a simple expression, (4.12*a*), and associated quantities, derived in § 4.2 for the reaction rate α_{rn}, and the exact expression (2.63) or (2.71) for the transport rate, the full time dependence of the recombination rate (2.122*a*) can be explored. Figure 1 illustrates the variation of $\alpha(t)$ with t for several values (1, 2, 3, 5, and 10) of the gas density N (in multiples of $N_{\mathrm{L}} = 2.69 \times 10^{19}\,\mathrm{cm}^{-3}$, the number density at s.t.p.). These rates are appropriate to a fictitious (but representative) case of equal masses ($M = 16$ a.m.u.) of the ionic species with mobility $2\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ in an equal-mass gas and with δ_{i} in (4.17) taken as 0.6 (Flannery 1978). Figure 1 exposes features of basic significance to the physics of recombination.

Since the initial ion distribution is assumed to be in Boltzmann equilibrium, the initial rate of

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recombination $\alpha(t=0)$ is simply the reaction rate α_{rn}, in accord with (2.124). The ions then begin their transport and replace the reacted ions within a time S^2/D. Since the recombination is determined by the rate-limiting step of reaction and transport, its variation with time is best observed at high gas densities N where $\alpha_{\mathrm{rn}} \gg \alpha_{\mathrm{tr}}$ such that α decreases from α_{rn} to α_{tr}, the steady-state limit at $t \gg S^2/D$. Variation of α with t for $N \approx 10N_{\mathrm{L}}$, for example, reflects the change in α from reaction controlled transport. The reaction rate at high $N\,(\gtrsim 5N_{\mathrm{L}})$ is so large because the radial extent S of the sink becomes so contracted that the Boltzmann distribution of ions at its boundary is locally very large and offsets the inherent reduction in cross section. For $N \approx N_{\mathrm{L}}$ and lower, the transport is always faster than the reaction such that the reaction rate limits the rate of recombination at all times, and a straight-line dependence is observed as in figure 1. The steady-state limit is, of course, independent of any initial condition adopted.

Measurement of the variation of α with t at high $N(\gtrsim N_{\mathrm{L}})$ would, therefore provide valuable information about the physics intrinsic to recombination, i.e. of the transport component at $t \gg S^2/D$ and, more significantly, of the reaction component at high densities when $t \lesssim S^2/D$. Such experiments are feasible with modern techniques such as laser spectroscopy. In figure 1 are indicated relevant time-scales. The radii S of the sinks are compressible (§4.2) as N is raised, and the unit of time (S^2/D) varies from 1.6×10^{-11} s at a gas pressure of about 1 atm to 3×10^{-12} s at *ca.* 10 atm. The laser can be tuned to some known molecular rotational or vibrational transition since electronic transitions are precluded because of the time-scale. The ion densities can then be determined by fluorescence.

Figure 1 is, therefore, a striking illustration of the transition in recombination from reaction alone to the limiting step of reaction or transport. Verification is feasible, not only by laboratory experiment but also by Monte-Carlo computer experiments such as those of Bates (1980*c*) and of Bardsley & Wadehra (1980), suitably generalized to include explicit time dependence.

The basic equation (2.89) can be written to incorporate both the condition (2.91*b*) for a finite rate α_{rn} of reaction and the possibility of a scavenger reaction proceeding in parallel at a rate γn, by

$$-\frac{\partial n}{\partial t}+\nabla\cdot\boldsymbol{j}-\gamma n = \Gamma_3 n\,\delta(R-S). \tag{2.129}$$

By Laplace transformation, we can show that the time-dependent solutions are given by $n\exp(-\gamma t)$ and $\alpha\exp(-\gamma t)$, with n and α given by (2.121*a*) and (2.122*a*), respectively.

Finally, transient solutions of (2.129) appropriate to other initial conditions are important, for example where intense ionization is deposited into or produced within a localized system either by a high energy beam of particles or by radiation such that many ions may diffuse out of the localized system before neutralization occurs. The rate of disappearance of ion–ion or electron–ion pairs scattered along the track of the ionization beam is time-dependent and is given by the appropriate solution of (2.129) applicable to 'columnar' recombination rather than 'volume' recombination as discussed here.

When $\mathcal{N}$ ions are generated instantaneously by a spherical surface source at distance R_0 from the central positive ion, i.e. R_0-ion pairs are produced, (2.89) is solved subject to

$$\left.\begin{aligned} n(R,t=0) &= \mathcal{N}\exp(-V/kT)\,\delta(R-R_0)/4\pi R_0^2,\\ j(S,t) &= \Gamma_3\, n(S,t),\\ n(R\to\infty,t) &= 0. \end{aligned}\right\} \tag{2.130}$$

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For the field-free case ($V = 0$), by analogy with the corresponding problem in heat conduction (Carslaw & Yeager 1959), the solution can be written in terms of the quantities χ and Ω associated with a continuous source at infinity as

$$n(R, t;\, R_0, S) = \frac{\mathscr{N}}{4\pi R R_0}\frac{1}{(4Dt)^{\frac{1}{2}}}\left\{\frac{1}{\sqrt{\pi}}[\exp(-\Omega_0^2) + \exp(-\Omega_1^2)] - 2\chi \exp\chi^2 \exp 2\Omega_1\chi \operatorname{erfc}(\chi+\Omega_1)\right\}, \tag{2.131}$$

where $$\Omega_0 = (R-R_0)/2(Dt)^{\frac{1}{2}}, \quad \Omega_1 = (R+R_0-2S)/2(Dt)^{\frac{1}{2}} \tag{2.132}$$

are similar to (2.102), and $$\chi(t) = (1+\alpha_3/\alpha_{\mathrm{d}})\,(Dt)^{\frac{1}{2}}/S, \tag{2.133}$$

as before (equation (2.101)) in terms of (2.91*c*) and (2.99). If the ions are generated at the reaction surface, $R_0 = S$ and $\Omega_0 = \Omega_1$. The volume external to the spherical surface of the sink is $\mathscr{V}$ so that the frequency (s^{-1}) of recombination is then

$$\begin{aligned}\nu_{\mathrm{r}}(t) &= -\int_{\mathscr{V}}\left(\frac{\partial n}{\partial t}\right)\mathrm{d}\boldsymbol{R} = 4\pi S^2\,\Gamma_3\,n(S, t;\, R_0 = S)\\ &= [\mathscr{N}\Gamma_3/(4Dt)^{\frac{1}{2}}]\,[2/\sqrt{\pi} - 2\chi(t)\exp\chi^2 \operatorname{erfc}\chi]\\ &\equiv -[\mathscr{N}\Gamma_3/(4Dt)^{\frac{1}{2}}]\,\mathrm{d}(e^{\chi^2}\operatorname{erfc}\chi)/\mathrm{d}\chi\end{aligned} \tag{2.134}$$

The initial frequency $\nu_{\mathrm{r}}(0)$ is $\mathscr{N}\Gamma_3/(\pi Dt)^{\frac{1}{2}}$, and as $t \to \infty$, $\nu_{\mathrm{r}} \to$ zero as $\nu_{\mathrm{r}}(0)/2\chi^2$. The total number of ions that have recombined after time t is

$$\mathscr{N}_{\mathrm{r}}(t) = \int_0^t \nu_{\mathrm{r}}(t)\,\mathrm{d}t = \mathscr{P}_{\mathrm{r}}\mathscr{N}[1-\exp\chi^2(t)\operatorname{erfc}\chi(t)] \to \begin{cases}(2/\sqrt{\pi}\,\mathscr{P}_{\mathrm{r}}\mathscr{N}\chi, & t\to 0,\\ \mathscr{P}_{\mathrm{r}}\mathscr{N}, & t \to\infty,\end{cases} \tag{2.135}$$

where the probability of recombination in the absence of the field V is

$$\mathscr{P}_{\mathrm{r}}(V\to 0) = \alpha_3/(\alpha_3+\alpha_{\mathrm{d}}) \tag{2.136}$$

and remains less than unity in the presence of outward diffusion.

For a general field $V(R)$, the general solution appropriate to (2.130) is obtained by use of transformation (2.105) and of (2.111*c*) to yield.

$$\begin{aligned}n(R, t;\, R_0, S) = \frac{\mathscr{N}\exp(-V/kT)}{4\pi R_0^2}\left(\frac{\tilde{R}_0}{\tilde{R}}\right)(4Dt)^{-\frac{1}{2}}&\left\{\frac{1}{\sqrt{\pi}}[\exp(-\Omega_0^2)\right.\\ &\left. + \exp(-\Omega_1^2)] - 2\tilde{\chi}_S\exp\tilde{\chi}_S^2\exp 2\Omega_1\tilde{\chi}_S\operatorname{erfc}(\tilde{\chi}_S+\Omega_1)\right\},\end{aligned} \tag{2.137}$$

in terms of the corresponding tilde quantities (2.105) and (2.122*b*). For a coincident source and sink, the recombination frequency is

$$\nu_{\mathrm{r}}(t) = [\mathscr{N}\Gamma_3/(4Dt)^{\frac{1}{2}}]\,[2/\sqrt{\pi} - 2\tilde{\chi}_S(t)\exp\tilde{\chi}_S^2\operatorname{erfc}\tilde{\chi}_S]\exp(-V(S)/kT), \tag{2.138}$$

where $\tilde{\chi}_S$ is given by (2.122*b*). The number of recombined pairs after time t is

$$\mathscr{N}_{\mathrm{r}}(t) = \mathscr{P}_{\mathrm{r}}\mathscr{N}[1-\exp\tilde{\chi}_S^2\operatorname{erfc}\tilde{\chi}_S], \tag{2.139}$$

where the probability of recombination in the presence of general V, in terms of the reaction and transport rates α_{rn} and α_{tr}, respectively, is

$$\mathscr{P}_{\mathrm{r}} = \alpha_{\mathrm{rn}}/(\alpha_{\mathrm{tr}}+\alpha_{\mathrm{rn}}), \tag{2.140}$$

as before (equation (2.77*d*)). Thus $\mathscr{P}_{\mathrm{r}}$ is controlled by the relative rates of reaction and transport. At low N, $\mathscr{P}_{\mathrm{r}} \to \alpha_{\mathrm{rn}}/\alpha_{\mathrm{tr}}$ while at high N, $\mathscr{P}_{\mathrm{r}} \to 1$. Expressions (2.121*a*), (2.122*a*), (2.137) and

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(2.138) represent the first time that analytical solutions of the Debye–Smoluchowski equation subject to conditions (2.90)–(2.92) and (2.130), respectively, have been developed for any (general) interaction $V(R)$.

The above analysis has therefore shown that the same key quantities appear in two distinct time-dependent problems: homogeneous recombination where the process is driven by a source operating continuously at infinity; and geminate recombination where the process is initially established by an instantaneous source of ion pairs within the medium (as produced by a laser burst) and is controlled by the relative reaction and transport rates.

For intense ionization, the interaction between the ions can no longer be assumed *ab-initio* to be pure coulomb. The interaction V must then be determined by self-consistent (with the recombination) methods as developed in § 4.

Competition between the increased number of sinks (assumed equivalent) for the flux incident from infinity is acknowledged by the last term of the following equation:

$$\partial\rho(R,t)/\partial t = \nabla\cdot\hat{\mathscr{J}}_{\mathrm{i}}\rho - \Gamma_3\rho\delta(R-S) - \alpha(t)\,\langle\rho(t)\rangle_S\,\rho(R,t),\, R \geqslant S, \tag{2.141}$$

for the concentration ρ in cm^{-6} of R-ion pairs such that $\rho\,\mathrm{d}\boldsymbol{R}$ is the concentration of ion pairs with internal separation $\boldsymbol{R}$ in the interval $\mathrm{d}\boldsymbol{R}$ about $\boldsymbol{R}$. In (2.141) the density of unreacted ion pairs (with $R > S$) is

$$\langle\rho(t)\rangle_S = \int_{\mathscr{V}}\rho(R,t)\,\mathrm{d}\boldsymbol{R} = \int_S^\infty 4\pi R^2\rho(R,t)\,\mathrm{d}R, \tag{2.142}$$

and the inward diffusional-drift operator $\hat{\mathscr{J}}_{\mathrm{i}}$ is given by (2.45) since we assume in addition that the diffusion coefficient D remains constant. Substitute

$$\rho(R,t) = C(t)\,g(R,t) \tag{2.143}$$

in (2.141) where C satisfies

$$\partial C(t)/\partial t = -\alpha\,\langle g(t)\rangle_S\,C^2(t), \tag{2.144}$$

such that the probability density or pair correlation function $g(R,t)$ satisfies the usual Debye–Smoluchowski equation,

$$\partial g/\partial t = \nabla\cdot\hat{\mathscr{J}}_{\mathrm{i}}g - \Gamma_3 g\delta(R-S) \tag{2.145}$$

for an isolated sink surrounding a positive ion (say).

