

Chapter 2

Theory of Scavenging and Recombination Kinetics

2.1 Introduction

This chapter sets out to introduce the theory of diffusion kinetics and its implementation in the simulation packages used as part of this work. Diffusion is the movement of particles from regions of high concentrations to regions of lower concentrations, driven by a concentration gradient which approaches steady state at long times. It is driven by entropy and the second law of thermodynamics which results in Fick's law (*vide infra*). As the spatial distribution of particles is non-homogeneous in nature within a spur, the recombination kinetics cannot be described by conventional theories of homogeneous reactions. This has led to the development of new theories which are able to describe the time-dependent intra-spur reactions, and are discussed in detail in this chapter.

Following the radiolysis of the solvent, localised clusters of highly reactive particles are formed which have a non-uniform distribution. After a short period of time, the clusters of ions spread by diffusion to form a uniform distribution which can be characterised by homogeneous theories of chemical kinetics. However, before scavenging steady state conditions can be achieved there is a transient period whose lifetime varies as $a^2/(\pi D')$ where a is the encounter radius and D' the mutual diffusion coefficient.

In the subsections below, a detailed review of the theories which underlie the diffusive behaviour and the chemical kinetics for both neutral and charged species are now presented.

2.2 Homogeneous Kinetics

Theories of diffusion-controlled reactions were first studied by Smoluchowski [1, 2] and form the foundation of many standard theories today. Considering a simple bimolecular reaction between the species A and B of the form



where k_d is the second order rate constant to form the encounter pair AB^* , while k_{-d} and k_a are the first order rate constants for the dissociation of the encounter pair and formation of products respectively. The rate of change of the transient $[AB]$ with respect to time can be expressed as

$$\frac{d[AB]}{dt} = k_d[A][B] - (k_{-d} + k_a)[AB] \quad (2.2)$$

Using the steady state approximation such that $d[AB]/dt = 0$ (which is appropriate when the lifetime of the encounter pair is short on the timescale of the reaction so that the concentration of pairs remains very small), Eq. (2.2) reduces to the form

$$[AB] = \frac{k_d[A][B]}{(k_{-d} + k_a)} \quad (2.3)$$

with the experimentally observed rate constant being of the form

$$k_{\text{obs}} = \frac{k_d k_a}{(k_{-d} + k_a)} \quad (2.4)$$

If $k_a \gg k_{-d}$, then $k_{\text{obs}} \approx k_d$ and the reaction is said to be *diffusion controlled*, and k_{obs} depends only on the relative rate of diffusion of species A and B. If however, $k_{-d} \gg k_a$ then the reaction is said to be *activation controlled* as the species A and B must have enough energy to surpass the activation energy barrier (E_a) threshold. In an intermediate region, k_{-d} and k_a may become comparable, in which case the rate of reaction is dependent on both the rate of diffusion k_d and the rate of crossing E_a and is termed *partly diffusion controlled*.

2.2.1 Neutral Species in Solution

In this section the foundations of the theory underlying chemical kinetics are presented. Based on the diffusion equation to describe Brownian motion together with Smoluchowski's theory [1, 2], a thorough derivation of the bulk reaction rate constant for neutral species for both diffusion and partially diffusion controlled reactions is presented. This theory is then extended for charged species in subsequent sections.

2.2.1.1 Diffusion Controlled Reactions

In the absence of any intermolecular forces, the diffusion of species B is considered random and can be characterised by its diffusion coefficient, which according to the

Stokes-Einstein relation is inversely proportional to the solvent viscosity. However, in Smoluchowski theory this independence is extended to the frame of reference on the A as well; each B particle diffuses relative to the A particle with a mutual diffusion coefficient D' . The flux of B particles per unit area (\mathbf{J}_B) is known to be dependent on the gradient operator (∇c) with respect to the coordinates relative to the position of A and mutual diffusion through the relation

$$\mathbf{J}_B = -D'\nabla c \quad (2.5)$$

where c is the concentration of B particles. In the above formulation, the motion of B particles relative to A is assumed to be independent and the negative sign simply implies that the diffusive flow is in the direction of lower concentration. *Fick's first law of diffusion* is of the same form as Eq. (2.5) but does not involve these extra assumptions, and is used to describe the diffusion of species in real space not the relative diffusion of two species. Smoluchowski recognised that Fick's first law might also be applicable in relative space as well.

