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A new and basic theory of ion-ion recombination in a dense gas has been developed from basic microscopic principles. The recombination rate is provided as a function of gas density, ion density and time. Various simplified treatments of ion-ion recombination are also presented. Research progress accomplished between January 1 - December 1981 is fully documented in seven published papers which appear as Appendices A - G of this report.
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Appendices A - G
Abstract

The research performed under AFOSR grant no. AFOSR-80-0055 during the period January 1, 1981 - December 31, 1981 is reported. The theory formulated and results obtained are fully documented by seven published papers which appear in Appendices A - G of this report and which represent a complete account of the work performed during the 1981 year. In particular, a new and basic theory of ion-ion recombination in a dense gas has been developed from basic microscopic principles and is fully described in Appendix F.
1. Refereed Research Publications under AFOSR Grant

1.1 January 1, 1980 - December 31, 1980


Separate copies of reprints of all of these publications (1) - (6) have already been forwarded during the course of the 1981-year and were fully documented in the interim report for the previous year (1980).

1.2 January 1, 1981 - December 31, 1981


Copies of all of the above papers #6-12 appear as Appendices A - G of this interim report. These papers represent the research work performed during 1981, under the present AFOSR grant.

2. Papers Presented at Scientific Meetings

3. Special Highlights: New Theoretical Developments in Present Research

A new and basic theory of ion-ion recombination as a function of gas density $N$ has been developed (M. R. Flannery, Phil. Trans. Roy. Soc. A) from basic microscopic principles. A key equation for the distribution in phase space of ion pairs has been derived together with an expression for the resulting recombination coefficient $\alpha$. Further development of the theory leads to interesting insights to a full variation with $N$ of $\alpha$, which is shown to yield the correct limits at low and high $N$. The recombination rate $\alpha$ is determined by the limiting step of the rate $\alpha_{RN}$ for ion reaction and of the rate $\alpha_{TR}$ for ion transport to the reaction zone. An accurate analytical solution of the time-dependent Debye-Smoluchowski equation which is a natural consequence of this theory, has been provided, for the first time, for transport/reaction under a general interaction $V$ in the cases of an instantaneous reaction ($\alpha_{RN} \gg \alpha_{TR}$) and of a finite rate ($\alpha_{RN} \sim \alpha_{TR}$) of reaction within a kinetic sink rendered compressible via variation of gas density. Expressions for the transient recombination rates $\alpha(t)$ have then been derived and illustrated. The exhibited time dependence lends itself to eventual experimental verification at high $N$.

A theory which investigates the variation of $\alpha$ with ion density $N^\pm$ has 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 have been illustrated as a function of $N$ via a simplified method for the reaction rate. Finally, two theoretical procedures for the solution of the general phase-space ion distributions have been proposed.
Appendix A

LETTER TO THE EDITOR

Thermal collisions of Rydberg atoms with neutrals

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Abstract. A new theoretical method outlined here for an important inelastic mechanism based on A—B⁺ encounters in A—B(n) thermal collisions indicates a substantial contribution to l-changing transitions which therefore cannot be viewed as proceeding via (e—A) encounters alone. Recent descriptions of l-changing thermal collisions which are based on an (e—A) impulse treatment appear defective in that they disregard certain impulse validity criteria and yield results which greatly exceed the upper limit specified by the basic impulse expression, and do not recognize the above important inelastic mechanism associated with the non-inertiality of the core.

In the collision process,

\[ A(i) + B(n) \rightarrow A(j) + \begin{cases} B(n') \\ B^+ + e \end{cases} \]  \hspace{1cm} (1)

between an incident atom (or molecule) A and a target atom B initially in a highly excited state with principal quantum number n, energy and momentum changes to the Rydberg electron (labelled 1) can be assumed, under certain conditions (see Flannery 1980 and below), to occur via a collision of 1 with the projectile A (labelled 3). A (1—3) inelastic encounter includes the additional possibility of simultaneous \((i \rightarrow j)\) transitions in the internal state of A. Based on this premise, a semiquantal treatment was developed (Flannery 1970, 1973) mainly for the ionisation channel in (1) and was recently derived (Flannery 1980) from the basic quantal impulse expression (cf Coleman 1969) in which the wavefunction for the ejected electron is replaced by a plane wave.

The three basic assumptions within the impulse approximation to A—B(n) collisions become fully transparent from a derivation (Flannery 1980) based on the two-potential formula and they are as follows.

(i) The interactions \(V_{12}\) and \(V_{32}\) of 1 and 3 with the core \(B^+\) (labelled 2) are switched off during the (1—3) collision time and \(V_{12}\) is invoked only to establish the initial and final quantal states of the target system.

(ii) The distortion of the motion of the projectile 3 in the field \(V_{32}\) due to the core 2 is neglected when interacting with both 2 and with the Rydberg electron 1.

(iii) Inelastic transitions in B are prohibited in direct (A—B⁺) encounters.

Although (i)–(iii) may be justified for many kinds of A—B(n) direct collision processes at sufficiently high \(n\) and collision speeds \(v_3 \gg v_1\), the orbital speed of the Rydberg electron, conditions (ii) and (iii) can be seriously violated, particularly when \(v_1 \ll v_3\). Various implications of (i)–(iii), discussed below, cast serious doubts on the overall validity of various models recently proposed (Matsuzawa 1979 and references...
therein, Hickman 1979, de Prunele and Pascale 1979) for angular momentum $l$-changing and quenching collisions between $B(nl)$ and rare-gas atoms at thermal energies (when $v_1 \gg v_3$), a subject of great current experimental interest and activity (Hugon et al. 1979, 1980 and references therein, Gallagher et al. 1977). Moreover, the models are based on further simplification such as a Born or $\delta$-function reduction within the basic impulse expression and, as such, entail additional validity criteria. The models yield results greatly in excess of the actual upper limit imposed by the basic impulse expression (cf. Flannery 1980). Also they neglect the effect of thermal ($2\rightarrow 3$) collisions which are, in fact, important.

(iv) Although not essential to the impulse treatment, 'on-the-energy-shell' ($1\rightarrow 3$) encounters in all applications to $A-B(n)$ collisions are tacitly assumed, a procedure valid only in the high-energy or weak-binding limit.

Assumptions (i)-(iii) above imply important conditions of special significance to $A-B(nl)$ thermal collisions.

**Condition A.** Switching off the core interactions $(V_{12} + V_{32})$ during the ($1\rightarrow 3$) collision time $\tau_c$ implies that energy can be controlled only to within an imprecision $\Delta E_1 \sim \hbar/\tau_c$ during the collision, i.e. the energy dependence of the electron-$1$-projectile-$3$ cross section $\sigma_{13}$ must not exhibit too rapid a variation as occurs, for example, in the neighbourhood of an electron-atom resonance in which a negative ion $A^-$ is temporarily formed, or in the vicinity of a Ramsauer minimum evident for $e$-$Ar$, $Kr$ and $Xe$ scattering. This implication is ignored by Matsuzawa (1979) in his resonance and $l$-changing studies, by Hickman (1979) and by others (e.g. de Prunele and Pascale). When $v_1 \gg v_3$, $\tau_c \sim A_1 n (au)$ where $A_1 (a_0)$ is the $(e-A)$ interaction distance such that during $\tau_c$ the energy imprecision $\Delta E_1 \sim (A_1 n)^{-1} au$ is comparable with the small impact energy $\frac{1}{2}v_1^2$. For $v_3 \gg v_1$, however, $\Delta E_1 \sim v_3/A_1$ which is very much less than $\frac{1}{2}v_1^2$ the relative energy over which $\sigma_{13}$ generally varies slowly.

**Condition B.** The momentum $P$ transferred (impulsively) to $1$ during the collision time $\tau_c$ must be very much greater than the momentum imparted to $1$ during the same time via the force $F$ due to its interaction $V_{12}$ with the core, i.e.

$$P \gg \int_{\tau_c} F dt \approx \langle \phi_{nl} | -\nabla V_{12} | \phi_{nl} \rangle \tau_c \approx \frac{\tau_c}{n^2 (l+\frac{1}{2})}$$

(2a)

where $\phi_{nl}$ is the electronic wavefunction for the Rydberg electron with orbital period $T_n \sim n^2$ au for each $l$ such that

$$\tau_c \ll T_n (l+\frac{1}{2}) P.$$ 

(2b)

If $V_{12}$ varies sufficiently slowly (but need not be necessarily small!) over the range $A_1$ of the collision interaction $V_{13}$, such that the force $F (\equiv -\nabla V_{12})$ due to the core is small in comparison with the impulsive force $(-\nabla V_{13})$ due to the Rydberg electron-projectile interaction, then (2) is satisfied; in this sense $V_{12}$ can be regarded as 'quasiclassical'.

For ionising collisions, $P \sim n^{-1}$, then $\tau_c \ll T_n$ for circular orbits ($l \sim n$) and $\tau_c \ll T_n/n$ for highly eccentric orbits ($l \sim 0$). Hence, the requirement $\tau_c \ll n^2$ covers electron ejection from all orbits. For non-ionising collisions, $P$ by (2) cannot become arbitrarily small, which could occur for quasi-elastic or $l$-changing collisions. At thermal energies, the electron speed $v_1 \sim n^{-1}$ au is greater than the incident speed $v_3 \sim 10^{-4}$ au of $A$ for most $n$ of interest, and the collision time $\tau_c \sim A_1 n$ for $e$-$rare$-gas atom scattering (where $A_1 \sim (1-7)a_0$) such that (2) implies that $P \gg A_1/n^2 (l+\frac{1}{2})$. The angular momentum
change (for fixed $n$) due to (e-A) impulsive encounters at $R_{12}$ from B$^+$ must satisfy
\[ \Delta L \sim P(R_{12}) \sim \frac{1}{2} P[3n^2 - l(l + 1)] \gg \frac{1}{2} A_4 [3n^2 - l(l + 1)]/n^2(l + \frac{1}{2}) \] (3)

which is, in general, fulfilled only at the highest initial $l$ when the permitted $\Delta L \gg A_4/l(l - n)$. Small initial $l$ require large changes $\Delta L \gg A_4$ for validity of the impulse model (since then the momentum imparted by the core on the highly elliptical orbits becomes considerably strengthened over that for circular orbits). The above considerations are absent in any previous $l$-changing study (Matsuzawa 1979, Hickman 1979, de Prunelé and Pascale 1979).

**Condition C.** Since the distortion of $V_{32}$ on the projectile 3 is neglected, the contribution to the basic impulse $T$-matrix element from (2-3) collisions is real and is non-vanishing only for elastic transitions in the target (Flannery 1980), the cross section for all elastic and inelastic events is, from the optical theorem, given in both the basic impulse expression and the semiquantum treatment by (Flannery 1980),
\[ \sigma_{13}^{\text{tot}}(v_3) = \int \frac{1}{v_3} \left| g_i(k_1) \right|^2 [v_{13} \sigma_{13}^{T}(v_{13})] \, dk_1 \] (4)

where $|g_i|^2$ is the probability that the Rydberg electron has momentum $k_1$, where $\sigma_{13}^{T}$ is the total cross section for all elastic and inelastic (1-3) collisions at relative speed $v_{13}$ and where $v_3$ is the speed of the projectile A in the (A-B$^+$) centre-of-mass reference frame. This cross section (4) is an upper limit to any collision process satisfying specific criteria for the validity of the impulse approximation and states that the rate $v_3 \sigma_{13}^{\text{tot}}$ for all A-B(n) elastic and inelastic processes is essentially limited to the total rate of free Rydberg e-A collisions. For $v_1 \gg v_3$, as in thermal collisions, then
\[ \sigma_{13}^{\text{tot}}(v_3) = \langle v_1 \sigma_{13}(v_1) \rangle/v_3 \approx \bar{v}_1 \sigma_{13}(v_1)/v_3 \] (5)

where the average is taken over the distribution in orbital speed $v_1$ of the Rydberg electron. de Prunelé and Pascale (1979) (and also Matsuzawa 1979) have correctly conjectured that (5) can be deduced from the semiquantum formulation of A-B(n) collisions. However, many treatments (Matsuzawa 1979, Hickman 1979) of $l$-changing collisions alone, which are simple derivatives of the basic impulse expression, yield results much larger than (4) or (5) in violation of the impulse upper limit. Curiously enough, their apparent agreement with experiment does not substantiate the assertion that $l$-changing collisions at thermal energies originate solely from slow Rydberg e-atom encounters. That the (1-3) impulse upper limit yields values much lower than experiment (see table 1 and semiquantum results calculated by de Prunelé and Pascale (1979)) simply infers that an important mechanism, discussed below and based on 2-3 encounters, has not been acknowledged.

**Condition D.** Assumption (ii) based on the neglect of distortion of $V_{32}$ on 3 while interacting with 1 implies that 1 and 2 behave as separate and as independent scatterers. This is valid provided (a) that the (1-2) separation $R_{12} = n_2a_0 \gg A_4$, the scattering lengths or amplitudes for (1-3) and (2-3) collisions, and (b) that the reduced wavelength $\lambda_{13}$ for (1-3) relative motion is very much less than $R_{12}$, so that $A_4$ is not affected by the presence of $A_2$ (and vice versa). In general, $\lambda_{13} \ll n^{-2}$ for high impact speeds $v_3 \gg v_1$, and for thermal-energy collisions when $v_1 \gg v_3$ such that $\lambda_{13} \sim v_1^{-1} \approx n$; and $A_{1,2} \ll n^{-2}$. Moreover, for (2-3) collisions at thermal energies $\lambda_{23} \sim k_3^{-1} = 10^{-1}$ (see table 1). Hence
$R_{12}^2 \gg \lambda_{13}A_4$ such that multiple scattering can be neglected. Curiously enough, condition D is the one most easily satisfied in A–B$(n)$ collisions and is the only condition of all here which receives consideration in previous studies.

**Condition E.** At thermal energies distortion of 3 due to the core 2 cannot be ignored, as in assumption (ii), and the cross section for $B^*$–A elastic thermal collisions are large, about $10^3 \text{Å}^2$ (cf Dalgarno 1970). The impulse expression customarily adopted (cf Coleman 1969) must be appropriately generalised. The result (Flannery 1980) involves a nine-dimensional integral for the $T$ matrix rather than the usual three dimensional integral, and appears valuable only in promoting deeper understanding. This condition of undistortion is closely related to $D$.

**Condition F.** However, the impulse model focuses attention on the (1–3) collision, whether distorted by $V_{32}$ or not and as such does not contain any inelastic electronic transitions due to direct (2–3) encounters (assumption (iii)). Effective allowance for inelastic transitions via (2–3) collisions due to the non-inertiality of the target core 2 can be readily obtained (Flannery 1980). Let the impulse procedure treat the (1–3) encounter, for which purpose it has been designed. Then in the absence of the interaction $V_{13}$ between the incoming projectile 3 and the Rydberg electron 1, the Hamiltonian for the complete A–B$(n)$ system of reduced mass $M_{AB}$ is

$$H = -\frac{\hbar^2}{2M_{12}} \nabla_2^2 - \frac{\hbar^2}{2M_{AB}} \nabla_3^2 + V_{23}(\mathbf{R}') - \frac{e^2}{r}$$

where the vector $\mathbf{R}'$ of 3 relative to 2, in terms of its position $\mathbf{R}$ relative to the (1–2) centre-of-mass and $r$ the vector separation of (1–2) of reduced mass $M_{12}$ is given by

$$\mathbf{R}' = \mathbf{R} + \frac{(M_1/M)r}{M} = M_1 + M_2$$

where $M_i$ is the mass of particle $i$. The (2–3) interaction can then be expanded as

$$V_{23}(\mathbf{R}') = V_{23}(\mathbf{R}) + \frac{(M_1/M)r}{M} \cdot \nabla V_{23}(\mathbf{R}) + \ldots$$

The full scattering solution for $H$ can be expanded in terms of the target basis $\{\phi_n(r)\}$, and a hierarchy of quantal and semiclassical approximations exist (to various degrees of sophistication) which are based on matrix elements,

$$V_{ji}(\mathbf{R}) = \langle \phi_j(r) | V_{23}(\mathbf{R}') | \phi_i(r) \rangle = V_{23}(\mathbf{R}) \delta_{ji} + (M_1/M) \langle \phi_j(r) | r | \phi_i(r) \rangle \cdot \nabla V_{23}(\mathbf{R}) + \ldots$$

In particular, Flannery (1980) has shown in the sudden limit to a semiclassical analysis, when the exponential phase factors $(i\epsilon_{nf}/\hbar)$ can be ignored, (i.e. the collision time $t$ is assumed small in comparison with the time $\hbar/\epsilon_{nf}$ for transitions between highly excited levels $n$ and $f$ with energy separation $\epsilon_{nf}$ or else the important levels $n$ and $f$ are assumed degenerate as in $l$-changing transitions), that the differential cross section for $(i \rightarrow f)$ transitions in the target B via A–B$^*$ (2–3) encounters is

$$\frac{d\sigma_i}{d\Omega} = |B_i(\rho, t \rightarrow \infty)|^2 \frac{d\sigma_{23}}{d\Omega}$$

where $(d\sigma_{23}/d\Omega)$ is the differential cross section for (2–3) elastic scattering and where

$$B_i(\rho, t \rightarrow \infty) = \langle \phi_f(r) | \exp \left[ i \frac{M_1}{\hbar M} r \cdot \int_{t \rightarrow \infty} \nabla V_{23}(\mathbf{R}(t)) \, dt \right] | \phi_i(r) \rangle$$

is the probability amplitude at impact parameter $\rho$ for the $i \rightarrow f$ transition. Since
Letter to the Editor

$(-\nabla V_{23})$ in (11) is the force on 2 due to 3, the 'impulse'

$$\int_{-\infty}^{\infty} F_{23} \, dt = M_{23}(v'_{23} - v_{23}) = M_2 v$$

(12)

is the momentum $M_2 v$ transferred to the core 2, where $v_{23}$ and $v'_{23}$ are the initial and final velocities of the (2-3) collision system with reduced mass $M_{23}$. Thus, the probability of the $(i \rightarrow f)$ transition is

$$|B_i(p, t \rightarrow \infty)|^2 = |\langle \phi_f(r) \exp(i M_{12} v \cdot r) \phi_i(r) \rangle|^2$$

(13)

the absolute square of the inelastic atomic form factor which, when summed over all final states, yields unity. A simple interpretation of (13), based on the recognition that the Rydberg electron which is bound to the core at rest before the collision, finds itself relative to a moving core after the collision, can be provided (Flannery 1980). Account of the translational factor so introduced (as in hydrogenic travelling orbitals $\phi_T$) and the sudden approximation $|\langle \phi_T | \phi_i \rangle|^2$ for the transition probability yields (13).

The total cross section for all elastic and inelastic transitions based on (2-3) collisions from (10) and (13) is given by

$$\sigma_{23}^{\text{tot}}(v_{32}) = \sigma_{23}^{\text{el}}(v_{32})$$

(14)

which is therefore an upper limit. A highly accurate representation of the integral elastic cross section is provided by the semiclassical expression (see Dalgarno 1970),

$$\sigma_{23}^{\text{el}}(v_{32}) = 1.0688 \times 10^3 \left( \frac{a M_{AB}}{k_3} \right)^{2/3} a_0^2$$

(15)

where $a a_3^3$ is the polarisability of 3 and where $k_3(au)$ is the momentum of the $(A^+ - B)$ system with reduced mass $M_{AB}(amu)$. A preliminary assessment based on the upper limits (5) and (15) can now be made.

The table illustrates (5) and (15) for thermal (520 K) collisions of Rb(15F) with rare gases RG(He, Ne, Ar, Kr and Xe) for which $v_1 \gg v_3$. The (e-RG) cross section $\sigma_{13}(v_1)$ were obtained from the phaseshifts of Yau et al. (1979, 1980) and were so normalised as to reproduce measurements (where available) of the scattering length $A_1$ (since for He, Ne and Ar the calculated scattering lengths were 13% lower, 11% lower and 40% higher than the respective measurements (cf Yau et al 1979, 1980)). The first value in the range $\sigma_{23}^{\text{el}}$ arising from (1-3) elastic collisions corresponds to $\sigma_{23}^{\text{el}} = 4\pi A_1^2$ at zero

Table 1. Maximum cross sections ($\AA^2$) for Rb(15F)-rare-gas (RG) collisions at 520 K based on the sum of (e-RG) elastic encounters with cross section $\sigma_{23}^{\text{el}}$ and on (Rb$^+$-RG) elastic encounters with cross section $\sigma_{23}^{\text{tot}}$. The relative speed, momentum and polarisability of the incident RG atom are $v_3$, $k_3$ and $a$ respectively. The measurements (Exp) are taken from table 1 of Hugon et al. (1979).

<table>
<thead>
<tr>
<th>RG</th>
<th>$v_3(10^{-4}$ au)</th>
<th>$k_3$(au)</th>
<th>$a (a_0^3)$</th>
<th>$\sigma_{23}^{\text{tot}} (\AA^2)$</th>
<th>$\sigma_{13}^{\text{tot}} (\AA^2)$</th>
<th>$(\sigma_{13}^{\text{tot}} + \sigma_{23}^{\text{tot}})A^2$</th>
<th>Exp($\AA^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>7.757</td>
<td>5.405</td>
<td>1.384</td>
<td>2.95$^2$</td>
<td>(4.28$^2$-4.41$^2$)</td>
<td>(7.23$^2$-7.63$^2$)</td>
<td>(8.1±1.6)$^2$</td>
</tr>
<tr>
<td>Ne</td>
<td>3.754</td>
<td>1.17</td>
<td>2.666</td>
<td>7.41$^2$</td>
<td>(5.65$^2$-1.74$^2$)</td>
<td>(7.98$^2$-9.15$^2$)</td>
<td>—</td>
</tr>
<tr>
<td>Ar</td>
<td>2.907</td>
<td>14.42</td>
<td>11.07</td>
<td>2.27$^3$</td>
<td>(1.82$^3$-3.52$^3$)</td>
<td>(4.09$^3$-2.62$^3$)</td>
<td>(2.5±0.5)$^3$</td>
</tr>
<tr>
<td>Kr</td>
<td>2.32</td>
<td>17.98</td>
<td>16.74</td>
<td>3.47$^3$</td>
<td>(1.78$^4$-3.66$^3$)</td>
<td>(2.13$^4$-7.13$^3$)</td>
<td>—</td>
</tr>
<tr>
<td>Xe</td>
<td>2.108</td>
<td>19.86</td>
<td>27.26</td>
<td>5.13$^3$</td>
<td>(6.80$^4$-1.00$^4$)</td>
<td>(7.31$^4$-1.51$^4$)</td>
<td>(2.0±0.7)$^4$</td>
</tr>
</tbody>
</table>

$^12.95^2 = 2.95 \times 10^2$. 
Appendix B

Vibrational deactivation of oxygen ions in low velocity $^{0}_2(X^2Π_g^0, v = 1) + ^0_2(X^3Σ_g^0, v = 0)$ collisions

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The deactivation of $^0_2(X^2Π_g^0, v = 1)$ ions in collisions with $^{0}_2(X^3Σ_g^0, v = 0)$ molecules has been examined using multistate impact parameter eikonal and orbital treatments. Cross sections for the formation of various product states in the charge exchange and direct scattering channels have been computed for ions with 0.5 to 8.0 eV c.m. kinetic energies. The relative probabilities for forming products in given vibrational states at the higher kinetic energies are similar for the eikonal and orbital approaches. At energies below several eV it is necessary to employ the multistate orbital treatment which takes explicit account of the strong ion–molecule scattering. Cross sections for reaction channels leading to de-excitation and/or excitation of the product $^0_2(X^2Π_g^0, v = 1)$ ions have been computed for both charge exchange and direct scattering processes. The channels leading to vibrationally deactivated $^0_2(X^2Π_g^0, v = 0)$ product ions are strongly favored at low velocities over the excitation processes in the charge exchange as well as in the direct scattering channels.

INTRODUCTION

As more information is assembled on the reactions of ions with neutral molecules, it is becoming evident that reaction rate constants for many processes depend strongly on the internal energy of the reactants. The magnitude of the cross sections for charge transfer reactions of atomic ions with neutral molecules varies widely depending on whether the reactant ions occupy the ground or excited electronic state. Likewise, cross sections for collision induced dissociation of various molecular ions depend on the vibrational and/or electronic state distributions of the ions. The influence of the neutral target molecule vibrational state has been examined in reactions of $^0_2$ and Ne$^+$ ions with $^0_2(X^1Σ^+_g, v)$, $^0_2(X^1Σ^+_g, v = 1)$ ions. The investigation by Albritton et al. has shown that the rearrangement reaction of $^0_2(X^2Π_g, v)$ with CH$_4$ producing CH$_3$O and CH$_3^+$ is strongly dependent on the $^0_2(X^2Π_g, v)$ vibrational state. This drift tube experiment has clearly demonstrated that a small amount of $^0_2(X^2Π_g, v = 0)$ gas, added to the Ar buffer gas, effectively quenches the hydrocarbon rearrangement reaction due to vibrational deactivation of $^0_2(X^2Π_g, v = 1)$ ions by charge exchange processes which result in the formation of the much less reactive $^0_2(X^2Π_g, v = 0)$ ions.

Previous theoretical investigations have examined charge transfer reactions in the symmetric $^0_2$–$^0_2$ system and have shown that vibrational excitation of the products occurs with high probability for ions in the keV range. Vibrational excitation processes are efficient in both the direct as well as the exchange channels due to strong coupling between these energy degenerate channels. Differential and integral charge transfer and direct scattering cross sections in the hundred eV range are adequately represented by the multistate eikonal treatment, but there is a lack of detailed information on these processes for the oxygen system at low (eV range) kinetic energies. The purpose of this investigation is to examine $^0_2(X^2Π_g, v = 1) + ^0_2(X^3Σ_g^0, v = 0)$ collisions in an effort to understand the competition between the various ionic excitation and de-excitation channels as a function of reactant ion kinetic energy.

RESULTS AND DISCUSSION

The multistate impact-parameter treatment has been used to examine vibrational transitions occurring in the symmetric ion–molecule system

$$^0_2(X^2Π_g, v_0 = 1) + ^0_2(X^3Σ_g^0, v_0 = 0) \rightarrow ^0_2(X^2Π_g, v'') + ^0_2(X^2Π_g, v'),$$  

(1a)

$$^0_2(X^2Π_g, v') + ^0_2(X^3Σ_g^0, v''),$$  

(1b)

where charge transfer reactions predominate. In Reaction (1a), the incident molecular $^0_2(X^2Π_g, v_0 = 1)$ ions initially in level $v_0$ capture an electron to form fast neutral $^0_2(X^3Σ_g^0, v'')$ molecules in vibrational level $v''$, while in the direct channel (1b) incident molecular ions are scattered with the fast product ions in level $v'$. Each of the charge transfer channels (1a) is degenerate in energy with a corresponding direct channel (1b) which leads to strong coupling between the charge transfer and direct processes in this symmetric ion–molecule system. Application of the multistate treatment to these reactions is made in the following sections.

Multichannel eikonal treatment

The wave function which represents the time-dependent response of the internal motions of the system under the influence of the mutual interaction $V(R, r)$ is described by

$$\psi_i(r, R) = \sum_{n=0}^{\infty} \sum_{l} \psi_n^0(R, \rho, Z) \exp\left[-(i E_n^0/l)\right],$$  

(2)

where $\psi_n^0(R, \rho, Z)$ are a complete set of molecular eigenfunctions (with electronic, vibrational, and rotational parts) describing the unperturbed Hamiltonian $H_0$ for the iso-
lated system at infinite center-of-mass separation $R$ with eigenenergies $E^2_{m}$. The index $\alpha$ denotes whether the labeled quantities refer to direct channels $D$ or to charge exchange channels $X$. The quantity $r$ denotes the collection of internal coordinates on each center. Substitution of the wave function (2) into the time-dependent Schrödinger equation results in the following set of coupled equations for the transition amplitudes $C^\alpha_i(t)$:

$$i\hbar C^\alpha_i(\rho, t)/\partial t = SV(R)P_{\Delta}C^\alpha_i(\rho, t)\exp(i\epsilon_{\rho, \Delta}),$$

$$f = 1, 2, \ldots, N,$$ (3)

which are solved numerically subject to the boundary condition that the direct channel $i$ is initially populated, i.e., $C^\alpha_i(\rho, -\infty) = \delta_{\rho, 0}$, $C^\alpha_i(\rho, -\infty) = 0$. Matrix elements $P_{\Delta}$ are equal to $F(\nu', \nu'')F(\nu', \nu'')$, where $F(\nu', \nu'')$ is the vibrational overlap for the $O^2(\chi^2 \Sigma^+_g, \nu = 1) - O^2(\chi^2 \Sigma^+_g, \nu''')$ transition. When $\alpha$ denotes $X$ in Eq. (3), $\alpha$ refers to $D$ and vice versa. Differences $\epsilon_{\rho, \Delta}$ in the internal energies between initial and final states of the system are given by $E^\alpha_i = E_{\alpha'}^\alpha$. The equation used to compute the scattering amplitude in the c.m. frame is

$$f^\alpha_i(\theta, \phi) = \left\{ \sqrt{i/2\hbar} \right\} \int \exp[i(K \cdot R + m_{\rho} \phi)]$$

$$\times \exp(i\epsilon_{\rho, \Delta}/\hbar\nu_{l}^f)(\delta C^\alpha_i(\rho, Z)/\delta R) dR,$$ (4)

where the incident velocity is $v_i = h k_i/u$, the momentum change $K$ during the collision is $k_i - k_f$ with the final momentum vector $k_f$ directed along $\phi$, and $m_{\rho, \Delta}$ is the change in azimuthal quantum number which is taken to be zero for the reactions under investigation here. The ion–molecule separation vector $R$ has spherical components $(\rho, \phi, Z)$, where $\rho$ is the impact parameter. For high energy collisions, a straight line trajectory is adequate with

$$R(t) = \rho + v_1 t,$$ (5)

where the velocity is taken to be along the $Z$ axis and is perpendicular to the impact parameter. In this situation the solution of Eq. (4) is simplified by noting that for heavy-particle collisions the $Z$ component of the momentum transfer can be approximated by

$$K_z = k_z - k_{z'} \cos \theta = k_z - k_{z'},$$ (6)

Equation (4) can be simplified to

$$f^\alpha_i(\theta, \phi) = -k_i^{1/2 \epsilon_{\rho, \Delta}} e^{i\Delta \phi}$$

$$\times \int_0^{\infty} J_{\Delta}(K')\left[ C^\alpha_i(\rho, -\infty) - \delta_{\rho, 0} \right] dp$$ (7)

by performing the $\phi$ integration. In Eq. (7), $\delta_{\rho, 0}$ is the Kronecker delta function and $J_{\Delta}$ are Bessel functions of integral order $\Delta = m_{\rho, \Delta}$, and $K' = (K^2 - K_z^2)^{1/2}$ is the momentum transfer perpendicular to the trajectory. From these scattering amplitudes given by Eq. (7), the differential cross section is

$$c^\alpha_i(\theta) = 2\pi K_{\nu}^f \left| f^\alpha_i(\theta, \phi) \right|^2.$$ (6)

Integrating Eq. (6) over angle yields the integral cross section $Q^\alpha_i(\nu_l)$ given by the equation

$$Q^\alpha_i(\nu_l) = \int_0^{\infty} c^\alpha_i(\theta) d\cos \theta$$

$$= 2\pi \int_0^{\infty} \left| C^\alpha_i(\rho, -\infty) - \delta_{\rho, 0} \right|^2 d\rho.$$ (9)

The interaction matrix elements $V(R)$ necessary to describe Reactions (1) are those used previously for this system and they are considered sufficiently accurate and suitable for this study. Energy defects and accurate vibrational overlaps for the respective transitions have been obtained from previously published wave functions which were constructed using RKR techniques. For the reactions of $O^2(\chi^2 \Pi_{1u}, \nu = 1)$ with $O^2(\chi^2 \Sigma^+_g, \nu = 0)$ molecules, the dominant product channels are those with small energy defects and favorable vibrational overlaps. Product channels with small energy defects are $1, 0; 0, 1; 0, 0; 0, 2; 1, 1; 2, 0; 0, 3$ (the vibrational level $\nu'$ of the production is denoted by the first number and the vibrational level $\nu''$ of the product neutral as the second number in the pair).