Thus

$$C(t) = C_0\Big/\left[1 + C_0\int_0^t \alpha(t)\,\langle g(t)\rangle_S\,\mathrm{d}t\right], \tag{2.146}$$

where C_0 is the initial concentration of ion pairs, describes the time decay of all ion pairs via recombination, and $g(R,t)$ describes the spatial distribution of R-ion pairs. The recombination rate

$$\alpha(t) = -\frac{\mathrm{d}}{\mathrm{d}t}\left[\int_S^\infty 4\pi R^2\rho(R,t)\,\mathrm{d}R\right]\Big/N^+N^-, \tag{2.147}$$

therefore satisfies

$$\alpha(t)\,\{1 - (\langle g(t)\rangle_S^2\,C^2(t)/N^+N^-)\} = \alpha_0(t)\,C(t)/N^+ \tag{2.148}$$

where α_0 is the rate that is obtained from appropriate solution of (2.145) for an isolated sink (or constant C). When the initial concentration C_0 and the recombination time t are sufficiently small that

$$C_0\int_0^t \alpha(t)\,\langle g(t)\rangle_S\,\mathrm{d}t \ll 1, \tag{2.149}$$

and $C(t)$ remains constant $\approx N^\pm$ then equations (2.147) and (2.148) reduce to the case of an isolated sink with associated rate α_0.

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3. 'GENERALIZED QUASI-EQUILIBRIUM', STEADY-STATE METHOD FOR THE REACTION AND TRANSPORT RATES

Rather than from the complete determination of α via solutions of (2.20) inserted in (2.52), or alternatively in (2.59) via α_3 of (2.44), intrinsic physics may yet be uncovered from the solution of (2.43) with (2.44) modified by a procedure suggested by (2.35): either neglect upward transitions k_{fi}; or, in effect, rewrite the energy-change frequency terms on the right-hand side of (2.47a), with the aid of the null-collision relation (2.41), as

$$N \sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}} \left(N_{\mathrm{i}}^{*} \sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} k_{\mathrm{if}} - \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} N_{\mathrm{f}}^{*} k_{\mathrm{fi}} \right) \approx N^{*} \nu(R), \tag{3.1}$$

where $\nu(R)$ is some averaged collision frequency v_{d}/λ in terms of a mean free path λ. With the aid of (2.46), (2.53) and of relation (2.10), (2.50) in this approximation yields,

$$4\pi R^2 D \left[\frac{\mathrm{d}n(R)}{\mathrm{d}R} + n(R) \frac{\mathrm{d}(V/kT_{\mathrm{eff}})}{\mathrm{d}R} \right] = \alpha_3(R)\, n(R) \approx 4\pi \int_0^{\min(R,\, R_E)} \nu(R)\, n(R)\, R^2\, \mathrm{d}R, \tag{3.2a}$$

$$= \begin{cases} \sim \dfrac{4\pi}{\lambda} D R^2 n(R), & R \leqslant R_E, \quad (3.2b) \\ F_{\mathrm{c}}(R_E), \quad \text{a constant}, & R \geqslant R_E, \quad (3.2c) \end{cases}$$

in which the speed v_{d} used for ion pairs within the collisional sink that extends to R_E is assumed to be mainly controlled by the speed D/R (cf. Flannery 1976) of *inward* diffusion due to the effect of the sink on the ion distribution. By use of an integrating factor $\exp(V/kT - R/\lambda)$, (3.2b) is solved to yield

$$n(R) \exp(V/kT) \exp(-R/\lambda) = n(R_E) \exp[V(R_E)/kT] \exp(-R_E/\lambda) \tag{3.3}$$

for $R \leqslant R_E$. For $R \geqslant R_E$ when the sink exerts a constant effect, the right-hand side of (3.2c) is constant so that the constant flux solution (2.58a) applies. Hence, continuity at R_E requires

$$n(R)\{\exp[V(R)/kT] \exp(R_E - R)/\lambda + [P(R_E)/\alpha_{\mathrm{h}}]\, \alpha_3(R)\} = N^{-}, \quad R \leqslant R_E, \tag{3.4}$$

where the constant flux F_{c} in (3.2c) is equivalent to $\alpha_3(R)\, n(R)$ for $R \geqslant R_E$. The overall recombination coefficient is,

$$\alpha = \frac{1}{N^{-}} [\alpha_3(R_E)\, n(R_E)] = \frac{\{\alpha_3(R_E) \exp[-V(R_E)/kT]\}\, \alpha_{\mathrm{h}}/P(R_E)}{\alpha_3(R_E) \exp[-V(R_E)/kT] + \alpha_{\mathrm{h}}/P(R_E)} \tag{3.5}$$

as before. Since α_{h} varies as N^{-1}, at low densities (and for small R), when the second term in the right-hand side of (3.4) can be neglected in comparison with the first,

$$\begin{aligned} n(R) &= N^{-} \exp[-V(R)/kT] \exp(R - R_E)/\lambda, \quad R \leqslant R_E \\ &= n_0(R) \exp(R - R_E)/\lambda. \end{aligned} \tag{3.6}$$

Hence (3.2a) yields

$$\alpha_3(R_E)\, n_0(R_E) = \frac{4\pi}{\lambda} N^{-} \exp(-R_E/\lambda) \int_0^{R_E} v_{\mathrm{d}} \exp[-V(R)/kT] \exp(R/\lambda)\, R^2\, \mathrm{d}R. \tag{3.7}$$

The speed $v_{\mathrm{d}} \exp(-V/kT)$ appropriate to the distribution (3.6) is taken as approximately its thermal value $\langle v \rangle$ corresponding to energies greater than $-E$. Hence, at low densities,

$$\alpha_3(R_E) \exp[-V(R_E)/kT] = (4\pi\langle v \rangle/\lambda^2)\{[2 - 2(R_E/\lambda) + (R_E/\lambda)^2] - 2\exp(-R_E/\lambda)\} \tag{3.8}$$

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which, in the low density limit, reduces to

$$\alpha_3(R_E)\exp[-V(R_E)/kT] = \frac{4\pi}{3}\frac{R_E^3\langle v\rangle}{\lambda}[1-\tfrac{1}{4}(R_E/\lambda)+\tfrac{1}{20}(R_E/\lambda)^2-\tfrac{1}{120}(R_E/\lambda)^3+\ldots], \tag{3.9}$$

which exhibits an N-variation ($\lambda \sim N^{-1}$) similar to the low density limit of the expression of Thomson (1924). At low densities $\alpha_\mathrm{h} \gg \alpha_3$, so that the actual recombination coefficient is

$$\alpha \xrightarrow{\text{low } N} \alpha_3(R_E)\exp[-V(R_E)/kT] \equiv \alpha_\mathrm{rn}, \tag{3.10}$$

the reaction rate.

At high gas densities $\alpha_3 \gg \alpha_\mathrm{h}$ such that the actual recombination coefficient (3.5) approaches the limit,

$$\alpha \xrightarrow{\text{high } N} \alpha_\mathrm{h}/P(R) \equiv \alpha_\mathrm{tr} \tag{3.11}$$

the transport rate. Hence, this procedure has shown again that

$$\alpha = \alpha_\mathrm{rn}\alpha_\mathrm{tr}/(\alpha_\mathrm{rn}+\alpha_\mathrm{tr}) \tag{3.12}$$

is limited by either the transport or the reaction rates whose variation with N is contained in (3.9)–(3.11).

The above simplified model, designed to reproduce the result of a detailed history of energy changes in ion pairs via ion–neutral collisions in a dense gas (which can be established) suggests introduction of phenomenological ion and ion-pair densities

$$\tilde{n}(R) = n(R)\exp(s/\lambda), \quad \tilde{N}(R) = N(R)\exp(s/\lambda), \tag{3.13}$$

where s is the radial length $R_E - R$ from some radius R_E within which energy-changing collisions are effective.† Hence, (3.2*b*) with T_eff replaced by T yields,

$$\frac{\mathrm{d}\tilde{n}(R)}{\mathrm{d}R} + \tilde{n}(R)\frac{\partial(V/kT)}{\partial R} = 0, \tag{3.14}$$

which can be solved to yield,

$$n(R) = N^-\exp(-V/kT)\exp(-s/\lambda) \equiv \sum_{\mathrm{i}=-\mathrm{V}}^{\mathrm{C}} n_\mathrm{i}(R,E_\mathrm{i}), \quad R \leqslant R_E, \tag{3.15}$$

where $n_\mathrm{i}(R,E_\mathrm{i})$ satisfies the system of equations (2.20) that describe microscopic events. When the effect of the sink operating in the ($-\mathrm{M} \rightarrow -\mathrm{V}$) range of energy levels is small, the right-hand side of (2.20) can be taken as approximately zero such that solution of the left-hand side set to zero yields the Maxwell–Boltzmann distribution $n_0(R,E_\mathrm{i})$ in (2.14) for ions in thermodynamic equilibrium. When n_0 is summed over all E_i, or integrated over all v_i as in (2.9) the Boltzmann term in (3.15) is obtained. Provided that the effect of the sink is small for ion pairs with internal energy greater than $-\mathrm{E}$, an iterative solution can be proposed by assuming the left-hand side of (2.20) to be zero, as if in full equilibrium, and then including the sink to first order by solving the equation

$$\int_0^R \mathrm{d}R\, N_\mathrm{i}^*(R,E_\mathrm{i}) \sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} k_\mathrm{if}(R) = \int_0^R \mathrm{d}R \sum_{\mathrm{f}=-\mathrm{M}(R)}^{\mathrm{C}} N_\mathrm{f}^*(R,E_\mathrm{f})\,k_\mathrm{fi}(R), \tag{3.16}$$

which follows from (2.20). Since the E_i- or v_i-averaged effect of the left-hand side of (2.20) is measured by $\mathscr{D}n(R)$ on the left-hand side of (2.47) and hence, in the approximation (3.2*a*) basic

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† In this sense Thomson (1924) displayed remarkable intuition in his concept of a trapping radius, a concept fully exploited in §2.4, §2.5 and §4.2 in the form of sinks compressible with N.

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to this section, by $\tilde{n}$ of (3.13), the small departures of the left-hand side of (2.20) from zero can be reintroduced by replacing N_i^* in (3.16) by the fictitious densities

$$\tilde{N}_i(R, E_i) = N_i^*(R, E_i) \exp(s/\lambda). \tag{3.17}$$

Provided the level $-\mathrm{E}$ is sufficiently high that departures from thermodynamic equilibrium are indeed small, and yet is sufficiently low in the bound spectrum that $v_i(R)$ on the left-hand side of (2.20) does not depart appreciably from zero, its value at the turning points, it follows that densities of bound ion-pairs with $E_i < -\mathrm{E}$ can still be obtained from (3.16); and replacement of N_i^* by $\tilde{N}_i$ will minimize any error in the original assumption.

The recombination coefficient α_3 associated with negative ion density $n(R)$ is therefore, in this approximation,

$$\alpha_3(R_E) = \frac{N}{N^+N^-}\int_0^{R_E} \exp(-s/\lambda)\, \mathrm{d}R \sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}} \left[\tilde{N}_i(R, E_i) \sum_{\mathrm{f}=-\mathrm{V}}^{-\mathrm{E}} k_{if}(R) - \sum_{\mathrm{f}=-\mathrm{M}(R)}^{\mathrm{C}} \tilde{N}_f(R, E_f)\, k_{fi}(R)\right], \tag{3.18}$$

and the overall recombination coefficient appropriate to the R-asymptotic density N^- can then be obtained from (2.52) directly or from (2.59).