For a steady state reaction, the rate of flow of B particles through any sphere of radius r containing the A particle (with a concentration gradient $\partial c/\partial r$) is constant,¹ with the pseudo first order rate constant (ζ) given by the expression

$$\zeta = D'4\pi r^2 \frac{\partial c}{\partial r} \quad (2.6)$$

where it is assumed that the concentration of B reactants around any A reactant is spherically distributed. With this simplification, only the radial part of the diffusion equation needs to be considered without the need to explicitly take into account its angular dependence (this assumption is made throughout this section). Integrating the above equation gives

$$c(r) = c(\infty) - \frac{\zeta}{4\pi D'r} \quad (2.7)$$

and using the inner boundary condition such that $c(a) = 0$, (instantaneous reaction at the encounter distance a) gives the well known solution for the steady state rate constant to be

$$\begin{aligned} k(\infty) &= \frac{\zeta}{c(\infty)} \\ &= 4\pi D'a \end{aligned} \quad (2.8)$$

If the encountering particles are of the same species, then the above equation becomes $k(\infty) = 2\pi D'a$, which avoids double counting every pair of reactants. Before steady state conditions can arise there is a period of transient kinetics which must be properly

¹ This assumes that the stationary A particle is at the centre of the sphere.

taken into account. This is because initially the inward diffusion of species B does not balance the rate of reaction of B at A and consequently the concentration gradient dynamically changes. More formally stated, the flux of B particles towards A (J_{B1}) is less than the flux of B particles leaving the chemical system (J_{B2}) via reaction. From the law of conservation of matter, the difference between J_{B1} and J_{B2} results in a change in the concentration. Using Fick's first law together with mass balance, the rate of change of the concentration in one dimension can be formally expressed as

$$\begin{aligned}\frac{\partial c}{\partial t} &= -\frac{\partial}{\partial x} J_B \\ &= \frac{\partial}{\partial x} \left(D' \frac{\partial c}{\partial x} \right)\end{aligned}\quad (2.9)$$

In the above formulation, it is again assumed that the motion of B particles relative to A is independent. If D' is constant then Eq. (2.9) simplifies to

$$\frac{\partial c}{\partial t} = D' \frac{\partial^2 c}{\partial x^2} \quad (2.10)$$

which is recognisable as *Fick's second law of diffusion* in one dimension.² For diffusion in three dimensions, Fick's second law becomes

$$\frac{\partial c}{\partial t} = D' \nabla^2 c \quad (2.11)$$

which is the three dimensional diffusion equation (∇^2 being the Laplacian operator). For the case in which D' is not constant, Fick's second law must be modified to the form

$$\frac{\partial c}{\partial t} = \nabla \cdot (D' \nabla c) \quad (2.12)$$

Probability distribution of B around A Letting $[B]_{\text{avg}}(r, t)$ represent the average concentration of B particles around the surviving A particles (normalised to the bulk concentration $[B]_0$), the density distribution of B about A can be expressed as

$$\rho_B(r, t) = \frac{[B]_{\text{avg}}(r, t)}{[B]_0} \quad 0 \leq \rho_B \leq 1 \quad (2.13)$$

where r is the distance between an A and B particle. Rewriting Eq. (2.11) in terms of $\rho_B(r, t)$ and considering only the radial dependence of the diffusion equation, one arrives at the expression for the distribution of B about A to be

$$\frac{\partial \rho_B(r, t)}{\partial t} = D' \left\{ \frac{\partial^2 \rho_B}{\partial r^2} + \frac{2}{r} \frac{\partial \rho_B}{\partial r} \right\} \quad (2.14)$$

² This equation is known as the diffusion equation in one dimension.

with $2D'/r$ term modelling the drift of the two particles away from each other, which is a geometric feature in a three dimensional space (in two dimensional space this would be D'/r and in one dimension this would be zero). To solve Eq. (2.14), the initial condition required is of the form

$$\rho_B(r, 0) = \begin{cases} 0 & r \leq a \\ 1 & r > a \end{cases} \quad (2.15)$$

which simply states that at zero time particles A are removed by reaction when $r < a$ or are uniformly distributed around A if $r > a$. The two other boundary conditions required are $\rho_B(a, t) = 0$, which is simply reasserting that two species react instantly on encounter at t (commonly referred to as *totally absorbing boundary*), and $\rho_B(r \rightarrow \infty, t) = 1$ with $t \geq 0$, thus establishing that $[B]_{\text{avg}}(r, t)$ approaches the bulk concentration $[B]_0$ with increasing distance at all times. The solution to Eq. (2.14) is shown below, which can be obtained in a straightforward manner by using the Laplace transform method [3].

$$\rho_B(r, t) = 1 - \frac{a}{r} \operatorname{erfc} \left(\frac{r-a}{\sqrt{4D't}} \right) \quad (2.16)$$

The erfc term arising in the above equation is the complementary error function which is defined as

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt \quad (2.17)$$

It can be seen that at long times such that $t \rightarrow \infty$, Eq. (2.16) reduces to $\rho_B(\infty) = 1 - (a/r)$, which gives the steady state distribution of B particles around any A particle. The time variation of this density distribution is shown in Fig. 2.1, which shows that with a given D' , the return to steady state is more rapid for regions close to A.