The computation of the cross sections for charge transfer and direct scattering processes requires solution of the coupled differential equations (3). These coupled differential equations are solved numerically by the Burroughs–Stoer rational extrapolation technique. Transition amplitudes $C_{\Delta, i}^\alpha(\rho, -\infty)$ determined as a function of $\rho$ from the multistate coupled equations are used to compute the complex transition amplitudes from Eq. (4) and transition probabilities $|C_{\Delta, i}^\alpha(\rho, -\infty)|^2$ for the charge exchange and direct scattering channels. It is necessary to explicitly consider a total of 14 product channels in order to obtain fully converged cross sections in the $O^2_2$–$O_2$ system at 8 eV center-of-mass kinetic energy. The competition between the various reaction channels is graphically displayed in Fig. 1 for the charge exchange channels where the relative transition probabilities are displayed as a function of impact parameter. The open area in the bottom portion of this figure represents the relative probability for the charge transfer channel forming slow $O^2_2(\chi^2 \Sigma^+_g, \nu = 1)$ ions and fast
FIG. 2. Relative probabilities (eikonal method) for formation of specific product channels in 8.0 eV c.m. $O_2^+(X^2\Pi_u, v''=1) + O_3(X^3\Sigma_g^+, v''=0)$ direct, inelastic scattering collisions as a function of impact parameter distance in atomic units. The numbers associated with each area denote the vibrational quantum numbers of the respective $O_2^+(X^2\Pi_u, v')$ and $O_3(X^3\Sigma_g^+, v'')$ reaction products.

$O_2(X^3\Sigma_g^+, v''=0)$ molecules at different values of $\rho$ for 8 eV collision energy. The cross-hatched area gives the relative probability for producing $O_2^+(X^2\Pi_u, v'=0) + O_3(X^3\Sigma_g^+, v=1)$ products. The designations of the other various areas in this figure refer to product channels in which the ion and neutral vibrational levels are $v'$ and $v''$, respectively. For example, at $R$ equal to 3.026 a.u., the relative probabilities for the $v', v''=1,0; 0,1; 0,0; 0,2; 1,1; 2,0$; and 0,3 channels are 0.5963, 0.0303, 0.0047, 0.1249, 0.1534, 0.0868, and 0.0036, respectively. At large values of internuclear distance the resonant charge transfer channel predominates; however, at smaller values of $R$ the inelastic charge transfer channels become important. Similar transition probabilities for the direct channels are displayed in Fig. 2. The notation in Fig. 2 is the same as in Fig. 1, where $v'$ and $v''$ symbols denote the product ion and neutral vibrational levels, respectively. The elastic 1, 0 direct channel is not displayed but rather only the direct inelastic channels, which are the topics of this paper, are given in Fig. 2. At large values of $R$ the 0, 1 channel, corresponding to de-excitation of the ion, predominates. As $R$ is reduced, the other inelastic channels become relatively more important.

The influence of lowering reactant ion kinetic energy on the relative transition probabilities is illustrated in Fig. 3. The relative contribution of the resonant 1, 0 exchange channel is larger at 1 eV than at 8 eV, i.e., the inelastic processes generally become less important as the ion kinetic energy is lowered. At an impact parameter of 1.0 a.u. the different regions in Fig. 3, from top to bottom, represent the 0, 3; 2, 0; 1, 1; 0, 0; 0, 1; and 1, 0 channels, respectively. It is to be noted that the area corresponding to the 0, 1 channel (vibrational de-excitation of the ion) is the dominant inelastic process at 1 eV. A similar situation occurs in the direct inelastic scattering channels shown in Fig. 4 with the 0, 1 de-excitation channel playing a more important role at lower ion kinetic energies.

The relative contributions of the different reaction channels to the integral multistate charge transfer cross sections are illustrated in Fig. 5. Integral cross sections for individual inelastic channels have been obtained from Eq. (9) for a range of kinetic energies. Cross sections for channels having large energy defects tend to increase with ion kinetic energy, a fact consistent with the transition probabilities presented in the previous figures. Integral cross sections for the direct channels are presented in Fig. 6 for the same kinetic energy range. The magnitudes of the direct-inelastic channels approximate those for the vibrationally inelastic charge transfer reactions. The direct channels with larger inelasticities begin to become important above several eV c.m. kinetic energy. Computation of accurate inelastic cross sections must take into account the curved trajectories as the reactant partners approach one another. The relative velocity range where the curved trajectories start to influence the inelastic pro-
Cross section will depend on the individual system and is examined in the following section.

Multichannel orbital treatment

The multistate orbital description of charge transfer uses Hamilton's equations to determine the actual relative trajectory $R(t)$ and the classical relative motion is evaluated using the "averaged" Hamiltonian

$$ R = \sum_{j=1}^{N} \frac{1}{2\mu_j} \langle \psi(r, t) | H | \psi(r, t) \rangle, $$

where the first term on the right-hand side represents

FIG. 5. Integral eikonal multistate cross sections ($\AA^2$) for excitation of specific product vibrational states in $\text{O}_2^+(X^2\Sigma_g^+, v' = 1) + \text{O}_2(X^2\Sigma_g^+, v'' = 0)$ charge exchange reactions. Cross sections for formation of specific ion and neutral product vibrational levels $v', v''$ given as a function of c.m. kinetic energy.

FIG. 6. Integral eikonal multistate cross sections ($\AA^2$) for excitation of specific product vibrational states in $\text{O}_2^+(X^2\Sigma_g^+, v' = 1) + \text{O}_2(X^2\Sigma_g^+, v'' = 0)$ charge exchange reactions. Cross sections for formation of specific ion and neutral product vibrational levels $v', v''$ given as a function of c.m. kinetic energy.

FIG. 7. Relative probabilities (orbital method) for formation of specific product channels in 8.0 eV c.m. $\text{O}_2^+(X^2\Sigma_g^+, v') + \text{O}_2(X^2\Sigma_g^+, v'')$ reaction products.

the kinetic energy of relative motion. With the use of the wave function $\psi(r, t)$, the second term reduces to

$$ \langle \psi(r, t) | H | \psi(r, t) \rangle = \mathbf{S} \langle | a_m \rangle \langle 1 | + \mathbf{S} a_m^* a_n V_{km}(R) e^{i\epsilon_{km}t} \rangle = V(R(t)), $$

which represents the averaged internal energy of the collision system. This term couples the response [Eq. (2)] of the collision partners to the relative motion via the expansion coefficients $a_n(t)$, analogous to $C_n(t)$, in Eq. (2) and Hamilton's equations become

$$ \frac{\partial a_n(t)}{\partial t} = \frac{p_j(t)}{\mu}, $$

where

$$ \frac{\partial a_n(t)}{\partial t} = -\mathbf{S} \sum_{m} a_m^* a_n(t) \frac{\partial V_{km}(R(t))}{\partial a_m} e^{i\epsilon_{km}t}, $$

a set of six equations, in general, or four for scattering in a plane, which must be solved simultaneously with a coupled set (3). In order to relate the flux that flows through the incident area $\rho d\rho d\phi$ to the scattering solid angle $d\Omega$, $d\rho$ is given by

$$ d\rho = (d\sigma/d\Omega)_{i\rightarrow f} d\Omega, $$

where $(d\sigma/d\Omega)_{i\rightarrow f}$ is the classical differential cross section for scattering by Eq. (11) and is just the Jacobian of the $(\rho, \Omega)$ transformation. The differential scattering cross section for the transition from state $i$ to state $f$ is computed from the equation

$$ a_{if}(\theta) = |a_f^*(\theta = \infty)|^2 (d\sigma/d\Omega)_{i\rightarrow f} d\Omega, $$

where $a_f^*(\theta)$ are the solutions of Eqs. (3) and (13), to be differentiated from $C_f^*$, the solutions of Eq. (3) with Eq. (5). If, however, more than one classical trajectory is scattered into solid angle $\Omega(\rho, \phi)$, then proper account of interference must be taken, including the phase of the contributing probability amplitude $a_f^*$. A full account of the procedure used here has already been given elsewhere in the full semiclassical treatment. The Burslsh–Stoer method was used to evaluate the $a_f^*$ from
which integral cross sections have been obtained using the relation

$$Q_N^R = 2\pi \int_0^\infty |\psi_R^N(\rho, t = \infty)|^2 \rho d\rho.$$  \hspace{1cm} (16)

Relative transition probabilities $|\psi_R^N(\rho, \infty)|^2$ for the charge exchange channels are shown in Fig. 7 for the reactions of 8 eV $O_2(X^2\Sigma\text{g}, v = 1)$ ions. The general features displayed in this figure are very similar to the multistate eikonal probabilities given in Fig. 1. This similarity is also reflected in the cross sections where the total multistate orbital charge transfer cross section, summed over all $X$ channels, is 31.8 Å$^2$, which is close to the corresponding eikonal value of 33.6 Å$^2$.

Relative transition probabilities for the 8 eV direct scattering channels in the orbital treatment are shown in Fig. 8. The overall behavior of these orbital probabilities for the $D$ channels is similar to that for the eikonal approach (Fig. 2) but with some structural differences between the two at small values of $R$.

The differences between the transition probabilities in the two computational approaches are further emphasized in Fig. 9, where relative orbital transition probabilities at 1 eV are given for both the $D$ and $X$ channels. There is very little structure in the 1 eV orbital transition probabilities for the inelastic scattering
processes with the $v', v'' = 0, 1$ channel dominating throughout the range of $R$, a fact in sharp contrast to data in Fig. 4. Likewise, the 1 eV orbital transition probabilities for charge exchange channels are relatively uncomplicated. The 1, 0 and 0, 1 channel transition probabilities are the largest at all impact parameters. The absence of contributions from reaction channels with larger energy defects in the orbital treatment is a result of the mutual scattering by the ion–molecule pair. The eikonal straight line approach artificially constrains the collision to be more "violent" at small values of $R$ and thus overestimates the translational to vibrational energy conversion processes. This is reflected in the integral cross sections computed in the orbital treatment for the inelastic X and D channels which are given in Figs. 10 and 11. Although the cross sections for the inelastic channels are similar at 8 eV for the eikonal and orbital treatments, they diverge as anticipated due to the translational to vibrational energy conversion processes. This is illustrated in Fig. 12, where the ratio summed over the X and D channels. Calculations were performed using the orbital method.

![Graph](image-url)

**Fig. 12.** Ratios of de-excitation $(0, 2u)$ to excitation $(1, 1) + (2, 0)$ cross sections for $O_2(X^2\Pi_g, v_0 = 1)$ ions as a function of c.m. kinetic energy in $O_2^-(X^2\Pi_g, v_0 = 1) + O_2(X^2\Pi_g, v'' = 0)$ collisions. The dashed curve illustrates the ratio for the charge transfer channels X; the dot-dashed curve gives the ratio for the direct scattering channels D; the solid curve illustrates the ratio summed over the X and D channels. Calculations were performed using the orbital method.

the fast reactant ion ends up as a vibrationally deactivated product ion.

The resonant charge transfer channel involving reactant $O_2(X^2\Pi_g, v_0 = 1)$ ions has the largest cross section of any other channel. The ratio of the cross sections for resonant to inelastic channels increases as the reactant ion kinetic energy is lowered. The inelastic processes dominant at low ion kinetic energies are those that lead to vibrational de-excitation of the incident $v_0 = 1$ ion beam. Quantitative measure of the vibrational de-excitation of the ions is given in Fig. 12, where the cross section ratio (sum of all X and D channels with product ion $v' = 0)/(sum of the two largest X and D excitation channels$ is presented. At low kinetic energies, the collisions that lead to vibrational de-excitation of the incident ion beam are approximately 200 times more probable than the vibrationally inelastic collisions. Thus, low velocity $O_2(X^2\Pi_g, v_0 = 1) + O_2(X^2\Pi_g, v'' = 0)$ collisions provide an effective means for quenching vibrational excitation in the incident ions.

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Appendix C

ION–ION RECOMBINATION AS A FUNCTION OF ION AND GAS DENSITIES

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We present a basic theory of the link between the low and high gas-density limits to ion–ion recombination under a general interaction \( V \) which now depends on the ion density and which is determined self-consistently with the recombination. Increase in ion density up to \( 10^{14} \, \text{cm}^{-3} \) causes little change to the recombination rates in direct contrast to that obtained in recent computer simulations.

Not only is the ion–ion recombination process†
\[
X^+ + Y^- + Z \rightarrow [XY] + Z
\]
(1)
of basic theoretical significance [1] in its own right, but it plays a key role in populating [2] the upper molecular electronic states of inert gas–halide lasers which operate not only at high densities \( N \approx 10^4 \sim 10^5 \, \text{atm} \) of the background gas \( Z \) but also at moderately high densities \( N \approx 10^{10} \sim 10^{14} \, \text{cm}^{-3} \) of the positive and negative ions \( X^+ \) and \( Y^- \). Reliable laboratory experiments are difficult and are as yet not forthcoming. All previous [3] theoretical treatments and experiments pertain tacitly to dilute ionization for which a coulombic ion–ion interaction is correct.

The purpose of this letter is to briefly outline a basic theory of the recombination rate \( \alpha \) (cm\(^3\) s\(^{-1}\)) of (1) versus gas and ion densities, \( N \) and \( N^\pm \), respectively and then to illustrate the key effects by appeal to a model version. In so doing, we will raise an interesting issue on the validity at all \( N \) of the ab initio adoption [4] of the Debye–Hückel interaction as a means of incorporating plasma sheathing effects when \( N^\pm \) is raised. Bates [5] has recently argued that this procedure is invalid at high \( N \).

**Recombination rate \( \alpha \).** Let the negative ions of density \( n^- (R, t) \) at time \( t \) stream across spheres of radius \( R \) each centered at each positive ion distributed \( N^\pm \) \( \text{cm}^{-3} \). The time-dependent continuity equation is
\[
\frac{\partial n^- (R, t)}{\partial t} - \nabla_R \cdot j = 0
\]
(2a)
where the net inward current (number of ions/s across unit area of an \( R \) sphere)
\[
j = D \left[ n^+ (R, t) + n^- (R, t) \nabla (V/\kT) \right]
\]
(2b)
arises from diffusional drift of the ions with relative diffusion coefficient \( D \) in the gas \( Z \) under an external field of potential \( V(R) \). The collisional-sink term is
\[
\left[ \frac{\partial n^- (R, E_i, t)}{\partial t} \right]_{\text{S}} = M(R) = N \sum_{f=-V(R)}^{N} n_f (R, E_f, t) \kT
\]
(3)
in terms of the phase-space densities \( n_f (R, E_f, t) \) of \( R_f \)-ion pairs (i.e. ion pairs with internal energy \( E_i \) and fixed internal separation \( R_f \)) and of the collisional frequencies \( \kT \) at which \( R_f \)-ion pairs are converted into \( R_f \)-ion pairs by collision with the gas bodies \( Z \) of density \( N \) (i.e. for \( E_i \rightarrow E_f \) collisional transitions). The collisional sink is effective only when the lowest bound level \(-V\) appropriate to fixed separation \( R \) lies at or
below the level $-S$ of energy $E_S$ below which the recombination is assumed to be stabilized against any upward collisional transitions, i.e. $-M = \max[-V, -S]$.

Although expression (2a) has been derived [1] from the full Boltzmann equation which describes the evolution of the phase-space densities $n_i^*(R, E_1, t)$ by gas collisions, it can be written down immediately from macroscopic principles. The microscopic origin of the macroscopic current $j$ of (2b) is the balance of all ineffective ion–neutral collisions in the absence of the sink, collisions which, in the presence of the sink, oversubscribe $j$ by the amount (3) summed over all states $f$ in (2a) between the lowest level $-V$ and the far continuum $C$. In a shell of radius $R$ and thickness $dR$ centered at each positive ion, distributed $N^+$ cm$^{-3}$, the number density $N^* dR$ of ion pairs is $4\pi R^2 dR N^+ n^-(R)$ which are assumed to decay explicitly with time as $e^{-\lambda t}$ so that (2) becomes

$$A N^+ \int_0^R 4\pi R^2 n^-(R) dR + 4\pi R^2 N^+ D \left[ \frac{d}{dR} + \frac{d(V/kT)}{dR} \right] n^-(R) = \alpha_3(R) n^-(R) N^+, \quad (4)$$

where the sink term (3) on integration over the volume of the $R_E$ sphere has been replaced by

$$\alpha_3(R) n^-(R) N^+ = \int_0^R dR \left[ \sum_{i=-E}^{C} \sum_{f=V}^{E} N_i^*(R, E_i) k_{if}(R) \right] - \sum_{f=-M}^{-E} N_j^*(R, E_f) k_{jf}(R), \quad (5)$$

the net balance between the rates of downflow and upflow of $R$-ion pairs past an arbitrary level $-E$ of negative energy. Although this replacement can be rigorously justified [1] it is physically correct and obvious.

Under thermodynamic equilibrium when the sink is neglected, the rhs of (5) vanishes. Since no effective collisional transitions occur at $R \geq R_E$, the outermost turning point associated with $-E$, the flux in the rhs of (4),

$$F_c(R) = \alpha_3(R) n^-(R) N^+ = \alpha N^+ N^-, \quad R \geq R_E, \quad (6)$$

is therefore constant for $R \geq R_E$. The lhs of (4) times $\exp(-\lambda t)$ then evolves with $R$ to the complete time derivative of $N^-$ with the result that the recombination coefficient appropriate to asymptotic ion density $N^-$ is

$$\alpha = \frac{\alpha_3(R_E) n^-(R_E)}{N^-}, \quad (7)$$

which is determined by the rhs of (5) evaluated at $R_E$. Note from (7) that $\alpha_3 \exp(-V/kT)$ is the recombination rate $\alpha_{RCTN}$ that would pertain provided a Boltzmann distribution $(N^- e^{-V/kT})$ of ions were maintained, i.e. a reaction rate. Although $\alpha$ in principle, is determined in (5) by energy-change rates $k_{if}$ and phase-space densities $n_i^*(R, E_1)$ of $R_i$-ion pairs, which, in turn, are solutions of a certain Boltzmann equation [1], a powerful approach based on prior or alternative knowledge of the “reaction rate” $\alpha_{RCTN}$ is as follows.

Neglect in (4) of the first term, which depends on $n^-(R)$ within $R_E$, implies,

$$f \int_0^{R_E} 4\pi R^2 n^-(R) dR \approx 1, \quad (8)$$

since $A \approx \alpha N^-$, such that $N^- \ll (\frac{4\pi R_E^2}{N^+})^{-1}$ and few ions are present in the recombination volume as measured by $R_E$. Then, integration of (4) under constant flux $(4\pi R^2 N^+)$ given by $F_c$ of (6) yields,

$$n^-(R) = N^- e^{-V/kT} [1 - (\alpha/\alpha_{TRNS})(P(R)/P(R_E))]$$

where the dimensionless quantity

$$P(R) = \int_R^{R_E} e^{V/kT} dR, \quad R_E = e^{2/kT}, \quad (9)$$

in terms of the natural unit $R_e$ of length, and where

$$\alpha_{TRNS}(R_E) = 4\pi k e/P(R_e) \approx \alpha_H/P(R_e) \quad (11)$$

tends at high $N$ to the correct Langevin–Harper rate [3,6] $\alpha_H$ for ions with relative mobility $K$ in gas. Hence (7) yields

$$\alpha = \frac{\alpha_{RCTV}(R_E) \alpha_{TRNS}(R_E)}{[\alpha_{RCTW}(R_E) + \alpha_{TRNS}(R_E)]^{-1}} \quad (12)$$
in terms of $a_H$, which is known, and which $\approx N^{-1}$, and of the reaction rate $a_{RCTN}$ and $V$, yet to be determined.

At low densities $N$, $a_H a_{\text{TRNS}} \rightarrow 0$ as $N^2$ such that the ion density (9) is Boltzmann and $a_{RCTN}$ may be uniquely identified with the low density limit to $a$. At low $N$, the reactivity of the ion pairs via three-body collisions with the gas is slow in comparison with the rate of ionic transport, so that this rate limiting step is characterized by $a_{RCTN}$. At high $N$, $a_H a_{\text{TRNS}} \rightarrow 1$ such that $n^-(R)$ in (9) departs appreciably from Boltzmann for $R \approx R_E$. As $N$ is increased the reactivity of the ion pairs via three-body collisions becomes so great compared with the rates of ionic transport that continued reaction at $R \approx R_E$ causes significant depletion in $t^-(R)$ over a localized region that $n^-(R)$ is far from Boltzmann. Hence the recombination process can be viewed as proceeding via ionic transport at rate $a_H a_{\text{TRNS}}$ followed by three-body reaction at rate $a_{RCTN}$ such that the overall rate (12) is controlled by the rate limiting step.

The above theory establishes a firm theoretical foundation for (12) which, as noted previously by Bates and Flannery [6] is intrinsic to the expression of Natanson [7] and which is based on the equality of the transport and reaction fluxes.

Interaction $V$. As $N^2$ is raised, the ion–ion interaction $V$ can no longer be assumed ab initio to be purely coulombic but is given by appropriate solution of Poisson’s equation

$$\nabla^2 V(R) = (4\pi e^2) \left[ n^+(R) - n^-(R) \right],$$

when the local positive and negative ion densities are $n^\pm(R)$ and where $\varepsilon$ is the dielectric constant of the gas $Z$. In the reference frame of the positive ion, $n^+(R)$ is the Boltzmann distribution $N^e e^{V/kT}$ such that (13) for an $R$-symmetric distribution reduces with the aid of (9) to

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial (V/kT)}{\partial R} \right) = (2R_S^2)^{-1} [e^{V/kT} - 1],$$

where the “screening” distance is

$$R_S = (8\pi N^2 e/e)^{1/2}.$$

The $[\cdot]$ term, which depends on $V$, $N$ and $R$ in (14), tends to unity at low $N$ for all $R$ and increases at high $N$, from zero at $R \approx R_E$ to unity as $R \approx \infty$. As $R_S \rightarrow \infty$, i.e. no plasma sheathing, the solution is coulombic so that an iterative solution valid for low $N^2$ (large $R_S$) and high $N$ in the vicinity of $R_E$ is

$$V_{HI}(R)/kT = -R_E/R + \frac{1}{12} (R/R_S)^2 \exp(-R/R_E),$$

which is pure coulombic for $R \ll R_S$, or for $R \ll 12R_E R_S^2$, i.e. when $N^2 \ll 10^{14}$ cm$^{-3}$ at $R \ll R_S$. For low $N$, both exponential terms in the rhs of (14) are important. When $R \rightarrow \infty$, then $V \ll kT$ such that the solution to (14) can be obtained for all $N$ linearizing the exponentials to give

$$V_{\text{DH}}(R) = -(e^2/R) \exp(-R/R_S), \quad R \rightarrow \infty,$$

the Debye–Hückel interaction which can be used as a starting condition for the inward integration of (14) from large $R$.

Thus, the present method involves self-consistent solutions of $a$ and $V$ via (12) and (14). If an analytic form of the reaction rate $a_{RCTN}$ which also depends on $V$ is also unknown, then (14) is coupled to (5) in terms of the energy-change rates $k_H$, and of the phase-space densities $n_i(R, E_i)$, which are solutions of a certain Boltzmann equation [1] which also includes $V$.

Reaction-rate model. Rather than solve directly for $n_i(R, E_i)$ and hence for $a$ from (5), assume that the sink term in (2a) can be replaced by a partially absorbing sphere of radius $R_E$ such that (2a) is, in effect,

$$\frac{\partial n^-(R,t)}{\partial t} = \frac{1}{R^2} \frac{\partial (R^2)}{\partial R} \Gamma_3 n^-(R) \delta(R - R_E),$$

where $\Gamma_3$ is the speed of reaction (via three-body collisions) for ions after being brought to $R_E$ by ionic transport. In steady state, (18) incorporates the boundary condition,

$$\Gamma_3 n^-(R) = \Gamma_3 n^-(R_E),$$

which when multiplied by $4\pi R_E^2$ is equivalent to (7) such that

$$a_3(R_E) = 4\pi R_E^2 \Gamma_3,$$

thereby confirming that the strength $\Gamma_3$ of the sink in (18) is the speed of reaction within $R_E$. The solutions

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(9) and (12) follow directly from (18). For \( \Gamma_3 \) large compared with the speed of ionic transport, as at high \( N \), the reactivity of the sink is effectively instantaneous and \( \alpha \) tends to \( \alpha_{\text{TRNS}} \) the transport rate, while low \( N \) implies \( \Gamma_3 \) small compared to the transport speed so that \( \alpha \) tends to the reaction rate \( \alpha_{\text{RCTN}} \). It is worth pointing out that when (18), with its rhs set to zero, is solved subject to the boundary condition \( n(R_E) = 0 \), then the expression of Bates \[8\] is recovered, i.e. \( \alpha \) is given entirely by \( \alpha_{\text{TRNS}} \).

From (19) this zero-density boundary condition is equivalent to assigning an infinitely fast reaction speed \( F \to 3 \) to the sink, as is the case at high \( N \). Thus (19), effectively allows for a finite reaction rate associated with a partially absorbing sink, rather than a fully absorbing sink implied by zero \( n(R_E) \), equates the transport current at the boundary with the current of absorbed ions, and is valid for all \( N \).

On recalling that each species of ion \( i \) have different mean free paths \( \lambda_i \) in the gas \( Z \) and different sink radii \( R_i \), the model for the rate \( \alpha_{\text{RCTN}} \) of reaction within \( R_E \) is therefore generalized from (20) to give

\[
\alpha_{\text{RCTN}}(R_1, R_2) = \pi \left[ R_1^2 \frac{W(Y_1)}{C_1^2 E_1} + R_2^2 \frac{W(Y_2)}{C_2^2 E_2} \right] - R_3^2 \frac{W(Y_1)}{W(Y_2)} G \langle u_{12} \rangle,
\]

where \( \langle u_{12} \rangle \) is some averaged ion–ion transport speed of approach, and where the probability for an ion \( i \)–neutral \( Z \) collision for ion pairs with internal separation \( R < R_i \) increases with gas density to unity as \[9\]

\[
W(Y_i) = 1 - \left( 1/2X_i^2 \right) \left[ 1 - \exp(-2X_i)(1 + 2X_i) \right],
\]

for a straight-line trajectory. The factor

\[
C_i = 1 + (2/3kT) \int_{R_i}^{R_i + \lambda_i} (\partial V/\partial R) \, dR
\]

acknowledges the focusing effect of the interaction on the assumed straight-line ion–ion trajectory between \( R_i + \lambda_i \) and \( R_i \). The minimum of \( R_1 \) and \( R_2 \) is \( R_S \) such that \( W(Y_1) W(Y_2) \) with \( Y_i = R_S/\lambda_i \) is the probability of simultaneous ion–neutral collisions within \( R_S \), a probability counted twice in the first two terms of (21a). Simple geometric arguments show that \( G \) in (21a) is either \( C_1 E_1 \) or \( C_2 E_2 \) depending on whether \( R_S \) is \( R_1 \) or \( R_2 \), respectively.