In the limit of low gas densities N, and low ion densities $N^\pm$, departures from thermodynamic equilibrium are indeed small, $\alpha \to \alpha_3$ and $\lambda \to \infty$ such that (3.18), on reordering integrations, can be rewritten as,

$$\alpha_3(-\mathrm{E}) = \frac{N}{N^+N^-}\sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}} \left[\sum_{\mathrm{f}=-\mathrm{D}}^{-\mathrm{E}} \int_0^{R_m} N_i^*(R, E_i)\, k_{if}(R)\, \mathrm{d}R - \sum_{\mathrm{f}=-\mathrm{S}}^{-\mathrm{E}} \int_0^{R_m} N_f^*(R, E_f)\, k_{fi}(R)\, \mathrm{d}R\right], \tag{3.19}$$

where $-\mathrm{D}$ is the lowest bound level of the system, $-\mathrm{S}$ is the stabilization level of energy $-E_S$, and $R_m = \min[R(E_i), R(E_f)]$, the minimum of the outermost turning points associated with levels E_i (bound and continuous) and E_f (bound) respectively. Since $(0 \to R_m)$ defines the full range accessible classically, i.e.

$$N_i(E_i)\, \langle k_{if}(E_i, E_f)\rangle = \int_0^{R_m} N_i^*(R, E_i)\, k_{if}(R; E_i, E_f)\, \mathrm{d}R, \tag{3.20}$$

for k_{if} given previously (Flannery 1980, 1981 *a*) we have

$$\alpha \xrightarrow{\text{low } N} \alpha_3(-\mathrm{E}) = \frac{N}{N^+N^-}\sum_{\mathrm{i}=-\mathrm{E}}^{\mathrm{C}} \left[N_i(E_i) \sum_{\mathrm{f}=-\mathrm{D}}^{-\mathrm{E}} \langle k_{fi}\rangle - \sum_{\mathrm{f}=-\mathrm{S}}^{-\mathrm{E}} N_f(E_f)\, \langle k_{fi}\rangle\right], \tag{3.21}$$

where the ion-pair number density in the classical accessible region is,

$$N_i(E_i) = \int_0^{R(E_i)} N_i^*(R, E_i)\, \mathrm{d}R \tag{3.22}$$

which, with the aid of (3.16) with integrations reordered, and of (3.20), satisfies

$$N_i(E_i) \sum_{\mathrm{f}=-\mathrm{D}}^{\mathrm{C}} \langle k_{if}\rangle = \sum_{\mathrm{f}=-\mathrm{S}}^{\mathrm{C}} N_f(E_f)\, \langle k_{fi}\rangle. \tag{3.23}$$

Equations (3.21) and (3.23) are identical with those originally introduced by Bates & Moffett (1966) and by Bates & Flannery (1968) in their effectively exact quasi-equilibrium treatment of the low density limit of ion–ion recombination. Because of this, and of the constant flux assumption implicit in (3.2*c*), the method represented by (3.16)–(3.18) and (2.59) is designated as the 'generalized-quasi-equilibrium-distribution' steady-state method to remind us of the underlying assumptions.

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4. Theory of ion–ion recombination as a function of ion density

All previous theoretical and experimental studies of ion–ion recombination pertain to a dilute degree of ionization with ion densities $N^\pm \sim 10^8\,\mathrm{cm^{-3}}$ for which a coulombic ion–ion interaction is correct. Ion–ion recombination plays a key role (Flannery 1979) in populating the upper laser electronic levels of rare gas–halide systems which operate not only at high gas pressure ($\frac{1}{2}$–10 atm) but also at relatively high ion densities $10^{12} \lesssim N^\pm \lesssim 10^{14}\,\mathrm{cm^{-3}}$. In § 4.1 is developed a theory for the variation of α with $N^\pm$. A useful procedure proposed in § 4.2 for the rapid evaluation of the reaction rate α_{rn} permits illustration of the variation of α with gas density N.

4.1. *General theory*

The interaction V between the positive and negative ions can no longer be assumed, *ab initio*, to be pure coulomb, but depends on the increased screening due to the other ions via their net charge-density distribution which, in turn, is coupled self-consistently to the recombination sink via α which contains an explicit dependence on V. Repulsion between like ions also becomes important. The interaction V between the ions is determined by appropriate solution of Poisson's equation

$$\nabla^2 V(R) = (4\pi e^2/\epsilon)\,[n^+(R) - n^-(R)], \tag{4.1}$$

where the local positive and negative ion densities are $n^\pm(R)$, and ϵ is the dielectric constant $1+4\pi Np$ of a gas with polarizability p and density N. For Xe, $\epsilon = (1+1.4\,10^{-3}\,N/N_{\mathrm{L}})$, in effect unity for $N \lesssim 25(N_{\mathrm{L}}$, the number density $(2.69\times 10^{19}\,\mathrm{cm^{-3}})$ at s.t.p.). In the steady-state limit when few unreacted ions are within the recombination sink measured by R_E of § 2, the net inward flux (in $\mathrm{s^{-1}}$) of positive ions towards the central positive ion is

$$F_{\mathrm{in}}^{++}(R) = -4\pi R^2\left[-D^+\frac{\mathrm{d}n^+(R)}{\mathrm{d}R} + n^+(R)\frac{K^+}{e}\frac{\partial V}{\partial R}\right], \tag{4.2}$$

where D^+ and K^+ are the relative quantities $2D_1$ and $2K_1$ in terms of the diffusion coefficient D_1 and mobility K_1 for a positive ion 1. The net inward flux of negative ions 2 towards a positive ion 1 is,

$$F_{\mathrm{in}}^{-+}(R) = 4\pi R^2\left[D\frac{\mathrm{d}n^-(R)}{\mathrm{d}R} + n^-(R)\frac{K}{e}\frac{\partial V}{\partial R}\right], \tag{4.3}$$

where D and K are the relative diffusion coefficients (D_1+D_2) and relative mobilities (K_1+K_2) for ions 1 and 2. In the reference frame of the central positive ions, assumed stationary, F_{in}^{++} vanishes, and integration of (4.2) yields the Boltzmann distribution

$$n^+(R) = N^+\exp\,[V(R)/kT], \tag{4.4}$$

where T is given by T_{eff} in (2.57) when the Einstein relation no longer holds. Hence, Poisson's equation for spherical distributions is

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial V}{\partial R}\right) = \left(\frac{4\pi e^2}{\epsilon}\right)\{N^+\exp\,[V(R)/kT] - n^-(R)\}. \tag{4.5}$$

For a single isolated sink, the steady-state density $n^-(R)$ of negative ions is given by (2.64), and

$$\frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2\frac{\partial(V/kT)}{\partial R}\right] = \frac{1}{2R_{\mathrm{s}}^2}\left\{\exp\,[V(R)/kT] - \left[1-\frac{\alpha}{\alpha_{\mathrm{tr}}}\frac{P(R)}{P(R_E)}\right]\exp\,[-V(R)/kT]\right\}, \tag{4.6}$$

where the 'screening' distance is

$$R_{\mathrm{s}} = (8\pi N^\pm R_e/\epsilon)^{-\frac{1}{2}}. \tag{4.7}$$

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The R-variation of the right-hand side of (4.6) is given explicitly by $V(R)$ and $P(R)$ and the interaction is contained implicitly within the recombination probability,

$$\alpha/\alpha_{\rm tr} = \alpha_{\rm rn}(R_E)/[\alpha_{\rm rn}(R_E)+\alpha_{\rm tr}(R_E)], \tag{4.8}$$

from (2.62), where $\alpha_{\rm rn}$ is the reaction rate (2.61), i.e. the recombination coefficient that would pertain provided a Boltzmann distribution of ions (with no net transport) were maintained as at low gas densities N, and $\alpha_{\rm tr}$ is the transport rate (2.63), i.e. the recombination coefficient that pertains for instantaneous reaction within R_E, as at high N. If an analytic expression for $\alpha_{\rm tr}$ is known in terms of V, as in § 4.2, then a self consistent V can be obtained from (4.6) with (4.8), since $\alpha_{\rm tr}$ is given in terms of V by the analytical expression (2.63). Otherwise, (4.5) must be coupled to the solution of

$$4\pi R^2\left[D\frac{{\rm d}n^-(R)}{{\rm d}R}+n^-(R)\frac{K}{e}\frac{\partial V}{\partial R}\right] \equiv 4\pi R^2 D\left\{\exp\left(-V/kT\right)\frac{{\rm d}}{{\rm d}R}[n^-(R)\exp\left(V/kT\right)]\right\}$$
$$= \alpha_3(R)\,n^-(R) = \alpha N^- \tag{4.9}$$

for $n^-(R)$, where the right-hand side of (4.9) is given by (2.50) in terms of the phase-space densities $n_{\rm i}(R,E_{\rm i})$ determined from (2.20) with collisional rates $k_{\rm if}(R)$, which in turn depend on V.

Hence the general theory involves the coupled solutions of the Poisson equation (4.5), of the flux equation (4.9), and of the Boltzmann equation (2.20), i.e. the interaction V is solved self-consistently with the recombination. Application of this general theory represents a formidable but yet a feasible task with the aid of new theoretical procedures for the solution of (2.20) for the phase-space densities $n_{\rm i}(R,E_{\rm i})$.

Note that it is only $\alpha_3(R)$ that depends on explicit knowledge of $n_{\rm i}(R,E_{\rm i})$ so that, provided the rate $\alpha_{\rm rn}$ of reaction can be provided analytically by alternative procedures, the above prescription reduces to the solution of (4.6) with (4.8). The term $1-(\alpha/\alpha_{\rm tr})\,[P(R)/P(R_E)]$, which depends on V, N and R, on the right-hand side of (4.6), tends to unity at low N for all R, and increases at high N, from zero at $R\sim R_E$ to unity as $R\rightarrow\infty$. As $R_{\rm s}\rightarrow\infty$ for no plasma sheathing, solution of (4.6) is pure coulomb so that a (first) iterative solution valid for low $N^{\pm}$ (large $R_{\rm s}$) and high N in the vicinity of R_E is

$$\frac{V_{\rm h}(R)}{kT} = -\frac{R_e}{R}+\frac{1}{12}\left(\frac{R}{R_{\rm s}}\right)^2\exp\left(-R_e/R_E\right), \quad R_E\lesssim R\ll R_{\rm s}, \tag{4.10}$$

where R_e is the natural unit (e^2/kT) of length. High-order iterations may be obtained. This interaction (4.10) is pure coulomb for $R\ll R_e$ as at high N, or else, for $R^3\ll 12R_eR_{\rm s}^2$, i.e. when $N^{\pm}\lesssim 10^{14}\,{\rm cm}^{-3}$ at $R\lesssim R_e$.

To facilitate numerical solution, equation (4.6) may be decomposed into three coupled first-order differential equations,

$$\left.\begin{aligned} {\rm d}v_1/{\rm d}r &= v_2(r),\\ {\rm d}v_2/{\rm d}r &= -(2/r)\,v_2(r)+(1/2r_{\rm s}^2)\,[\exp v_1(r)-v_3(r)\exp -v_1(r)],\\ {\rm d}v_3/{\rm d}r &= (\alpha/\alpha_{\rm h})\exp v_1(r)/r^2, \end{aligned}\right\} \tag{4.11a}$$

where all distances $r=R/R_e$ are expressed in natural units, $v_1=V/kT$, and v_3 is the fractional departure $n^-/N^-\exp\left(-V/kT\right)$ of the ion density from Boltzmann equilibrium. The first two coupled equations are equivalent to the Poisson equation (4.5), and the third equation represents diffusional drift (equation (4.9)).