Using the spherical symmetry of the concentration of B about A, the inward flux towards the A particle can be described using Fick's law as

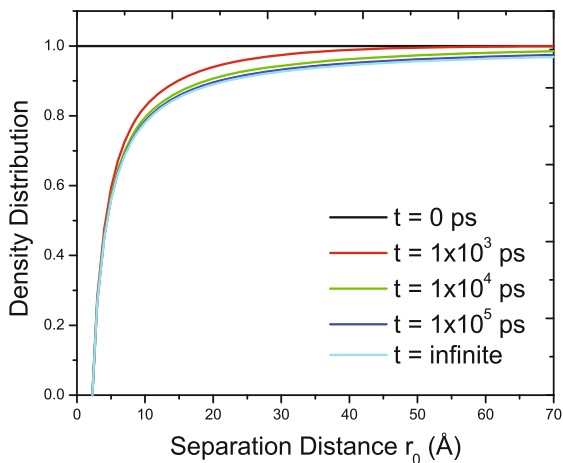
$$J_B(a) = D' \left. \frac{\partial [B]_{\text{avg}}}{\partial r} \right|_{r=a} = D' [B]_0 \left. \frac{\partial \rho_B}{\partial r} \right|_{r=a} \quad (2.18)$$

Differentiating Eq. (2.16) and taking the condition $r = a$ (i.e. at the reactive boundary), the magnitude of the flux at a can be written in the form

$$J_B(a) = D' [B]_0 \left(\frac{1}{a} + \frac{1}{\sqrt{\pi D't}} \right) \quad (2.19)$$

The rate of reaction is then simply the magnitude of the inward flux of the B particle across a sphere of radius a containing the A particle, which is $4\pi a^2 J_B(a)$. Thus the

Fig. 2.1 Density distribution of B species around an A species as a function of distance at five different time scales. $D' = 0.44 \text{ \AA}^2 \text{ ps}^{-1}$ and encounter distance $a = 2.2 \text{ \AA}$ (typical values for the $\cdot\text{OH} + \cdot\text{OH}$ reaction)



overall reaction rate is given by

$$[A][B]_0 4\pi a^2 D' \left[\frac{1}{a} + \frac{1}{\sqrt{\pi D' t}} \right] \quad (2.20)$$

with the second-order rate time dependent rate coefficient found to be

$$k(t) = 4\pi a D' \left(1 + \frac{a}{\sqrt{\pi D' t}} \right) \quad (2.21)$$

The units of the second-order rate constant are $\text{m}^3 \text{s}^{-1}$ and should be converted to the more commonly used units of $\text{M}^{-1} \text{s}^{-1}$ by introducing a multiplicative factor $10^3 N_A \text{ dm}^3 \text{ m}^{-3}$, where N_A is Avogadro's constant. Equation (2.21) shows that the time-scale of the transient period is given by $a/\sqrt{\pi D' t} \approx 1$; so for example using the parameters $a = 2.52 \text{ \AA}$ and $D' = 0.44 \text{ \AA}^2 \text{ ps}^{-1}$ (typical values for the $\text{OH} + \text{OH}$ reaction) gives a transient period of $\approx 4.5 \text{ ps}$. The transient period using these parameters is shown diagrammatically in Fig. 2.2. It should be noticed that the timescale of the transient period scales with the square of the encounter radius ($t = a^2/\pi D'$), highlighting the importance of the transient kinetics for chemical systems with larger reaction systems such as polymers and structures like micelles.

Problems with Smoluchowski theory Smoluchowski theory makes the assumptions such that: (1) the central particle A is fixed at the origin and (2) the central sink is indestructible. Many workers [4–6] have attempted to apply the theory where the central sink is destroyed by reaction or when the central A particle is not stationary. It is not immediately clear how the theory can describe either of these effects. The worst case scenario for Smoluchowski's theory is to consider the situation where the central A particle moves in a 'sea' of stationary B particles. Fixing on the frame of

Fig. 2.2 Transient period of the kinetics for the $\cdot\text{OH} + \cdot\text{OH}$ recombination in comparison with the steady state rate constant. The parameters used were $a = 2.52 \text{ \AA}$ (encounter radius) and $D' = 0.44 \text{ \AA}^2 \text{ ps}^{-1}$