The trapping radii \( R_i \) may now be deduced from kinematical considerations. The initial kinetic energy of relative motion of the positive ion \( 1 \) and negative ion \( 2 \)

\[
T_0 = \frac{3}{2}kT + \int R^+ \left( \partial V/\partial R \right) dR,
\]

since the ions on average are uninterrupted by collision only for separations between \( R + \lambda \) and \( R \). Ion pairs upon collision with a neutral become incapable of expanding outwards from \( R \) to \( R + \lambda \) provided their final kinetic energy \( T_f \) is barely sufficient to provide the necessary energy required to increase \( R \) to \( R + \lambda \) against the attractive force, i.e. when

\[
T_f \leq \frac{1}{2}kT \int R + \lambda \left( \partial V/\partial R \right) dR.
\]

Introduce a collision parameter \( \delta \) to be fixed later such that the energy change \( T_0 - T_f = \delta T_f \). Thus the criteria (23) with (22) yields

\[
V(R_E + \lambda) - V(R_E) = \frac{3}{2}kT/8,
\]

to be solved for the trapping radii \( R_{Ei} \) corresponding to mean free paths \( \lambda_i \) where the subscript \( i \) is attached to quantities associated with each species of ion. In this strong-collision model, the interaction need only be specified at the trapping radii \( R_{Ei} \). Solution of (24) for pure Coulomb field is

\[
R_i = \frac{2}{3} \lambda_i \left[ (1 + 4\delta R_T/\lambda_i) \right]^{1/2} - 1
\]
tion (14) which can now be solved to yield

\[ V_L(R_E)kT = -R_e/R_E + \frac{1}{12}(R_E/R_S)^2 B(\delta), \]  

(26a)

where

\[ B(\delta) = \exp(3/2\delta) - \exp(-3/2\delta). \]  

(26b)

This potential which reduces to pure coulombic for \( R \ll R_e \) and \( N^\pm \lesssim 10^{14} \text{ cm}^{-3} \) is almost identical to (16) appropriate to high \( N \). At low \( N \), the trapping radii in (24) are therefore solutions of

\[ B(\delta/18) R^3_{E0} + R_{E0} = \delta R_T \]  

(27)

and, for all \( N \) are given in terms of this solution \( R_{E0} \) by

\[ R_E = \frac{1}{2}(1 + 4 R_{E0}/\lambda)^{1/2} - 1 \]

\( \rightarrow R_{E0} \), \( \lambda \rightarrow \lambda \) \( \rightarrow \lambda \) \( \rightarrow \lambda \)

(28)

in analogy with (25). Finally the low-density \( N \) limit to (21a) is

\[ \alpha_{\text{TRANS}} - \alpha_L = \alpha_{L1} + \alpha_{L2} = C_1 \delta^3 \alpha_{T1} + C_2 \delta^2 \alpha_{T2}, \]  

(29a)

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

\[ \alpha_{T1} = \frac{4}{3} \pi R^3_{T1} (v_{12})/\lambda_i \]  

(29b)

is the Thomson partial recombination coefficient as \( \lambda \rightarrow 0 \). The ratio \( R_{Ti} \) of the exact low gas-density limit as given by the effectively exact microscopic theory of Bates and Flannery [10] to (29b) has been provided [11] over an extensive range of systems such that the collision parameter \( \delta_i \) introduced above can now be uniquely obtained from solution of

\[ \delta^3_i + \delta^2_i - R_{Ti} = 0 \]  

(30)

and \( \alpha_{RCTN} \) tends, therefore, at low \( N \) to the exact quasi-equilibrium value [10].

Results of the present procedure, represented by (12) with \( \alpha_{RCTN} \) given by (21) in terms of trapping radii (28), for the rate of

\[ \text{Kr}^+ + F^- + \text{Ar} \rightarrow \text{KrF}^* + \text{Ar} \]  

(31)

at 300 K are illustrated in fig. 1 as a function of gas density \( N \) for various ion densities \( N^\pm \) up to \( \approx 10^{14} \text{ cm}^{-3} \), the validity limit of the present analysis. Results from the universal Monte Carlo plot procedure of Bates [12] for low \( N^\pm \) are also shown together with the direct Monte Carlo computer simulations of Morgan et al. [4] who adopted ab initio the Debye–Hückel interaction (17) for higher \( N^\pm \). The general agreement between the various methods at low \( N^\pm \) can be considered excellent, but significant departure occurs at higher \( N^\pm \approx 10^{14} \text{ cm}^{-3} \). The origin of the discrepancy at high \( N \) is due to the factor \( P(R) \) in (11) which is much larger for the Debye–Hückel interaction (17) than for the interaction (16) predicted here; and, at low \( N \), to the trapping radii given by (24) which for (17) are much smaller than those for (26) predicted here. The Debye–Hückel interaction (17) contains much stronger repulsion than either of (16) or (26). The theory outlined here predicts little departure of rates \( \alpha \) up to \( N^\pm \approx 10^{14} \text{ cm}^{-3} \). The theory indicates via (14) that the Debye–Hückel interaction is only valid at asymptotic \( R \) of little significance to the recombination. At high \( N \), the ion distribution at \( R_E \) is far from Boltzmann equilibrium, and \( V \gg kT \) such that linearization of even an equilibrium distribution is not valid at these \( R \) of significance to recombination.

In summary, therefore, we have provided here a timely theory of \( \alpha \) as a function of gas and ion densities, have shown how the overall recombination may be viewed as proceeding via ion transport followed by
reaction such that the overall rate is determined by the rate-limiting step of transport/reaction, and have raised a timely, interesting and important question concerning validity of the ab initio assumption of the Debye–Hückel interaction in recombination studies. It will be of great interest to see whether improved Monte Carlo simulations which do not rely on this assumption will confirm the present theoretical predictions which are based on the \((\alpha, V)\) self-consistent solution of the interaction \(V\) in the presence of the recombination \(\alpha\). Finally, it is worth mentioning that transient “time-dependent” rates \(\alpha(t)\) can be obtained \([1]\) from (18) and these are important in medical radiology and in situations where intense ionization is deposited into or produced as a track within a localized system either by a high-energy beam of particles or radiation.

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References

Appendix D

Exact Closed Form Solution of the Generalized Debye-Smoluchowski Equation.

EXACT CLOSED-FORM SOLUTION OF THE GENERALIZED DEBYE-SMOLUCHOWSKI EQUATION

M. R. Flannery

Exact Closed-Form Solution of the Generalized Debye-Smoluchowski Equation

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The first exact solution of the time-dependent Debye-Smoluchowski equation for diffusional drift under a general interaction in the presence of a reactive sink is presented. Associated time-dependent rates of chemical reactions in a dense gas are formulated and display the basic physical transition from reaction control to transport control as time progresses for a system initially in Boltzmann equilibrium.

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The number density $n(R,t)$ at time $t$ of some species $A$ (e.g., negative ions) drifting under interaction $V(R)$ across a sphere of radius $R$ towards a central species $B$ (positive ion) in a gas $Z$ (or liquid) under the action of a reactive spherical sink of extent $S$ from $B$ is governed by the generalized Debye-Smoluchowski equation,

$$-\frac{dn(R,t)}{dt} = -\frac{\partial n(R,t)}{\partial t} + R^{-2} \frac{\partial}{\partial R} [R^2 j(R,t)]$$

$$= \Gamma_s n(R,t) \delta (R-S).$$

Here $\Gamma_s$ is the speed of reaction (via ion-pair-gas collisions) for ions after being brought to $S$. by the net inward diffusional-drift current,

$$j(R,t) = D \exp \left( -\frac{V}{kT} \right) \frac{\partial}{\partial R} \left[ n(R,t) \exp \left( \frac{V}{kT} \right) \right],$$

in terms of the diffusion coefficient $D$ (cm$^2$ s$^{-1}$) for relative diffusion of $A$ and $B$ in $Z$. The number density $N_s$ of all ion pairs $AB$ with internal separation $R \geq S$ then decays at a rate,

$$-\frac{dN_s}{dt} = -\frac{d}{dt} \int_S^\infty 4\pi R^2 N_s n(R,t) dR$$

$$= -\frac{\partial N_s}{\partial t} + N_s [ F - 4\pi S^2 j(S-\epsilon,t)]$$

$$= 4\pi S^2 \Gamma_s n^-(S,t) N^+ = \alpha(t) N^+ N^-, \quad (3)$$

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where \( F \) is the rate \((s^{-1})\) of generation of negative ions at infinity, and where \( \alpha \) is the time-dependent rate \((cm^{3} s^{-1})\) of recombination appropriate to asymptotic ion densities \( N^* \). If the ion current approaching \( S \) is absorbed by reaction within \( S \), then \( \lim_{t \to 0} j(S-\epsilon, t) = 0 \). In steady state, the rate \( 4\pi R^2 j(R, t) \) from (1) is constant for \( R \gg S + \epsilon \) and equals the production rate \( F \) in (3).

Equation (1) automatically incorporates the boundary condition

\[
\Gamma_j n^-(S, t) = \lim_{\epsilon \to 0} j(S+\epsilon, t)
\]

which follows on integration of (1) between \( S \pm \epsilon \) and which equates the transported and absorbed currents at the boundary. At asymptotic \( R \) the correct solution of (1) tends to the Boltzmann distribution.

\[
n^-(R \to \infty, t) = N^- \exp(-V/kT). \tag{5}
\]

Equation (1) is of basic significance not only to ion-ion recombination in gases\(^1\) and ionic solutions but also to chemical reactions in a dense medium, to coagulation of colloids, to medical radiology, to diffusion and field controlled reactions in metabolizing systems (as enzyme-substrate reactions in a cell\(^2\)), and to diffusion across a membrane. While an exact time-dependent solution to (1) can be obtained\(^2\) for the field-free \((V = 0)\) case, no exact solution has yet been determined for general \( V \) although a large body of literature exists on various approximate techniques\(^3\) for the Coulomb case. We provide here the first analytical exact solution of (1) subject to the condition that \( n^- (R, t = 0) \) is prepared as the Boltzmann distribution (5).

The following exact solution is based on the novel transformation from \( R \) to the variable

\[
\tilde{R} = \int_{R}^{\infty} \exp\left[V(R)/kT\right] R^{-2} dR \;^{-1};
\]

\[
d\tilde{R}/dR = (\tilde{R}/R)^2 \exp(V/kT), \tag{6}
\]

which is not without its physical significance. It is related\(^4\) to the probability that an \( R \)-ion pair will further contract by diffusion under \( V \), in the presence of an instantaneous sink at \( S \). Let,

\[
n_\epsilon(R, t) = n^-(R, t) \exp(V/kT) \tag{7}
\]

such that (1) with (6) reduces to

\[
\frac{\partial n_\epsilon(\tilde{R}, t)}{\partial t} = \frac{\tilde{D}}{\tilde{R}^2} \frac{\partial}{\partial \tilde{R}} \left[ \tilde{R}^2 \frac{\partial n_\epsilon(\tilde{R}, t)}{\partial \tilde{R}} \right] \tag{8}
\]

subject to (4). The transformed diffusion coefficient \((cm^2 s^{-1})\) is

\[
\tilde{D} = D \left(\frac{dR}{d\tilde{R}}\right)^2. \tag{9}
\]

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,

\[
\tilde{\varphi} = (\tilde{R}/\bar{S}) - 1, \quad \tilde{\tau} = \tilde{D}t/\bar{S}^2, \quad \nu^* = (\bar{R}/\bar{S}) n_\epsilon(\tilde{R}, t) \tag{10}
\]

such that (8) reduces to

\[
\frac{\partial \nu^*}{\partial \tilde{\tau}} = \frac{\partial \nu^*}{\partial \tilde{\varphi}}. \quad \tag{11}
\]

This can be now solved by the method of Laplace transformation which automatically incorporates the initial condition. The full solution of (1) appropriate to spontaneous \( \nu^* \to \nu \infty \) in (4) is then, after some analysis,

\[
n^S(R, t) = N^- \exp\left(-\frac{\tilde{S}}{kT}\right) \left[1 - \text{erfc}\left(\frac{(\bar{R} - \bar{S})}{2(\tilde{D}t)^{1/2}}\right)\right]. \tag{12}
\]

The associated recombination rate is then

\[
\alpha^S(t) = 4\pi S^2 j(S, t)/N^- \tag{13}
\]

which tends at long time \( t \gg S^2/D \) to the steady-state transport rate

\[
\alpha^\text{TRANS} = 4\pi S D = 4\pi D R_e/P(S), \tag{14}
\]

where the natural unit of length \( R_e \) is \((e^2/kT)\) and where

\[
P(S) = R_e/\bar{S} = R_e \int_{\bar{S}}^{\infty} \exp(V/kT) R^{-2} dR. \tag{15}
\]

Under condition of equilibrium with the field, the Einstein relation \((D R_e = K e)\) between \( D \) and the mobility \( K \) is valid. For a Coulombic attraction, the steady-state solution (14) is then

\[
\alpha^\text{TRANS} = 4\pi K e/\left[1 - \exp(-R_e/\bar{S})\right] \tag{16}
\]

in accord with that of Bates.\(^4\)

The boundary condition (4) for finite reaction under a field is,

\[
\Gamma_j S n^-(S, t) = D \exp\left(\frac{-V(S)kT}{kT}\right) \left[\frac{\partial}{\partial \bar{S}} \nu(S) \exp\left(-\frac{V(S)}{kT}\right)\right]_{\bar{S}} \tag{17}
\]

which yields, in the transformed representation (6),

\[
n_\epsilon(S, t) = \frac{\bar{D}}{\Gamma_j S} \left(\frac{d\nu^*}{d\bar{S}}\right)_{\bar{S}}. \tag{18}
\]
where the transformed speed of reaction is
\[ \tilde{\Gamma}_3 = \Gamma_3 (d\tilde{R}/dR). \] (19)

Hence, the full time-dependent solution obtained from Laplace transformation of (11) subject to the initial Boltzmann distribution is, for a general interaction, given by
\[ n^\ast(R, t) = N^\ast \exp\left(-V/kT\right) \left[ 1 + \left( \frac{\tilde{\alpha}}{\tilde{\alpha}_L} \right) \frac{\tilde{S}}{R} \right] \exp\left(2\tilde{\alpha} - \tilde{\alpha}_L\right) \exp\left(\tilde{\chi}^2\text{erfc}(\tilde{\chi} + \tilde{\alpha}) - \text{erfc}\tilde{\alpha}ight). \] (20a)

Here the associated quantities are defined as
\[ \tilde{\chi}(t) = (1 + \tilde{\alpha}_3/\tilde{\alpha}_L) (D\tilde{t})^{1/2} / \tilde{S}, \] (20b)
\[ \tilde{\alpha}(t) = (R - \tilde{S}) / 2(D\tilde{t})^{1/2}, \] (20c)
and
\[ \tilde{\alpha} = \tilde{\alpha}_3/\tilde{\alpha}_L, \] (20d)
in terms of the transformed reaction and transport rates,
\[ \tilde{\alpha}_3 = 4\pi \tilde{S}^2 \tilde{\Gamma}_3, \quad \tilde{\alpha}_L = 4\pi \tilde{S} \tilde{D}. \] (20e)

The ratio of these rates is, however, unchanged and given by
\[ \frac{\tilde{\alpha}_3}{\tilde{\alpha}_L} = \frac{4\pi \tilde{S}^2 \Gamma_3 \exp[-V(S)/kT]}{\alpha_{\text{TRANS}}}. \] (21)

Here \( \alpha_{\text{RCTN}} \) denotes the reaction rate which from (3) is the recombination rate that would pertain provided a Boltzmann distribution of ions were maintained as at low gas densities when \( j \) in (2) vanish-es. The full time-dependent recombination rate is now given by (20a) in (2) as
\[ \alpha(t) = 4\pi S^2 \Gamma_3 n^\ast(S, t) / N^\ast = \alpha_\ast \left[ 1 + (\alpha_{\text{RCTN}}/\alpha_{\text{TRANS}}) \exp(\tilde{\chi}^2\text{erfc} \tilde{\chi}) \right], \] (22a)
where \( \tilde{\alpha}(R = S) \) in (20c) vanishes, \( \tilde{\chi} \) in (20b) is, with the aid of (6), (9), and (21),
\[ \tilde{\chi} = (1 + \alpha_{\text{RCTN}}/\alpha_{\text{TRANS}}) [(D\tilde{t})^{1/2}/S] \exp[V(S)/kT] \left[ S \int_S^\infty \exp(V/kT)R^{-2}dR \right]^{-1}, \] (22b)
and where
\[ \alpha_\ast = \alpha_{\text{RCTN}} \alpha_{\text{TRANS}} / (\alpha_{\text{RCTN}} + \alpha_{\text{TRANS}}) \] (22c)
is the steady-state rate of recombination which is controlled by the rate limiting step of reaction versus transport and which exhibits a form characteristic of physical mechanisms in series. At high gas densities \( N \), \( \alpha_{\text{TRANS}} \ll \alpha_{\text{RCTN}} \) such that \( \alpha_\ast = \alpha_{\text{TRANS}} \), the transport rate. At low \( N \), \( \alpha_{\text{TRANS}} \gg \alpha_{\text{RCTN}} \) such that \( \alpha_\ast = \alpha_{\text{RCTN}} \). As \( t \) increases from zero, then
\[ \exp(\chi^2\text{erfc} \chi - 1 - \frac{2}{\sqrt{\pi}} \chi + \chi^2 - \frac{4}{3\sqrt{\pi}} \chi^3 + \ldots \] (23)
such that
\[ \alpha(t = 0) = \alpha_{\text{RCTN}} \left[ 1 - \frac{2}{\sqrt{\pi}} \left( \frac{\alpha_{\text{RCTN}}}{\alpha_{\text{TRANS}}} \right) (D\tilde{t})^{1/2} \exp[V(S)/kT] \left[ S \int_S^\infty \exp(V/kT)R^{-2}dR \right]^{-1} \right] \] (24)
decreases initially from the reaction rate \( \alpha_{\text{RCTN}} \). As \( t \to \infty \),
\[ \exp(\chi^2\text{erfc} \chi - \frac{1}{\chi^{1/4}} \left( 1 - \frac{1}{\chi^{1/2}} + \frac{3}{4\chi^3} \ldots \right) \] (25)
such that the long-time dependence is
\[ \alpha(t = \infty) = \alpha_\ast \left[ 1 + \left( \frac{\alpha_\ast}{\alpha_{\text{TRANS}}} \right) \frac{S\exp[-V(S)/kT]}{(\pi D\tilde{t})^{1/2}} \left[ S \int_S^\infty \exp(V/kT)R^{-2}dR \right] \right]^{-1} \] (26)
which tends eventually to the steady-state rate \( \alpha_\ast \) for \( t \gg (S^2/D) \).
The ion density (20a) tends to the steady-state limit

\[ n^-(r, t \to \infty) = N^- \exp(-V/kT) \left[ 1 - \left( \frac{\alpha_\infty}{\alpha_{\text{TRNS}}} \right) P(R) \right] \]

which at low \( N \) is approximately Boltzmann but departs appreciably from Boltzmann at high \( N \) (\( \alpha_\infty \sim \alpha_{\text{TRNS}} \)) particularly in the region of the sink.

The full time dependence in (22a) for \( \alpha \) is contained in (22b) for \( \xi \) which, for a pure Coulomb attraction, varies as

\[ \bar{\xi}(\tau) = \left( 1 + \frac{\alpha_{R\text{CTN}}}{\alpha_{\text{TRNS}}} \right)^{1/2} \tau^{1/2} \left( \frac{R_\text{S}}{S} \right)^{1/2} \left[ \exp \left( \frac{R_\text{S}}{S} \right) - 1 \right]^{-1}, \]

where the scaled time is

\[ \tau = \frac{t}{(S^2/D)} \]

in the units of \((S^2/D)\), the time approximately required for an ion to diffuse from the boundary to the center of the sink.

In Fig. 1 the time dependence is illustrated for the recombination rates \( \alpha(t) \) resulting from (22) for various gas densities \( N \) (in units of \( N_L \), the number density \( 2.69 \times 10^{19} \text{ cm}^{-3} \) at STP). The transport rate \( \alpha_{\text{TRNS}} \) is given by (14) and the reaction rate \( \alpha_{R\text{CTN}} \) for a fictitious (but representative) case of ions of equal mass (16 amu) and mobility 2 cm\(^2\)/Vs recombining in an equal mass gas at 300 K is obtained from a model\(^1\) which yields the exact quasiequilibrium rates\(^6\) at low \( N \).

For high \( N \), \( \alpha(t) \) decreases initially from \( \alpha_{R\text{CTN}} \), which is \( \gg \alpha_{\text{TRNS}} \), to its steady-state limit which is \( \alpha_{\text{TRNS}} \), i.e., for the assumed initial Boltzmann distribution, reaction first occurs spontaneously for the ions within \( S \) and then ion transport is initiated in an attempt to compensate for the resulting hole in the distribution. For low \( N \approx N_L \) (\( \approx 1 \text{ atm} \)), a linear variation of \( \alpha(t) \) with \( t \) is exhibited since the reaction rate \( \alpha_{R\text{CTN}} \ll \alpha_{\text{TRNS}} \) is always the rate limiting step. Thus the transition from reaction to transport is best observed for dense gases. Also shown in Fig. 1 are the characteristic time scales \((S^2/D)\) for diffusion across a sink of radius \( S \) which is compressible with \( N \). This effect could therefore be detected by modern laser spectroscopic techniques based on rotational or vibrational transitions in molecular ions. The steady-state rates are of course independent of the initial condition.

In summary, we have presented here the first exact closed-form analytical solution of the generalized Debye-Smoluchowski equation for diffusional drift in the presence of a reactive sink or source. The evolution of the rate of the overall process for an initial Boltzmann distribution exhibits the interesting phenomenon of control by reaction to control by transport, and illustrates the competition between these basic physical mechanisms as time progresses. This phenomenon is directly important to many areas as fluorescence quenching in solutions and in the disappearance rate of ionization tracks.

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Appendix E

Ion–Ion Recombination in Dilute and Dense Plasmas

M. R. FLANNERY
Ion–Ion Recombination in Dilute and Dense Plasmas

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Abstract

Theory of ion–ion recombination in a gas is provided as a function of gas density \( N \), ion density \( N^\pm \), and time. An approximate analytical solution to the generalized time-dependent Debye–Smoluchowski equation for reaction and diffusional drift under general ion–ion field is provided for an initial Boltzmann distribution of ions. The transition in the time-dependent rates \( \alpha(t) \) of recombination from reaction to the rate limiting step of reaction and transport is illustrated for various \( N \), together with the variation of the steady-state limit \( \alpha \) with \( N \). The method and results are of basic significance for situations ranging from medical radiological and biophysics to the rate of disappearance of ionization tracks.

1. Introduction

In this article we outline the first basic theory \([1]\) of the recombination process

\[
X^+ + Y^- + Z \rightarrow [XY] + Z
\]

as a function of the density \( N \) of the gas \( Z \), of the density \( N^\pm \) of the ions \( X^+ \) and \( Y^- \) and of the time \( t \). The problem is fairly complex in that various macroscopic effects such as diffusion, mobility and the recombination sink must be initially addressed \([1]\) in language of their microscopic collisional origin, so that various effects are not twice included (unwittingly) via some particular graft of macroscopic phenomena and microscopic principles. This detailed history has recently been established \([1]\) via the Boltzmann equation and in this paper a simplified version which correctly blends microscopic and macroscopic effects is provided and the important results are illustrated. The work is significant also to chemical reactions in dense gases, to recombination in dilute ionic solutions and to the time rate of disappearance or diffusion of ionization tracks produced by a high-energy laser or beam of particles.

2. Recombination Rate

Let the negative ions of density \( n^- (R,t) \) at time \( t \) stream across spheres of radius \( R \) each centered at each positive ion distributed \( N^\pm \) cm\(^{-3}\). The time-dependent continuity equation is

\[
\frac{\partial n^-}{\partial t} (R,t) - \nabla_R \cdot j = - \frac{C}{\sum_{i=-V(R)}} \left[ \frac{\partial n^+_i}{\partial t} (R,E_i,t) \right]_S
\]

\* The square brackets denote that the product may not remain bound.

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where the net inward current (number of ions/s across unit area of an $R$ sphere)
\[
j = D[\nabla n^-(R,t) + n^-(R,t)\nabla (V/kT)]
\]
\[
\equiv -D \exp(-V/kT)(d/dR)[n^- \exp(V/kT)]\dot{R}
\]  
(3)
arises from diffusional drift of the ions with relative diffusion coefficient $D$ in
the gas $Z$ under an external field of potential $V(R)$. The collisional-sink term is
\[
\left[\frac{\partial n_i^-}{\partial t} (R,E_i,t)\right]_S = N \sum_{f=-V(R)}^{-M(R)} n_f^-(R,E_{f},t) k_{fi}(R)
\]  
(4)
in terms of the phase-space densities $n_i^-(R,E_{i},t)$ of $R_i$ ions (which form ion pairs
with internal energy $E_i$ and fixed internal separation $R$) and of the collisional
frequencies $Nk_{fi}$ at which an $R_i$ ion pair is converted into an $R_f$ ion pair by
collision with the gas bodies $Z$ of density $N$ (i.e., for $E_i \rightarrow E_f$ collisional
transitions). The collisional sink is effective only when the lowest bound level $-V$
appropriate to fixed separation $R$ lies at or below the level $-S$ of energy $E_S$
below which the recombination is assumed to be stabilized against any upward
collisional transitions, i.e., $-M$ is max$[-V, -S]$. Although expression (2) has
been derived [1] from the full Boltzmann equation which describes the evolution
of the phase-space densities $n_i^-(R,E_{i},t)$ by gas collisions, it can be written im-
mediately from macroscopic principles. The microscopic origin of the macro-
scopic current $j$ of Eq. (3) is the balance of all ineffective ion-neutral collisions
in the absence of the sink—collisions which, in the presence of the sink, over-
subscribe $j$ by the amount in Eq. (3) summed over all states $i$ in Eq. (2) between
the lowest level $-V$ and the far continuum $C$.

On integrating over the volume of each $R$ sphere,
\[
-N^+ \frac{\partial}{\partial t} \int_0^R \left[4\pi R^2 n^-(R,t)dR + 4\pi R^2 N^+ j(R,t)\right] = \alpha_3(R)n^-(R,t)N^+
\]  
(5)
where the sink term which effects recombination has been replaced by [1]
\[
\alpha_3(R)n^-(R,t)N^+ = N \int_0^R dR \left[ \sum_{E=-E}^{E=-E} \left( N_i^*(R,E_i,t) \sum_{f=-V}^{f=-V} k_{fi}(R) \right) - \sum_{f=-M}^{f=-M} k_{fi}(R) \right]
\]  
(6)
the net balance between the collisional rates of downflow and upflow of $R$ ion
pairs past some arbitrary bound level $-E$ of negative energy. In the shells of radii
$R$ and thickness $dR$, the number density of $R_i$ ion pairs (or radial two-particle
correlation function) is
\[
N_i^*(R,E_i,t) = (4\pi R^2 dR)N^+ n^-(R,E_i,t)
\]  
(7)
We note for $R \geq R_E$, the outermost turning point associated with level $-E$, that
Eq. (6) tends to a constant since collisions with the gas atoms can be assumed impulsive [2] and change only the internal energy \( E_i \) of the ion pair and not their internal separation \( R \). Hence, the flux \( F_e(R,t) \) due to recombination,

\[
F_e(R,t) = \alpha_3(R)n^-(R,t)N^+ = -\frac{dN^\pm}{dt} = \alpha N^+N^-, \quad R \geq R_E
\]

is therefore constant for \( R \geq R_E \) and since the left-hand side of Eq. (5) evolves to the complete time derivative of the ion density, the overall recombination coefficient \( \alpha \) in Eq. (7) appropriate to asymptotic ion density \( N^- \) is therefore,

\[
\alpha(t) = \frac{\alpha_3(R_E)n^-(R_E,t)}{N^-}
\]

which is determined by Eq. (6) from a knowledge of the phase space ion-pair densities \( N_i^\prime \) and the collisional rates \( k_{ji}(R) \) for energy change.

By appeal to the Boltzmann equation for motion of an ion under an external electric field of intensity \( E = (-\nabla V) \), the phase-space densities evolve in phase space and time as,

\[
\frac{\partial n_i^-(R,v_i,t)}{\partial t} + v_i \cdot [\nabla_R n_i^-(R,v_i,t)] + \left[ \frac{eE}{m} \right] \cdot \nabla v_i n_i^-(R,v_i,t)
\]

\[
= \left( \frac{\partial n_i^-(R,v_i,t)}{\partial t} \right)_{EL} - \left( \frac{\partial n_i^-(R,v_i,t)}{\partial t} \right)_S
\]

where \( v_i \) is the velocity of the negative ion at time \( t \). Here the explicit time rate of change \( (\partial n_i^-(R,v_i,t)/\partial t) \) results from the following four mechanisms.

1. The continuous transport (diffusion) of \( R_i \) ions across the \( R \) sphere is due to the \( R \)-inhomogeneity in \( n_i \).
2. The continuous drift in velocity space due to \( E \) produces an acceleration \( (eE/m) \) in each of the \( n_i \Delta R \) ions initially with velocity points \( v_i \) within the phase element \( \Delta v_i \Delta R \), i.e., the \( R_i \) ions drift in velocity space at the common rate \( (eE/m) \) and are therefore lost from the initial elementary region.
3. The quasi-discontinuous change \( (\partial n_i^-(R,v_i,t)/\partial t)_{EL} \) of ions with velocities within \( \Delta v_i \) removes ions upon elastic ion-neutral collisions from one velocity element \( \Delta v_i \) to another. Replenishment to \( \Delta v_i \) is due to similar displacements from other elements of velocity space. Hence,

\[
\left[ \frac{\partial n_i^-(R,v_i,t)}{\partial t} \right]_{EL} = \int_{v_0} \left[ n_i^-(R,v_f,t)N_0(R,v_0,t) - n_i^-(R,v_i,t)N_0(R,v_0,t) \right] dv_0,
\]

\[
\int_{\Omega} [g\sigma(g,\psi)d\Omega] dv_0, \quad g = (v_i - v_0)
\]

where \( N_0(R,v_0,t) \) is the phase-space density of neutral gas species, and where the ion-neutral differential cross section at relative velocity \( g = (v_i - v_0) \) for elastic scattering by angle \( \psi \) into solid angle \( d\Omega \) is \( ad\Omega \). The \( \Omega \) integration is over that scattering region \( \Omega' \) made accessible for the production of final ion and neutral velocities \( v_f \) and \( v_0 \), respectively, consistent with initial fixed \( v_i \) and \( v_0 \).
Note, however, that these elastic scattering terms produce energy changes (inelastic effects) in the internal energy $E_i$ of an ion-pair system.

(4) 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 $R$.