When $v_1\ll 1$ as at large r, the exponentials in (4.11 a) may be linearized to provide

$$v_3\approx 1-\alpha/\alpha_{\rm h}r \tag{4.11b}$$

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so that the consistent and appropriate solution of the Poisson equation

$$\frac{1}{r}\frac{\mathrm{d}^2(rv_1)}{\mathrm{d}r^2} = \frac{1}{r_\mathrm{s}^2}\left(v_1 + \frac{\alpha}{\alpha_\mathrm{h}}\frac{1}{r}\right), \tag{4.11c}$$

is

$$v_1(r) = \frac{V}{kT} = -\frac{1}{r}\left(1 - \frac{1}{2}\frac{\alpha}{\alpha_\mathrm{h}}\right)\exp\left(-r/r_\mathrm{s}\right) - \frac{\alpha/\alpha_\mathrm{h}}{2r}, \tag{4.11d}$$

which yields the coulomb attraction (C) for $r \ll r_\mathrm{s}$.

At low N,

$$v_1 \rightarrow -(1/r)\exp\left(-r/r_\mathrm{s}\right), \tag{4.11e}$$

the Debye–Hückel interaction D.H. (cf. McDaniel 1964), while at large N when $\alpha \approx \alpha_\mathrm{h}$,

$$v_1 \rightarrow -(1/2r)\left[1 + \exp\left(-r/r_\mathrm{s}\right)\right] \tag{4.11f}$$

the mean of C and D.H. For intermediate N, v_1 contains various mixtures of C and D.H.

Direct numerical inward solution of (4.11 *a*) subject to (4.11 *b*) and (4.11 *d*) as initial conditions at large r shows that (4.11 *d*) remains an excellent solution by reproducing the actual numerical results to within 2 % for all $r \geqslant 0.1$, for α/α_h between zero and unity and for $N^{\pm} \leqslant 10^{13}\,\mathrm{cm}^{-3}$. As α/α_h decreases from unity the accuracy becomes even better.

The criterion $v_1 \ll 1$ is satisfied at $r \sim 1$ (the important region at low N) and at small α/α_h when $r_\mathrm{s} \gg 1$ which with (4.7), implies that $\frac{4}{3}\pi R_\mathrm{s}^3 N^{\pm} = \frac{1}{6}r_\mathrm{s} \gg 1$. Many ions are then present within the R_s-sphere, and $N^{\pm} \ll 2 \times 10^{14}\,\mathrm{cm}^{-3}$.

As N increases, the extent R_E of the reaction sink decreases as $(R_e/N)^{\frac{1}{2}}$ (see § 4.2), such that (4.11 *f*) is pure coulomb at R_E in the high N-limit. For lower N, the situation is not as clear, without resort to explicit knowledge of the rate α of reaction.

4.2. *Simplified method for reaction rate*

Rather than solving the Boltzmann equation (2.20) directly for the phase-space densities $n_\mathrm{i}(R, E_\mathrm{i})$ and hence α_rn from (2.50), let us adopt a procedure based on the analysis in § 2.4 of the finite reaction rate α_rn within a collisional sink of radial extent S. Since the X^+ and Y^- ions $(i = 1, 2)$ have in general different mean free paths λ_i in the gas Z and since both ions have different sink radii R_i, the expression (2.84) or (2.91 *c*) for the rate of reaction within S is therefore generalized to give

$$\alpha_\mathrm{rn}(R_1, R_2) = \pi\left[R_1^2 W(X_1)\, C_1 E_1 + R_2^2 W(X_2)\, C_2 E_2 - R_\mathrm{m}^2\, W(Y_1)\, W(Y_2)\, G\right]\langle v_{12}\rangle, \tag{4.12a}$$

where $\langle v_{12}\rangle$ is some averaged ion–ion thermal or transport speed of approach, and where the probability for an ion i-neutral Z collision for ion pairs with internal separation $R \leqslant R_i$ increases with gas density to unity as (Loeb 1955)

$$W(X_i) = 1 - (1/2X_i^2)\left[1 - \exp\left(-2X_i\right)\left(1 + 2X_i\right)\right], \quad X_i = \lambda_i/R_i, \tag{4.12b}$$

for a straight-line trajectory. Since α_rn pertains to a Boltzmann distribution, the factor

$$E_i = \exp\left[-V(R_i + \lambda_i)/kT\right], \tag{4.12c}$$

in (4.12 *a*) acknowledges the Boltzmann enhancement of the ion density N^- due to the field at $R_i + \lambda_i$ at which the last ineffective ion–neutral collision occurs just before the ion enters the recombination sink within R_i. The factor

$$C_i = 1 + \frac{2}{3kT}\int_{R_i}^{R_i+\lambda_i}\frac{\partial V}{\partial R}\,\mathrm{d}R, \tag{4.12d}$$

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acknowledges the focusing effect of the interaction on the assumed straight-line trajectory between $R_i+\lambda_i$ and R_i in the cross section πR_i^2. The smaller of R_1 and R_2 is R_m such that $W(Y_1)\,W(Y_2)$, with $Y_i = \lambda_i/R_m$, is the probability of simultaneous ion–neutral collisions within R_m, a probability counted twice by the sum of the first two terms of (4.12*a*). Simple geometric arguments show that G in (4.12*a*) is equal to either C_1E_1 or C_2E_2 depending on whether R_m is equal to R_1 or R_2, respectively.

The trapping radii R_i may now be deduced from simple kinematical considerations. The kinetic energy of (1, 2) relative motion before the i–Z collision is

$$T_b = \tfrac{3}{2}kT + \int_{R_i}^{R_i+\lambda_i} \frac{\partial V}{\partial R}\,dR, \tag{4.13}$$

since the ions on average are uninterrupted by collision only for separations between $R_i+\lambda_i$ and R_i, within which the acceleration due to the field is effective. Ion pairs upon collision with Z become incapable of expanding outwards from R_i to $R_i+\lambda_i$ provided their kinetic energy T_a after collision is barely sufficient for provision of the energy required to increase R_i to $R_i+\lambda_i$ against the force of attraction, i.e. when

$$T_a \leqslant \int_{R_i}^{R_i+\lambda_i} \frac{\partial V}{\partial R}\,dR. \tag{4.14}$$

We can show (Flannery 1978) from the full expression (Bates & Flannery 1968) for the energy change that, to a good approximation,

$$T_a = T_b(1+\delta), \tag{4.15}$$

where δ is a parameter depending only on the masses M_i of the interacting species. Here we simply adopt δ as a convenient collision parameter chosen to normalize the low-density limit of the expression (4.12*a*) for α_{rn} to the exact quasi-equilibrium results of Bates & Flannery (1968). Thus, the stabilization criteria (4.14) with (4.13) yields

$$V(R_i+\lambda_i) - V(R_i) = \tfrac{3}{2}kT/\delta_i, \tag{4.16}$$

to be solved for the trapping radii R_i associated with mean free paths λ_i and collision parameters δ_i.

In this strong-collision model, (4.16) provides a valuable relation satisfied by the general interaction V at two points. Solution of (4.16) for a pure coulomb attraction is

$$R_i = \tfrac{1}{2}\lambda_i[(1+4\delta_i R_T/\lambda_i)^{\frac{1}{2}}-1] \rightarrow \begin{cases} \delta_i R_T, & \text{as} \quad N\rightarrow 0, \\ (\delta_i R_T \lambda_i)^{\frac{1}{2}}, & \text{as} \quad N\rightarrow\infty, \end{cases} \tag{4.17}$$

which decreases monotonically as λ_i decreases from infinity and which is constrained by (4.16) to satisfy $R_i(R_i+\lambda_i) = \delta_i\lambda_i R_T$, where R_T is the Thomson trapping radius $2e^2/3kT$. The sink is therefore compressible with N, as in the model of Natanson (1959).

At low gas densities the reaction rate

$$\alpha_{rn} \rightarrow C_1\delta_1^2\alpha_{T1} + C_2\,\delta_2^2\alpha_{T2}, \tag{4.18}$$

where C_i, by (4.16), is $1+\delta_i^{-1}$ and

$$\alpha_{Ti} = \tfrac{4}{3}\pi R_T^3\,\langle v_{12}\rangle/\lambda_i \tag{4.19}$$

is the Thomson partial recombination coefficient (1.3). The ratio

$$\mathscr{R}_{Ti} = \alpha_{q.e.}(N\rightarrow 0)/\alpha_{Ti} \tag{4.20}$$

of the exact low density limits $\alpha_{q.e.}$, as given by the quasi-equilibrium theory of Bates & Flannery (1968), has been provided (Flannery 1981*a*) for an extensive range of physical systems represented by

$$X^+ + Y^- + Z \rightarrow [XY] + Z, \tag{4.21}$$

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where energy-change transitions occur via elastic ion–neutral collisions. Also, the $\mathscr{R}_{\mathrm{T}i}$ have been provided (Flannery 1980) for a wide range of systems represented by

$$X^+ + Y^- + X \rightarrow [XY] + X, \tag{4.22}$$

where in addition to an elastic (Y^-–X) encounter a symmetrical resonance charge transfer encounter occurs, or by

$$X^+ + Y^- + Y \rightarrow [XY] + Y. \tag{4.23}$$

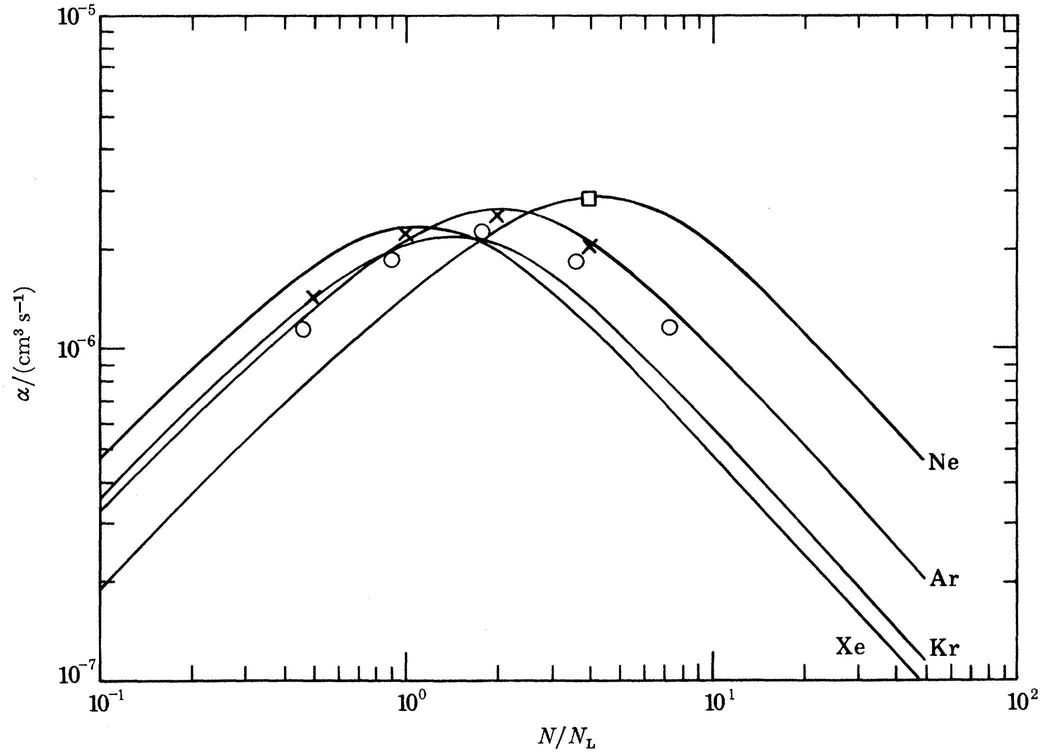

FIGURE 2. Recombination rate coefficient α at 300 K for Kr^+–F^- in rare gases (Ne, Ar, Kr, Xe) as a function of gas density N (in multiples of the Loschmidt number density $N_{\mathrm{L}} = 2.69 \times 10^{19}$ at s.t.p.). ——: Present treatment; ×, □: universal Monte-Carlo (hard-sphere) plot (Bates 1980*b*) for Ar and Ne, respectively; ○: Monte-Carlo (polarization) results (Morgan *et al.* 1980) for Ar.