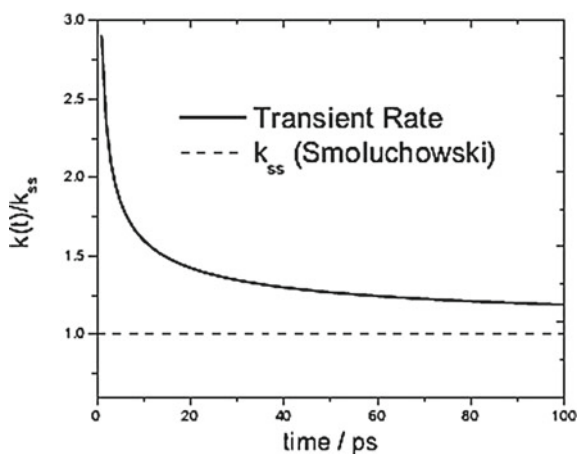
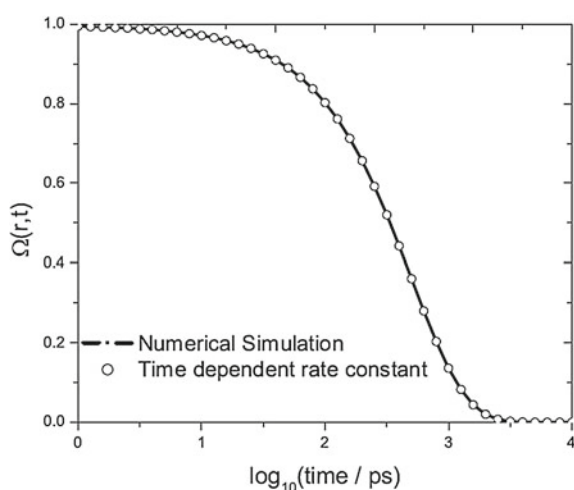


Fig. 2.3 Survival probability of a hydroxyl radical in a concentration of 1 M of scavengers. Encounter radius was 0.77 \AA and the mutual diffusion coefficient (D') set to $0.315 \text{ \AA}^2 \text{ ps}^{-1}$. Scavenging rate constant was $1.9 \times 10^{-3} \text{ M}^{-1} \text{ ps}^{-1}$



reference of the A particle, the relative movement of the B particles relative to A is *correlated*, whereas in Smoluchowski's theory the motion of the B particles is strictly *uncorrelated*. It is found that even with this neglect of the correlation between the A–B particles, the theory accurately predicts the survival probability of the A particle (as shown in Fig. 2.3), in comparison with numerical simulations, which treats the scavengers explicitly and takes into account the correlation of the B particles.

In the frame of reference of particle A, B particles diffusing into A are removed instantly by reaction, setting up a concentration gradient where inward diffusion balances reaction. Hence, the rate of reaction is equal to the rate of first encounter in solution, and the rate of flow into A is the rate of reaction per A molecule. In order to describe this from a theoretical point of view, one must set up a model of transport for Brownian motion. Although there are many models available (as discussed in

Sect. 2.3.4) currently the only solvable realistic model is the diffusion equation. From the viewpoint of spin dynamics, this theory is considered incomplete, since for a spin-controlled reaction the species are required to be in the correct spin state for reaction to occur. An alternative treatment for spin controlled reactions is presented later in this Sect. 2.7.1), which analytically treats re-encounters differently to first encounter and still retains the diffusion equation.

2.2.1.2 Partially Diffusion Controlled Reactions

Treating partially diffusion controlled reaction involves replacing the inner boundary condition such that $\rho_B(a, t) = 0$ with a radiation boundary condition [7] of the form

$$k_{\text{act}}\rho_B(a) = 4\pi a^2 D' \left. \frac{\partial \rho_B}{\partial r} \right|_{r=a} \quad (2.22)$$

where k_{act} is the second-order rate constant, describing the rate at which the particle crosses the activational energy barrier to react. The right hand side of Eq. (2.22) is simply Fick's first law describing the flux of B particles towards a single A particle. The radiation boundary condition assumes that the rate of reaction is proportional to the concentration of B particles at the encounter distance (a), where k_{act} is the constant of proportion. The relationship between k_{act} and the reactivity of the surface (v) can be expressed through the equation $k_{\text{act}} = 4\pi a^2 v$, with v having units of velocity. Both k_{act} and v are simply alternative ways of parameterising the boundary rate; however it is more convenient to use the parameter v , as (i) k_{act} is second order and (ii) the effect of the encounter radius is factored out on the overall reactivity.

The probability distribution of the B particles around the A particle using this boundary condition can be obtained using the Laplace transform technique to give [3]

$$\begin{aligned} \rho_B(r, t) = & 1 - \frac{a}{r} \frac{k_{\text{act}}}{k_{\text{act}} + 4\pi a D'} \times \left[\text{erfc} \left\{ \frac{r-a}{\sqrt{4D't}} \right\} \right. \\ & - \exp \left\{ \frac{(4\pi a D' + k_{\text{act}})(r-a)}{4\pi a^2 D'} \right\} \\ & \times \exp \left\{ \frac{(4\pi D'a + k_{\text{act}})^2 t}{(4\pi a^2)^2 D'} \right\} \\ & \left. \times \text{erfc} \left\{ \frac{4\pi a D' + k_{\text{act}}}{4\pi a^2 (D'/t)^{1/2}} + \frac{r-a}{\sqrt{4D't}} \right\} \right] \end{aligned} \quad (2.23)$$