The elastic term in Eq. (11) produces inelastic transitions $(E_i \rightarrow E_f)$ in an $R_i$ ion pair and on integrating over $1/4\pi d^2\theta_i$ an expression equivalent to Eq. (11) can therefore be written as,

$$\left[ \frac{\partial n_i^−(R,E_i,t)}{\partial t} \right]_{EL} = N \left[ \sum_{\nu} \sum_{\delta=\nu} n_f(R,E_f,t) k_{\delta\nu}(R) - n_i(R,E_i,t) \sum_{\delta=\nu} k_{\delta\nu}(R) \right]$$

where the internal energy $E_i$ is $\frac{1}{2}m_v^2 + V(R)$.

Because of their continuous development in phase space, mechanisms (1) and (2) provide the “streaming” or transport terms. We note that the ion density $N^\pm$ must be sufficiently low ($\leq 10^{16} \text{ cm}^{-3}$) 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 Eq. (11). Hence $N_0$ in Eq. (11) can be taken as the Maxwell–Boltzmann distribution such that Eq. (10) with Eqs. (11) and (4) is then the “linear” Boltzmann equation.

The recombination rate $\alpha(t)$ is therefore, in principle, determined as a general function of gas density $N$, ion density $N^\pm$, and time from Eqs. (9) and (6) via the time-dependent solutions of Eq. (10) for the phase-space densities. The interaction $V(R)$ between the ions can no longer be assumed $ab initio$ to be pure Coulomb as $N^\pm$ is raised. It is the appropriate solution of Poisson’s equation

$$\nabla^2 V = \frac{4\pi e^2}{\epsilon} \left[ n^+(R,t) - n^−(R,t) \right]$$

where the local positive and negative ion densities are

$$n^\pm(R,t) = 4\pi \int n^\pm(R,v_i,t)v_i^2 dv_i$$

and where $\epsilon$ is the dielectric constant of the gas $Z$. In the reference frame of the positive ion, $n^+(R,t)$ is simply the Boltzmann distribution

$$n^+(R,t) = N^+ \exp(V/kT)$$

Recombination is therefore fully determined by the solutions of Boltzmann’s equation (10), Poisson’s equation (13), and the kinetic equation (6) coupled together. Various theoretical procedures have been already proposed [1] for the solution of Boltzmann’s equation (10) for the phase-space densities.

Rather than solve Boltzmann’s equation (10) directly, assume that the sink term, Eq. (4) in Eq. (2), can be replaced by a partially absorbing sphere of radius $S(=R_E)$, an assumption suggested by the constancy at $R \geq R_E$ of the microscopic kinetic expression (6) for the loss rate, such that Eq. (2) is in effect equivalent to the generalized Debye–Smoluchowski equation,

$$\frac{\partial n^-(R,t)}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} [R^2 j(R,t)] = \Gamma_3 n^-(R,t) \delta(R-S)$$  \hspace{1cm} (16)

where $\Gamma_3$ is the speed of reaction (via three-body collisions) for ions after being brought to $S$ by the diffusional-drift current,

$$j(R,t) = D \exp(-V/kT) - \frac{\partial}{\partial R} [n(R,t) \exp(V/kT)]$$  \hspace{1cm} (17)

On integrating Eq. (16) over $4\pi R^2 dR$, then the continuous-source result is identical with Eq. (8) provided

$$j(S,t) = \Gamma_3 n^-(S,t)$$  \hspace{1cm} (18)

such that

$$\alpha_3(S) = 4\pi S^2 \Gamma_3$$  \hspace{1cm} (19)

thereby confirming that the strength $\Gamma_3$ of the sink in Eq. (16) is the speed of reaction within $S$. As $\Gamma_3 \to \infty$, then

$$n^-(S,t) = 0$$  \hspace{1cm} (20)

for an instantaneous-reactive sink. Note that Eq. (16) is equivalent to the homogeneous equation (16) with its right-hand side set equal to zero solved subject to $\alpha_3(S)n^-(S,t)$ equal to $\alpha(t)N^-$.

Equation (16) is of basic significance not only to ion–ion recombination and chemical reactions in a dense medium but also to medical radiology, diffusion and field controlled reactions in metabolizing systems (as enzyme-substrate reactions in a cell [3], and diffusion across a membrane. While an exact time-dependent solution to Eq. (16) can be obtained [3] for the field-free ($V = 0$) case, no exact solution has yet been determined for general $V$ although a large body of literature exists on various approximate techniques [4] and numerical solutions [5] for the Coulomb case. We provide here an analytical solution of Eq. (16) for general $V(R)$, subject to the condition that $n^-(R,t = 0)$ is initially prepared as the Boltzmann distribution, Eq. (15).

The following approximate solution is based on the novel transformation from $R$ to the variable

$$R = \left\{ \int_R^\infty \exp[V(R)/kT] \frac{dR}{R^2} \right\}^{-1}; \quad \frac{d\tilde{R}}{dR} = \left[ \frac{\tilde{R}}{R} \right]^2 \exp(V/kT)$$  \hspace{1cm} (21)

a transformation not without its physical significance. It is related [1] to the
probability $P_c$ that an $R_0$ ion pair will further contract by diffusion under $V$, in the presence of an instantaneous sink at $S$ (or else expand by diffusion expansion against $V$ to infinite internal separation).

Let,

$$n_0(R,t) = n(R,t) \exp(V/kT)$$

such that Eq. (16) with Eq. (21) reduces to

$$\frac{\partial n(\hat{R},t)}{\partial t} = \frac{\hat{D}}{\hat{R}^2} \frac{\partial}{\partial \hat{R}} \left[ \hat{R}^2 \frac{\partial n(\hat{R},t)}{\partial \hat{R}} \right]$$

where the transformed diffusion coefficient (cm$^2$ s$^{-1}$) is

$$\hat{D} = D \left[ \frac{d\hat{R}}{dR} \right]$$

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

$$\hat{r} = (\hat{R}/\hat{S}) - 1, \hat{\tau} = Dt/\hat{S}^2, n' = (\hat{R}/\hat{S}) n_0(\hat{R},t)$$

such that Eq. (23) under assumption of constant $\hat{D}$ reduces to

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

which can be solved by the method of Laplace transformation which incorporates the initial condition.

The full solution of Eq. (16) appropriate to spontaneous reaction Eq. (20) is therefore, after some analysis,

$$n(S)(R,t) = N^{-} \exp(-V/kT) \left\{ 1 - \frac{\hat{r}}{\hat{R}} \operatorname{erfc} \left[ \frac{(\hat{R} - \hat{S})}{2\sqrt{D\hat{\tau}}} \right] \right\}$$

The recombination rate then reduces to

$$\alpha^{(S)}(t) = 4\pi S^2 j(S,t)/N^{-} = \alpha_{TR} \left\{ 1 + \frac{S^2 \exp[-V(S)/kT]}{S(\pi D\hat{\tau})^{1/2}} \right\}$$

where the steady-state transport rate

$$\alpha_{TR} = 4\pi \hat{S} D = 4\pi DR_e/P(S)$$

with

$$P(S) = R_e/\hat{S} = R_e \int_{S}^{\infty} \exp(V/kT) \frac{dR}{R^2}$$

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

$$\alpha^{(S)}_{TR} = 4\pi Ke/[1 - \exp(-R_e/S)]$$

The boundary condition Eq. (18) for finite reaction under a field is,

$$\Gamma(S)n^{-}(S,t) = D \exp[-V(S)/kT] \left\{ \frac{\partial}{\partial R} \left[ n(R,t) \exp(V/kT) \right] \right\}$$  \hspace{1cm} (32)

which yields, in the transformed representation of Eq. (21),

$$n_{e}(S,t) = \frac{\bar{D}}{\Gamma(S)} \left[ \frac{dn_{e}}{d\bar{R}} \right]_{S}$$  \hspace{1cm} (33)

where the transformed speed of reaction is

$$\bar{\Gamma} = \Gamma \left( d\bar{R}/dR \right)$$  \hspace{1cm} (34)

Hence, after exercising due care, the full time-dependent solution obtained from the Laplace transformation of Eq. (26) subject to the initial Boltzmann distribution is given by, for a general interaction

$$n^{-}(R,t) = N^{-} \exp(-V/kT) \left[ 1 + \left[ \frac{\tilde{\alpha}}{\tilde{\alpha}_{D}} \right] \left( \frac{S}{\bar{S}} \right) \right]$$

$$\times \left\{ \exp(2\tilde{\alpha}_{3} \bar{\bar{\chi}}) \exp\bar{\bar{\chi}}^{2} \text{erfc}(\bar{\bar{\chi}} + \tilde{\bar{\bar{\chi}}}) - \text{erfc} \tilde{\bar{\bar{\chi}}} \right\}$$  \hspace{1cm} (35a)

where

$$\bar{\bar{\chi}}(t) = \left[ 1 + \frac{\tilde{\alpha}_{3}}{\tilde{\alpha}_{D}} \right] \left( \frac{\bar{\bar{D}}t}{\bar{\bar{S}}} \right)^{1/2} \equiv \left[ 1 + \frac{\tilde{\alpha}_{3}}{\tilde{\alpha}_{D}} \right]^{1/2} \left( \frac{D\bar{\bar{D}}^{1/2} \bar{\bar{S}}}{\bar{\bar{S}}} \right) \exp(V/S)/kT$$  \hspace{1cm} (35b)

where,

$$\tilde{\bar{\bar{\chi}}}(t) = (\bar{\bar{R}} - \bar{\bar{S}})/(2\bar{\bar{D}}t)^{1/2} \equiv (R - S)/(2Dt)^{1/2}$$  \hspace{1cm} (35c)

since \(\bar{\bar{D}}\) is assumed constant in eq. (24) and where

$$\tilde{\alpha} = \frac{\tilde{\alpha}_{3}\tilde{\alpha}_{D}}{\tilde{\alpha}_{3} + \tilde{\alpha}_{D}}$$  \hspace{1cm} (35d)

in terms of

$$\tilde{\alpha}_{3} = 4\pi \bar{\bar{S}}^{2}\bar{\bar{\Gamma}}; \tilde{\alpha}_{D} = 4\pi \bar{\bar{S}}\bar{\bar{D}}$$  \hspace{1cm} (35e)

The ratio of \(\tilde{\alpha}_{3}\), the transformed reaction rate to \(\tilde{\alpha}_{D}\), the transformed transport rate in Eq. (35) is therefore

$$\frac{\tilde{\alpha}_{3}}{\tilde{\alpha}_{D}} = \frac{\alpha_{3} \exp[-V(S)/kT]}{\alpha_{TR}} = \frac{\alpha_{RN}}{\alpha_{TR}}$$  \hspace{1cm} (36)

where \(\alpha_{RN}\) is used to denote the recombination rate that would pertain provided a Boltzmann distribution of ions were maintained at as low gas densities, i.e.,

$$\alpha_{RN}(S) = 4\pi \bar{\bar{S}}^{2} \bar{\bar{\Gamma}}_{3} \exp[-V(S)/kT]$$  \hspace{1cm} (37)

from Eqs. (19) and (36) such that Eq. (37) is the rate of reaction within \(S\).
The full time-dependent recombination rate now follows from Eq. (35a) as,

$$\alpha(t) = \alpha_3 n^-(S,t)/N^- = \alpha \left[ 1 + \frac{\alpha_{RN}}{\alpha_{TR}} \exp \tilde{x}^2 \text{erfc} \tilde{x} \right], \quad (38a)$$

where $\Omega(R = S)$ in Eq. (35c) vanishes, where $\tilde{x}$ in Eq. (35b) is, with the aid of Eqs. (21), (24) and (36),

$$\tilde{x} = \left( 1 + \frac{\alpha_{RN}}{\alpha_{TR}} \right) \frac{(Dt)^{1/2}}{S} \exp[V(S)/kT] \times \left[ S \int_S^\infty \exp(V/kT)R^{-2} dR \right]^{-1} \quad (38b)$$

and where

$$\alpha = \frac{\alpha_{RN}\alpha_{TR}}{(\alpha_{RN} + \alpha_{TR})} \quad (38c)$$

is the steady-state rate of recombination. Hence the radiation boundary condition (33) can be written as

$$n'(o,t) = (\alpha/\alpha_{RN}) \left( \frac{\partial n}{\partial r} \right)$$

which incorporates the full absorption ($\alpha_{RN} \gg \sigma$) and vanishing absorption ($\alpha \gg \alpha_{RN}$) conditions appropriate to diffusion-controlled and reaction-controlled processes respectively.

Thus the steady-state recombination rate $\alpha$ is controlled by the rate-limiting step of reaction versus transport. At high gas densities $N_0 \alpha_{TR} \ll \alpha_{RN}$ such that $\alpha \rightarrow \alpha_{TR}$ the transport rate. At low $N_0 \alpha_{TR} \gg \alpha_{RN}$ such that $\alpha \rightarrow \alpha_{RN}$.

As $t$ increases from zero, then

$$\exp \frac{\chi^2}{2} \text{erfc} \chi \rightarrow 1 - \frac{2}{\sqrt{\pi}} \chi + \frac{\chi^2}{3\sqrt{\pi}} + \ldots \quad (39)$$

such that,

$$\alpha(t \rightarrow 0) = \alpha_{RN} \left[ 1 - \frac{2}{\sqrt{\pi}} \frac{(Dt)^{1/2}}{S} \frac{\alpha_{RN}}{\alpha_{TR}} \exp[V(S)/kT] \times \left[ S \int_S^\infty \exp(V/kT)R^{-2} dR \right]^{-1} \right] \quad (40)$$

decreases initially from the reaction rate $\alpha_{RN}$. As $t \rightarrow \infty$, then

$$\exp \frac{\chi^2}{2} \text{erfc} \chi \rightarrow \frac{1}{\chi \sqrt{\pi}} \left[ 1 - \frac{1}{2\chi^2} + \frac{3}{4\chi^4} + \ldots \right] \quad (41)$$
such that the long-time dependence is

\[
\alpha(t \to \infty) = \alpha \left[ 1 + \frac{\alpha}{\alpha_{TR}} \right] \frac{S \exp(-V(S)/kT)}{(\pi D t)^{1/2}} \times \left[ S \int_{S}^{\infty} \exp(V/kT) R^{-2} dR \right]
\]  

(42)

which tends eventually to the steady-state rate \( \alpha \) for \( t \gg (S^2/D) \).

The transient rates, Eqs. (40) and (42), for short and long intervals of time are best observed at high gas densities when \( \alpha_{RN} \gg \alpha_{TR} = \alpha \), respectively. The full transient densities (35) and rates (37) are of basic significance to all diffusion-drift phenomena in gases or dilute solutions, as ion–ion, ion–atom, and atom–atom recombination in dense gases, or as coagulation of colloids in ionic solutions and in general to chemical reactions in dense gases.

The steady-state ion density from Eq. (33a) is

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

(43)

The full time dependence in Eq. (38a) for \( \alpha \) is contained in Eq. (38b) for \( \bar{\chi} \) which, for a pure Coulomb attraction, varies as

\[
\bar{\chi}(\tau) = \left[ 1 + \frac{\alpha_{RN}}{\alpha_{TR}} \right]^{1/2} \left( \frac{R_e}{S} \right) \left[ \exp(R_e/S) - 1 \right]^{-1}
\]  

(44)

where the scaled time is

\[
\tau = t/(S^2/D)
\]  

(45)

in units of \( (S^2/D) \), the time approximately required for an ion to diffuse from the boundary to the center of the sink.

4. Simple Model for Reaction Rate

Assume that a reaction occurs following strong collisions between gas atoms and ion pairs with internal separations \( R_i \leq R_i \). The trapping radii appropriate to interaction \( V \) is then the root of [7]

\[
V(R_i + \lambda_i) - V(R_i) = \frac{3}{2} kT/\delta_i
\]  

(46)

where \( \lambda_i \) is the mean free path of the ion \( i(=1,2) \) in the gas \( Z \) and where \( \delta_i \) is a collision parameter so chosen that the deduced reaction rate reproduces in the limit of low \( N \) results [8] obtained from the quasiequilibrium microscopic treatment of ion–ion recombination at low \( N \). Condition (46) originates from the requirement that an ion pair upon collision with \( Z \) is rendered incapable of expanding outwards from \( R_i \) to \( R_i + \lambda \) where the next collision would occur. It is a generalization of Natanson’s condition [9] and as \( \lambda \to \infty \), Eq. (46) reduces to Thomson’s criterion [10].
On recalling that each species of ion $i$ have different mean free paths $\lambda_i$ in the gas $Z$ and different sink radii $R_i$, the model for the rate $\alpha_{RN}$ of reaction within $R_E$ is therefore generalized from Eq. (37) to give [7]

$$\alpha_{RN}(R_1, R_2) = \pi \left[ R_i^3 W(X_i) C_i E_i + R_j^3 W(X_j) C_j E_j - R_k^3 W(Y_1) W(Y_2) G \right] (v_{12}) \quad (47a)$$

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

$$W(X_i) = 1 - \left( \frac{1}{2} X_i \right) \left[ 1 - \exp[-2X_i](1 + 2X_i) \right], \quad X_i = R_i/\lambda_i \quad (47b)$$

for a straight line trajectory. The factor

$$E_i = \exp\left[-V(R_i + \lambda_i)/kT\right] \exp\left[V(R)/kT\right] \exp\left(-3/2\delta_i\right) \quad (47c)$$

acknowledgments the Boltzmann enhancement in the ion number density 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

$$C_i = \left[ 1 + \left( \frac{2}{3kT} \right) \int_0^{R_i + \lambda_i} \frac{dV}{dR} \, dr \right] \left[ 1 + \delta_i^{-1} \right] \quad (47d)$$

acknowledges the focusing effect of the interaction on the assumed straight-line ion–ion trajectory between $(R_i + \lambda_i)$ and $R_i$. The minimum of $R_1$ and $R_2$ is $R_M$ such that $W(Y_1)W(Y_2)$ with $Y_i = R_M/\lambda_i$ is the probability of simultaneous ion-neutral collisions within $R_M$, a probability counted twice in the first two terms of Eq. (47a). Simple geometric arguments show that $G$ in Eq. (47a) is either $C_1E_1$ or $C_2E_2$ depending on whether $R_M$ is $R_1$ or $R_2$, respectively.

5. Interaction $V$

On inserting the steady-state ion density of Eq. (43) into Eq. (13), Poisson’s equation become

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left[ R^2 \frac{\partial}{\partial R} \left( V/kT \right) \right] = \left[ \frac{1}{2R_S^3} \right] \left[ \exp(V/kT) \right. \left. - \left[ 1 - \left( \frac{\alpha}{\alpha_{TR}} \right) \frac{P(R)}{P(R_E)} \right] \exp(-V/kT) \right], \quad R \geq R_E \quad (48)$$

where the “screening” distance is

$$R_S = (8\pi N^2 R_d/\epsilon)^{-1/2} \quad (49)$$

and where $R_E$ is the sink radius $S$ of Sec. 3. An analogous time-dependent equation follows by inserting $n^-(R,t)$ of Eq. (35a) into Poisson’s equation, Eq. (13).

Hence the $[\ ]$ term of Eq. (48) contains an explicit dependance on $V(R)$ via $P(R)$ of Eq. (30) and implicit and explicit dependances via $\alpha_{TR}$ of Eq. (29) and
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\( \alpha_{RN} \) of Eq. (47a) in Eq. (38c). The interaction must therefore be solved from Eq. (48) self-consistently with the recombination.

At low \( N \), the | | term of Eq. (48) tends to unity at all \( R \), while, at high \( N \), it increases from zero, at \( R \approx R_F \), to unity at asymptotic \( R \). For no plasma sheathing \( (R_S \rightarrow \infty) \), the interaction \( V \) is Coulombic.

When \( V \ll kT \), the exponentials in Eq. (48) may be linearized to yield the solution

\[
V(R) = -\frac{e^2}{R} \left[ 1 - \frac{\alpha}{2\alpha_H} \right] \exp(-R/R_S) - \frac{(\alpha/\alpha_H)e^2}{2R}
\]

where

\[
\alpha_H = 4\pi D R_e = 4\pi Ke
\]

is the Langevin transport rate. Direct numerical integration of Eq. (48) which may be replaced by equivalent three coupled first-order differential equations shows that Eq. (50) remains a highly accurate solution for \( R \gtrsim 0.1R_e \). When \( \alpha \ll \alpha_H \) as at vanishing \( N \), Eq. (50) yields

\[
V^{DH}(R) = -\frac{e^2}{R} \exp(-R/R_S)
\]

the Debye–Hückel interaction (DH). The recent Monte-Carlo simulations [12] based on this interaction DH are therefore invalid [11, 13] for the range of gas densities \( N \) covered. The interaction of Eq. (52) is valid only in the limit of vanishing gas density, i.e., as \( N \rightarrow 0 \) when the rate \( \alpha \) of recombination is vanishingly small compared to the rate of ion transport. When \( \alpha \approx \alpha_H \) as at high gas densities \( N \), Eq.(50) is Coulombic \((C)\) at \( R \approx R_F \) which is much smaller than \( R_S = 1.5R_e \) appropriate to \( N^* \approx 10^{14} \text{ cm}^{-3} \), and Eq. (50) tends to the mean of \( C \) and \( DH \) at asymptotic \( R \) which is self-consistent with the choice \( \alpha = \alpha_H \).

6. Transient and Steady-State Rates

In Figure 1 is illustrated the time-dependence of the recombination rates \( \alpha(t) \) obtained from Eq. (38) for various gas densities \( N \) (in units of \( N_L \), the number density \( 2.69 \times 10^{19} \text{ cm}^{-3} \) at STP). The transport rate \( \alpha_{TR} \) is given by Eq. (31) and the reaction rate \( \alpha_{RN} \) is obtained from Eq. (47) for a fictitious (but representative) case of ions of equal mass (16 amu) and mobility 2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) recombining in an equal mass gas (for which \( \delta_i = 0.6 \) [7]) at 300 K.

For high \( N,\alpha(t) \) decreases initially from \( \alpha_{RN}, \) which is \( \gg \alpha_{TR}, \) to its steady-state limit which is \( \alpha_{TR}, \) i.e., for the assumed initial Boltzmann distribution, reaction first occurs for the ions within \( S \) and then ion transport begins in an attempt to compensate for the resulting hole in the distribution. For low \( N \lesssim N_L, \) \((\approx 1 \text{ atm.)}, \) a linear variation of \( \alpha(t) \) with \( t \) is exhibited since the reaction rate \( \alpha_{RN} \ll \alpha_{TR} \). Thus the transition from reaction to transport is best observed for dense gases. Here the large reaction rates originate from the greatly enhanced
Boltzmann factors $E_i$ in Eq. (47a) which more than offsets the inherent reduction in the trapping radii $R_t$. Also shown in Figure 1 are the characteristic time scales $(S^2/D)$ for diffusion across a sink of radius $S$ which from Eq. (46) is compressible.
with \( N \). This effect could therefore be detected by modern laser spectroscopic techniques based on rotational or vibrational transitions in molecular ions. The steady-state rates are independent of the initial condition.

In Figure 2 is illustrated the variation of the steady-state rates \( \alpha(t \rightarrow \infty) \) for the realistic case

\[
\text{Kr}^+ + \text{F}^- + \text{Rg} \rightarrow \text{KrF}^* + \text{Rg}
\]

(53)

at 300 K with gas density \( N \) of various gases \( \text{Rg} = \text{Ne, Ar, Kr, Xe} \). Agreement with Monte-Carlo computer simulations [12, 14] is very good for low \( N^+ \). Figure 2 essentially shows the variation with \( N \) of the asymptotic limits of Figure 1.

Both figures therefore provide a comprehensive account of the recombination rate \( \alpha \) as a function of time, and gas density. The present theory is also significant in other situations involving the rate of disappearance of a dense ionization track produced by a directed high energy beam of particles or radiation.

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**Bibliography**


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Appendix F

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 $\alpha$. 
of recombination. Further development of the theory leads to interesting insights into the full variation with \( N \) of \( a \), which is shown to yield the correct limits at low and high \( N \). The recombination rate \( a \) is determined by the limiting step of the rate \( a_{rn} \) for ion reaction and of the rate \( a_{tr} \) 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 \( (a_{rn} \gg a_{tr}) \) and for a finite rate \( (a_{rn} \approx a_{tr}) \) of reaction within a kinetic sink rendered compressible by variation of gas density. Expressions for the transient recombination rates \( a(t) \) 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 \( a \) with ion density \( N^+ \) is also developed. Here the ion–ion interaction \( V \) can no longer be assumed \textit{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 (1978a), 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 \( a \) with gas density \( N \), consistent with the initial nonlinear ascent with \( N \) as given in the phenomenological
treatment of Thomson (1924). However, at pressures greater than 1 atm\(^\dagger\) (at 0 °C), the Thomson model predicts saturation in \(a\), 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 1978a, 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 1980a, b; Bates & Mendag 1978, Bardsley & Wadehra 1980, Morgan et al. 1980) which, although they produce numerical coefficients \(a\), 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 1980c). 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 \(10^{12} \leq N^+ \leq 10^{14}\) 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 \(N^+\), 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 \(\alpha\) of

\[\text{X}^+ + \text{Y}^- + \text{Z} \rightarrow [\text{XY}] + \text{Z}\]  

(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 \(v\) of the positive and negative ions \(\text{X}^+\) and \(\text{Y}^-\), labelled 1 and 2, respectively, is governed by \(v_0\), the drift velocity \((K_1 + K_2)E\) acquired from the 1–2 mutual electrostatic field of intensity \(E\) by the ions with mobilities \(K_{1,2}\) in the neutral gas \(Z\), labelled 3. The ion–neutral collision frequency \((\nu/\lambda_i)\) in terms of the mean free path \(\lambda_i\) of either ion \(i\) is very high and \(v_0\) is therefore in equilibrium with the field. The constant steady-state \(v_0\) is achieved as the balance between accelerations in the field direction between 1–3 collisions, and decelerations during 1–3 collisions. The net (inward) flux \(F_n^-\) (cm\(^{-3}\)s\(^{-1}\)) of negative ions crossing spheres of radii \(R_X\) centred at each positive ion, distributed with frequency \(N^+\) cm\(^{-3}\), is about \(4\pi R_X^2 v_0 N^+ N^-\) so that, under the assumption that all ion pairs with separations \(R\) less than \(R_X\)

\(\dagger\) atm = 101325 Pa.
are assured of eventual recombination, the recombination rate at high gas densities $N$ is equal to the rate of (drift) transport:

$$\alpha_n = \frac{1}{N \cdot N^-} \frac{dN^\pm}{dt} = \frac{F_{i\to i}^+}{N^+ \cdot N^-} = 4 \pi e (K_1 + K_2), \quad (1.2)$$

This is the Langevin result, which decreases as $N^{-1}$. The rate (1.2) is the rate $\alpha_{nn}$ of ionic transport in the absence of diffusion, which is appropriate only at asymptotic $R$, and is valid when the rate $\alpha_{nn}$ of reaction (by three-body collisions within $R_x$) is much faster than $\alpha_{nn}$, 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 ($\S$ 2.4) must be solved.