With this knowledge, the collision parameters δ_i may now be uniquely determined by solution of

$$\delta_i^3 + \delta_i^2 - \mathscr{R}_{\mathrm{T}i} = 0, \tag{4.24}$$

and α_{rn} of (4.12*a*) tends therefore at low N to the exact quasi-equilibrium values (Flannery 1980, 1981*a*). This model of the reaction rate acknowledges the decrease in survival probability due to diffusion for ion–neutral collisions within the R_i-trapping spheres, and, with the inclusion of the quasi-equilibrium δ_i, is the 'strong-collision' analogue to the microscopic method provided in § 3. The strong-collision parameter δ_i is, in general, a function of ion-density $N^{\pm}$.

4.3. *Results for* $[(Kr^+ - F^-) + M]$ *recombination*

For a pure coulomb interaction associated with dilute ionization, the collision parameters δ_i have been given (Flannery 1981*b*) for various combinations of rare gas (He^+, Ne^+, Ar^+, Kr^+, Xe^+) and halide (F^-, Cl^-) ions in a parent or unlike background gas M. In figure 2 are illustrated the variations of the rate

$$\alpha = \alpha_{\mathrm{rn}}\alpha_{\mathrm{tr}}/(\alpha_{\mathrm{rn}} + \alpha_{\mathrm{tr}}) \tag{4.25}$$

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for the recombination of Kr^+ and F^- with density N of the background gas M, taken respectively as Ne, Ar, Kr and Xe, at 300 K. The reaction rate α_{rn} was obtained from (4.12), with (4.17) for R_i and the solution of (4.24) for δ_i, and the transport rate from

$$\alpha_{\mathrm{tr}} = 4\pi e\{K_1/[1-\exp(-R_e/R_1)] + K_2/[1-\exp(-R_e/R_2)]\}. \tag{4.26}$$

Results from the universal Monte-Carlo plot procedure of Bates (1980*b*) are also shown in figure 2 together with the direct Monte-Carlo computer simulations of Morgan *et al.* (1980) at low $N^\pm$. The general agreement as shown can be considered excellent. At low N, $\alpha_{\mathrm{rn}} \ll \alpha_{\mathrm{tr}}$ while at high N, $\alpha_{\mathrm{rn}} \gg \alpha_{\mathrm{tr}}$ so that α is given by the rate-limiting step in each region. As N increases, α_{rn} increases with respect to α_{tr} until the maximum is obtained where $\alpha_{\mathrm{rn}} \approx \alpha_{\mathrm{tr}}$. Figure 2 can be made universal for all temperatures T by simply relabelling the ordinate and abscissa axes as $(T/300)^{\frac{3}{2}}\,\alpha$ and $(300/T)^{\frac{3}{2}}\,N$ respectively as pointed out by Bates (1980*c*). Analogous results for other systems are presented elsewhere (Flannery 1981*b*).

At higher $N^\pm$, the interaction between the ions varies in general with α, and is accurately determined by (4.11) which therefore must be coupled to the equation (whether basic as (2.52) or phenomenological as (4.12)) for α. At high gas densities ($N > \frac{1}{2}N_{\mathrm{L}}$), Morgan *et al.* (1980) simply adopted *ab initio* the D.H. interaction (4.11*e*) as a means of incorporating plasma sheathing effects when $N^\pm$ is raised. As shown in § 4.2 this assumption is without foundation unless $N \rightarrow 0$ and leads to greatly reduced rates which are in error particularly at intermediate and high gas densities N (Bates 1981, Flannery 1981*c*). Although increase in the ion density to about $10^{12}\,\mathrm{cm}^{-3}$ is not expected to cause appreciable change (Flannery 1981*c*) to the rates of figure 2, direct calculation based on the theory of § 4.1 is under way.

5. Theoretical solution of the phase density

Since the phase-space density of ions in thermodynamic equilibrium separates quite naturally into a product of two functions – one of R alone and the other of v_{i} alone – as in (2.13), it remains convenient initially to express the set in terms of these natural (R, v_{i}) variables rather than (R, E_{i}) the set more natural for expression of the sink. Upon differentiation of (2.20) with respect to R or from (2.12) directly, we find with the aid of (2.10), that

$$v_{\mathrm{i}}\left\{4\pi R^2 \frac{\partial}{\partial R}[N_{\mathrm{i}}^*(R, v_{\mathrm{i}})/4\pi R^2] - \frac{4\pi v_{\mathrm{i}}^2}{m v_{\mathrm{i}}}\frac{\partial}{\partial v_{\mathrm{i}}}[N_{\mathrm{i}}^*(R, v_{\mathrm{i}})/4\pi v_{\mathrm{i}}^2]\frac{\partial V}{\partial R}\right\}$$

$$= \int\!\!\int_{\Omega'} [N_{\mathrm{f}}^*(R, v_{\mathrm{f}})\,N_0(\boldsymbol{v}_0') - N_{\mathrm{i}}^*(R, v_{\mathrm{i}})\,N_0(\boldsymbol{v}_0)]\,[g\sigma(g,\psi)\,\mathrm{d}\Omega]\,\mathrm{d}\boldsymbol{v}_0 \tag{5.1a}$$

$$= N\left[\sum_{\mathrm{f}=-\mathrm{M}(R)}^{\mathrm{C}} N_{\mathrm{f}}^*(R, E_{\mathrm{f}})\,k_{\mathrm{fi}}(R) - N_{\mathrm{i}}^*(R, E_{\mathrm{i}}) \sum_{\mathrm{f}=-\mathrm{V}(R)}^{\mathrm{C}} k_{\mathrm{if}}(R)\right], \tag{5.1b}$$

which is a set of *linear* integro-differential equations in two variables (rather than *quadratic* in $N(R, v_{\mathrm{i}})$ since the gas density $N_0(\boldsymbol{v}_0)$ has already been set in (5.1*b*) to its thermodynamic value, as implied by the condition $N^\pm \ll N_0$). The speeds v_0' and v_{f} in (5.1*a*) are given by energy conservation with fixed v_{i}, v_0 and Ω'. The recombination sink at internal energies below E_{s} requires that N_{f}^* vanishes for

$$v_{\mathrm{f}} \leqslant v_{\mathrm{f}0} = \{2/m[E_{\mathrm{s}} - V(R)]\}^{\frac{1}{2}}, \quad R \leqslant R(E_{\mathrm{s}}). \tag{5.2}$$

The equilibrium phase density (2.13) in (5.1) ensures that the left-hand side of (5.1) vanishes. This left-hand side includes the streaming (incompressible) terms while the right-hand side is the collisional integral that attempts to drive the momentum-space distribution of the system

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towards a Maxwellian distribution. For small energy transfers the collision integral reduces (Flannery 1971, 1972) to that given by the Fokker–Planck equation (which essentially describes diffusion in momentum space) derived via description of recombination as a Markov process (Flannery 1971, 1972). For high gas densities and for high ion densities (more than several N_L) the decreased effect of accelerations and the increased ion–ion screening effect ensures respectively that the interaction $V \ll kT$ such that energy transfers are indeed small, such that the right-hand side of (5.1) is then best described by the Fokker–Planck equation.

For dilute ionization, $N^{\pm} \ll N$, two new procedures are proposed with the above comments in mind for the solution $N_i^*(R, v_i)$ of (5.1) subject to certain boundary conditions.

5.1. *Separable-equations method*

In expression (5.1), let

$$N_i^*(R, v_i) = N_0(R, v_i)\,[1 - \Phi_i(R, v_i)], \tag{5.3}$$

in terms of the equilibrium density

$$N_0(R, v_i) = 4\pi R^2 \exp\,(-V/kT)\,F_0(v_i), \tag{5.4}$$

where the Maxwellian speed distribution is

$$F_0(v_i) = 4\pi v_i^2 (m/2\pi kT)^{\frac{3}{2}} \exp\,(-\tfrac{1}{2}mv_i^2/kT). \tag{5.5}$$

Since energy is conserved in the binary ion–neutral encounters,

$$N_0(R, v_i)\,N_0(v_0) = N_0(R, v_f)\,N_0(v_0'), \tag{5.6}$$

and hence, after some analysis, Φ_i satisfies the set

$$\begin{aligned} v_i\left[\frac{\partial}{\partial R}\Phi_i - \frac{1}{mv_i}\frac{\partial V}{\partial R}\frac{\partial \Phi_i}{\partial v_i}\right] &= \int\!\!\int_{\Omega'} N_0(\boldsymbol{v}_0)\,[\Phi_f(R, v_f) - \Phi_i(R, v_i)]\,(g\sigma\,\mathrm{d}\Omega)\,\mathrm{d}\boldsymbol{v}_0 \\ &= N\left\{\left[\sum_{\mathrm{f}=-\mathrm{M}(R)}^{\mathrm{C}} \Phi_f(R, E_f) - \sum_{\mathrm{f}=-\mathrm{V}(R)}^{\mathrm{C}} \Phi_i(R, E_i)\right] k_{if}(R)\right\} \end{aligned} \tag{5.7}$$

subject to the boundary conditions that

$$\begin{aligned} \Phi_i(R, E_i) &\rightarrow 0 \quad \text{for} \quad E_i \rightarrow \infty, \quad \text{or for} \quad R \rightarrow \infty \\ &\rightarrow 1 \qquad \text{for}\; E_i \leqslant E_s, \quad R \leqslant R(E_s). \end{aligned} \tag{5.8}$$

In the limit of low gas densities N, the net rate of change of each of the streaming terms contained within all classical accessible configuration space between zero and $R_i(E_i)$, the outermost turning point, effectively balance, since the sink rate is small by comparison, i.e.

$$\int_0^{R_i} 4\pi R^2 \frac{\partial}{\partial R}\left[\frac{N_i^*(R, v_i)}{4\pi R^2}\right] \mathrm{d}R \approx \frac{4\pi v_i^2}{m}\frac{\partial}{\partial v_i}\left[\frac{1}{4\pi v_i^2}\int_0^{R_i} N_i^*(R, v_i)\,\frac{\partial V}{\partial R}\,\mathrm{d}R\right]. \tag{5.9}$$

The average rate over all accessible R-space of collisional transitions between levels with energies E_i and E_f can be written as,

$$\langle k_{if}(E_i, E_f)\rangle = \frac{1}{N_i^*(E_i)}\int_0^{R_i} N_i^*(R, E_i)\,k_{if}(E_i, E_f, R)\,\mathrm{d}R, \tag{5.10}$$

where
$$N_i(E_i) = \int_0^{R_i} N_i^*(R, E_i)\,\mathrm{d}R. \tag{5.11}$$

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Hence, (5.1) reduces, with the aid of (5.9), to

$$N_i(E_i)\sum_{f=-D}^{C}\langle k_{if}(E_i,E_f)\rangle = \sum_{f=-S}^{C} N_f(E_f)\,\langle k_{if}(E_i,E_f)\rangle \tag{5.12}$$

which is the 'quasi-equilibrium' result of Bates & Moffett (1966) and of Bates & Flannery (1968) for ion densities N_i appropriate to the limit of low gas densities N and valid when the left-hand side of (5.7) can be neglected.

As N is raised the first (spatial diffusion) term on the left-hand side of (5.7) becomes increasingly important while the second (acceleration) term eventually dominates in the high N-limit. Note, however, that *both* these terms must be included from the outset since their combination is required for thermodynamic equilibrium. Neglect of the acceleration term on the left-hand side of (5.1) does *not* yield, upon substitution of (5.3), the expression (5.7) with its acceleration term set to zero. Effects of diffusion and acceleration are so coupled that various schemes of approximation are best constructed from (5.7) as origin, rather than from (5.1).