where as before r is the separation distance of the A and B particle and D' is the mutual diffusion coefficient. As expected, for an infinitely fast reactivity boundary, it is seen that the solution reduces to Eq. (2.8) (Smoluchowski's totally absorbing boundary condition). Taking the limit $t \rightarrow \infty$, the steady state limit of $\rho_B(r, \infty)$ can be found to be

$$\rho_B(r, t \rightarrow \infty) = 1 - \frac{a}{r} \left[\frac{k_{\text{act}}}{k_{\text{act}} + 4\pi D'a} \right] \quad (2.24)$$

which shows that for a partially diffusion controlled reaction, there is a greater concentration of species B around A than what is predicted by Smoluchowski's totally absorbing boundary conditions.

The time dependent rate constant $k(t)$ may be written in the form $k(t) = k_{\text{act}}\rho_B(a, t)$, which simply states that the rate is proportional to the concentration of B particles around the A particles multiplied by the reactivity of the surface. The explicit form for $k(t)$ is then

$$k(t) = \frac{4\pi a D' k_{\text{act}}}{4\pi a D' + k_{\text{act}}} \left[1 + \frac{k_{\text{act}}}{4\pi a D'} \exp \left[\frac{D't}{a^2} \left(1 + \frac{k_{\text{act}}}{4\pi a D'} \right)^2 \right] \right. \\ \left. \times \operatorname{erfc} \left\{ \frac{\sqrt{D't}}{a} \left(1 + \frac{k_{\text{act}}}{4\pi a D'} \right) \right\} \right] \quad (2.25)$$

which can be simplified by using the asymptotic form such that $\lim_{x \rightarrow \infty} \exp(x^2) \operatorname{erfc}(x) = 1/x\sqrt{\pi}$ to give the rate at long times to be

$$k(t) = \frac{4\pi a D' k_{\text{act}}}{4\pi a D' + k_{\text{act}}} \left[1 + \frac{k_{\text{act}} a}{(4\pi D' a + k_{\text{act}})(\sqrt{\pi D' t})} \right] \quad (2.26)$$

For comparison with the diffusion controlled case, expressing Eq. (2.26) in the form of Eq. (2.21) gives

$$k(t) = 4\pi a'_{\text{eff}} D' \left[1 + \frac{a'_{\text{eff}}}{\sqrt{\pi D' t}} \right] \quad (2.27)$$

with the 'effective' encounter radius (a'_{eff}) defined as

$$a'_{\text{eff}} = a \left(\frac{k_{\text{act}}}{4\pi a D' + k_{\text{act}}} \right) \quad (2.28)$$

The steady state rate constant is then simply

$$k(\infty) = 4\pi a'_{\text{eff}} D' \quad (2.29)$$

It can be seen that within the steady state limit the encounter distance is reduced by a factor of $(k_{\text{act}} + 4\pi D'a)/k_{\text{act}}$ in comparison to Smoluchowski's totally absorbing boundary.

Equation (2.29) can be decomposed into two processes [8] as

$$k(\infty)_{\text{obs}}^{-1} = (k_{\text{diff}})^{-1} + (k_{\text{act}})^{-1} \quad (2.30)$$

which simply states that using the radiation boundary condition, the overall time required for species A and B to react involves: (i) the time required for diffusion [the first term in Eq. (2.30)] and (ii) time required to react once within this encounter distance [the second term in Eq. (2.30)]. If the condition $k_{\text{act}} \gg 4\pi a D'$ is true, then the rate limiting step is diffusion towards the boundary and in this instance reactions are said to be *diffusion controlled*. If the converse is true, such that $k_{\text{act}} \ll 4\pi a D'$, then reaction on the boundary is the rate determining step (*kinetic control*) and the rate can be approximated as

$$k(t) = k_{\text{act}} \left[1 + \frac{k_{\text{act}}}{4\pi a D'} \frac{a}{\sqrt{\pi D' t}} \right] \quad (2.31)$$

Problems with the radiation boundary Some of the problems with using the radiation boundary condition to model chemical systems have been discussed in the literature [9]. The most important of these are (1) for particles close to the encounter distance, it is not possible to specify a non-zero probability for reaction, since an infinite number of encounters follow an unsuccessful first encounter resulting in reaction (as shown by Collins and Kimball [7]). (2) Schell and Kapral [10] have shown that the probability of reaction on encounter should scale with the ratio of D' and a (D' is the mutual diffusion coefficient and a the encounter distance) for radiation boundary condition to be applicable. (3) All re-encounters are treated in the same manner.

Sometimes for a spin controlled reaction, the probability of reaction of first encounter has a physical origin, and if this first encounter is unreactive then the spin state is also unreactive, and therefore all subsequent rapid re-encounters will not react either [due to condition (3)]. The radiation boundary condition is clearly not appropriate to use for such reactions, where an appropriate model for spin dynamics is not incorporated.