At low gas densities $N$, ion–neutral collision frequencies are vanishingly small, so the relative 1–2 approach velocity $v$ 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 $R \leq R_T$ 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 $N$, $\alpha$ increases linearly with $N$ as

$$\alpha_{10} = K_{eq}(R_T) \langle \langle v \rangle / \lambda_1 + \langle v \rangle / \lambda_2 \rangle \equiv \frac{3}{2} \pi R_T^2 N \sigma_d \langle v \rangle, \quad (1.3)$$

in terms of some averaged collision frequency $\langle v \rangle / \lambda_1$ and of $K_{eq}$, the equilibrium constant ($\frac{3}{2} \pi R_T^2$) averaged over all energies for formation of $R$-ion pairs with internal separations $R \leq R_T$. The sum of the diffusion cross sections for each i–3 encounter is $\sigma_d$. 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 $\alpha_{10}$ increases to such an extent that its effect on the number density $N_i(R)$ 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 $P_3(R_T/\lambda_i)$ of effective† ion–neutral collisions, for ion pairs with $R \leq R_T$, eventually increased to unity as

$$P_3(X) = W(X_1) + W(X_2) - W(X_1) W(X_2), \quad X_i = R_T/\lambda_i, \quad (1.4)$$

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

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

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 collisions.\

† In the sense of promoting the reaction phase of the recombination.
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 ($\S$ 2). Thus the Thomson rate is essentially the rate of reaction $\alpha_{rn}$ 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 $\alpha_{rn}$, of ion pairs (via three-body effective collisions) brought together by ion net transport at a rate $\alpha_{tr}$ such that the rate $\alpha$ of recombination is determined by the rate-limiting step, i.e. by

$$\alpha = \alpha_{rn}\alpha_{tr}/(\alpha_{rn} + \alpha_{tr})$$  \hspace{1cm} (1.6a)

where

$$\alpha_{rn} \sim (\pi R_T^2) P_3(X) \exp[-V(R_T)/kT] \langle v_{12} \rangle$$  \hspace{1cm} (1.6b)

is the rate of reaction within $R_T$, and

$$\alpha_{tr} = 4\pi D \int_{R_T}^{\infty} \exp(KV/De) R^{-2} dR = 4\pi Ke[1-\exp(-\epsilon^2/R_TkT)]^{-1}$$  \hspace{1cm} (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 $\alpha$ 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 $\alpha_{rn}$ is the recombination rate that would pertain ($\S$ 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

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

- \( \alpha \): recombination rate \((\text{cm}^3\text{s}^{-1})\), (2.51)
- \( \alpha_{r0}, \alpha_{10} \): reaction rate \((\text{cm}^3\text{s}^{-1})\) or recombination rate appropriate to a Boltzmann distribution of ions, recombination rate at low gas densities, (2.61)
- \( \alpha_3 \): \( \alpha_{r0} \exp \left[ V(R)/kT \right] \), (2.44), such that \( \alpha_3(R) \) is frequency of reaction within \( R \)-sphere.
- \( \alpha_h \): Langevin rate \((4\pi eK_e)\), (1.2)
- \( \alpha_{tr}(R) \): transport rate \( \left[ \alpha_h \left( R_e \right) \right] \exp \left[ V/kT \right] R^{-2} dR \), (2.63)
- \( \alpha_{bl} \): \( \alpha_{tr}(R_e) \); 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)
- \( D \): diffusion tensor, (2.37)
- \( D \): relative diffusion coefficient \((\text{cm}^3\text{s}^{-1})\) of positive and negative ions, (2.43)
- \( D_s \): diffusion coefficient in the presence of a sink, (5.49)
- \( \mathcal{D} \): diffusion drift operator, (2.46a)
- \( \delta \): collision parameter, (4.15)
- \( E \): electric field intensity, (2.3)
- \( -E \): energy of arbitrary bound level \((-E)\) of ion pair, (2.47a)
- \( E_{-S}, E_{-V}, E_{-M} \): energy of bound levels \(-S\), \(-V\), and \(-M\) of ion pair such that \( E_{-M} = \max \left[ E_{-V}, E_{-S} \right] \), (2.49)
- \( E_i \): internal energy of the ion pair in state i
- \( e \): electronic charge \((4.80324 \times 10^{-10} \text{e.s.u})\)
- \( F \): inward flux \((\text{negative ions s}^{-1})\) across a sphere centred at a positive ion, (2.69)
- \( F_0(v_i) dv_i \): Maxwellian distribution of speeds, (2.13)
- \( g, \tilde{g} \): ion–neutral relative speed, and velocity, (2.4)
- \( j(R,t) \): current \((\text{negative ions cm}^{-2}\text{s}^{-1})\) across an \( R \)-sphere centred at a positive ion, (2.45b)
- \( k \): Boltzmann constant \((1.38066 \times 10^{-23} \text{JK}^{-1})\)
- \( K \): relative mobility \((\text{cm}^2\text{Stat V}^{-1}\text{s}^{-1})\) of positive and negative ions, (2.38), (2.43)
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$k_{1t}(R)$, collisional rate coefficient (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)

$L(v_i)$ peculiar path length of ions with speed $v_i$ in absence of recombination sink, (5.34, 5.35)

$l_1(R, E_i)$ peculiar path length of ions in recombination process, (5.31)

$\lambda$ mean free path averaged over all speeds of ions in equilibrium, (1.3)

$-\mathbf{M}$ bound level of energy $E_{-\mathbf{M}}$ such that $E_{-\mathbf{M}} = \max \{E_{-\mathbf{M}}(R), E_{-\mathbf{M}}\}$, (2.11)

$N$ gas bulk density (cm$^{-3}$), (1.3)

$N_0(R, v_0, t)$ gas density (2.69 x 10$^{13}$ cm$^{-3}$) at s.t.p. (Loschmidt's number), after (2.128)

$N^i$ ion bulk density (cm$^{-3}$), (1.2)

$N_0(R, v_0, t)$ phase-space gas density (cm$^{-3}/$(cm s$^{-1}$))$^3$, i.e. gas density per unit $dv_0$-interval, (2.4)

$N(R, t)$ configuration-space gas density (cm$^{-3}$) $\int N_0(R, v_0, t) dv_0$, (2.34)

$n(R, v, t)$ phase-space density of negative ions, (2.2), (2.3)

$n(R, v, t)$ density of negative ions per unit speed-interval about $v$, (2.8)

$n_0(R, v_i)$ Maxwell–Boltzmann ion density per unit $dv_i$-interval, (2.13)

$n(R, v_i)$ configuration-space negative ion density (cm$^{-3}$) $\int n_i(R, v_i, t) dv_i$, (2.26)

$n^+_{ei}(R, E_i, t)$ configuration density of $R_i$-ion pairs per unit $dR$-interval, $4\pi R^2 n(R, E_i, t) N^i$ (cm$^{-4}$) with internal energy $E_i < 0$, or per unit $dR dv_i$-interval for $E_i > 0$, (2.10)

$n^+_{ei}(R, E_i, v_i)$ phase-space density of $R_i$-ion pairs, i.e. configuration density per unit $dv_i$-interval, (2.2)

$N_0(R, E_i)$ Maxwell–Boltzmann ion pair density per unit $dR dE_i$-interval, (2.14)

$P_0(R)$ probability of an ion-pair–neutral collision, (1.4)

$P_0(R), P(R)$ $R_{ei}^{\infty} \exp (V/kT) R^{-2} dR$, (2.56), which is such that $P(R_0)/P(R_K)$ is the probability $\mathcal{P}^{pe}$ that an $R_p$-ion pair contracts by diffusional drift in the presence of an instantaneous sink at $R_{Ki}$, (2.77)

$\mathcal{P}^{pe}(R, R_K)$ for instantaneous sink and (2.77b) for finite-rate sink.

$\mathcal{P}^{pe}(R, R_K)$ probability that an $R$-ion pair expands by diffusion to infinite internal separation against attractive force, (2.78)

$Q^{E,X}$ 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 $e^2K/D_e$) appropriate to coulomb attraction, (2.57) $\approx 55.7$ nm at 300 K.

$R_K, R(E)$ 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)

$R_f$ 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 $S$, (2.70, 2.82)
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 $\alpha$ of recombination. An exact expression for the steady-state $\alpha$ is provided (§ 2.3) in terms of the rates for ion 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 $n_i(R, v_i, t)$ and velocity $v_i$ at time $t$ under interaction $V(R)$ across spheres of radius $R$ centred on each positive ion, which are distributed with density $N^+ \text{cm}^{-3}$, so that the number density $N^*_i(R, E_1, t)$ of ion pairs with reduced mass $M_{12}$, within the $R$-shells of thickness $dR$, with internal energy

$$E_1 = \frac{1}{2} M_{12} v_i^2 + V(R),$$

(2.1)

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

$$N^*_i(R, E_1, \hat{v}_i, t) \, dR = 4\pi R^2 \, dR n_i(R, v_i, t) \, N^+. \quad (2.2)$$

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 $E = -\nabla V/e$ (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

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

$$\frac{\partial n_i(R, v, t)}{\partial t} + v \cdot \nabla n_i(R, v, t) + \left( \frac{eE}{m} \right) \cdot \nabla_{v_i} n_i(R, v, t) = \left( \frac{\partial n_i}{\partial t} \right)_{1} - \left( \frac{\partial n_i}{\partial t} \right)_{S},$$

(2.3)

in which the explicit time rate of change \( \left( \frac{\partial n_i}{\partial t} \right)_{1} \) results from the following four mechanisms.

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

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

(c) The quasidiscontinuous change \( \left( \frac{\partial n_i}{\partial t} \right)_{S} \) of ions with velocities within $\Delta v_i$ upon elastic ion-neutral collisions which therefore remove ions from one velocity element $\Delta v_i$ to another. Replenishment to $\Delta v_i$ is due to similar displacements from other elements of velocity space. Hence,

$$\frac{\partial n_i}{\partial t} = \int_{v_o} \int_{\Omega} \left[ \left( \frac{\partial N_0(R, v_o, t)}{\partial t} \right)_{S} - \left( \frac{\partial n_i}{\partial t} \right)_{1} \right] \sigma(g \vartheta, \varphi) d\Omega d\varphi,$$

(2.4)

where $N_0(R, v_o, t)$ is the phase-space density of neutral gas species, and where the ion-neutral differential cross section at relative velocity $g_{i} = (v_i - v_o)$ for elastic scattering by angle $\vartheta$ into solid angle $d\Omega = \sigma d\Omega$. The $\Omega$-integration is over that scattering region $\Omega'$ made accessible for the production of speeds associated with final ion and neutral velocities $v_f(v_i, v_o, \Omega)$ and $v_0(v_i, v_o, \Omega)$, respectively consistent with initial fixed $v_i$ and $v_o$. 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 \( \left( \frac{\partial n_i}{\partial t} \right)_{S} \) due to the recombination sink tends to cause a redistribution in internal energies $E_i$ of an ion pair with fixed internal separation $R$ 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 $10^{16}$ 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.
As already mentioned, (2.4) produces inelastic transitions \((E_i \rightarrow E_f)\) in an \(R_i\)-ion pair and on integrating over \(v_i^2 \, d\Omega\), an equivalent expression for (2.4) can, on replacing \(v_i\) by (2.1), therefore be written as,

\[
\left[ \frac{\partial n_i(R, E_i, t)}{\partial t} \right]_{R_i} = N \left[ \sum_{E_f = V}^{C} n_i(R, E_i, t) k_{nf}(R) - n_i(R, E_i, t) \sum_{E_f = V}^{C} k_{nf}(R) \right],
\]

(2.5)

where \(N\) is the number density of gas atoms (or molecules) \(Z\), and \(Nk_{nf}(R)\) 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.

\[
N \sum_{t = -V}^{t + \Delta t} \left[ k_{nf}(E_i, E_f, R) \right] dE_t = \int_{v_{\text{min}}}^{v_{\text{max}}} \left[ 4\pi N_0(v_0) \int_{g} g\sigma(g, \psi) \, d\phi \right] v_{\text{f}}^2 \, dv_0 \, d(\cos \theta_i);
\]

(2.6)

where \(v_{\text{min}}, v_{\text{max}}\) and \(\Omega'\) are such that a final speed \(v_f\) of ion–ion relative motion is obtained from a given \(v_i\) and \(g\) and where \(\Delta f\) is the number of states in the energy interval \(dE_f\) 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)

\[
\sum_{t = -V}^{t + \Delta t} k_{nf}(E_i, E_f, R) = \int_{v_{\text{min}}}^{v_{\text{max}}} F_0(v_0) \, dv_0 \left[ v_{\text{f}}^2 - (v_i^2 + 2\Delta[M_1]) \right],
\]

(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 \(\Delta = T_f - T_i\), the change in initial and final kinetic energies \(\frac{1}{2}M_1(1 + c) v_{\text{f}}^2\), 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 \(k_{nf}\) 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 \(-V\), 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 \(N_0(v_0)\) in gas velocities is isotropic, is independent of both time \(t\) and position \(R\) 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 \(E\) and transferred subsequently by collision with the gas \(Z\) have a completely negligible effect on \(N_0(v_0)\). 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 \(R\)- and \(v\)-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

\[
n_i(R, v_i, t) = 4\pi v_i^2 n_i(R, v_i, t) \equiv n_i(R, E_i, t),
\]

(2.8)

\[
\sum_{v_i = -V}^{V} n_i(R, E_i, t) = 4\pi \int_{0}^{\infty} n_i(R, v_i, t) \, v_i^2 \, dv_i = \int_{0}^{\infty} n_i(R, v_i, t) \, dv_i.
\]

(2.9)

Also the density \(N_i^\ast\) of ion pairs in the \(R\)-shell of thickness \(dR\) is related to the negative-ion density \(n_i\) by

\[
N_i^\ast(R, v_i, t) \, dR = \left( 4\pi R^2 \, dR \right) n_i(R, v_i, t) \, N_i^\ast \equiv N_i^\ast(R, E_i, t) \, dR.
\]

(2.10)
(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,

\[
\frac{\partial n_i(R, E_i, t)}{\partial t} = N \sum_{t=-V(R)}^{M(R)} n_t(R, E_t, t) k_{tt}(R) - \frac{N}{4\pi R^2 N^+} \sum_{t=-V(R)}^{M(R)} N^*_t(R, E_t, t) k_{tt}(R)
\]

(2.11)

where the energy of the bound level \(-M\) is \(E_{-M} = \max[E_{-V}(R), E_{-S}]\) in which \(E_{-S}\) is the negative energy of the bound level \(-S\) below which recombination is assumed stabilized against any upward collisional transitions in energy. If the level \(-V(R)\) of energy \(E_{-V}(R)\) at \(R\) is above \(-E_S\), 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 \(-V\) and \(-M\) 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

\[
\frac{\partial n_i(R, v_i, t)}{\partial t} + v_i \left\{ \frac{\partial n_i(R, v_i, t)}{\partial R} - \frac{4\pi v^3_i}{m v_i} \frac{\partial}{\partial v_i} \left[ n_i(R, v_i, t) \frac{\partial V}{\partial R} \right] \right\} = \int \frac{C}{4\pi^2} \left[ n_t(R, v_t, t) N_0(\mathbf{v}_0) - n_i(R, v_i, t) N_0(\mathbf{v}_0) \right] g(\sigma, \psi) d\Omega d\mathbf{v}_0
\]

(2.12)

as the basic equation for the solution of the phase-space densities of negative ions. The corresponding equation for phase-space densities \(N^*_t(R, E_i, t)\) of ion pairs follows directly from (2.12) with the aid of (2.10) and of \(\partial/\partial v_i = m v_i \partial/\partial E_i\) 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

\[
n_0(R, v_i) dv_i = N^+ \exp \left[ -V(R)/kT \right] F_0(v_i) dv_i
\]

(2.13a)

\[
= N^+ \exp \left[ -V(R)/kT \right] \left[ 4\pi v^3_i (m/2\pi kT)^{3/2} \exp \left( -\frac{1}{2} m v^2_i / kT \right) dv_i \right],
\]

(2.13b)

where \(F_0(v_i) dv_i\) 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 \(dR\) and with internal energy in the interval \(dE_i\) about \(E_i\) is, therefore, with (2.1) and (2.2),

\[
N_0(R, E_i) dR dE_i = 4\pi R^2 dR \int_{E_i - V(R)}^{E_i} \left[ \frac{1}{2\pi^3 (kT)^{3/2}} \exp \left( -E_i/kT \right) dE_i \right] N^+ N^-
\]

(2.14)

of which one half move inward and one half move outward across the \(R\)-sphere, respectively. Also the rates \(k_{tt}\) satisfy the detailed balance relation (Flannery 1981 a)

\[
N_0(R, E_i) k_{tt}(R) = N_0(R, E_i) k_{tt}(R)
\]

(2.15)

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

\[
N_0(R) dR = dR \int_{E_i - V(R)}^{+\infty} N_0(R, E_i) dE_i = 4\pi R^2 dR \exp \left[ -V(R)/kT \right] N^+ N^-
\]

(2.16)
The equilibrium number density of ion pairs bound with negative energy in the interval \( dE \) about \( E \) is

\[
N_0(E) \, dE = dE \int_0^{R_{E}(K)} N_0(R, E) \, dR = \frac{8\pi^3}{kT} [C(E) \exp \left( -E/kT \right) \, dE] N^+ N^-,
\]

where \( R_{E}(E) \) is the outermost turning point obtained from \( E = V(R_{E}) \), and where for a pure coulomb attraction

\[
C(E) = \int_0^{\sqrt{E}} (\varepsilon^2 - |E|)^{\frac{3}{2}} R^2 \, dR = \frac{1}{4\pi\varepsilon^2} |E|^{\frac{3}{2}},
\]

(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 \( N^I_v \) where \( v_i \) 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 \( v_i^{-1} \) between collisions so that the explicit time derivative in (2.12) is negligible with respect to the right-hand side. Hence, by setting

\[
N(R, E_1, t) = N^I_v(R, E_1) \exp \left[-A(E_1) \, t\right],
\]

(2.19)

in (2.12) and by ignoring the small decay frequency \( A(E_1) \) of level \( i \) in comparison with \( v_i \), as in a steady-state solution, we have

\[
v_i \left[ \int_0^R 4\pi R^2 \frac{\partial}{\partial R} \left[ N^I_v(R, v_i) \right] \, dR - \frac{4\pi v_i^2}{m v_i} \frac{\partial}{\partial v_i} \left[ \int_0^R N^I_v(R, v_i) \frac{\partial V}{\partial R} \, dR \right] \right]
\]

\[
= \int_0^\alpha \left[ N^I_v(R, v_I) N_0(v_0') - N^I_v(R, v_I) N_0(v_0) \right] (gs \, d\Omega) \, dv_0
\]

\[
= N \left[ \int_0^R \, dR \sum_{t=-M(R)}^C N^I_v(R, E_1) k_{II}(R) - N^I_v(R, E_1) \sum_{t=-V(R)}^C k_{II}(R) \right]
\]

(2.20a)

as the basic set of coupled integro-differential equations to be solved in general for the steady-state \( (R, E_1) \)-distributions of the ion-pair number densities \( N^I_v(R, E_1) \). This set is solved subject to the boundary conditions that

\[
N^I_v(R, v_i) = N^I_v(R, E_1) = \begin{cases} N_0(R, E_i), & E_i > 0, \quad R \to \infty, \\ N_0(R, E_i), & E_i \to \infty, \quad \text{all accessible } R, \\ 0, & E_i < -E_s, \quad R < R_s(E_s), \end{cases}
\]

(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 \( R_0 \) of \( E_i = V(R_0) \), where \( v_i(R_0, E_1) \) vanishes, then upon assuming that the left-hand side of (2.20) vanishes everywhere in this range we have

\[
N^I_v(E_i) \sum_{t=-V}^C \langle k_{II} \rangle = \sum_{t=-V}^C N^I_v(E_i) \langle k_{II} \rangle
\]

(2.22)

where \(-V\) is the lowest bound energy level, the averaged rate is

\[
\langle k_{II}(E_i, E_i) \rangle = \frac{1}{N^I_v(E_i)} \int_0^{R_{E}(E_1)} N^I_v(R, E_1) k_{II}(E_i, E_1, R) \, dR, \quad R_{M} = \min [R(E_1), R(E_1)],
\]

(2.23)

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

\[
N^I_v(E_i) = \int_0^{R_{E}(E_1)} N^I_v(R, E_1) \, dR.
\]

(2.24)
THEORY OF ION–ION RECOMBINATION

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 recombinations 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 \( \alpha \) from derived equations of continuity, momentum and flux

To develop an expression for the recombination coefficient \( \alpha \) 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 \((R, \mathbf{v}_i)\)-phase space occupied by the incoming negative ions of density \( n_i(R, \mathbf{v}_i, t) \), we write the \( \mathbf{v}_i \)-averaged value of some physical quantity \( P_i(R, \mathbf{v}_i, t) \) as

\[
P(R, t) = \langle P_i \rangle = \frac{1}{n(R, t)} \int n_i(R, \mathbf{v}_i, t) P_i(R, \mathbf{v}_i, t) \, d\mathbf{v}_i,
\]

where the configuration-space density is

\[
n(R, t) = \int n_i(R, \mathbf{v}_i, t) \, d\mathbf{v}_i.
\]

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

\[
\frac{\partial \langle P_i \rangle}{\partial t} - n \frac{\partial \langle P_i \rangle}{\partial R} + \nabla_R \cdot \left[ n \langle P_i \mathbf{v}_i \rangle \right] - n \langle \mathbf{v}_i \cdot \nabla_R P_i \rangle - n \langle \frac{eE}{m} \cdot \nabla_{\mathbf{v}_i} P_i \rangle = \int_{\mathbf{v}_i} P_i(R, \mathbf{v}_i, t) \left( \frac{\partial n_i}{\partial t} \right)_{\mathbf{v}_i} d\mathbf{v}_i - \int_{\mathbf{v}_i} P_i(R, \mathbf{v}_i, t) \left( \frac{\partial n_i}{\partial t} \right)_{\mathbf{v}_i} d\mathbf{v}_i.
\]

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

\[
\int_{\mathbf{v}_i} \int_{\mathbf{v}_o} \int_{\Omega} P_i n_i N_0 \left[ g_i \sigma(g_i, \psi) \right] d\Omega d\mathbf{v}_i d\mathbf{v}_o = \int_{\mathbf{v}_i} \int_{\mathbf{v}_o} \int_{\Omega} P_i n_i N_0 \left[ g_i \sigma(g_i, \psi) \right] d\Omega d\mathbf{v}_i d\mathbf{v}_o,
\]

since the collision is elastic \( (g_i = g_o) \), and since \( d\mathbf{v}_i d\mathbf{v}_o = d\mathbf{v}_o d\mathbf{v}_i \), so that, with the aid of (2.4),

\[
\int_{\mathbf{v}_i} \int_{\mathbf{v}_o} \int_{\Omega} \left[ P_i(R, \mathbf{v}_i, t) - P_i((R, \mathbf{v}_i, t) \right] n_i N_0 \left[ g \sigma(g, \psi) \right] d\Omega d\mathbf{v}_i d\mathbf{v}_o.
\]

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

\[
\frac{\partial n(R, t)}{\partial t} + \nabla_R \cdot n(R, \mathbf{v}_i) \langle \mathbf{v}_i \rangle = -\int_{\mathbf{v}_i} \langle \frac{\partial n_i}{\partial t} \rangle_{\mathbf{v}_i} d\mathbf{v}_i,
\]

the equation of continuity in the presence of the sink \( S \). When \( P_i \) is taken as the vector \( m \mathbf{v}_i \), since

\[
m(\mathbf{v}_i - \mathbf{v}_o) = \mu (g_i - g_o),
\]

where \( \mu \) is the ion–neutral reduced mass, we can show, after some analysis, that

\[
\int_{\mathbf{v}_i} m \mathbf{v}_i \left( \frac{\partial n_i}{\partial t} \right)_{\mathbf{v}_i} d\mathbf{v}_i = -\mu \int_{\mathbf{v}_i} R_D(g_i) n_i(R, \mathbf{v}_i, t) N_0(R, \mathbf{v}_o, t) d\mathbf{v}_i d\mathbf{v}_o,
\]

where

\[
R_D(g_i) = \int g_i (1 - \cos \psi) \sigma(g, \psi) d\Omega
\]
is the momentum-transfer rate \((\text{cm}^3\text{s}^{-1})\) which, for an ion–neutral pure polarization attraction, is independent of \(g_i\), the relative speed \(|(v_i - v_0)|\). Since the gas is, on average, considered at rest (with respect to the centre of mass of the ion pair), \(\langle v_0 \rangle\) is zero such that

\[
\int_{v_i} v_i \left( \frac{\partial n_i}{\partial t} \right) dv_i = -n(R, t) \langle v_i \rangle \left[ \frac{\mu}{m} R D R, t \right] = -n(R, t) \langle v_i \rangle v, \tag{2.33}
\]

where the configuration-space density of neutrals is

\[
N(R, t) = \int n_0'(R, v_0, t) dv_0, \tag{2.34}
\]

and the term in square brackets, the frequency \(\nu\) 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

\[
n(R, t) \langle v_i \rangle v = N \sum_{i} C v_i \sum_{r} C [n(R, E_i, t) k_{tt}(R) - n_i(R, E_i, t) k_{tt}]. \tag{2.35}
\]

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

\[
\frac{\partial (n(R, t) \langle v_i \rangle)}{\partial t} + \nabla R [n(R, t) \langle v_i v_i \rangle] - \frac{eE}{m} n(R, t) = -n(R, t) \langle v_i \rangle v + \int_{v_i} v_i \left( \frac{\partial n_i}{\partial t} \right) dv_i, \tag{2.36}
\]

where the \(jk\)-element of the direct product \(\langle v_i v_i \rangle\) tensor is \(v_i^{(0)} v_i^{(k)}\), the product of cartesian components \([v_i^{(j)}, j = x, y, z]\) of the velocity \(v_i\).

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 \(n \langle v_i \rangle v\); (b) the characteristic time for substantial variation of \(n(R, t) \langle v_i \rangle\) is much longer than the mean time \(\nu^{-1}\) 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 \(D \cdot \nabla R n(R, t)\) both in equilibrium (Maxwellian) and in non-equilibrium situations, where the diffusion (symmetric) tensor is

\[
D = \langle v_i v_i \rangle / \nu \quad (\text{cm}^2\text{s}^{-1}) \tag{2.37}
\]

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 \(KE n(R, t)\) where the mobility is

\[
K = e/mv \quad (\text{cm}^2\text{StatV}^{-1}\text{s}^{-1}). \tag{2.38}
\]

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

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

\[
J(R, t) = n(R, t) \langle v_i \rangle = -D \cdot \nabla R n(R, t) + KE n(R, t), \tag{2.39}
\]
which together with the equation of continuity (2.30) implies
\[
\frac{\partial n(R, t)}{\partial t} + \nabla_R \cdot [-D \cdot \nabla_R n(R, t) + KE n(R, t)] = \int_{\mathcal{S}_1} \left[ \frac{\partial n_i(R, \vec{v}_n, t)}{\partial t} \right] d\vec{v}_n,
\]
\[
eq - \frac{C}{i=-V(R)} \left[ \frac{\partial n_i(R, \vec{v}, t)}{\partial t} \right]_{\mathcal{S}_s}, \tag{2.40}
\]
in which the summation or integration over all states \(i\) between \(-V(R)\) and \(C\) is equivalent to the \(\vec{v}_i\)-integration for spherical \(R\)-symmetry. On introduction of the null collision quantity,
\[
\frac{C}{i=-A} \left\{ N_i^*(R, E_i, t) \sum_{k=N_1}^N k_{N_1}(R) - \sum_{i=-V}^N N_i^*(R, E_i, t) k_{N_1}(R) \right\} = 0, \tag{2.41}
\]
where \(-A\) is an arbitrary bound level, the sink term in (2.40) and given by (2.11) may be written as
\[
\sum_{i=-V(R)}^C \left[ \frac{\partial n_i(R, \vec{v}, t)}{\partial t} \right]_{\mathcal{S}_s} = N \left\{ \sum_{i=-V(R)}^C N_i^*(R, E_i, t) \sum_{k=N_1}^N k_{N_1}(R) - \sum_{i=-V, k=-M}^N N_i^*(R, E_i, t) k_{N_1}(R) \right\} (4\pi R^2 N^+)^{-1}. \tag{2.42}
\]

On integration of (2.40) over \(R\) and with the aid of Gauss's theorem, of spherical symmetry and of (2.2), we have, on replacing \(E\) by \(- (\nabla V)/\epsilon\), the appropriate flux equation
\[
\frac{\partial}{\partial t} \int_0^R N^*(R, t) dR - 4\pi R^2 \left[ D \frac{\partial n(R, t)}{\partial R} + n(R, t) \frac{\partial V}{\partial R} \right] N^+ = - \alpha_n(R) n(R, t) N^+, \tag{2.43}
\]
in terms of the net depletion (recombination) rate \((\text{cm}^{-3} \text{s}^{-1})\)
\[
\alpha_n(R) n(R, t) N^+ = N \int_0^R dR \left\{ \sum_{i=-V}^C N_i^*(R, E_i, t) \sum_{k=N_1}^N k_{N_1}(R) - \sum_{i=-M}^N N_i^*(R, E_i, t) k_{N_1}(R) \right\}, \tag{2.44}
\]
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 \(-E\); II, from \(-E\) to \(-M\); and III, from \(-M\) to \(-V\). 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
\[
\hat{\mathcal{J}_1} = D \nabla + (K/\epsilon) \nabla V \equiv D \exp (-V/kT) \nabla \exp (V/kT), \tag{2.45}
\]
such that the inward current \(j\) \((\text{cm}^{-2} \text{s}^{-1})\) is \(\hat{\mathcal{J}_1} n(R, t)\), and the flux operator \(\mathcal{D}\) which is such that the flux across the spheres each of radius \(R\) and surface area \(\mathcal{S}\) is
\[
\mathcal{D} [4\pi R^2 N^+ n(R, t)] = - N \int_{\mathcal{S}_1} \hat{\mathcal{J}_1} \cdot d\mathcal{S} \equiv 4\pi R^2 N^+ j(R, t). \tag{2.46}
\]
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
\[
- \frac{\partial}{\partial t} \int_0^R N_i^*(R, t) dR + \mathcal{D} N_i^*(R, t) = N \int_0^R dR \sum_{i=-E}^C \left( N_i^* \sum_{k=N_1}^N k_{N_1} - \sum_{i=-M}^N N_i^* k_{N_1} \right), \tag{2.47a}
\]
on making use of the null collision relation (2.41) with \(-A\) taken as \(-E\), and where explicit dependences in the right-hand side are omitted. The right-hand side of (2.47a) is constant for \(R \geq R_E\), the outermost turning point associated with \(-E\), i.e. \(V(R_E) = -E\). For region II,
\[
- \frac{\partial}{\partial t} \int_0^R N_{i1}^*(R, t) dR + \mathcal{D} N_{i1}^*(R, t) = N \int_0^R dR \sum_{i=-M}^C \left( N_i^* \sum_{k=N_1}^N k_{N_1} - \sum_{i=-M}^N N_i^* k_{N_1} \right), \tag{2.47b}
\]
while for region III,

\[ \frac{\partial}{\partial t} \left[ \int_0^R N^*_\text{III}(R,t) \, dR \right] + \partial N^*_\text{III}(R,t) = - N \int_0^R dR \sum_{t=-M}^{C} \sum_{i=-V}^{E} N^*_i k_\text{II}. \]  

(2.47c)

For all three regions the number densities \( N^*_r(R,E_i,t) \) 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 \( R(E_i) \) 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

\[ N^*_r(R,E_i,t) \sum_{t=-V}^{C} k_\text{II}(R) \approx \sum_{t=-M}^{C} N^*_i(R,E_i,t) k_\text{II}(R); \quad -E \geq E_i \geq E_M, \]  

(2.48)

as for quasi-equilibrium at each \( R \). Thus the right-hand side of (2.47b) 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 \(-E_M\) have recombined and are irretrievably lost to the recombination in progress, \( N^*_r(R,,E_M \to E_-) \) vanishes, so that (2.48) implies, in the above approximation, that

\[ \sum_{t=-M}^{C} N^*_i(R,E_i,t) k_\text{II}(R) \approx 0, \quad E_M \geq E_i \geq E_V, \]  

(2.49)

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

\[ \frac{\partial}{\partial t} \int_0^R N^*(R,t) \, dR = \int_0^R dR \sum_{i=-E}^{C} \sum_{t=-V}^{E} \left( N^*_i k_\text{II} - \sum_{t=-M}^{C} N^*_i k_\text{II} \right) \]  

\[ = a_3(R) n(R,t) N^*. \]  

(2.50)

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

\[ F_\infty = -N^+ \int_{\varphi=-\infty}^R J \cdot dS \]  

so that

\[ -d(N^+)/dt + F_\infty = \alpha_3(R_\infty) n(R_\infty) N^+ = \alpha N^+ N^-, \]  

(2.51)

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

\[ \alpha = \alpha_3(R_\infty) n(R_\infty)/N^- \]

\[ = \left( \frac{N^+}{N^+ + N^-} \right) \int_0^{R_\infty} \sum_{i=-E}^{C} \sum_{t=-V}^{E} \left[ N^*_i(R,E_i) \sum_{t=-M}^{C} k_\text{II}(R) - \sum_{t=-M}^{C} N^*_i(R,E_i) k_\text{II}(R) \right], \]  