For example, as N is raised, the speed distribution remains essentially Maxwellian while diffusion effects change, i.e. the correction Φ_i in (5.3) to the Maxwell–Boltzmann distribution N_0 exhibits an R-variation alone. Hence the acceleration term in (5.7) can be neglected in comparison with the diffusion term, and with the substitution in (5.7) of

$$\Phi_i(R,v_i) = \Phi_i^{I}(R,v_i)\exp(-R/L_i), \tag{5.13}$$

where the length

$$L_i(v_i) \equiv L_i(R,E_i) = v_i/N\sum_f k_{if}(R) \tag{5.14}$$

is a function only of v_i (see Appendix B) then, after some analysis and reduction, Φ_i^{I} satisfies the set of first-order coupled differential equations

$$\frac{\partial \Phi_i^{I}(R,E_i)}{\partial R} = \frac{N}{v_i}\sum_{f=-M(R)}^{C}\Phi_f^{I}(R,E_f)\,k_{if}(R)\exp\left[-R(L_f^{-1}-L_i^{-1})\right], \tag{5.15}$$

which, by standard numerical techniques, can be solved easily subject to the boundary conditions (5.8).

The above set exhibits a striking similarity to the time-dependent set obtained in collision treatments based on Dirac's method of variation of constants (cf. Bates 1961). In fact, perturbation procedures based on the strength of the coupling terms k_{if} result in a full hierarchy of computational schemes of varying degrees of sophistication. For example, the $\{k_{if}\}$-matrix is dominated by its diagonal (elastic) elements (cf. Flannery 1981 *a*) such that to zero-order the non-diagonal elements are neglected, to give

$$\frac{\partial \Phi_i^{I}}{\partial R} \approx \frac{\partial \Phi_i^{(0)}}{\partial R} = \frac{N}{v_i}k_i(R)\,\Phi_i^{(0)} \tag{5.16}$$

with solution

$$\Phi_i^{(0)}(R,v_i) = \exp\left[-\frac{N}{v_i}\int_0^R k_{ii}(R)\,\mathrm{d}R\right]; \quad v_i(R) \geqslant v_{f0} \tag{5.17}$$

which ensures that $N_i(R=0,v_i)/N_0(R=0,v_i)$ in (5.3) vanishes.

In this approximation, the phase density is

$$N_i^{I}(R,E_i) = N_0(R,v_i)\left\{1-\exp\left[-RN\sum_f k_{if}(R)/v_i\right]\exp\left[-N\int_0^R k_{ii}(R)\,\mathrm{d}R/v_i\right]\right\}, \tag{5.18}$$

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which tends to N_0 as $R \to \infty$. It is worthwhile noting, even for approximation (5.18), that α given by (2.52) predicts a general nonlinear variation with gas density N for which the acceleration term in (5.7) can be neglected. Since off-diagonal terms are also ignored in this approximation to $\Phi_{\mathrm{i}}^{\mathrm{I}}$, there is no coupling with the sink, and (5.18) is valuable only in providing interesting insight to the manner in which the diffusion term on the left-hand side of (5.7) affects the R-distribution of ion pairs. Full coupling with the sink is provided only by solution of the full set of coupled equations (5.15).

In the limit of high N, (5.18) predicts zero α, and the diffusion (R-gradient) term in (5.7) may therefore be neglected in comparison with the acceleration (v_{i}-gradient) term. With the substitution

$$\Phi_{\mathrm{i}}(R, v_{\mathrm{i}}) = \Phi_{\mathrm{i}}^{\mathrm{II}}(R, v_{\mathrm{i}}) \exp(v_{\mathrm{i}}/V_{\mathrm{i}}), \tag{5.19}$$

where the effective speed is

$$V_{\mathrm{i}}(R, E_{\mathrm{i}}) = \left(\frac{\partial V}{\partial R}\right) \Big/ mN \sum_{\mathrm{f}} k_{\mathrm{if}} \equiv a(R)\, \tau_{\mathrm{i}}(R, E_{\mathrm{i}}), \tag{5.20}$$

in terms of the acceleration $a(R)$ and of time $\tau_{\mathrm{i}} \equiv L_{\mathrm{i}}(v_{\mathrm{i}}^2)/v_{\mathrm{i}}$ between collisions, the set (5.7), with diffusion ignored, yields, after some analysis and reduction, the set of first-order coupled differential equations

$$\frac{\partial \Phi_{\mathrm{i}}^{\mathrm{II}}(R, E_{\mathrm{i}})}{\partial v_{\mathrm{i}}} = -\frac{N}{a(R)} \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} \Phi_{\mathrm{f}}^{\mathrm{II}}(R, E_{\mathrm{i}})\, k_{\mathrm{if}}(R) \exp[(v_{\mathrm{f}}/V_{\mathrm{f}}) - (v_{\mathrm{i}}/V_{\mathrm{i}})] \tag{5.21}$$

analogous to the previous set (5.15). This set can also be solved to various degrees of sophistication. As before, the zero-order approximation follows by neglect of the off-diagonal elements to yield,

$$\frac{\partial \Phi_{\mathrm{i}}^{\mathrm{II}}}{\partial v_{\mathrm{i}}} \approx \frac{\partial \Phi_{\mathrm{i}}^{(0)}}{\partial v_{\mathrm{i}}} = -\frac{N}{a(R)} k_{\mathrm{ii}}(R)\, \Phi_{\mathrm{i}}^{(0)}, \tag{5.22}$$

such that

$$\Phi_{\mathrm{i}}^{(0)}(R, v_{\mathrm{i}}) = \exp\left[-\frac{N}{a(R)} \int_0^{v_{\mathrm{i}}} k_{\mathrm{ii}}(R)\, \mathrm{d}v_{\mathrm{i}}\right], \tag{5.23}$$

which vanishes as $R \to \infty$. Hence in this approximation the phase density is

$$N_{\mathrm{i}}^{\mathrm{II}}(R, E_{\mathrm{i}}) = N_0(R, v_{\mathrm{i}}) \left\{1 - \exp\left[Nmv_{\mathrm{i}} \sum_{\mathrm{f}} k_{\mathrm{if}} \Big/ \frac{\partial V}{\partial R}\right] \exp\left[-\frac{Nm}{\partial V/\partial R} \int_0^{v_{\mathrm{i}}} k_{\mathrm{ii}}(R)\, \mathrm{d}v_{\mathrm{i}}\right]\right\} \tag{5.24}$$

which exhibits an increasing or decreasing variation with N, depending on the kinetics of the collision.

For general N however, both diffusion and acceleration terms in (5.7) are effective. With the assumption that the first solution $\Phi_{\mathrm{i}}^{\mathrm{I}}(R, v_{\mathrm{i}})$ contains most of the R-variation and that $\Phi_{\mathrm{i}}^{\mathrm{II}}(R, v_{\mathrm{i}})$ contains most of the v_{i}-variation, a working approximation for the general case (5.7) is

$$\Phi_{\mathrm{i}}(R, v_{\mathrm{i}}) \approx \tfrac{1}{2}(\Phi_{\mathrm{i}}^{\mathrm{I}} + \Phi_{\mathrm{i}}^{\mathrm{II}}), \tag{5.25}$$

where $\Phi_{\mathrm{i}}^{\mathrm{I},\,\mathrm{II}}$ are the full solutions of (5.15) and (5.21), respectively.

In the zero-order approximation that ignores the effect of the sink, we have

$$\begin{aligned} N_{\mathrm{i}}^{*}(R, v_{\mathrm{i}}) = N_0(R, v_{\mathrm{i}}) \Bigg\{1 &- \tfrac{1}{2}\exp\Big(-NR \sum_{\mathrm{f}} k_{\mathrm{if}}/v_{\mathrm{i}}\Big) \exp\left(-\frac{N}{v_{\mathrm{i}}} \int_0^R k_{\mathrm{ii}}\, \mathrm{d}R\right) \\ &- \tfrac{1}{2}\exp\left[Nmv_{\mathrm{i}} \sum_{\mathrm{f}} k_{\mathrm{if}} \Big/ \frac{\partial V}{\partial R}\right] \exp\left[-\frac{Nm}{\partial V/\partial R} \int_0^{v_{\mathrm{i}}} k_{\mathrm{ii}}\, \mathrm{d}v_{\mathrm{i}}\right]\Bigg\} \end{aligned} \tag{5.26}$$

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which tends to N_0 when $R \to \infty$ or when $v_\mathrm{i} \to \infty$. This 'one-channel' result is useful in providing insight into the overall effect of the diffusion and acceleration terms on the ion distribution. With (5.26) as a background density, various corrections may then be obtained. The effect of the sink is, of course, acknowledged by the full solution of (5.15) and (5.21).

Calculations based on the procedures outlined above are under way and will be presented in future reports.

5.2. '*Distribution in length between collisions*' *method: the frequency equation*

The second and very effective approach for solution of (5.1) for the ion-phase densities is based on the recognition that the collisional integral, the right-hand side of (5.1), in contrast to the 'incompressible' streaming terms of the left-hand side, attempts via quasi-discontinuous collisions to drive the momentum-space part of the distribution towards Maxwellian at a given ion–ion separation R. With this in mind set the ion-pair distribution as,

$$N_\mathrm{i}(R, v_\mathrm{i}) = [4\pi R^2 \tilde{n}(R)\, N^+]\, F_0(v_\mathrm{i})\, [1 + \Phi_\mathrm{i}(R, v_\mathrm{i})], \tag{5.27}$$

where $\tilde{n}(R)$ is some negative-ion configuration-space density yet to be determined, and where Φ_i, which represents the departure of the momentum distribution from the Maxwellian $F_0(v_\mathrm{i})$, will provide coupling to the recombination sink. On substituting (5.27) in (5.1), by noting that the acceleration term operating on the Maxwellian produces

$$-\frac{4\pi v_\mathrm{i}^2}{m}\frac{\partial}{\partial v_\mathrm{i}}\left[\frac{F_0(v_\mathrm{i})}{4\pi v_\mathrm{i}^2}\right] = v_\mathrm{i}\, F_0(v_\mathrm{i})\, \frac{\partial(V/kT)}{\partial R}, \tag{5.28}$$

after some reduction, we obtain (5.1) exactly as

$$\begin{aligned} v_\mathrm{i}\, F_0(v_\mathrm{i}) \left\{\hat{\mathrm{D}}\tilde{n}(R) + \frac{\partial}{\partial R}[\Phi_\mathrm{i}\, \tilde{n}(R)] - \tilde{n}(R)\, \frac{\partial(V/kT)}{\partial R}\, \frac{\partial \Phi_\mathrm{i}}{\partial T_\mathrm{i}}\right\} \\ = \tilde{n}(R)\, F_0(v_\mathrm{i}) \left[\iint_{\Omega'} N_0(\boldsymbol{v}_0)\, (\Phi_\mathrm{f} - \Phi_\mathrm{i})\, (g\sigma\, \mathrm{d}\Omega)\, \mathrm{d}\boldsymbol{v}_0\right], \end{aligned} \tag{5.29}$$

where the $\hat{\mathrm{D}}$-operator is such that

$$\hat{\mathrm{D}}\tilde{n} \equiv \left[\frac{\mathrm{d}}{\mathrm{d}R} + \frac{\mathrm{d}(V/kT)}{\mathrm{d}R}\right] \tilde{n}(R), \tag{5.30}$$

and where T_i, the normalized kinetic energy of ion–ion relative motion is $\frac{1}{2}\mathrm{m}v_\mathrm{i}^2/kT$. The separation of the collision integral (the right-hand side of (5.29)) into its various components suggests the solution

$$\Phi_\mathrm{i}(R, v_\mathrm{i}) = -[1/\tilde{n}(R)]\, \hat{\mathrm{D}}\tilde{n}(R)\, l_\mathrm{i}(v_\mathrm{i}^2, R) \tag{5.31}$$

where l_i is an unknown function principally of v_i^2, but only because of the recombination sink will depend, in general, on R and E_i. In thermodynamic equilibrium, Φ_i is zero and $\tilde{n}(R)$ is $N^- \exp(V/kT)$ such that $\hat{\mathrm{D}}\tilde{n}$ vanishes. Hence the $\hat{\mathrm{D}}$-operator in effect projects out the background R-variation due to outward diffusion and inward mobility and leaves only that R-variation due to the presence of the sink alone. When departures from thermodynamic equilibrium are not too strong we need not restrict $\hat{\mathrm{D}}\tilde{n}$ to be small but its derivative $\mathrm{d}(\hat{\mathrm{D}}\tilde{n})/\mathrm{d}R$ must vanish. Under this sole approximation (5.29) reduces with the aid of substitution (5.31), and after some analysis, to

$$v_\mathrm{i}\left[1 - \frac{\partial l_\mathrm{i}(v_\mathrm{i}^2, R)}{\partial R} + \frac{\partial(V/kT)}{\partial R}\, \frac{\partial l_\mathrm{i}(v_\mathrm{i}^2, R)}{\partial T_\mathrm{i}}\right] = N\left[l_\mathrm{i}(R, E_\mathrm{i}) \sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} k_\mathrm{if}(R) - \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} l_\mathrm{f}(R, E_\mathrm{f})\, k_\mathrm{if}(R)\right]. \tag{5.32}$$