Noyes [8], Wilemski and Fixman [11] have pointed out that it is not strictly correct to apply Smoluchowski [1] or radiation [7] boundary conditions to the diffusion equation to model bimolecular chemical reactions. Both Teramoto and Shigesada [12] and Wilemski and Fixman [11] have proposed a modified diffusion equation by introducing a sink term to represent the reaction rate at a set of relative phase-space coordinates of two reacting species. Let a simple diffusive process be described as

$$\frac{\partial \rho_B}{\partial t} - D' \nabla^2 \rho_B = -\frac{k}{4\pi a^2} \delta(r - a) \rho_B \quad (2.32)$$

with k being a second order rate constant, $\delta(x)$ the Dirac delta function and ∇^2 the Laplacian operator. Assuming spherical symmetry, Wilemski and Fixman [11] have shown that integrating Eq. (2.32) over the entire volume gives an expression for the rate of change for the total number (n) of unreacted particles to be

$$\frac{dn}{dt} = -k \rho_B(a, t) \quad (2.33)$$

where the term $\partial\rho_B/\partial t$ is required to vanish at the reactive surface a due to reaction. Integrating Eq. (2.32) again, but with $r \geq a + \epsilon$, Wilemski and Fixman [11] further obtain

$$\frac{dm}{dt} = -4\pi(a + \epsilon)^2 \left. \frac{\partial\rho_B}{\partial r} \right|_{r=a+\epsilon} \quad (2.34)$$

with m being the number of unreacted particles from a spherical surface of radius $a + \epsilon$, which is centered at the origin. By letting Eqs. (2.33) and (2.34) be equal and taking the limit $\epsilon \rightarrow 0$ (such that there is no surface extending from a), one retrieves the radiation boundary condition as given in Eq. (2.22). Clearly the radiation boundary is not appropriate to use if reaction is possible at multiple interparticle distances and one must instead use Wilemski and Fixman's method. Another important reason to use Wilemski and Fixman's method is that the Green's function can be more readily found (in comparison with the radiation boundary) which is described on the full configuration space, and can be used to solve the general diffusion equation.

2.2.2 Ions in Solution

In the analysis so far, it is assumed both particles A and B to be uncharged. If however, both the particles are now ions, the diffusion of B reactants about a given A particle has to be modified due to the drift exerted by the electrostatic forces. The steady state solution for both diffusion controlled and partially diffusion controlled reactions is now presented.

2.2.2.1 Diffusion Controlled Reactions

Diffusion controlled recombination of an ion pair is influenced by the random dispersive forces (also present for non-charged species) and the strong Coulombic electrostatic interactions. The diffusion equation [13, 14] governing the diffusive motion of charged species is known as the Debye-Smoluchowski equation [15], which can be expressed as

$$\frac{\partial\rho_B}{\partial t} = D'\nabla^2\rho_B + \frac{D'}{k_B T} \nabla \cdot (\rho_B \nabla U) \quad (2.35)$$

where as before ρ_B is the probability distribution of B about A, and U is the electrostatic potential energy at a separation r . The explicit form for U can be written as (in the absence of any screening potential)

$$U = \frac{k_B T z_i z_j r_c}{r} \quad (2.36)$$

with r_c representing the Onsager distance [14] (the distance at which the Coulombic interaction equals $k_B T$), which is defined as

$$r_c = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (2.37)$$

In Eqs. (2.36) and (2.37) $z_i e$ and $z_j e$ are the charges on ion i and j respectively, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the solvent, k_B is the Boltzmann constant and T is the temperature. The sign of r_c is important and it depends on whether the encountering pair are of the same charge (in which case $r_c > 0$) or of different charge (in which case $r_c < 0$). In the absence of any external field, the diffusion tensor and potential energy of interaction is assumed to be spherically symmetrical, so the diffusive motion becomes independent of angles ϕ and θ . Substituting the expression for U , the radial part of Eq. (2.35) becomes

$$\frac{\partial \rho_B}{\partial t} = D' \left[\frac{\partial^2 \rho_B}{\partial r^2} - \frac{\partial}{\partial r} \frac{(2r + r_c) \rho_B}{r^2} \right] \quad (2.38)$$

In the steady state limit ($\partial \rho_B / \partial t = 0$) Eq. (2.38) can be reduced to

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho_B}{\partial r} \right) - r_c \frac{\partial \rho_B}{\partial r} = 0 \quad (2.39)$$

which when integrated gives

$$\left(r^2 \frac{d \rho_B}{dr} \right) - \rho_B r_c = A \quad (2.40)$$

where A is the constant of integration. Using standard integration techniques together with boundary conditions $\rho_B(a, t) = 0$ and $\rho_B(r \rightarrow \infty, t)$, the expression for the steady state distribution of B about A is then

$$\rho_B(r, \infty) = \frac{1 - \exp\left(\frac{r_c}{a} - \frac{r_c}{r}\right)}{1 - \exp\left(\frac{r_c}{a}\right)} \quad (2.41)$$