(2.52)

where the number densities \( N^*_i(R,E_i) \) 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 \( \alpha \).
i s then a general function of $N$. We note that (2.51) equates the steady-state inward flux $\alpha N^-$ or $4\pi R^2 \int n\,dR$ with $\alpha_a(R_E) \pi(R_E)$ 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 $N^+(R, E, t)$, and the appropriate equation (2.50) or equivalent expression (2.52) for the recombination coefficient $\alpha$ 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, $N^+ F_e(R)$, 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

$$N^+ F_e(R_E) = AN^+ \int_0^{R_E} 4\pi R^2 n^-(R) \,dR + 4\pi R^2 N^+ D \exp\left(-V/kT\right) \frac{\partial}{\partial R} \left[n^-(R, t) \exp\left(V/kT\right)\right]$$

$$= \alpha_a(R) n^-(R) N^+ = \alpha N^+ N^-, \quad R \geq R_E. \quad (2.53)$$

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

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

since $A \sim \alpha N^-$, such that

$$N^- \ll (\frac{3}{2} \pi R_E^2)^{-1}, \quad (2.54b)$$

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, $N^\pm \ll 10^{16} \text{cm}^{-3}$ 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

$$N^- - n^-(R) \exp\left(V/kT_{\text{eff}}\right) = \left[F_e(R_E)/\alpha_h\right] P(R), \quad R \geq R_E, \quad (2.55)$$

where $\alpha_h = 4\pi DR_e$, the high density Langevin limit (1.2);

$$P(R) = R_e \int_0^\infty \exp\left(V/kT_{\text{eff}}\right) \,dR/R^2, \quad (2.56)$$

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

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

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 $T_{\text{eff}}$ 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:

$$n^-(R) = N^- \exp\left(-V/kT\right) \left[1 - \frac{\alpha}{\alpha_h} P(R)\right] = \frac{N^- \exp\left(-V(R)/kT\right) \left[\alpha_h/P(R)\right]}{\alpha_a(R) \exp\left(-V(R)/kT\right) + \alpha_h/P(R)}, \quad R \geq R_E, \quad (2.58a)$$
in which $T_{eff}$ is denoted here by $T$ for brevity;

$$n^{-}(R) = N^{-} \exp \left( -V/kT \right) \exp \left[ -\frac{R_{E}}{\alpha_{n}} \int_{R}^{\infty} \alpha_{3}(R) R^{-2} dR \right]. \quad (2.58b)$$

Hence the overall recombination coefficient $\alpha$ from (2.53) is

$$\alpha = \frac{\alpha_{3}(R_{E}) n^{-}(R_{E}) / N^{-}}{\alpha_{3}(R_{E}) \exp \left[ -V(R_{E}) / kT \right]} = \text{const.} \quad (2.59)$$

in terms of $\alpha_{n}$ which is known, and of $\alpha_{3}(R_{E})$ which is yet to be determined. Since $\alpha_{3}$ is internally dependent on the phase densities, $N^{*}_{i}(R, E)$, through (2.44), we note that $\alpha$, 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 $t \gg R_{E}/D$ for high $N$ (see § 2.5), and are independent of condition (2.54). Since $\alpha_{n} \sim N^{-1}$, from (2.58), at low gas densities $N$,

$$n^{-}(R) \approx N^{-} \exp \left( -V(R) / kT \right), \quad R \geq R_{E}, \quad (2.60)$$

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

$$\alpha_{10} = \frac{\alpha_{3}(R_{E}) \exp \left[ -V(R_{E}) / kT \right]}{\alpha_{3}(R_{E}) \exp \left[ -V(R_{E}) / kT \right]} = \alpha_{10}(R_{E}), \quad (2.61)$$

which is from (2.53) the recombination coefficient that would pertain provided the Boltzmann ion-distribution were maintained (as at low $N$), i.e. $\alpha_{10}$ in the absence of net ionic transport (as in a Boltzmann distribution) measures the rate of reaction within $R_{E}$. Thus, (2.59) reads,

$$\alpha = \frac{\alpha_{10} \alpha_{tr}}{\alpha_{10} + \alpha_{tr}}, \quad (2.62)$$

where the recombination coefficient $\alpha_{hi}$ at high gas densities is,

$$\alpha_{hi} = 4\pi D \int_{R_{E}}^{\infty} \exp \left( KV / De \right) R^{-2} dR = \left[ \frac{\alpha_{n}}{P(R_{E})} \right] = \alpha_{tr} \quad (2.63)$$

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

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

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 \textit{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 $10^{8}$ cm$^{-3}$ to about $10^{14}$ cm$^{-3}$. Use of an interaction, self-consistent with the ionic distribution and recombination sink, is the correct procedure (see § 4).
THEORY OF ION-ION RECOMBINATION

We note that $\alpha_3$ and hence $\alpha_{10}$ 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 $\alpha_{11}$, and of the rate of ion-ion reaction (by effective three-body collisions), as measured by $\alpha_{rn}$. 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 $\alpha_{rn}$ of reaction can be deduced without explicit knowledge of the phase densities $N^+(R, E_i)$, 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

$$\frac{\partial n^-(R, t)}{\partial t} + \nabla \cdot J = - \sum_{i=1}^{C} \frac{\partial n_i(R, E_i, t)}{\partial t} \bigg|_{s},$$

(2.65)

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

$$J = - D \left[ \nabla n^-(R, t) + n^-(R, t) \nabla (V/kT) \right] \equiv - D \exp (- V/kT) \frac{d[n^-(V/kT)]/dR}{\hat{R}},$$

(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,

$$\alpha_s(R, t) n^-(R, t) \big|_{n^-(R, t) = 0},$$

(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 $n_i(R, E_i, t)$ 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 $R \leq S$. Also, the physical meaning of $P$ in (2.63) becomes apparent. Thus (2.65) is equivalent, with $J = -J$, to,

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

(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

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

(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 $S$, at as high $N$,

$$n^-(R, t) = 0, \quad R \leq S,$$

$$n^-(R, t) = N^-, \quad R \rightarrow \infty,$$

(2.70)

such that (2.68) yields,

$$\alpha_{tr} = \alpha_{nl} = F/N^- = 4\pi D \int_0^\infty \exp (V/kT) dR/R^2,$$

(2.71)
the transport rate, which at high $N$ is equivalent to the recombination rate. This reduces to
\[ \alpha_d = 4\pi DS \] (2.72)
when the interaction $V$ between the ions is neglected, and to
\[ \alpha_{hi} = 4\pi DR_e/[1 - \exp(-R_e/S)], \] (2.73)
for pure coulomb attraction
\[ V/kT = -Z_1Z_2e^2/RkT \equiv -(R_e/R) \] (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 $\epsilon$, 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 $n_i(R, E_1, t)$. However, with this knowledge of $n_i$, the steady-state $\alpha$ 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 $\alpha$ for the homogeneous case where the process is driven by the boundary condition (2.70) for $n(R \to \infty)$ and the probability $\mathcal{P}(R_0, R_K)$ for the diffusional-drift contraction of ions generated at $R_0$. Between $R_0$ and an instantaneous sink at $R_K < R_0$, (2.69) then yields
\[ n^{-}(R) \exp (V/kT) = (F_c/4\pi D) [P(R_K) - P(R)], \quad R_K \leq R \leq R_0, \] (2.75)
where $F_c$ is the net inward flux at $R$. In the presence of a sink at infinity,
\[ n^{-}(R) \exp (V/kT) = (F_c/4\pi D) P(R), \quad R_0 \leq R \leq \infty, \] (2.76)
where $F_c$ is the net outward flux at $R$. The probability that an isolated $R_0$-ion pair contracts by diffusional-drift is
\[ \mathcal{P}(R_0, R_K) = F_c(R_0)/[F_c(R_0) + F_c(R_0)], \] (2.77a)
where the subscript (s) denotes that this \( \mathcal{P} \) 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

\[
\mathcal{P}_{(s)}(R_0, R_E) = \frac{F_e(R_0)}{[F_e(R_0) + F_e(R_0)]} = 1 - P(R_0) \cdot P(R_E).
\]

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

\[
n^-(R) = N^{-} \exp\left(-\frac{V}{kT}\right)[1 - (\alpha/\alpha_{tr}) \mathcal{P}_{(s)}(R, R_E)] 
\]

\[
\mathcal{P}_{(s)}(R, R_E) \xrightarrow{N \to \infty} N^{-} \exp\left(-\frac{V}{kT}\right) \mathcal{P}_{(s)}(R, R_E),
\]

where \( \mathcal{P}_{(s)} \) 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

\[
\alpha_{tr} = 4\pi R_i D \exp\left(-\frac{V}{kT}\right) \mathcal{P}_{(s)}(R, R_E) / \alpha R = \alpha_B / P(R_E),
\]

where \( \alpha_B \) is the Langevin rate \( 4\pi DR_e \) and \( \mathcal{P}_{(s)} \) 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

\[
\mathcal{P}_{(s)}(R) \sim \exp\left(-\frac{V}{kT}\right),
\]

and

\[
\mathcal{P}_{(s)}(R) \sim 1 - \exp\left(-\frac{V}{kT}\right)
\]

in agreement with Onsager (1938), and \( n^-(R) \approx N^{-} \exp\left(-\frac{V}{kT}\right) \exp\left(-\frac{R_e}{R}\right) \).

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

\[
j(R, t) = \Gamma_a n^-(R, t), \quad R = S,
\]

where \( \Gamma_a(R) \) 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 \( \Gamma_a \) 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 \( \Gamma_a(S) \) 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

\[
F = 4\pi R^2 j = (4\pi R^2 \Gamma_a) n^-(R, t) = \alpha(t) N^{-},
\]

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

\[
\alpha_{tr} = (4\pi R^2 \Gamma_a) \exp\left(-\frac{V}{kT}\right) \equiv \alpha_3(R) \exp\left(-\frac{V}{kT}\right),
\]

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 \( \alpha \) and \( \Gamma \).

Hence, (2.82) is simply

\[
\alpha_3(S) n^-(S, t) = 4\pi S^2 j(S, t) = \alpha N^{-},
\]

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

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

which yields the following steady-state recombination coefficient:

\[
\alpha(t \to \infty) = \frac{\alpha_0(S) \exp\left(-V(S)/kT\right) \alpha_{tr}}{\alpha_0(S) \exp\left(-V(S)/kT\right) + \alpha_{tr}} = \frac{\alpha_{rn} \alpha_{tr}}{\alpha_{rn} + \alpha_{tr}} \tag{2.87a}
\]
in agreement with the results (2.64) and (2.58) of the previous subsection.

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

\[
\nu - (R,t) = N^{-} \exp\left(-V/kT\right) P(R) \tag{2.77c}
\]

so that

\[
n^-(R) = N^{-} \exp\left(-V/kT\right) \mathcal{P}^<(R,R_E) \tag{2.79b}
\]

and

\[
\alpha = 4\pi R^2 D \exp\left(-V/kT\right) \left[\frac{\partial \mathcal{P}^<}{\partial R}\right]_{R=E} \tag{2.80b}
\]

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

\[
\mathcal{P}^<(R,R_E) = \frac{\alpha P(R)}{\alpha_{tr} P(R_E)} \equiv 1 - \mathcal{P}^<(R,R_E), \tag{2.77d}
\]

where the probability of recombination

\[
\mathcal{P}_r = \frac{\alpha_{rn}}{\alpha_{rn} + \alpha_{tr}} = \mathcal{P}^<(R,E,R) \left\{\begin{array}{ll}
\frac{\alpha_{rn}}{\alpha_{tr}}, & \alpha_{rn} \ll \alpha_{tr}, \\
1, & \alpha_{rn} \gg \alpha_{tr},
\end{array}\right. \tag{2.77d}
\]
is simply the contraction probability for ion pairs generated with internal separations equal to the sink radius, i.e. \(\mathcal{P}_r \ll 1\) 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

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

which uniquely identifies the strength of the sink as the speed of three-body recombination; for \(\Gamma_3\) large compared with the rate of ionic transport, the reactivity of the sink is effectively instantaneous, and \(\alpha\) is given then by (2.73); while (2.87) pertains when \(\Gamma_3\) is comparable with the ion transport rate. No deactivating reaction implies zero \(\Gamma_3\), and hence zero rate of recombination.
The number density $N_i$ of all ion pairs $AB$ with internal separation $R > S$ then decays at a rate

$$\frac{dN_i}{dt} = -\sum_b \frac{d}{dS} \int_N^{\infty} 4\pi R^2 N^+ n^- (R, t) dR = \left[ 4\pi S^2 \Gamma_1 n^- (S, t) - \left( F_x - 4\pi S^2 j (S - \varepsilon, t) \right) \right] N_i$$

$$= \alpha(t) N_i (N_+ N_- - F_x N_i), \quad (2.88b)$$

where $F_x$ is the rate ($s^{-1}$) of generation of negative ions at infinity, and $\alpha$ is the time-dependent rate ($cm^3 s^{-1}$) of recombination appropriate to asymptotic ion densities $N_\pm$. If the ion current approaching $S$ is absorbed by reaction within $S$, then $\lim_{s \to 0} j(S - \varepsilon, t) \to 0$. In steady state, the rate $4\pi R^2 j(R, t)$ from (2.88a) is constant for $R > S + \varepsilon$ and equals both the production and absorption rates $F_x$ and $4\pi S^2 \Gamma_1 n^-$, respectively, in (2.88b).

In conclusion, this subsection has emphasized the decomposition of the recombination rate $\alpha$ into its reaction and transport components, $\alpha_{re}$ and $\alpha_{tr}$, respectively, which act in series so that $\alpha = \alpha_{re} \alpha_{tr}$ in terms of the recombination probability $\alpha_r$ of (2.77d), and is determined by the rate limiting step $\alpha_{re}$ or $\alpha_{tr}$ in the limit of low $N$ and high $N$ respectively. Also the relation has been developed between $\alpha_r$ and $\alpha_{re}$ for the homogeneous case with the escape probability $\alpha$ 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 $\alpha_r$ is simply the probability $\alpha_{re}$ for contraction of those geminate $R_+$ 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. $R_e (R, \lambda_e)^\dagger$ 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 ($\alpha_r \to 1$ or $I \to \infty$). 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 $R^{-1}$-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
approximate yet accurate analytical time-dependent solution, and associated recombination rates, of the equation

\[
\frac{\partial n(R,t)}{\partial t} = \frac{1}{R^2} \frac{\partial}{\partial R} \left[ R^2 j \right]
\]  

(2.89a)

with a general diffusional-drift current

\[
j(R,t) = D \exp \left( -\frac{V}{kT} \right) \partial [n(R,t) \exp \left( \frac{V}{kT} \right) / \partial R.
\]  

(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

\[ n(R \rightarrow \infty, t) = N - \exp \left( -\frac{V}{kT} \right), \]  

(2.90)

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

\[ n(R,t) = 0, \quad R \leq S, \]  

(2.91a)

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

\[ \Gamma_3 n(S,t) = j(S,t), \]  

(2.91b)

for a partially absorbing sink where \( \Gamma_3 \) is, as before, the speed of (three-body) reaction for ion pairs brought to internal separation S by ion transport such that

\[ \alpha_3 = 4\pi S^2 \Gamma_3. \]  

(2.91c)

The initial \((t = 0)\) distribution

\[ n(R,t = 0) = N - \exp \left( -\frac{V}{kT} \right), \]  

(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

\[ r = \frac{R}{S} - 1, \quad \tau = Dt/S^2, \]  

(2.93)

and let

\[ n'(R,t) = (R/S) n(R,t), \]  

(2.94)

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

\[
\frac{\partial n'(r,\tau)}{\partial \tau} = \frac{\partial^2 n'(r,\tau)}{\partial r^2}.
\]  

(2.95)

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

\[ n_{0d}^d(R,t) = N^- \left[ 1 - \left( \frac{S}{R} \right) \operatorname{erfc} \left[ \left( \frac{R-S}{2(Dt)^{1/2}} \right) \right] \right], \]  

(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)

\[ \operatorname{erfc} \chi = \frac{2}{\sqrt{\pi}} \int_{\chi}^{\infty} \exp \left( -\chi^2 \right) d\chi. \]  

(2.97)

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

\[ \alpha_{0d}^d(t) = 4\pi S^2 j(S,t) / N^- = \alpha_d \left[ 1 + S/(\pi Dt)^{1/2} \right], \]  

(2.98a)

where

\[ \alpha_d = 4\pi SD \]  

(2.98b)
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 \(N_R\) of diffusing species outside \(S\) can be evaluated directly from,

\[
\frac{dN_R}{dt} = N - \frac{d}{dt}\int_S^{\infty} 4\pi SR \text{erfc}\left[\frac{(R-S)/2(Dt)^1}{dR}\right] dR = \alpha_3 N',
\tag{2.99}
\]

where the derived \(\alpha_3^{(0)}\) is identical with (2.98), as expected from (2.89a). Under the condition (2.91 b) for finite \((f)\) reaction and diffusive transport,

\[
n_0^{(f)}(R, t) = N^{-1} \{1 + (\alpha/\alpha_3) (S/R) \{\exp(2\Omega\chi) \exp(\chi^2 \text{erfc}(\chi + \Omega) - \text{erfc} \Omega)\} \},
\tag{2.100}
\]

where the time dependence is contained in

\[
\chi(t) = (1 + \alpha/\alpha_3) (Dt)^{1/2} S \equiv \left(\alpha_3/\alpha\right) (Dt)^{1/2} S,
\tag{2.101}
\]

and in

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

which vanishes at the sink, and

\[
\alpha = \alpha_3 \alpha_4/\left(\alpha_3 + \alpha_4\right)
\tag{2.103}
\]

in terms of (2.91 c) and (2.99). When the rate \(\alpha_3\) of reaction is much larger than the rate \(\alpha_4\) of ion transport, \(\chi \to \infty, \alpha = \alpha_4\), 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

\[
\alpha_3^{(f)}(t) = \alpha_3 n_0^{(f)}(S, t)/N' = \alpha \{1 + (\alpha_3/\alpha_4) \exp(\chi^2 \text{erfc} \chi)\},
\tag{2.104}
\]

and \(\alpha\) is therefore the steady-state \((t \to \infty)\) solution (since \(\text{erfc} \to 0\)). The rate (2.104) also follows directly from \(4\pi S^2 D(dn_4/dR)S\) as expected from (2.91 b). At \(t = 0\) the recombination rate \(\alpha_3^{(f)}(0)\) is simply the rate \(\alpha_3\) 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

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

a transformation not without its physical significance. It is related to the probability \(P_{(n)}\) in (2.77 a) that an \(R_o\)-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

\[
\Psi_{(n)}(R_o, S) = \tilde{R}(S)/\tilde{R}(R_o) = S/\tilde{R}_o.
\tag{2.106}
\]

Let

\[
n_{(f)}(R, t) = n(R, t) \exp(V/kT),
\tag{2.107}
\]

such that (2.89) becomes

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

where the transformed diffusion coefficient \((\text{cm}^2\text{s}^{-1})\) is

\[
\tilde{D} = D(dR/dR)^2.
\tag{2.109}
\]
The form of this equation is, in the transformed $\vec{R}$-representation, identical with that for the field-free case in the original $R$-representation. Accordingly, introduce scaled quantities (2.93) and

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

such that (2.108) reduces to

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

(2.111a)

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

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

(2.111b)

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

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

(2.112)

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

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

(2.111c)

the one-dimensional diffusion equation in $r, \tau$-space.

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

$$n^{(0)}(R, t) = N^- \exp \left( -V/kT \right) \left\{ 1 - \frac{S}{R} \operatorname{erfc} \left( \frac{(R-S) dR}{2(Dt) \frac{1}{2} dR} \right) \right\}$$

(2.113)

The recombination rate then reduces to

$$\alpha^{(0)}(t) = 4\pi S^2 j(S, t) / N^- = \alpha_{\text{tr}} \left\{ 1 + \frac{S^2 \exp \left( -V(S)/kT \right)}{S(p) \frac{1}{4} \exp \left( -V(S)/kT \right)} \right\}$$

(2.114)

where the steady-state transport rate

$$\alpha_{\text{tr}} = 4\pi S D = 4\pi DR_e P(S) = \alpha_{\text{hi}}$$

(2.115)

with

$$P(S) = R_e / S = R_e \int_S^\infty \exp \left( V/kT \right) \frac{dR}{R^2}$$

(2.116)

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

$$\alpha_{\text{hi}}^{(0)} = 4\pi Ke \left[ 1 - \exp \left( -R_e / S \right) \right]$$

(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 $(dR/d\tau)$ is assumed in (2.111b), $(R-S)(dR/d\tau)$ can be replaced by $R - S$ which yields a result also obtained via (2.111c).

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

$$\Gamma_3(S) n^-(S, t) = D \exp \left( -V(S)/kT \right) \left\{ \delta(n(R, t) \exp \left( -V/kT \right) / \partial R \right\}$$

(2.118)
The theory of ion-ion recombination, which for (2.111b) and (2.111c) transforms as

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

and

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

respectively, where

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

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 (2.111b) subject to boundary conditions (2.90) and (2.119a), and to the Boltzmann initial condition (2.92):

\[
n(R, t) = N - \int_0^\infty \exp \left( -\frac{V}{kT} \right) \left[ 1 + \left( \frac{\alpha}{\alpha_{tr}} \right) \left( \frac{S}{\tilde{R}} \right) \exp \left( \frac{2\tilde{\Gamma} \chi}{\tilde{\Omega}} \right) \exp \left( \frac{\chi^2}{\tilde{\Omega}} \right) - \text{erfc} \left( \frac{\chi}{\tilde{\Omega}} \right) \right] \, d\tilde{R} \tag{2.121a}
\]

where

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

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

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

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

\[
\alpha(t) = \alpha_3 \n(S, t) / N = \alpha \left[ 1 + \left( \frac{\alpha_{rn}}{\alpha_{tr}} \right) \exp \left( \frac{\chi^2}{\tilde{\Omega}} \right) \text{erfc} \left( \frac{\chi}{\tilde{\Omega}} \right) \right], \tag{2.122a}
\]

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

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

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 \( (d\tilde{r}/d\tilde{r}) \) can be assumed constant in (2.111a).

As \( t \) increases from zero,

\[
\exp \chi^2 \text{erfc} \chi \to 1 - \frac{2}{\sqrt{\pi}} \chi + \chi^2 - \frac{4}{3\sqrt{\pi}} \chi^3 + \ldots \tag{2.123}
\]

such that

\[
\alpha(t \to 0) = \alpha_{rn} \left[ 1 - \frac{2}{\sqrt{\pi}} \frac{\alpha_{rn} (\tilde{D}t)^{\frac{1}{2}}}{S} \exp \left[ \frac{V(S)/kT}{S} \right] \right] \tag{2.124}
\]

decreases initially from the reaction rate \( \alpha_{rn} \). As \( t \to \infty \),

\[
\exp \chi^2 \text{erfc} \chi \to \left( 1 / \chi \sqrt{\pi} \right) \left( 1 + 1/2 \chi^2 + 3/4 \chi^4 + \ldots \right) \tag{2.125}
\]

such that the long-time dependence is

\[
\alpha(t \to \infty) = \alpha \left[ 1 + \frac{\alpha}{\alpha_{tr}} \frac{S \exp \left[ -V(S)/kT \right]}{\left( \pi D \right)^{\frac{1}{2}}} \right] \int_S^\infty \exp \left( V/kT \right) R^{-2} dR \right], \tag{2.126}
\]
The transient rates (2.124) and (2.126) for short and long intervals of time are best observed at high gas densities when $\alpha_{rn} \gg \alpha_{tr} \approx \alpha$ 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.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Explicit time dependence of recombination rate $\alpha(t)$ at various gas densities $N$ (in multiples of the Loschmidt number $N_L = 2.69 \times 10^{18} \text{ cm}^{-3}$ at s.t.p.). Characteristic times $(S^2/D)$ for diffusion are $(16, 11, 8, 5, 3) \times 10^{-12} \text{ s}$ for $N/N_L = 1, 2, 3, 5, 10$ respectively.}
\end{figure}

The full time dependence in (2.122a) for $\alpha$ is contained in (2.122b) for $\chi_S$ which, for a pure coulomb attraction, varies as

$$\chi_S(\tau) = (1 + \alpha_{rn}/\alpha_{tr}) \tau R_c/S \exp (R_c/S - 1)/1,$$  \hspace{1cm} (2.127)

where the scaled time is

$$\tau = t/(S^2/D)$$ \hspace{1cm} (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, (4.12a), and associated quantities, derived in § 4.2 for the reaction rate $\alpha_{rn}$, and the exact expression (2.63) or (2.71) for the transport rate, the full time dependence of the recombination rate (2.122a) 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 $N_L = 2.69 \times 10^{18} \text{ cm}^{-3}$, the number density at s.t.p.). These rates are appropriate to a fictitious (but representative) case of equal masses ($M = 16 \text{ a.m.u.}$) of the ionic species with mobility $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in an equal-mass gas and with $\delta_i$ 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
recombination \( \alpha(t = 0) \) is simply the reaction rate \( \alpha_{rn} \), 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 \( \alpha_{rn} \gg \alpha_{tr} \) such that \( \alpha \) decreases from \( \alpha_{rn} \) to \( \alpha_{tr} \), the steady-state limit at \( t \gg S^2/D \). Variation of \( \alpha \) with \( t \) for \( N \approx 10N_e \), for example, reflects the change in \( \alpha \) from reaction controlled transport. The reaction rate at high \( N(\gtrsim 5N_e) \) 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 \( N \approx N_e \) 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 \( \alpha \) with \( t \) at high \( N(\gtrsim N_e) \) 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 \( t \ll S^2/D \). 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 \( 1.6 \times 10^{-11} \text{s} \) at a gas pressure of about 1 atm to \( 3 \times 10^{-12} \text{s} \) 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 (1980c) 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 (2.91b) for a finite rate \( \alpha_{rn} \) of reaction and the possibility of a scavenger reaction proceeding in parallel at a rate \( \gamma n \), by

\[
-\frac{\partial n}{\partial t} + \nabla \cdot j - \gamma n = \Gamma_0 n \delta(R - S). \tag{2.129}
\]

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 \( \alpha \) given by (2.121a) and (2.122a), 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

\[
\begin{align*}
\left. n(R, t = 0) = \mathcal{N} \exp\left(-V/kT\right)\delta(R - R_0)/4\pi R_0^2 \right| \\
j(S, t) = \Gamma_0 n(S, t), \\
n(R \to \infty, t) = 0.
\end{align*}
\tag{2.130}
\]

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 \( \alpha \) given by (2.121a) and (2.122a), respectively.
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 \(\chi\) and \(\Omega\) associated with a continuous source at infinity as

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

where \(\Omega_0 = (R - R_0)/2(4Dt)^{\frac{1}{2}}\), \(\Omega_1 = (R + R_0 - 2S)/2(4Dt)^{\frac{1}{2}}\) are similar to (2.102), and \(\chi(t) = (1 + \alpha_3/\alpha_d) (4Dt)^{\frac{1}{2}}/S\) as before (equation (2.101)) in terms of (2.91c) 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 \(\mathcal{V}\) so that the frequency \((s^{-1})\) of recombination is then

\[
\nu_r(t) = -\int_R \frac{dR}{\nu_r(t)} = 4\pi S^2 \mathcal{N}_3 n(S, t; R_0 = S) = \left\{ \begin{array}{ll}
\mathcal{N}_3 \nu_r S^2 \mathcal{N}_3 - \chi(t) \text{erfc} \chi(t), & t \to 0, \\
\mathcal{N}_3 \nu_r, & t \to \infty,
\end{array} \right.
\]

where the probability of recombination in the absence of the field \(V\) is

\[
\mathcal{P}_r(V \to 0) = \alpha_0/(\alpha_d + \alpha_0)\]

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 (2.111c) to yield.

\[
n(R, t; R_0, S) = \frac{N}{4\pi R_0^2} \left( \frac{R_0}{R} \right) (4Dt)^{-\frac{1}{2}} \left\{ \frac{1}{\sqrt{\pi}} \left[ \exp \left( -\Omega_0^2 \right) + \exp \left( -\Omega_1^2 \right) \right] - 2\chi_\mathcal{S} \exp \chi_\mathcal{S} \exp \left( -V(S)/kT \right) \right\},
\]

in terms of the corresponding tilde quantities (2.105) and (2.112b). For a coincident source and sink, the recombination frequency is

\[
\nu_r(t) = \left\{ \begin{array}{ll}
\mathcal{N}_3 \nu_r S^2 \mathcal{N}_3 - \chi_\mathcal{S}(t) \text{erfc} \chi_\mathcal{S}(t), & t \to 0, \\
\mathcal{N}_3 \nu_r, & t \to \infty,
\end{array} \right.
\]

where \(\chi_\mathcal{S}\) is given by (2.122b). The number of recombined pairs after time \(t\) is

\[
\mathcal{M}_r(t) = \mathcal{P}_r \mathcal{N}_r (1 - \exp \chi_\mathcal{S} \text{erfc} \chi_\mathcal{S}),
\]

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

\[
\mathcal{P}_r = \alpha_{rn}/(\alpha_{tr} + \alpha_{rn}),
\]

as before (equation (2.77d)). Thus \(\mathcal{P}_r\) is controlled by the relative rates of reaction and transport. At low \(N\), \(\mathcal{P}_r \to \alpha_{rn}/\alpha_{tr}\) while at high \(N\), \(\mathcal{P}_r \to 1\). Expressions (2.121a), (2.122a), (2.137) and
(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 \textit{ab-initio} to be pure coulomb. The interaction \( V \) must then be determined by self-consistent (with the recombination) methods as developed in \S\ 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:

\[
\frac{\partial \rho(R, t)}{\partial t} = \nabla \cdot \mathbf{j}_R \rho - \Gamma_3 \rho \delta(R - S) - \alpha(t) \langle \rho(t) \rangle_R \rho(R, t), R \geq S, \tag{2.141}
\]

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

\[
\langle \rho(t) \rangle_R = \int_R^\infty \rho(R, t) dR = \int_S^\infty 4\pi R^2 \rho(R, t) dR, \tag{2.142}
\]

and the inward diffusional-drift operator \( \mathbf{j}_R \) 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

\[
\frac{\partial C(t)}{\partial t} = - \alpha \langle g(t) \rangle_R C^2(t), \tag{2.144}
\]

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

\[
\frac{\partial g}{\partial t} = \nabla \cdot \mathbf{j}_R g - \Gamma_3 g \delta(R - S) \tag{2.145}
\]

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

Thus

\[
C(t) = C_0 \left[ \frac{1 + C_0 \int_0^t \alpha(t) \langle g(t) \rangle_R dt}{1 + C_0 \int_0^t \alpha(t) \langle g(t) \rangle_R dt} \right], \tag{2.146}
\]

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

\[
\alpha(t) = \frac{1}{\tau} \left[ \int_S^\infty 4\pi R^2 \rho(R, t) dR \right] / N^+ N^- \tag{2.147}
\]

therefore satisfies

\[
\alpha(t) \left\{ 1 - \langle g(t) \rangle_R \frac{\langle C(t) \rangle_R / N^+ N^-} \right\} = \alpha_0(t) C(t) / N^+ \tag{2.148}
\]

where \( \alpha_0 \) 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

\[
C_0 \int_0^t \alpha(t) \langle g(t) \rangle_R dt \ll 1, \tag{2.149}
\]

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 \( \alpha_0 \).
Rather than from the complete determination of $\alpha$ via solutions of (2.20) inserted in (2.52), or alternatively in (2.59) via $\alpha_3$ 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 $k_{ii}$; 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

$$N \sum_{i \in E} \left( \sum_{t \in t} k_{tt} - \sum_{t \in t} N^* k_{ii} \right) \approx N^* \nu(R),$$

(3.1)

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

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

(3.2a)

$$= \begin{cases} \frac{4\pi v_d}{\lambda} DR^2 n(R), & R \leq R_E, \\ F_c(R_E), & \text{a constant}, \ R \geq R_E, \end{cases}$$

(3.2b)

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

$$n(R) \exp(V/kT) \exp(-R/\lambda) = n(R_E) \exp(V(R_E)/kT) \exp(-R_E/\lambda)$$

(3.3)

for $R \leq R_E$. For $R \geq R_E$ 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

$$n(R) \{ \exp(V(R)/kT) \exp(R_E - R)/\lambda + [P(R_E)/\alpha_b] \alpha_3(R_E) \} = N^-, \ R \leq R_E,$$

(3.4)

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

$$\alpha = \frac{1}{N^-} \left[ \alpha_3(R_E) n(R_E) \right] = \frac{\{ \alpha_3(R_E) \exp(-V(R_E)/kT) \} \alpha_b/P(R_E)}{\alpha_3(R_E) \exp(-V(R_E)/kT) + \alpha_b/P(R_E)}$$

(3.5)

as before. Since $\alpha_b$ 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,

$$n(R) = N^- \exp(-V(R)/kT) \exp(R - R_E)/\lambda, \ R \leq R_E$$

$$= n_0(R) \exp(R - R_E)/\lambda,$$

(3.6)

Hence (3.2a) yields

$$\alpha_3(R_E) n_0(R_E) = \frac{4\pi}{\lambda} N^- \exp(-R_E/\lambda) \int_0^{R_E} v_d \exp(-V(R)/kT) \exp(R/\lambda) R^2 dR.$$

(3.7)

The speed $v_d \exp(-V/kT)$ 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,

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

(3.8)
which, in the low density limit, reduces to
\[ \alpha_3(R_e) \exp[-V(R_e)/kT] = \frac{4\pi R_e^2 \langle v \rangle}{3} \left[ 1 - \frac{1}{4} \left( \frac{R_e}{\lambda} \right)^2 + \frac{1}{2} \left( \frac{R_e}{\lambda} \right)^4 - \frac{1}{10} \left( \frac{R_e}{\lambda} \right)^6 + \ldots \right], \]
(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 \( \alpha_h \gg \alpha_3 \), so that the actual recombination coefficient is
\[ \alpha \longrightarrow \alpha_3(R_e) \exp[-V(R_e)/kT] = \alpha_{\text{tn}}, \]
the reaction rate.