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The frequency ν_{i} of ion–neutral collisions is

$$\nu_{\mathrm{i}}(v_{\mathrm{i}}) = N \sum_{\mathrm{f}=-\mathrm{V}}^{\mathrm{C}} k_{\mathrm{if}}(R), \tag{5.33}$$

such that the interval τ_{i} between collisions for ions of speed v_{i} is ν_{i}^{-1} and the mean length L_{i} of their free paths is

$$L_{\mathrm{i}}(v_{\mathrm{i}}) = v_{\mathrm{i}}\,\tau_{\mathrm{i}} = v_{\mathrm{i}}/\nu_{\mathrm{i}}. \tag{5.34}$$

When the ion–neutral collision cross section Q^{E} or Q^{X} for elastic or charge-transfer collisions is independent of the relative speed, the path length peculiar to speed v_{i} is, as shown in the Appendix B,

$$L_{\mathrm{i}}(v_{\mathrm{i}}) = \pi^{\frac{1}{2}} X_{\mathrm{i}}/NQ^{\mathrm{X,E}}[(2X_{\mathrm{i}}+1)\tfrac{1}{2}\pi^{\frac{1}{2}}\Phi_{\mathrm{E}}(X_{\mathrm{i}}^{\frac{1}{2}}) + X_{\mathrm{i}}^{\frac{1}{2}}\exp(-X_{\mathrm{i}})], \tag{5.35}$$

where Φ_{E} is the error function which is a function of

$$X_{\mathrm{i}} = \tfrac{1}{2}Mv_{\mathrm{i}}^2/kT \tag{5.36}$$

in terms of the reduced mass M of the ion-pair–neutral system. As $X_{\mathrm{i}} \to \infty, L_{\mathrm{i}} \to (NQ)^{-1} \equiv l_{\infty}$. Hence, (5.32) can be rewritten as

$$v_{\mathrm{i}}\left[\frac{l_{\mathrm{i}}(R,E_{\mathrm{i}})}{L_{\mathrm{i}}(v_{\mathrm{i}})} - 1 + \frac{\partial l_{\mathrm{i}}(R,v_{\mathrm{i}}^2)}{\partial R} - \frac{\partial(V/kT)}{\partial R}\frac{\partial l_{\mathrm{i}}(R,v_{\mathrm{i}}^2)}{\partial T_{\mathrm{i}}}\right] = N \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} l_{\mathrm{f}}(R,E_{\mathrm{f}})\,k_{\mathrm{if}}(R), \tag{5.37}$$

the basic equation to be solved for l_{i} under appropriate boundary conditions.

The negative ion density n_{i} is from (5.27) and (5.31) given by

$$n_{\mathrm{i}}(R,E_{\mathrm{i}}) = [\tilde{n}(R) - \hat{\mathrm{D}}\,\tilde{n}(R)\,l_{\mathrm{i}}(R,E_{\mathrm{i}})]\,F_0(v_{\mathrm{i}}) \tag{5.38}$$

which tends to n_0 as $E_{\mathrm{i}} \to \infty$, i.e.

$$\tilde{n}(R) - \hat{\mathrm{D}}\,\tilde{n}(R)\,l(R,\infty) = N^{-}\exp(-V/kT). \tag{5.39}$$

With use of (5.30) and an integrating factor, (5.39) is solved to yield

$$\tilde{n}(R) = N^{-}\exp(-V/kT)\exp[R/l(R,\infty)]\int_R^{\infty}\frac{\exp[-R/l(R,\infty)]}{l(R,\infty)}\,\mathrm{d}R, \tag{5.40}$$

which tends to the appropriate thermodynamic value $N^{-}\exp(-V/kT)$ as $R \to \infty$. Hence, the overall phase density is

$$\begin{aligned} n_{\mathrm{i}}(R,E_{\mathrm{i}}) = N^{-}\exp(-V/kT)\,F_0(v_{\mathrm{i}})&\left\{\frac{l_{\mathrm{i}}(R,E_{\mathrm{i}})}{l(R,\infty)} + \left[1 - \frac{l_{\mathrm{i}}(R,E_{\mathrm{i}})}{l(R,\infty)}\right]H(E_{\mathrm{i}})\right.\\ &\left.\times\exp[R/l(R,\infty)]\int_R^{\infty}\frac{\exp[-R/l(R,\infty)]}{l(R,\infty)}\,\mathrm{d}R\right\}, \end{aligned} \tag{5.41}$$

where the Heaviside step function H is unity only for energies E_{i} in the continuum (as implied by the $R \to \infty$ limit).

As $E_{\mathrm{i}} \to \infty$, (5.41) ensures that $n_{\mathrm{i}} \to n_0$; and as $R \to \infty$, $n_{\mathrm{i}} \to n_0$ implies that

$$l_{\mathrm{i}}(R,E_{\mathrm{i}}) \to l_{\mathrm{i}}(\infty,E_{\mathrm{i}}) = l(\infty,\infty) \equiv l_{\infty}. \tag{5.42}$$

Hence the set (5.37) is solved subject to the condition (5.42). As $E_{\mathrm{i}} \to \infty$, the right-hand side of (5.37) vanishes, $L_{\mathrm{i}} \to l_{\infty}$ and hence

$$\frac{l(R,\infty)}{l_{\infty}} - 1 + \frac{\partial l(R,\infty)}{\partial R} - \frac{\partial(V/kT)}{\partial R}\left[\frac{\partial l_{\mathrm{i}}(R,E_{\mathrm{i}})}{\partial T_{\mathrm{i}}}\right]_{T_{\mathrm{i}}\to\infty} = 0. \tag{5.43}$$

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For infinite E_i or T_i, the last term on the left-hand side of (5.43) vanishes and the resulting equation can be solved, subject to the condition of vanishing $l_i(R \rightarrow 0, \infty)$, to give

$$l(R, \infty) = l_\infty[1-\exp(-R/l_\infty)], \tag{5.44}$$

which satisfies (5.42) and which also ensures that $(\partial l_i/\partial R)_{R\rightarrow\infty}$ vanishes. Hence the phase density is given by (5.41) in terms of (5.44) and of $l_i(R, E_i)$, the solution of (5.37) over a spectrum of (R, E_i)-values subject to $l(R, \infty)$ as $E_i \rightarrow \infty$. Each solution will depend on the gas density N through l_∞.

At high gas densities, $l_\infty \rightarrow 0$, $l(R, \infty) \rightarrow \infty$, and (5.41) tends to its thermodynamic equilibrium value, as expected. At low gas densities $l_\infty \rightarrow \infty$, and

$$l_i(R, E_i) \rightarrow l(R, \infty)\,\gamma(E_i), \tag{5.45}$$

where $\gamma(E_i)$ is a function only of E_i and is unity for $E_i \geqslant 0$. Hence (5.41) yields

$$n_i(R, E_i) = N^- \exp(-V/kT)\,F_0(v_i)\,\{\gamma(E_i)+[1-\gamma(E_i)]\,H(E_i)\}. \tag{5.46}$$

The expression (5.37) for the distribution in the lengths $l_i(R, E_i)$ between collisions for use in (5.41) and hence in the recombination coefficient α in (2.52) is, apart from the neglect of $\mathrm{d}[\hat{\mathrm{D}}\,\tilde{n}(R)]/\mathrm{d}R$ in (5.29), exact. The chief distinction between this proposed method and the previous method is that l_i is, in the absence of the recombination sink, a function only of v_i^2, while Φ_i in (5.3) is a function of both R and v_i. Hence the R-dependence in $l_i(R, v_i^2)$ results only from the sink; the background R-dependence due to outward diffusion and mobility being acknowledged already by $\tilde{n}(R)$.

The physical meaning of the functions $\tilde{n}$ and l_i in (5.27) and (5.31) becomes apparent by noting that the current density (ions cm^{-2}s^{-1}) is

$$\boldsymbol{J}_S = \tilde{n}(R)\,\boldsymbol{v}_\mathrm{d} = \int n_i(R, v_i)\,\boldsymbol{v}_i\,d\boldsymbol{v}_i, \tag{5.47}$$

which with the aid of (5.27) and (5.31) reduces, after some analysis, to

$$\boldsymbol{J}_S = -D_S\left[\frac{\mathrm{d}\tilde{n}}{\mathrm{d}R}+\tilde{n}(R)\,\frac{\partial(V/kT)}{\partial R}\right]\hat{\boldsymbol{R}} \tag{5.48}$$

where

$$D_S = \frac{1}{3}\int_{v_{i0}(R)}^{\infty} F_0(v_i)\,v_i\,l_i(v_i^2)\,\mathrm{d}v_i\ (\mathrm{cm^2\,s^{-1}}) \tag{5.49}$$

is the diffusion coefficient in the presence of the sink for ions with the radial distribution $\tilde{n}(R)$. The factor of $\frac{1}{3}$ in (5.49) arises by adopting the radial direction $\hat{\boldsymbol{R}}$ as the Z-axis for v_i-integration of (5.47). Hence $l_i(v_i^2)$ is an actual path length at ion speed v_i (and not a phenomenological mean free path), such that the diffusion coefficient that would be measured in a recombination experiment is

$$D_S \equiv \tfrac{1}{3}\langle l_i v_i\rangle\ (\mathrm{cm^2\,s^{-1}}), \tag{5.50}$$

an average over the ion-distribution in the presence of the recombination sink. In light of this relation and of (5.34), the basic equation (5.37) which provides the average rate of increase of l_i between collisions can be referred to as *the frequency equation.*

As before, a hierarchy of approximate computational schemes can be proposed for evaluation of $l_i(R, E_i)$ from (5.37). Since $\tilde{n}(R)$ contains most of the background R-dependence, we can assume, with the aid of (5.44), that on the left-hand side of (5.32)

$$\frac{\partial l_i(R, v_i^2)}{\partial R} \approx \frac{\partial l(R, \infty)}{\partial R} = \exp(-R/l_\infty), \tag{5.51}$$

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and neglect initially the acceleration term $\partial(V/kT)/\partial R$. The resulting set of equations,

$$v_{\mathrm{i}}\left[\frac{l_{\mathrm{i}}(R, E_{\mathrm{i}})}{L_{\mathrm{i}}(v_{\mathrm{i}}^2)} - 1 + \exp\left(-R/l_{\infty}\right)\right] = N \sum_{\mathrm{f}=-\mathrm{M}}^{\mathrm{C}} l_{\mathrm{f}}(R, E_{\mathrm{f}})\, k_{\mathrm{if}}(R) \tag{5.52}$$

can be evaluated by normal computational techniques.

6. SUMMARY

In this paper a basic microscopic theory of ion–ion recombination as a function of gas density N has been presented. We have developed a basic equation (2.20), a *linear Boltzmann equation*, for the distribution in phase space of ion pairs, and have proposed in § 5 effective methods – the ‘separable-equations’ method and the ‘distribution in length between collisions’ method – for its steady-state solution. An expression (2.52) for the recombination coefficient α in terms of the phase-space distributions has been constructed from *the flux equation* (2.43), a combination of *the equation of continuity* (2.30) and of *the momentum equation* (2.36), both of which have been derived from basic microscopic principles, i.e. the macroscopic effects are truly addressed in language of their microscopic origins in the presence of the recombination sink.