Fick's first law in the presence of electrostatic forces can be written as

$$\mathbf{J}_B = D' \left[\nabla \rho_B + \frac{\rho_B}{k_B T} \nabla U \right] \quad (2.42)$$

which gives an expression for the steady state rate constant to be

$$k(\infty) = 4\pi a^2 D' \left[\frac{\partial \rho_B}{\partial r} + \frac{\rho_B(a, \infty)}{k_B T} \frac{dU}{dr} \right] \quad (2.43)$$

Using the derivative of Eq. (2.41) and substituting into Eq. (2.43) finally gives the steady state rate constant for ions to be

$$k(\infty) = 4\pi r_c D' \left[\exp\left(\frac{r_c}{a}\right) - 1 \right]^{-1}. \quad (2.44)$$

2.2.2.2 Partially Diffusion Controlled

Like the neutral case, the inner boundary condition must be replaced from Smoluchowski's condition to $\rho_B(a) = k_{\text{act}}\rho_B$. The required inner boundary condition for charged species then takes the form

$$4\pi a^2 D' \left[\nabla \rho_B + \frac{\rho_B}{k_B T} \nabla U \right]_a = k_{\text{act}} \rho_B \quad (2.45)$$

where the left hand side of Eq. (2.45) simply representing the diffusive flux across a sphere of radius a (with the A particle located at the centre). Upon solving with the required boundary conditions one obtains an expression for the steady state rate constant to be $k(\infty) = 4\pi a'_{\text{eff}} D'$, with a'_{eff} representing

$$a'_{\text{eff}} = r_c \left[\left(1 + \frac{4\pi r_c D'}{k_{\text{act}}} \right) \exp(r_c/a) - 1 \right]. \quad (2.46)$$

2.3 Diffusion as a Stochastic Process

2.3.1 Introduction

Until now diffusion has been treated as a macroscopic physical process driven by entropy, however, the diffusion equation implies a microscopic interpretation in terms of stochastic trajectories. Since much of the work in this thesis uses and develops simulation methods at this microscopic level, it is necessary to introduce the fundamental concepts of this theory.

Markov process A stochastic process is a random process in which the evolution from a state $X(t_n)$ to $X(t_{n+1})$ is indeterminate (i.e. governed by the laws of probability) and can be expressed by a probability distribution function. Diffusion can be classified as a stochastic process in a continuous state space (τ) possessing the *Markov property* as

$$\begin{aligned} P(X(t_{n+1}) \in \tau | X(t_1) = x_1, X(t_2) = x_2, \dots, X(t_n) = x_n) \\ = P(X(t_{n+1}) \in \tau | X(t_n) = x_n) \end{aligned} \quad (2.47)$$

In diffusion terms of a stochastic process, the above equation simply states that the future trajectory of a particle is independent of the trajectory the particle followed to reach its current state.

Strong markov process For a diffusion process, the Markov property can be extended to a sequence of random times known as the *strong Markov property* and can be expressed as follows: let $T_n, n = 1, 2, \dots$ be an increasing sequence of stopping times³ for the process $X(t_n), n \geq 0$, and suppose $X(T) = x_n$; the Markov chain $X(T_{n+1}), X(T_{n+2}), \dots, X_{T+n}$ behaves as if the process had started anew at $X(T_n) = x_n$, and is independent of the Markov chain of events $X(T_1), \dots, X(T_{n-1})$. It should be noticed that a Markov process does not necessarily obey the strong Markov property because of subtle links between the random times. The converse is however true.

Time homogeneous process Finally a diffusion process is time-homogeneous in that the process is independent of the time origin. This can be written more formally as

$$P((X(T_n) = x_n) | X(T_{n-1}) = x_{n-1}) = P(X(T_n - T_{n-1}) = x_n | X(0) = x_{n-1}) \quad (2.48)$$

which simply states that the diffusion process starts afresh, and that the new position x_n only depends on the elapsed time since the most recently specified position x_{n-1} . A diffusion process is only time homogeneous if it obeys the above property. Not all diffusion process obey this property such as a conditioned diffusion process, where the time origin is of significant importance.

2.3.2 One Dimensional Diffusion Process

The mathematical model of a one dimensional diffusion is the Wiener process (W_t), which satisfies the following three conditions: (1) $W_0 = 0$, (2) W_t is continuous with independent increments and (3) the trajectory of $[W_{t+\delta t} - W_t]$ can be sampled from a normal distribution with mean (μ) of zero and variance (σ^2) of δt (strong Markov property).