At high gas densities \( \alpha_3 \gg \alpha_h \) such that the actual recombination coefficient (3.5) approaches the limit,
\[ \alpha \longrightarrow \alpha_h/\rho(R) \equiv \alpha_{\text{tr}} \]
(3.11)
the transport rate. Hence, this procedure has shown again that
\[ \alpha = \alpha_{\text{tn}} \alpha_{\text{tr}}/(\alpha_{\text{tn}} + \alpha_{\text{tr}}) \]
(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
\[ \tilde{n}(R) = n(R) \exp(s/\lambda), \quad \tilde{N}(R) = N(R) \exp(s/\lambda), \]
(3.13)
where \( s \) is the radial length \( R_e - R \) from some radius \( R_e \) within which energy-changing collisions are effective.\(^\dagger\) Hence, (3.26) with \( T_{\text{eff}} \) replaced by \( T \) yields,
\[ \frac{d\tilde{n}(R)}{dR} + \tilde{n}(R) \frac{\partial(V/kT)}{\partial R} = 0, \]
(3.14)
which can be solved to yield,
\[ n(R) = N^{-} \exp(-V/kT) \exp(-s/\lambda) = \sum_{i=-V}^{C} n_i(R, E_i), \quad R \leq R_e, \]
(3.15)
where \( n_i(R, E_i) \) satisfies the system of equations (2.20) that describe microscopic events. When the effect of the sink operating in the \( (-M \rightarrow -V) \) 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 \( n_0(R, E_i) \) in (2.14) for ions in thermodynamic equilibrium. When \( n_0 \) is summed over all \( E_i \) or integrated over all \( v_1 \) 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 \( -E \), 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
\[ \int_0^R dR N_i^*(R, E_i) \sum_{t=-V}^{C} k_{it}(R) = \int_0^R dR \sum_{t=-M(R)}^{C} N_i^*(R, E_i) k_{it}(R), \]
(3.16)
which follows from (2.20). Since the \( E_i \) or \( v_1 \)-averaged effect of the left-hand side of (2.20) is measured by \( \partial n(R) \) on the left-hand side of (2.47) and hence, in the approximation (3.2a) basic
\(^\dagger\) 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 \( N \).
to this section, by \( \delta \) of (3.13), the small departures of the left-hand side of (2.20) from zero can be reintroduced by replacing \( N^+ \) in (3.16) by the fictitious densities

\[
\tilde{N}^+_i(R, E_i) = N^+_i(R, E_i) \exp \left( \frac{s}{\lambda} \right).
\]

(3.17)

Provided the level \(- E\) 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 \( E_i < - E \) 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 \( \alpha_3 \) associated with negative ion density \( n(R) \) is therefore, in this approximation,

\[
\alpha_3(R, E) = \frac{N}{N^+ N^-} \int_{-\lambda}^{R_E} \exp \left( -\frac{s}{\lambda} \right) dR \sum_{i=-E}^{C} \frac{-E}{t = -S} \tilde{N}^+_i(R, E_i) \sum_{i} \frac{-E}{t = -S} k_{hi}(R) \left( \sum_{i} \frac{-E}{t = -S} N^+_i(R, E_i) k_{ii}(R) \right),
\]

(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 \( N^- \), 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,

\[
\alpha_3(-E) = \frac{N}{N^+ N^-} \sum_{i=-E}^{C} \left[ \frac{-E}{t = -D} \int_{0}^{R_m} N^+_i(R, E_i) k_{ii}(R) dR - \frac{-E}{t = -S} \int_{0}^{R_m} N^+_i(R, E_i) k_{ii}(R) dR \right],
\]

(3.19)

where \(- D\) is the lowest bound level of the system, \(- S\) 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.

\[
N_i(E) \langle k_{hi}(E_i, E_f) \rangle = \int_{0}^{R_m} N^+_i(R, E_i) k_{ii}(R; E_i, E_f) dR,
\]

(3.20)

for \( k_{ii} \) given previously (Flannery 1980, 1981a) we have

\[
\alpha \to \alpha_3(-E) = \frac{N}{N^+ N^-} \sum_{i=-E}^{C} \left[ N_i(E_i) \langle k_{hi} \rangle - \frac{-E}{t = -D} N_i(E_i) \langle k_{ii} \rangle \right],
\]

(3.21)

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

\[
N_i(E) = \int_{0}^{R_m} N^+_i(R, E_i) dR
\]

(3.22)

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

\[
N_i(E_i) \sum_{t = -D}^{C} \langle k_{hi} \rangle = \sum_{t = -S}^{C} N_i(E_f) \langle k_{ii} \rangle.
\]

(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 (3.2c), 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.
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 $N^\pm \sim 10^6 \text{cm}^{-3}$ 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 $10^{12} \leq N^\pm \leq 10^{14} \text{cm}^{-3}$. In § 4.1 is developed a theory for the variation of $\alpha$ with $N^\pm$. A useful procedure proposed in § 4.2 for the rapid evaluation of the reaction rate $\alpha_{\text{eff}}$ permits illustration of the variation of $\alpha$ 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 $\alpha$ 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

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

(4.1)

where the local positive and negative ion densities are $n^\pm(R)$, and $\epsilon$ is the dielectric constant $1 + 4\pi N \rho$ of a gas with polarizability $\rho$ and density $N$. For Xe, $\epsilon = (1 + 1.4 \times 10^{-3} N/N_L)$, in effect unity for $N \leq 25 N_L$, the number density $2.69 \times 10^{19} \text{cm}^{-3}$ 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 $\text{s}^{-1}$) of positive ions towards the central positive ion is

$$F_{\text{in},+}^+(R) = -4\pi R^2 \left[ -D^+ \frac{dn^+(R)}{dR} + n^+(R) \frac{K^+}{\epsilon} \frac{\partial V}{\partial R} \right],$$

(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,

$$F_{\text{in},-}^+(R) = 4\pi R^2 \left[ D \frac{dn^-(R)}{dR} + n^-(R) \frac{K}{\epsilon} \frac{\partial V}{\partial R} \right],$$

(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, $F_{\text{in},+}^+$ vanishes, and integration of (4.2) yields the Boltzmann distribution

$$n^+(R) = N^+ \exp \left[ \frac{V(R)}{kT} \right],$$

(4.4)

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

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

(4.5)

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

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial (V/kT)}{\partial R} \right) = \frac{1}{2R_s^2} \left\{ \exp \left[ \frac{V(R)}{kT} \right] - \left[ 1 - \frac{\alpha}{\alpha_{\text{eff}} P(R_E)} \right] \exp \left[ -\frac{V(R)}{kT} \right] \right\},$$

(4.6)

where the 'screening' distance is

$$R_s = (8\pi N^\pm R_E/e)^{-1}.$$  

(4.7)
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,

$$ \alpha/\alpha_{tr} = \alpha_{rn}(R_e)/[\alpha_{rn}(R_e) + \alpha_{tr}(R_e)], $$  

(4.8)

from (2.62), where $\alpha_{rn}$ 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 $\alpha_{tr}$ 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 $\alpha_{tr}$ 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 $\alpha_{tr}$ is given in terms of $V$ by the analytical expression (2.63). Otherwise, (4.5) must be coupled to the solution of

$$ 4\pi R^2 \left[ D \frac{dn^-(R)}{dR} + n^-(R) K_0 V \right] = 4\pi R^2 D \left[ \exp \left( -V/kT \right) \frac{d}{dR} [n^-(R) \exp (V/kT)] \right] $$

$$ = \alpha_3(R) n^-(R) = \alpha N $$

(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 $n_i(R,E_i)$ determined from (2.20) with collisional rates $k_{i1}(R)$, 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 $n_i(R,E_i)$.

Note that it is only $\alpha_3(R)$ that depends on explicit knowledge of $n_i(R,E_i)$ so that, provided the rate $\alpha_{rn}$ of reaction can be provided analytically by alternative procedures, the above prescription reduces to the solution of (4.6) with (4.8). The term $1 - (\alpha/\alpha_{tr}) [P(R)/P(R_e)]$, 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 $R \to \infty$. As $R \to \infty$ for no plasma sheathing, solution of (4.6) is pure coulomb so that a (first) iterative solution valid for low $N \pm$ (large $R_s$) and high $N$ in the vicinity of $R_e$ is

$$ V_h(R) = -\frac{R_e}{R} + \frac{1}{12} \left( \frac{R}{R_e} \right)^2 \exp (-R_e/R), \quad R_e \lesssim R \ll R_s, $$

(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 $R \ll R_s$ as at high $N$, or else, for $R^3 \ll 12R_s^2$, i.e. when $N \lesssim 10^{14}$ cm$^{-3}$ at $R \lesssim R_e$.

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

$$ dv_1/dr = v_2(r), $$

$$ dv_2/dr = -\left( \frac{2}{r} - v_2(r) + (1/2r^2) [v_1(r) - v_3(r)] \exp (v_1(r) - v_3(r)) \right), $$

(4.11a)

$$ dv_3/dr = \left( \frac{\alpha}{\alpha_{tr}} \right) \exp v_1(r)/r^2, $$

where all distances $r = R/R_e$ are expressed in natural units, $v_i = V/kT$, and $v_3$ is the fractional departure $n^-/N^- \exp (V/kT)$ 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 (4.11a) may be linearized to provide

$$ v_3 \approx 1 - \alpha/\alpha_{tr} r $$

(4.11b)
so that the consistent and appropriate solution of the Poisson equation

$$\frac{1}{r} \frac{d^2 v_i}{dr^2} = \frac{1}{r_a} \left( v_i + \frac{\alpha}{2 \alpha_n} \right),$$

(4.11c)

is

$$v_i(r) = \frac{V}{kT} = -\frac{1}{r} \left( 1 - \frac{\alpha}{2 \alpha_n} \right) \exp \left( -\frac{r}{r_a} \right) - \frac{\alpha}{2r_a},$$

(4.11d)

which yields the coulomb attraction \((C)\) for \(r \ll r_a\).

At low \(N\),

$$v_i \to -\left( \frac{1}{2r} \right) \left[ 1 + \exp \left( -\frac{r}{r_a} \right) \right],$$

(4.11e)

the Debye–Hückel interaction D.H. (cf. McDaniel 1964), while at large \(N\) when \(\alpha \approx \alpha_n\),

$$v_i \to -\left( \frac{1}{2r} \right) \left[ 1 + \exp \left( -\frac{r}{r_a} \right) \right] \exp \left( -\frac{r}{r_a} \right) - \frac{\alpha}{2r_a},$$

(4.11f)

the mean of \(C\) and D.H. For intermediate \(N\), \(v_i\) contains various mixtures of \(C\) and D.H.

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

The criterion \(v_i \ll 1\) is satisfied at \(r \approx 1\) (the important region at low \(N\)) and at small \(\alpha/\alpha_n\) when \(r_s \gg 1\) which with (4.7), implies that \(\frac{\pi R_s}{r_a} N \approx \frac{1}{2} \pi r_s / r_a \approx 1\). Many ions are then present within the \(R_s\)-sphere, and \(N \approx 2 \times 10^{14}\) 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 (4.11f) 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 \(\alpha\) of reaction.

### 4.2. Simplified method for reaction rate

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

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

(4.12a)

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

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

(4.12b)

for a straight-line trajectory. Since \(\alpha_{rn}\) pertains to a Boltzmann distribution, the factor

$$E_i = \exp \left[ -V(R_i + \lambda_i)/kT \right],$$

(4.12c)

in (4.12a) 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

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

(4.12d)
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 $\pi R_i^2$. 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 (4.12a). Simple geometric arguments show that $G$ in (4.12a) is equal to either $C_1 E_1$ or $C_2 E_2$ 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

$$T' = \frac{\delta k T}{2} + \frac{\lambda_i}{R_i} \int_{R_i}^{R_i + \lambda_i} \frac{\partial V}{\partial R} dR,$$

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 $T'_1$ 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

$$T'_1 \leq \int_{R_i}^{R_i + \lambda_i} \frac{\partial V}{\partial R} dR.$$

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

$$T'_1 = T'_2 (1 + \delta),$$

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

$$V(R_i + \lambda_i) - V(R_i) = \frac{\delta k T}{2} \frac{\lambda_i}{R_i},$$

to be solved for the trapping radii $R_i$ associated with mean free paths $\lambda_i$ and collision parameters $\delta_i$.

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

$$R_i = \frac{1}{2} \lambda_i \left[ \left( 1 + 4 \delta_i R_T / \lambda_i \right)^{1/2} - 1 \right],$$

which decreases monotonically as $\lambda_i$ 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 $2e^2/3k T$. The sink is therefore compressible with $N$, as in the model of Natanson (1959).

At low gas densities the reaction rate

$$\alpha_m \rightarrow C_1 \delta_i \alpha_{Ti} + C_2 \delta_i^2 \alpha_{T2},$$

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

$$\alpha_{Ti} = \frac{\delta k R_T^2}{2} \langle v_{1x} \rangle / \lambda_i$$

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

$$\alpha_{T2} = \alpha_{q.e.} (N \rightarrow 0) / \alpha_{Ti}$$

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

$$X^+ + Y^- + Z \rightarrow [XY] + Z,$$

(4.21)
where energy-change transitions occur via elastic ion-neutral collisions. Also, the $\mathcal{A}_{ti}$ have been provided (Flannery 1980) for a wide range of systems represented by

$$X^+ + Y^+ + X \rightarrow [XY] + X,$$  \hspace{1cm} (4.22)

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

$$X^+ + Y^+ + Y \rightarrow [XY] + Y.$$  \hspace{1cm} (4.23)

With this knowledge, the collision parameters $\delta_i$ may now be uniquely determined by solution of

$$\delta_i^2 + \delta_i^2 - \mathcal{A}_{ti} = 0,$$  \hspace{1cm} (4.24)

and $\alpha_{rn}$ of (4.12a) tends therefore at low $N$ to the exact quasi-equilibrium values (Flannery 1980, 1981a). 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 $\delta_i$, the 'strong-collision' analogue to the microscopic method provided in §3. The strong-collision parameter $\delta_i$ 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 $\delta_i$ have been given (Flannery 1981b) 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

$$\alpha = \frac{\alpha_{rn} \alpha_{tr}}{(\alpha_{rn} + \alpha_{tr})}$$  \hspace{1cm} (4.25)
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 \( \alpha_{rn} \) was obtained from (4.12), with (4.17) for \( R_i \) and the solution of (4.24) for \( \delta_i \), and the transport rate from

\[
\alpha_{tr} = 4\pi e^2 \left( \frac{K_1}{1 - \exp (-R_i/R_1)} + \frac{K_2}{1 - \exp (-R_i/R_2)} \right). \tag{4.26}
\]

Results from the universal Monte-Carlo plot procedure of Bates (1980b) are also shown in figure 2 together with the direct Monte-Carlo computer simulations of Morgan et al. (1980) at low \( N^+ \). The general agreement as shown can be considered excellent. At low \( N \), \( \alpha_{rn} \ll \alpha_{tr} \) while at high \( N \), \( \alpha_{rn} \gg \alpha_{tr} \) so that \( \alpha \) is given by the rate-limiting step in each region. As \( N \) increases, \( \alpha_{rn} \) increases with respect to \( \alpha_{tr} \) until the maximum is obtained where \( \alpha_{rn} \approx \alpha_{tr} \). Figure 2 can be made universal for all temperatures \( T \) by simply relabelling the ordinate and abscissa axes as \( (T/300)^{\frac{3}{4}} \alpha \) and \( (300/T)^{\frac{3}{4}} N \) respectively as pointed out by Bates (1980c). Analogous results for other systems are presented elsewhere (Flannery 1981b).

At higher \( N^+ \), the interaction between the ions varies in general with \( \alpha \), 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 \( \alpha \). At high gas densities \( (N > \frac{1}{2}N_L) \), Morgan et al. (1980) simply adopted \( \text{ab initio} \) the D.H. interaction (4.11e) as a means of incorporating plasma sheathing effects when \( N^+ \) is raised. As shown in \$4.2 \) this assumption is without foundation unless \( N^- \) and leads to greatly reduced rates which are in error particularly at intermediate and high gas densities \( N \) (Bates 1981, Flannery 1981c). Although increase in the ion density to about \( 10^{12} \text{cm}^{-3} \) is not expected to cause appreciable change (Flannery 1981c) 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

\[
v_i \left( 4\pi \frac{R^2}{c} \frac{\partial}{\partial R} \left[ N^*_i(R, v_i)/4\pi R^2 \right] - \frac{4\pi \eta^2}{m v_i^2 c v_i} \frac{\partial}{\partial v_i} \left[ N^*_i(R, v_i)/4\pi v_i^2 \right] \frac{\partial V}{\partial R} \right)
\]

\[
= \int \int dR \int d v_i \frac{c}{\Gamma(R)} \left( N^*_i(R, v_i) N_o(v_o) - N^*_i(R, v_i) N_o(v_i) \right) [g \sigma(g, \psi) \frac{\partial \Omega}{\partial v_i} d v_i \] \tag{5.1a}
\]

\[
N \left[ \frac{c}{\Gamma(R)} N^*_i(R, E_i) \kappa_i(R) - N^*_i(R, E_i) \sum_{t=-N(B)} k_i(R) \right], \tag{5.1b}
\]

which is a set of linear integro-differential equations in two variables (rather than quadratic in \( N(R, v_i) \) since the gas density \( N_o(v_i) \) has already been set in (5.1b) to its thermodynamic value, as implied by the condition \( N^+ = N^0 \)). The speeds \( v_6 \) and \( v_t \) in (5.1a) are given by energy conservation with fixed \( v_i, v_o \) and \( \Omega \). The recombination sink at internal energies below \( E_b \) requires that \( N^*_i \) vanishes for

\[
v_t < v_t = (2/m[E_b - V(R)])^{\frac{1}{2}}, \quad R < R(E_b). \tag{5.2}
\]

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...
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 \(N_i\)) 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

\[
N^*_i(R,v_i) = N_0(R,v_i) \left[1 - \Phi_i(R,v_i)\right],
\]

(5.3)
in terms of the equilibrium density

\[
N_0(R,v_i) = 4\pi R^2 \exp\left(-\frac{V_i}{kT}\right) F_0(v_i),
\]

(5.4)
where the Maxwellian speed distribution is

\[
F_0(v_i) = \frac{4\pi v_i^2}{(m/2\pi kT)^{3/2}} \exp\left(-\frac{1}{2} \frac{mv_i^2}{kT}\right).
\]

(5.5)

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

\[
N_0(R,v_i) N_0(v_o) = N_0(R,v_f) N_0(v_f'),
\]

(5.6)
and hence, after some analysis, \(\Phi_i\) satisfies the set

\[
v_i \left[\frac{\partial}{\partial R} \Phi_i - \frac{1}{mv_i} \frac{\partial}{\partial v_i} \Phi_i\right] = \int_{\Omega} N_0(v_0) \left[\Phi_i(R,v_i) - \Phi_i(R,v_i)\right] (g d\Omega) dv_0
\]

\[
= N \left\{ \sum_{E_i = -M(R)} \Phi_i(R,E_i) - \sum_{E_i = V(R)} \Phi_i(R,E_i) \right\} k_{if}(R)
\]

(5.7)
subject to the boundary conditions that

\[
\Phi_i(R,E_i) \rightarrow 0 \quad \text{for} \quad E_i \rightarrow \infty, \quad \text{or for} \quad R \rightarrow \infty
\]

\[
\rightarrow 1 \quad \text{for} \quad E_i \leq E_S, \quad R \leq R(E_S).
\]

(5.8)

In the limit of low gas densities \(N\), the net rate of change of each of the streaming terms con-
tained 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.

\[
\int_0^{R_i} 4\pi R^2 \frac{\partial}{\partial R} \left[ \frac{N^*_i(R,v_i)}{4\pi R^2} \right] dR \\
\approx \frac{4\pi v_i^2}{m} \frac{\partial}{\partial v_i} \left[ \frac{1}{4\pi v_i^2} \int_0^{R_i} N^*_i(R,v_i) \frac{\partial V}{\partial R} dR \right].
\]

(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,

\[
\langle k_{if}(E_i,E_f) \rangle = \frac{1}{N_i^*(E_i)} \int_0^{R_i} N^*_i(R,E_i) k_{if}(E_i,E_f,R) dR,
\]

(5.10)
where

\[
N_i(E_i) = \int_0^{R_i} N^*_i(R,E_i) dR.
\]

(5.11)
Hence, (5.1) reduces, with the aid of (5.9), to
\[
N_i(E_t) \sum_{t=-D}^{C} \langle k_{tt}(E_t,E_t) \rangle = \sum_{t=-S}^{C} N_i(E_t) \langle k_{tt}(E_t,E_t) \rangle
\]
(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 approxi-
mation 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 \(\Phi_i\) 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 com-
parison with the diffusion term, and with the substitution in (5.7) of
\[
\Phi_i(R,v_i) = \Phi^0_i(R,v_i) \exp (-R/L_i),
\]
(5.13)

where the length
\[
L_i(v_i) = L_i(R,E_i) = v_i/N \sum_{t} k_{tt}(R)
\]
(5.14)
is a function only of \(v_i\) (see Appendix B) then, after some analysis and reduction, \(\Phi_i^0\) satisfies the
set of first-order coupled differential equations
\[
\frac{\partial \Phi_i^0(R,E_t)}{\partial R} = \frac{N}{v_i} \sum_{t=-S(R)}^{C} \Phi_i^0(R,E_t) k_{tt}(R) \exp [-R(L_i^{-1} - L_i^{-1})],
\]
(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, pertur-
bation procedures based on the strength of the coupling terms \(k_{tt}\) result in a full hierarchy of
computational schemes of varying degrees of sophistication. For example, the \(\{k_{tt}\}\)-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
\[
\frac{\partial \Phi_i}{\partial R} \approx \frac{\partial \Phi_i^0}{\partial R} = \frac{N}{v_i} k_i(R) \Phi_i^0
\]
(5.16)

with solution
\[
\Phi_i^0(R,v_i) = \exp \left[ -\frac{N}{v_i} \int_{R_o}^{R} k_i(R) dR \right]; \quad v_i(R) \geq v_{to}
\]
(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
\[
N_i^0(R,E_t) = N_0(R,v_i) \left[ 1 - \exp \left[ -RN \sum_{t} k_{tt}(R)/v_i \right] \exp \left[ -N \int_{0}^{R} k_{tt}(R) dR/v_i \right] \right],
\]
(5.18)
which tends to $N_0$ as $R \to \infty$. It is worthwhile noting, even for approximation (5.18), that $\alpha$ 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 $\Phi_1$, 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 $\alpha$, 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

$$\Phi_i(R,v_i) = \Phi_i^{(1)}(R,v_i) \exp \left( v_i / V_i \right), \quad (5.19)$$

where the effective speed is

$$V_i(R,E_i) = \left( \frac{\partial V}{\partial R} \right)_i \int mN \sum k_{ii} = a(R) \tau_i(R,E_i), \quad (5.20)$$

in terms of the acceleration $a(R)$ and of time $\tau_i = L_i(v_i^2) / v_i$ between collisions, the set (5.7), with diffusion ignored, yields, after some analysis and reduction, the set of first-order coupled differential equations

$$\frac{\partial \Phi_i^{(1)}(R,E_i)}{\partial v_i} = -\frac{N}{a(R)} \sum_{i=1}^{C} \Phi_i^{(1)}(R,E_i) k_{ii}(R) \exp \left[ (v_i / V_i) - (v_i / V_i) \right] \quad (5.21)$$

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,

$$\frac{\partial \Phi_i^{(0)}(R,v_i)}{\partial v_i} = -\frac{N}{a(R)} k_{ii}(R) \Phi_i^{(0)}, \quad (5.22)$$

such that

$$\Phi_i^{(0)}(R,v_i) = \exp \left[ -\frac{N}{a(R)} \int_0^{v_i} k_{ii}(R) \, dv_i \right], \quad (5.23)$$

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

$$N_i^{(1)}(R,E_i) = N_0(R,v_i) \left[ 1 - \exp \left[ \frac{Nm}{a(R)} \sum k_{ii} \frac{\partial V}{\partial R} \exp \left[ -\int_0^{v_i} k_{ii}(R) \, dv_i \right] \right] \right] \quad (5.24)$$

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 $\Phi_i^{(1)}(R,v_i)$ contains most of the $R$-variation and that $\Phi_i^{(1)}(R,v_i)$ contains most of the $v_i$-variation, a working approximation for the general case (5.7) is

$$\Phi_i(R,v_i) \approx \frac{1}{2} (\Phi_i + \Phi_i^{(1)}), \quad (5.25)$$

where $\Phi_i^{(1)}$ 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

$$N_i^*(R,v_i) = N_0(R,v_i) \left[ 1 - \frac{1}{2} \exp \left( -NR \sum k_{ii} / v_i \right) \exp \left( \frac{-N}{v_i} \int R k_{ii} \, dR \right) \right]$$

$$- \frac{1}{2} \exp \left[ Nm \sum k_{ii} \frac{\partial V}{\partial R} \right] \exp \left[ -\frac{Nm}{\partial V/\partial R} \int_0^{v_i} k_{ii} \, dv_i \right] \quad (5.26)$$
which tends to $N_0$ when $R \to \infty$ or when $v_1 \to \infty$. 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,

$$N_i(R, v_1) = \frac{4\pi R^2 \bar{n}(R) N^+}{4\pi v_1^2} F_0(v_1) [1 + \Phi_1(R, v_1)],$$  \hspace{1cm} (5.27)

where $\bar{n}(R)$ is some negative-ion configuration-space density yet to be determined, and where $\Phi_1$, which represents the departure of the momentum distribution from the Maxwellian $F_0(v_1)$, 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

$$\frac{-4\pi v_1^2}{m} \frac{\partial}{\partial v_1} \left[ F_0(v_1) \frac{\partial}{\partial R} \right] = v_1 F_0(v_1) \frac{\partial}{\partial R} \left[ \frac{V}{kT} \right],$$  \hspace{1cm} (5.28)

after some reduction, we obtain (5.1) exactly as

$$v_1 F_0(v_1) \left\{ \hat{D} \bar{n}(R) + \frac{\partial}{\partial R} \left[ \Phi_1 \bar{n}(R) \right] - \bar{n}(R) \frac{\partial}{\partial R} \left[ \Phi_1 \right] \right\} \hspace{1cm} (5.29)