An alternative expression (2.59) for α has been derived in terms of α_{rn}, the rate of reaction or, equivalently, the recombination coefficient that would pertain provided a Boltzmann distribution of ions were maintained, and of α_{tr}, the rate of ionic transport by diffusional drift. The steady-state recombination rate is determined at any gas density N by the rate-limiting steps of reaction and transport which proceed in series. This expression not only provides interesting insights into the internal workings of recombination, as in § 2.4, but is also very valuable when alternative means (as in § 4.2) are used to deduce reliable reaction rates α_{rn} alone, without the necessity of solving the linear Boltzmann equation (2.20). Further theoretical development of this expression reveals in § 3 an N-variation of α consistent with both the nonlinear rise at low N of Thomson's expression, which therefore can be identified with the reaction rate, and with the N^{-1}-decrease in Langevin's result which is the transport rate.

The basic time evolution of recombination is developed in § 2.4 where the Debye–Smoluchowski time-dependent equation (2.89), which is a natural consequence of the present basic theory, is solved for the time dependence of the density of ions undergoing diffusional drift in an arbitrary spherical potential and a reactive sink. This solution enables us to investigate analytically the explicit variation of the recombination rate $\alpha(t)$ with time. For an initial Boltzmann distribution, $\alpha(t)$ is initially determined by the reaction rate, as expected, and tends at large $t (\gg S^2/D)$ to its steady-state limit determined by the limiting rate of reaction or transport. For $N \lesssim N_{\mathrm{L}}$, a straight-line dependence of $\alpha(t)$ with t is noted, since the reaction rate is always much slower, while high $N > N_{\mathrm{L}}$ produces the interesting effect of transition between reaction (initially) and transport, which are the two series components of recombination. This time variation is such that it would permit verification by techniques of modern laser spectroscopy and by appropriate Monte-Carlo computer experiments. Such time dependences will be very important in many applications ranging from medical radiology and biophysics to ionization tracks.

As $N^{\pm}$ is raised, the ion–ion interaction V is, in general, obtained as described in § 4 from the self-consistent solution of the linear Boltzmann equation (2.20) for the phase-space densities, coupled to Poisson's nonlinear equation (4.5) for the radial number densities. The recombination rate α can then be determined as a function of both N and $N^{\pm}$. Otherwise, if the analytic reaction

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rate α_{rn} is known in terms of V as in § 4.2, then Poisson's equation can be solved directly for V. Use of a model for α_{rn} has been illustrated for Kr$^+$–F$^-$ recombination as a function of N for various rare gases.

In conclusion, basic theory has been presented here that thoroughly investigates the recombination rate as a function of gas density, ion density and time.

APPENDIX A. ANALOGY WITH CONDUCTING SPHERE

Introduce a single conducting sphere of radius S held at constant potential ϕ_S into a field of constant potential ϕ_0. The potential ϕ at any point $\boldsymbol{R}$ from the centre of the sphere satisfies Laplace's equation,

$$\nabla^2\phi = 0, \tag{A 1}$$

with solution

$$\phi(R) = \phi_0[1-(S/R)(1-\phi_S/\phi_0)]. \tag{A 2}$$

The total charge induced on the sphere is

$$q_i = -\frac{1}{4\pi}\int \nabla\phi\cdot \mathrm{d}\boldsymbol{S} = -S\phi_0(1-\phi_S/\phi_0). \tag{A 3}$$

For recombination, the steady-state diffusional-drift current $\boldsymbol{j}$ towards a central positive ion satisfies (2.68), i.e.

$$\nabla\cdot\boldsymbol{j} = \nabla\cdot[D\exp(-V/kT)\nabla n^- \exp(V/kT)] = 0, \tag{A 4}$$

subject to $n = N^-$ at infinity and to $n = n_S$ at the surface of the sink of radius S, respectively. When the field V is neglected, the resulting Laplace's equation is solved to give the density

$$n^-(R) = N^-[1-(S/R)(1-n_S/N^-)]. \tag{A 5}$$

The flux across any R-sphere is,

$$F^- = 4\pi SD(1-n_S/N^-)N^- \equiv \alpha_d(1-n_S/N^-)N^- = \alpha N^-, \tag{A 6}$$

where α_d is the recombination rate α appropriate to instantaneous reaction $(n_S = 0)$. Analogy with electrostatics then follows by identifying the local ion density n^- with the local potential ϕ, and the flux of ions across S with the induced charge. Hence, the recombination rate α is equivalent to $4\pi D$ times the 'induced charge q_i' per unit 'external potential ϕ_0', and the transport rate α_d is $4\pi D$ times the 'induced charge q_i' per unit 'potential difference $(\phi_S-\phi_0)$'. Introduce a reaction rate α_3 at S by

$$\alpha_3 n_S = \alpha N^-, \tag{A 7}$$

which equates the incident flux with the rate (s^{-1}) of reaction. Thus the reaction rate α_3 is $4\pi D$ times the 'induced charge q_i' per 'unit surface potential ϕ_S'. Thus α, α_3 and α_d may be regarded as appropriate capacitances of the sphere associated with potentials ϕ_0, ϕ_S and $\phi_S-\phi_0$, respectively. From (A 6) and (A 7),

$$1/\alpha = 1/\alpha_3 + 1/\alpha_d, \tag{A 8}$$

showing that the overall rate (cm^3 s^{-1}) is equivalent to a capacitance associated with potential ϕ_S joined in series to a capacitance with potential $\phi_S-\phi_0$. This analogy is similar in spirit to that of Bates (1974).

For non-zero V, (A 4) can be reduced to Laplace's equation (A 1) via transformations (2.105) and (2.107). The above analogy between ϕ in (A 1)–(A 3) and $n\exp(V/kT)$ is preserved in $\tilde{R}$-space. The equivalent solution is then

$$n^-(R) = N^-\exp(-V/kT)\{1-(\tilde{S}/\tilde{R})(1-n_S\exp[V(S)/kT]/N^-)\}, \tag{A 9}$$

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which is analogous with (A 2). With the aid of (2.105), the inward flux across any R-sphere is

$$F^- = 4\pi R^2 D \exp(-V/kT)\,[\mathrm{d}\,n(R)\exp(V/kT)\,/\mathrm{d}R] \tag{A 10}$$

$$= 4\pi D\, N^- \tilde{S}\{1-(n_s/N^-)\exp[V(S)/kT]\}, \tag{A 11}$$

such that, with (A 7),

$$1/\alpha = 1/\alpha_{\mathrm{rn}} + 1/\alpha_{\mathrm{tr}} \tag{A 12}$$

where the diffusional-drift transport rate that replaces α_d is

$$\alpha_{\mathrm{tr}} = 4\pi\tilde{S}D \equiv 4\pi D \Big/ \int_S^\infty \exp(V/kT)\,R^{-2}\,\mathrm{d}R \tag{A 13}$$

as in (2.115), and where the reaction rate is

$$\alpha_{\mathrm{rn}} = \alpha_3 \exp[-V(S)/kT]. \tag{A 14}$$

This analogy may be extended to cover the case where there are many non-overlapping conducting and identical spheres. A charge on one reference sphere induces on the remaining spheres an image charge that can be replaced by an induced charge and a dipole located at each centre. A self-consistent set of charges and dipoles are set up. The recombination coefficient pertinent to a large number of positive ions is then given by $4\pi D$ times the self-consistent 'induced charge' per unit potential ϕ_0 at infinity. This analogy furnishes a method whereby the competition for flux between the various non overlapping sinks can be acknowledged and is therefore relevant to the case of high ion density.

Appendix B. The peculiar mean free path

The path length of an ion moving with speed v_i in a gas of density N is defined by equation (5.14) as

$$L_i(v_i) = v_i/[N \sum_f k_{if}(R)], \tag{B 1}$$

where the denominator is the frequency ν_i for all elastic ion–neutral collisions that leave an R-ion pair in all states of binding (bound and dissociative) at fixed internal separation R. Thus, the collisional rate (cm³ s⁻¹) between an ion i and a gas atom 3 is

$$\sum_f k_{if}(R) \equiv \int_{-\infty}^{\infty} k'(E_i, E_f, R)\,\mathrm{d}E_f = \frac{1}{2}\int_0^\infty G(v_3)\,\mathrm{d}v_3 \int_\Omega g\sigma(g,\psi)\,\mathrm{d}(\cos\psi)\,\mathrm{d}\phi \int_{-1}^{+1}\mathrm{d}\mu, \tag{B 2}$$

where

$$\boldsymbol{g} = \boldsymbol{v}_1 - \boldsymbol{v}_3; \quad \mu = \hat{\boldsymbol{v}}_1\cdot\hat{\boldsymbol{v}}_3 \tag{B 3}$$

and where G is the distribution of gas speeds v_3. The differential cross section for i–3 scattering in the i–3 centre-of-mass reference frame is σ, which for isotropic (hard-sphere) scattering independent of the (thermal) impact speed is $Q/4\pi$ in terms of the integral cross section Q. Hence

$$\sum_f k_{if}(R) = Q\int_0^\infty G(v_3)\,\mathrm{d}v_3(v_1 + \tfrac{1}{3}v_3^2/v_1), \quad v_1 > v_3,$$

$$= Q\int_0^\infty G(v_3)\,\mathrm{d}v_3(v_3 + \tfrac{1}{3}v_1^2/v_3), \quad v_1 < v_3, \tag{B 4}$$

which reduces, for a Maxwellian distribution with respect to the centre of mass of the ion pair, to

$$\sum_f k_{if}(R) = \tfrac{1}{2}Q\,\langle v_3\rangle[(2X_i^{\frac{1}{2}} + X_i^{-\frac{1}{2}})\,\tfrac{1}{2}\pi^{\frac{1}{2}}\,\Phi_E(X_i^{\frac{1}{2}}) + \exp(-X_i)], \tag{B 5}$$

where

$$X_i = (\tfrac{1}{2}Mv_i^2/kT) \tag{B 6}$$

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in terms of the reduced mass M of the (ion-pair–gas) system, where

$$\Phi_{\mathrm{E}}(X_{\mathrm{i}}^{\frac{1}{2}}) = \frac{2}{\sqrt{\pi}}\int_0^{X_{\mathrm{i}}^{\frac{1}{2}}} \exp(-t^2)\,\mathrm{d}t = \frac{1}{\sqrt{\pi}}\int_0^{X_{\mathrm{i}}} E^{-\frac{1}{2}}\exp(-E)\,\mathrm{d}E, \tag{B 7}$$

is the probability integral (or error function), and where $\langle v_3\rangle$ is the mean thermal speed $(8kT/\pi M)^{\frac{1}{2}}$ of the gas atoms. The total rate (B 5) tends to $Q\langle v_3\rangle$ and to $Q\,v_{\mathrm{i}}$ as $v_{\mathrm{i}} \rightarrow 0$ and as $v_{\mathrm{i}} \rightarrow \infty$, respectively. Equation (5.35) for L_{i} in the text is therefore recovered from (B 1) and (B 5.) We note that

$$L_{\mathrm{i}}(v_{\mathrm{i}})/L_{\mathrm{i}}(\infty) = \pi^{\frac{1}{2}} X_{\mathrm{i}}/[(2X_{\mathrm{i}}+1)\,\tfrac{1}{2}\pi^{\frac{1}{2}}\,\Phi_{\mathrm{E}}(X_{\mathrm{i}}^{\frac{1}{2}}) + X_{\mathrm{i}}^{\frac{1}{2}}\exp(-X_{\mathrm{i}})], \tag{B 8}$$

increases monotonically with v_{i} from zero to unity. The results (B 5) and (B 8) hold for either elastic or charge-transfer ion–neutral collisions with cross sections Q assumed to be independent of the relative speed.

This research is sponsored by the U.S. Air Force Office of Scientific Research under grant no. AFOSR-80-0055.

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