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

$$\hat{D} \bar{n} = \left[ \frac{d}{dR} + \frac{d(V/kT)}{dR} \right] \bar{n}(R),$$  \hspace{1cm} (5.30)

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

$$\Phi_1(R, v_1) = -N_0(E_1) \int \bar{n}(R) \, d\nu_1,$$  \hspace{1cm} (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, $\Phi_1$ is zero and $\bar{n}(R)$ is $N^+ \exp \left( \frac{V}{kT} \right)$ such that $\hat{D} \bar{n}$ vanishes. Hence the $\hat{D}$-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 $\bar{n}(R)$ to be small but its derivative $d(\bar{n}(R))/dR$ must vanish. Under this sole approximation (5.29) reduces with the aid of substitution (5.31), and after some analysis, to

$$v_1 \left[ 1 - \frac{\partial l_i(v_i^2, R)}{\partial R} + \frac{\partial (V/kT)}{\partial R} \frac{\partial l_i(v_i^2, R)}{\partial T_i} \right] = N \left[ l_i(R, E_1) \sum_{t=+}^C k_{tt}(R) - \sum_{t=-}^C l_i(R, E_1) k_{tt}(R) \right].$$  \hspace{1cm} (5.32)
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The frequency \( v_i \) of ion–neutral collisions is

\[
v_i(v_i) = N \sum_{t=-v}^{c} k_{tt}(R),
\]

such that the interval \( \tau_i \) between collisions for ions of speed \( v_i \) is \( v_i^{-1} \) and the mean length \( L_i \) of their free paths is

\[
L_i(v_i) = v_i \tau_i = v_i/v_i.
\]

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,

\[
L_i(v_i) = \pi X_{\bar{q}}/NQ X_{\bar{q}} [(2X_{\bar{q}} + 1)\frac{1}{2}\pi \Phi_E(X_{\bar{q}}) + X_{\bar{q}}^2 \exp (-X_{\bar{q}})],
\]

where \( \Phi_E \) is the error function which is a function of

\[
X_{\bar{q}} = \frac{iM q_0 \sqrt{kT}}{R},
\]

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

\[
v_i \left[ \frac{l_i(R, E_i)}{L_i(v_i)} - 1 + \frac{\partial l_i(R, v_i^2)}{\partial R} - \frac{\partial (V/kT)}{\partial R} \frac{\partial l_i(R, v_i^2)}{\partial T_i} \right] = N \sum_{t=-v}^{c} l_t(R, E_i) k_{tt}(R),
\]

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

\[
n_i(R, E_i) = [\hat{n}(R) - \hat{D} \hat{n}(R) l_i(R, E_i)] F_0(v_i)
\]

which tends to \( n_0 \) as \( E_i \to \infty \), i.e.

\[
\hat{n}(R) - \hat{D} \hat{n}(R) l_i(R, \infty) = N^\infty \exp (-V/kT).
\]

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

\[
\hat{n}(R) = N^\infty \exp (-V/kT) \exp \left[ R/l(R, \infty) \right] \int_R^{\infty} \frac{\exp \left[ -R/l(R, \infty) \right]}{l(R, \infty)} \mathrm{d}R,
\]

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

\[
n_i(R, E_i) = N^\infty \exp (-V/kT) F_0(v_i) \left[ \frac{l_i(R, E_i)}{l_i(R, \infty)} + \left[ 1 - \frac{l_i(R, E_i)}{l_i(R, \infty)} \right] H(E_i) \right]
\]

\[
\times \exp \left[ R/l(R, \infty) \right] \int_R^{\infty} \frac{\exp \left[ -R/l(R, \infty) \right]}{l(R, \infty)} \mathrm{d}R,
\]

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 \( E_i \to \infty \), (5.41) ensures that \( n_i \to n_0 \); and as \( R \to \infty, n_i \to n_0 \) implies that

\[
l_i(R, E_i) \to l_i(\infty, E_i) = l(\infty, \infty) \equiv l_\infty.
\]

Hence the set (5.37) is solved subject to the condition (5.42). As \( E_i \to \infty \), the right-hand side of (5.37) vanishes, \( L_i \to l_\infty \) and hence

\[
\frac{l(R, \infty)}{l_\infty} - 1 + \frac{\partial l(R, \infty)}{\partial R} - \frac{\partial (V/kT)}{\partial R} \frac{\partial l(R, \infty)}{\partial T_i} \bigg|_{T_i \to \infty} = 0.
\]
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 $l_i(R \to 0, \infty)$, to give

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

(5.44)

which satisfies (5.42) and which also ensures that $(\partial l_i / \partial R)_{R \to \infty}$ 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 $E_i \to \infty$. Each solution will depend on the gas density $N$ through $l_\infty$.

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

$$l_i(R, E_i) \to l(R, \infty) \gamma(E_i),$$

(5.45)

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

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

(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 $\alpha$ in (2.52) is, apart from the neglect of $d[l \dot{n}(R)] / dR$ in (5.29), exact. The chief distinction between this proposed method and the previous method is that $l_1$ is, in the absence of the recombination sink, a function only of $v_i^2$, while $\Phi_1$ 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 $\dot{n}(R)$.

The physical meaning of the functions $\dot{n}$ and $l_1$ in (5.27) and (5.31) becomes apparent by noting that the current density (ions cm$^{-2}$s$^{-1}$) is

$$J_s = \dot{n}(R) v_d = \int n_i(R, v_i) v_i dv_i,$$

(5.47)

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

$$J_s = - D_s \left[ \frac{d\dot{n}(R)}{dR} + \dot{n}(R) \frac{\partial (V / kT)}{\partial R} \right] R$$

(5.48)

where

$$D_s = \frac{1}{3} \int_{v_0(R)}^{\infty} F_0(v_i) v_i l_i(v_i^2) dv_i \text{ (cm}^2 \text{s}^{-1})$$

(5.49)

is the diffusion coefficient in the presence of the sink for ions with the radial distribution $\dot{n}(R)$. The factor of $\frac{1}{3}$ in (5.49) arises by adopting the radial direction $\dot{R}$ 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

$$D_s \equiv \frac{1}{3} \langle l_i v_i \rangle \text{ (cm}^2 \text{s}^{-1}),$$

(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 $l_1$ 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 $\dot{n}(R)$ 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)

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

(5.51)
and neglect initially the acceleration term $\partial (V/kT)/\partial R$. The resulting set of equations,

$$v_l \left[ \frac{I_l(R, E_l)}{l_l(t)} - 1 + \exp \left(-\frac{R}{l_m}\right) \right] = N \sum_{t=-M}^{C} I_t(R, E_t) k_{th}(R)$$

(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 $\alpha$ 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 $\alpha$ has been derived in terms of $\alpha_{rn}$, the rate of reaction or, equivalently, the recombination coefficient that would pertain provided a Boltzmann distribution of ions were maintained, and of $\alpha_{tr}$, 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 $\alpha_{rn}$ 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 $\alpha$ 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 $N \leq N_L$, a straight-line dependence of $\alpha(t)$ with $t$ is noted, since the reaction rate is always much slower, while high $N > N_L$ 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 $N^2$ 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 $\alpha$ can then be determined as a function of both $N$ and $N^2$. Otherwise, if the analytic reaction
rate \( x_{rn} \) 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 \( x_{rn} \) 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 \( \phi_S \) into a field of constant potential \( \phi_0 \). The potential \( \phi \) at any point \( R \) from the centre of the sphere satisfies Laplace's equation,

\[
\nabla^2 \phi = 0,
\]

with solution

\[
\phi(R) = \phi_0 \left[ 1 - \left( \frac{S}{\sqrt{R}} \right) \left( 1 - \frac{\phi_S}{\phi_0} \right) \right].
\]

The total charge induced on the sphere is

\[
q_1 = -\frac{1}{4\pi} \int \nabla \phi \cdot dS = -S \phi_0 \left( 1 - \frac{\phi_S}{\phi_0} \right).
\]

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

\[
\nabla \cdot j = \nabla \cdot \left[ D \exp \left( -\frac{V}{kT} \right) \nabla n - \exp \left( \frac{V}{kT} \right) \right] = 0,
\]

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

\[
n^-(R) = N - \left[ 1 - \left( \frac{S}{\sqrt{R}} \right) \left( 1 - \frac{n_S}{N -} \right) \right].
\]

The flux across any \( R \)-sphere is,

\[
F^- = 4\pi SD \left( 1 - \frac{n_S}{N^-} \right) N^- \equiv \alpha_d \left( 1 - \frac{n_S}{N^-} \right) N^- = \alpha N^-,
\]

where \( \alpha_d \) is the recombination rate \( \alpha \) appropriate to instantaneous reaction \( (n_S = 0) \). Analogy with electrostatics then follows by identifying the local ion density \( n^- \) with the local potential \( \phi \), and the flux of ions across \( S \) with the induced charge. Hence, the recombination rate \( \alpha \) is equivalent to \( 4\pi D \) times the 'induced charge \( q_1 \)' per unit 'external potential \( \phi_0 \)', and the transport rate \( \alpha_d \) is \( 4\pi D \) times the 'induced charge \( q_1 \)' per unit 'potential difference \( (\phi_S - \phi_0) \)'. Introduce a reaction rate \( \alpha_3 \) at \( S \) by

\[
\alpha_3 n_S = \alpha N^-,
\]

which equates the incident flux with the rate \( (s^{-1}) \) of reaction. Thus the reaction rate \( \alpha_3 \) is \( 4\pi D \) times the 'induced charge \( q_1 \)' per unit 'surface potential \( \phi_S \)'. Thus \( \alpha, \alpha_d \) and \( \alpha_3 \) may be regarded as appropriate capacitances of the sphere associated with potentials \( \phi_0, \phi_S \) and \( \phi_S - \phi_0 \), respectively.

From (A 6) and (A 7),

\[
1/\alpha = 1/\alpha_d + 1/\alpha_3,
\]

showing that the overall rate \( (cm^2 s^{-1}) \) is equivalent to a capacitance associated with potential \( \phi_0 \) 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 \( \phi \) in (A 1)-(A 3) and \( n \exp \left( \frac{V}{kT} \right) \) is preserved in \( R \)-space. The equivalent solution is then

\[
n^-(R) = N^- \exp \left( -\frac{V}{kT} \right) \left[ 1 - \left( \frac{S}{\sqrt{R}} \right) \left( 1 - n_S \exp \left[ \frac{V(S)}{kT} \right] / N^- \right) \right],
\]
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which is analogous with (A 2). With the aid of (2.105), the inward flux across any R-sphere is

\[ F^- = 4\pi R^2 D \exp \left( - V/kT \right) \left[ \frac{d n(R) \exp \left( V/kT \right)}{dR} \right] \]

\[ = 4\pi D N^- \left( 1 - n_v/(N^-) \right) \exp \left( V(S)/kT \right) \]

\[ \tag{A 10} \]

\[ \tag{A 11} \]

such that, with (A 7),

\[ 1/\alpha = 1/\alpha_{rn} + 1/\alpha_{tr} \]

\[ \tag{A 12} \]

where the diffusional-drift transport rate that replaces \( \alpha_d \) is

\[ \alpha_{tr} = 4\pi S D = 4\pi D \int_0^{R_{\infty}} \exp \left( V/kT \right) R^{-2} dR \]

\[ \tag{A 13} \]

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

\[ \alpha_{rn} = \alpha_d \exp \left[ - V(S)/kT \right]. \]

\[ \tag{A 14} \]

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 \( \phi_o \) 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

\[ L_i(v_i) = v_i/[N \sum \kappa_{it}(R)], \]

\[ \tag{B 1} \]

where the denominator is the frequency \( v_i \) 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 \( \text{(cm}^3\text{s}^{-1}) \text{between an ion } i \text{ and a gas atom } 3 \) is

\[ \sum \kappa_{it}(R) \equiv \int_{-\infty}^{\infty} k'(E_i, E_t, R) dE_t \frac{1}{2} \int_{0}^{\infty} G(v_3) dv_3 \int_{0}^{\pi} g \sigma(g, \psi) d (\cos \psi) d\phi \int_{-1}^{+1} d\mu, \]

\[ \tag{B 2} \]

where

\[ g = v_i - v_3; \quad \mu = \hat{v}_i \cdot \hat{v}_3 \]

\[ \tag{B 3} \]

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 \( \sigma \), 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

\[ \sum \kappa_{it}(R) = Q \int_{0}^{\infty} G(v_3) dv_3 (v_1 + \frac{1}{2} v_3^2/v_1), \quad v_1 > v_3, \]

\[ = Q \int_{0}^{\infty} G(v_3) dv_3 (v_3 + \frac{1}{2} v_3^2/v_3), \quad v_1 < v_3, \]

\[ \tag{B 4} \]

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

\[ \sum \kappa_{it}(R) = \frac{1}{2} Q \langle v_3 \rangle [(2X_i^1 + X_i^2) \frac{1}{2} \pi k T \Phi_k(X_i^2) + \exp (- X_i^2)], \]

\[ \tag{B 5} \]

where

\[ X_i = (\frac{1}{2} M v_i^2/k T) \]

\[ \tag{B 6} \]

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in terms of the reduced mass $M$ of the (ion-pair-gas) system, where
\[ \Phi_E(X_i) = \frac{2}{\sqrt{\pi}} \int_0^{X_i} \exp(-t^2) dt = \frac{1}{\sqrt{\pi}} \int_0^{X_i} E^{-1/2} \exp(-E) dE, \] (B 7)
is the probability integral (or error function), and where $\langle v_2 \rangle$ is the mean thermal speed \((8kT/\pi M)^{1/2}\) of the gas atoms. The total rate (B 5) tends to $Q \langle v_2 \rangle$ and to $Q v_i$ as $v_i \to 0$ and as $v_i \to \infty$, respectively. Equation (5.35) for $L_i$ in the text is therefore recovered from (B 1) and (B 5).

We note that
\[ L_i(v_i)/L_i(\infty) = \pi^{1/2} X_i/[(2X_i + 1) \frac{1}{2}\pi^{1/2} \Phi_E(X_i^2) + X_i^2 \exp(-X_i^2)], \] (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.

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Appendix G

Analytical solution of the Debye-Smoluchowski equation for geminate and homogeneous recombination and for fluorescence quenching

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Closed-form analytical time-dependent solutions of the Debye-Smoluchowski equation with a general spherical interaction are obtained for the important cases of geminate and homogeneous recombination by diffusional drift in a gas of liquid medium. A relationship between the time-dependent probability for recombination or escape in geminate recombination and the transient rate for homogeneous recombination is established. An expression for the rate of decay of emitted intensity in fluorescence quenching is also derived.

When a dissociated pair $A$ and $B$ is generated instantaneously within a gas or liquid medium then the $(A-B)$ pair may react internally or escape by diffusional drift in the presence of a sink to infinite separation. The key quantity in this geminate recombination process is the probability $P(t)$ or $\Sigma(t)$ for recombination or survival, respectively, of the dissociating pair at time $t$. When reaction occurs between a central species $A$ and another of the species $B$ created within the medium by a continuous source at infinity (or else by escape from geminate recombination), then this recombination is homogeneous and is characterized by an effective two-body coefficient $\alpha(t)$ cm$^3$s$^{-1}$ appropriate to termolecular reactions. Contact has recently been established$^1$ between the basic microscopic (phase-space) theory of chemical reactions influenced by diffusional drift in a medium and the (Debye-Smoluchowski) macroscopic equation of continuity

$$ -\frac{\partial n(R,t)}{\partial t} + \nabla \cdot J_i(R,t) = \alpha_3 n(R,t) \delta(\bar{R} - \bar{S}) $$

(1)

for the probability density $n(R,t)$ for finding an $AB$ pair with internal separation $R \geq S$. Here $\alpha_3$ is the local rate of reaction (via three-body $AB$ collisions with the medium) for $AB$ pairs brought to internal separation $S$ by the diffusional-drift current $\bar{J} = - J_i$ with

$$ J_i(R,t) = D \nabla n(R,t) + (K/e) n(R,t) \nabla V(R) $$

(2a)

$$ \equiv D \left[ \exp(-V/kT) \nabla n(R,t) \exp(V/kT) \right] $$

(2b)

expressed as a generalized Fick's law by use in (2a) of the Einstein relation ($D_e = K kT$) between the diffusion coefficient $D$ (cm$^2$s$^{-1}$) and mobility $K$ (cm$^2$/statvolt s) for relative $AB$ motion in the gas or liquid medium. Equation (1) is equivalent to the corresponding homogeneous equation solved subject to the partially absorbing boundary condition

$$ 4\pi S^2 J_i(S,t) = \alpha_3 n(S,t) $$

(3)

which assumes that the net inward radial diffusional-drift current at $S$ is absorbed by reaction within $S$.

It has recently been shown$^1$ how analytical time-dependent solutions of (1) for an arbitrary spherical interaction can, in general, be obtained in closed form via introduction of the transformation$^1$ from the variable $R$ to

$$ \bar{R} = \left[ \int_R^\infty \exp(V/kT)R^{-2}dR \right]^{-1} $$

(4)

which then reduces (1) to a form capable of exact solution for $R \geq$ the natural unit (n.u.) at which the thermal ($kT$) and potential ($V$) energies are equal. It is the purpose of this communication to briefly summarize the key results obtained for geminate and homogeneous recombination.

Recombination is used here in its most general sense of any chemical reaction influenced by diffusional drift in a gas or liquid (electron-ion and ion-ion neutralization, coagulation of colloids, electrolytic reactions, chemical conversions, etc.).

On setting
\[ n'(\vec{r}, \tau) = \frac{-R}{S} n(R, t) \exp V(R)/kT; \]
\[ F = \frac{-R}{S}; \]
\[ \tau =Dt/S^2 \quad (5) \]
then the homogeneous equation corresponding to (1) reduces to
\[ \frac{\partial n'}{\partial \tau} (\vec{r}, \tau) \quad \frac{\partial^2 n'}{\partial \vec{r}^2} (\vec{r}, \tau) \]
\[ = \frac{\partial^2 n'}{\partial \vec{r}^2} + \left( \frac{\partial}{\partial \vec{r}} \left( \frac{\partial^2 n'}{\partial \vec{r}^2} \right) \right) \frac{\partial n'}{\partial \vec{r}} \quad (6) \]
which suggests the following two procedures for solution: Assume \( \frac{\partial}{\partial \vec{r}} \right(\frac{\partial^2 n'}{\partial \vec{r}^2} \right) \) remains constant such that introduction of
\[ \tau(\vec{r}) = \left( \frac{\partial}{\partial \vec{r}} \right)^2 \tau \quad (7a) \]
in (6) yields
\[ \frac{\partial n'}{\partial \vec{r}} (\vec{r}, \tau) = \frac{\partial^2 n'}{\partial \vec{r}^2} (\vec{r}, \tau) \quad (7b) \]
which is the field-free diffusion equation in \( (\vec{r}, \tau) \) space. Alternatively, since the coefficient on the right hand side of (6),
\[ \left( \frac{\partial}{\partial \vec{r}} \left( \frac{\partial^2 n'}{\partial \vec{r}^2} \right) \right) \frac{\partial n'}{\partial \vec{r}} \]
vanishes to \( O(R^{-3}) \) for the Coulomb interaction and is negligible for \( R^3 \geq SR_0^2 \equiv S(e^2/kT)^2 \),
then
\[ \frac{\partial n'}{\partial \vec{r}} (r, \tau) = \frac{\partial^2 n'}{\partial \vec{r}^2} (r, \tau), \quad (8b) \]
the one-dimensional diffusion equation in \( (r, \tau) \) space. The radiation boundary condition (3) in cases (7b) and (8b) is
\[ \left( \frac{\partial n'}{\partial \vec{r}} \right) \left|_{0} = \left( \frac{\alpha_{RN}}{\alpha} \right) n'(0, t) \quad (9a) \]
or
\[ \left( \frac{\partial n'}{\partial \vec{r}} \right) \left|_{0} = \left( \frac{\alpha_{RN}}{\alpha} \right) \left( \frac{\vec{S}}{S} \exp \frac{V(S)}{kT} \right) n'(0, t), \quad (9b) \]
respectively, where
\[ \alpha = \frac{\alpha_{RN} \alpha_{TR}}{\alpha_{RN} + \alpha_{TR}} \quad (10a) \]
in terms of the reaction rate at \( S \),
\[ \alpha_{RN} = \alpha \exp \left[ -V(S)/kT \right] \quad (10b) \]
at \( S \), and of the transport rate at \( S \): \[ \alpha_{TR} = 4\pi D \bar{S} \quad (10c) \]
When \( \alpha_{RN} >> \alpha \), as at high \( N \), then (9a) implies full absorption with zero \( n'(0, t) \) and when \( \alpha_{RN} << \alpha \), as a low \( N \), then (9a) implies partial absorption with zero \( \left( \frac{\partial n'}{\partial \vec{r}} \right) \). For *geminate* recombination, the solution of (1), subject to the initial condition
\[ n(R, t = 0) = N_0 \delta(R - R_0)/4\pi R_0^2 \quad (11a) \]
for instantaneous generation of \( N_0 \)
\[ \equiv N \exp \left[ -V(R_0)/kT \right] \] \( \) species \( A \) at a fixed distance \( R_0 \) from the central, and subject to the boundary condition
\[ n(R \rightarrow \infty, t) = 0 \quad (11b) \]
is determined from (8b) and (9b) to be
\[ n(R, t; R_0, S) = \frac{N \exp \left[ -V(kT)/R \right]}{(4\pi R_0^2 / (4Dt)^{1/2})} \]
\[ \times \left[ \frac{1}{\sqrt{\pi}} \left[ \exp (-\Omega_0^2) + \exp (-\Omega_1^2) \right] \]
\[ -2 \chi \exp (\chi^2) \exp (2\Omega_1 \chi) \text{erfc} (\chi + \Omega_1) \right] \quad (12a) \]
in terms of (4), and of the dimensionless quantities
\[ \Omega_0(R, t) = \left( \frac{R - R_0}{4Dt} \right)^{1/2}, \quad \Omega_1(R, t) = \left( \frac{R + R_0 - 2S}{4Dt} \right)^{1/2}, \quad (12b) \]
\[ \chi(t) = \left[ \frac{\alpha_{RN}}{\alpha} \right] \left( \frac{D t}{S} / S \right)^{1/2} \exp \left( \frac{V(S)/kT}{S} \right). \]
For *homogeneous* recombination, the solution of (1) subject to the initial and boundary conditions
\[ n(R, t = 0) \]
\[ n(R \rightarrow \infty, t) = N_0 \exp \left[ -V(R)/kT \right] \quad (13) \]
of a Boltzmann equilibrium distribution, is similarly
\[ n(R,t) = N_0 \exp\left(-\frac{V}{kT}\right) \times \left[ 1 + \frac{\alpha}{\alpha_{TR}} \frac{S}{R} \right] \]
\[ \times \left[ \exp(2\Omega x) \exp\left(\chi + \Omega\right) - \text{erfc}(\chi) \right], \]

(14a)

where \( \Omega(t) \) is defined in (12b), and where

\[ \Omega(R,t) = \frac{(R-S)}{(4Dt)^{1/2}} \equiv \frac{(R-S)}{(4Dt)^{1/2}} \frac{dR}{dR}, \]

(14b)

since \((dR/dR)\) is assumed constant. The solutions (12a) and (14a) are exact at all times over the region \( R > S \) when \( S > R_e \). The steady-rate solutions obtained from (7b) are exact over all \( R \) and are identical with the \( (t \to \infty) \) limit of (12a) and (14a). Both methods based on (7b) and (8b), respectively, yield results which depend on the density of the medium and therefore valid when \( R > 3R_e \), \( R_e \), and 0.2\( R_e \) at 0.1, 1, and 20 atm, respectively, for Coulombic attraction.

The survival probability that each \( AB \) pair has not reacted in geminate recombination, \( \Sigma(t) \), is best evaluated indirectly from

\[ \Sigma(t) = 1 - \mathcal{P}(t) = 1 - \frac{1}{\mathcal{N}^0} \int_0^t \nu(t) dt, \]

(15b)

where the frequency of recombination is

\[ \nu(t) = -\int_{\mathcal{S}} \left[ \frac{\partial n}{\partial t} \right] d\mathcal{R} = \alpha_n(S,t;R_0,S) \]

(15c)

since \( J_i \) vanishes at infinity and within \( \mathcal{S} \).

Without loss of generality, a coincident source and sink \( (R_0 = S) \) can be assumed in (15b) with (15c) and (12a), so that the recombination probability is

\[ \mathcal{P}(t) = \frac{\alpha}{\alpha_{TR}} \left[ 1 - \exp(2\nu(t)) \text{erfc}(\nu(t)) \right] \]

(15d)

which tends at long times \( t >> S^2/D \) to \( \alpha_{RN}/(\alpha_{RN} + \alpha_{TR}) \). From the rate of decrease in the number of diffusional-drift species outside \( S \) the rate coefficient \( \alpha(t) \) for homogenous recombination is

\[ \alpha(t) = -\frac{1}{N_0} \left[ \frac{d}{dt} \int \mathcal{R}(R,t)d\mathcal{R} - \mathcal{F}_\infty \right] \]

\[ = \alpha_n(S,t)/N_0, \]

(16)

where \( \mathcal{F}_\infty \) is the net inward flux generated continuously at infinity. With the aid of (14a),

\[ \alpha(t) = \alpha \left[ 1 + \left( \frac{\alpha_{RN}}{\alpha_{TR}} \right) \exp(\nu(S,t)\text{erfc}(\nu(S,t)) \right]. \]

(17)

From (15d), (17), and (10a), we obtain

\[ \alpha(t) = \alpha_{RN} \Sigma(t) \to \alpha_{TR} \mathcal{P}(\infty) \]

(18)

between the transient rate \( \alpha(t) \) for homogeneous recombination and the transient recombination and escape probabilities \( \mathcal{P}(t) \) and \( \Sigma(t) \), respectively.

When instantaneous generation of \( A \) occurs at \( R_0 = S \), i.e., reaction may immediately follow, then the fractional number of \( A \) that can be found at time \( t \) within a spherical shell of thickness \( dR \) and centered at \( B \) is

\[ \mathcal{F}(R,t)dR = 4\pi R^2 n(R,t;S,S)dR \mathcal{N}_0, \]

(19)

for geminate recombination.

Figure 1 is a three-dimensional display of the variation of \( \mathcal{F}(R,t) \) with both interseparation \( R \) [in units of the natural length \( (e^2/kT) \)] and in intervals of 0.05 from \( R = 1.0 \), the assumed radius of the sink, to \( R = 2.2 \) and time \( t \) [in units of \( S^2/D \) and in intervals of 0.05 from 0.05 to 0.70] for geminate recombination between positive and negative ions. Here equal rates of transport and reaction are assumed such that \( \mathcal{P}(\infty) \) and \( \Sigma(\infty) \) equal 0.5. Each approximately right-to-left curve provides the fixed-R variation of \( \mathcal{F}(R,t) \) with \( t \) while each left-to-right curve provides the fixed-time variation of \( \mathcal{F}(R,t) \) with \( R \). The boundary curve \( \mathcal{F}(S,t) \) provides the variation with time of the recombination frequency \( \nu(t) \) which decreases to zero as expected. This figure is a striking illustration of the evolution with time and separation of an ion pair subject to reaction and diffusional drift, i.e., of the geminate recombination process.

Figure 2 displays the time variation of the probability (15d) for geminate recombination. The initial variation \( \sim 0.5 (1 - 1.3t^{1/2}) \) at short times is
rapid in comparison with that ≈ 0.5 (1 − 0.5τ −1/2 ) at asymptotic times. The bulk of the probability for geminate recombination (19) is achieved effectively instantaneously within a few $S^2/D$ (e.g., $S^2$ increases to 0.3 and 0.4 at $τ = 1$ and 5, respectively), a feature apparent also for the homogeneous case 2 with an initial Boltzmann distribution and continuous source of ionization, particularly for low gas densities. Fluorescence quenching of excited fluorophors $A^*$ of density $n_A(t)$ after an initial incident laser pulse of excitation is governed by

$$\frac{dn_A(t)}{dt} = -[τ_A^{-1} + α(t)n_B(t)]n_A(t), \quad (20)$$

$$n_A(t) = n_A(0)\exp \left[ -t/τ_A - \int_0^t α(t)n_B(t)dt \right], \quad (21)$$

where $τ_A$ is the unquenched radiative lifetime of $A^*$ and where $n_B$ is the density of the quenching species $B$ with an initial Boltzmann distribution.

If the quenching species $B$ are chemically inert or if $n_B >> n_A$, then $n_B$ is effectively constant.

With $α(t)$ given by (17), the integral

$$\int_0^t α(t)dt = αt \left[ 1 + \left( \frac{αRN}{αTR} \right) \sqrt{\frac{π}{2}} \frac{1}{X} \left( 1 - \frac{2X}{\sqrt{π}} \right) \right],$$

(22)

which varies as $αRN[1 - 0(t^{1/2})]$ and as $αt[1 - 0(t^{-1/2})]$ at short and long times, respectively. Thus the decay law (21) is known exactly at all times. Note that the collisional quenching part of $n_A(t)$ decreases initially as $\exp(-αRNt)$ and after long times as $\exp[-α(∞)t]$, as expected.

The full transient fluorescence is governed by (21) and (22) which is capable of experimental verification for any fluorphor-quencher system in a gas or liquid medium.

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3$D$ is measured as constant when the electric-field intensity $E$ divided by the gas density $N ≤ 20 \times 10^{-17}$ cm$^2$ V$^2$, i.e., for a Coulomb attraction then $R ≥ S_m = (0.85N_L/N)^{1/2}(T/300)R_s$, where $N_L$ is $2.69 \times 10^{19}$ cm$^{-3}$.