A Wiener process has the additional property $\mathbb{E}(X(t_{n+1}) | X_1 \dots X(t_n) = X(t_n))$ i.e. the expectation value for a future event X_{n+1} , conditioned on it having evolved to $X(t_n)$ is $\mathbb{E}[X(t_n)]$ and no information is needed regarding any previous or future events. In diffusion terms of a stochastic process, this means that the expectation value of a new position of the particle at $X(t_{n+1})$ is equal to its position at $X(t_n)$ and is known as the *martingale property*.

More generally, a diffusion process from a state $X(t)$ to $X(t + \delta t)$ of a particle in one dimension can be characterised by two parameters, namely μ representing the

³ T is said to be a stopping time for the sequence $\{X(t_i)\}$, if the event $\langle X(T) = n \rangle$ is independent of $X(T_{n+1}), X(T_{n+2}), X(T_{n+3}) \dots$ for $n = 1, 2, \dots$

mean (drift) and σ^2 representing the variance (dispersion)

$$\begin{aligned}\mu &= \lim_{\delta t \rightarrow 0} \frac{\mathbb{E}(\delta X)}{\delta t} \\ \sigma^2 &= \lim_{\delta t \rightarrow 0} \frac{\mathbb{E}(\delta X^2)}{\delta t}\end{aligned}\quad (2.49)$$

All higher moments are zero for a diffusion process. The stochastic differential equation [16] which governs the change in the particle's position (dX) in an infinitesimal time space (dt) is well known to be

$$dX = \mu dt + \sigma dW_t \quad (2.50)$$

with dW_t representing the random increment of the standard Wiener process over the time interval dt . Analytical solution in terms of stochastic process that can be sampled exactly is only possible in some cases; where this is not possible, numerical simulations become necessary. There are many discretisation methods available [17], with the simplest being the Euler method (which is adopted for the purposes of this work). The solution to Eq. (2.50) is only possible when dt is infinitesimal, and must be approximated by time discretisation, which replaces dX and dt in Eq. (2.50) with δX and δt . Using the definition of a Wiener process [condition (3)], dW_t can be replaced with a normally distributed random variable with $\mu = 0$ and $\sigma = \delta t$ giving

$$\delta X = \mu \delta t + \sigma \sqrt{\delta t} N(0, 1) \quad (2.51)$$

For the Wiener process the transition density on going from a state x_0 to y is a simple Gaussian of the form

$$p(x_0, y, t) = \frac{1}{\sigma \sqrt{2\pi t}} \exp \left[-\frac{(y - x_0 - \mu t)^2}{2\sigma^2 t} \right] \quad (2.52)$$

A Wiener process $\{X(t), t \geq 0\}$ with $X(0) = 0$, $\mu = 0$ and $\sigma = 1$ is commonly referred to as the *standard Wiener process*. Using this transition density, both the *forward* and *backward* equations (see Sect. 2.3.2.1 for a detailed explanation) can be derived, for which Eq. (2.52) is a solution [18].

2.3.2.1 Kolmogorov Diffusion Equation

Defining $p(x, y, t)$ as the probability (or more formally the transition density) of the particle diffusing from position x to y at a given time t , Kolmogorov [13] (and later by Cox and Miller [19]) has shown that $p(x, y, t)$ satisfies Eqs. (2.53) and (2.54), formally known as the Kolmogorov forward and backward equations [13].

Forward equation:

$$\frac{\partial p}{\partial t} = \frac{\partial^2}{\partial y^2} \left(\frac{\sigma^2(y)p}{2} \right) - \frac{\partial}{\partial y} (\mu(y)p) \quad (2.53)$$

Backward equation:

$$\frac{\partial p}{\partial t} = \frac{1}{2} \sigma^2(x) \frac{\partial^2 p}{\partial x^2} + \mu(x) \frac{\partial p}{\partial x} \quad (2.54)$$

In the language of applied maths, $p(x, y, t)$ is the Green's function for the diffusion process. It is important to note that in the forward equation, differentiation is carried out with respect to y (the current position) and with respect to x (the initial position) in the backward equation. In the simulation of chemical systems, the drift term (μ) arising in Kolmogorov's equation is normally due to the Coulombic interaction between charged species and can be expressed as

$$\mu(x) = -\frac{D'}{k_B T} \frac{\partial U}{\partial x} \quad (2.55)$$

with D' being the diffusion coefficient, k_B the Boltzmann constant, T the temperature and U the potential energy. If D' does not depend on either the position or time, then Eqs. (2.53) and (2.54) can be rewritten as the one dimensional Debye-Smoluchowski equation with variance $2D'$ as

Forward equation:

$$\frac{\partial p}{\partial t} = D' \frac{\partial^2 p}{\partial y^2} + \frac{D'}{k_B T} \frac{\partial}{\partial y} \left(p \frac{\partial U}{\partial y} \right) \quad (2.56)$$

Backward equation:

$$\frac{\partial p}{\partial t} = D' \frac{\partial^2 p}{\partial x^2} - \frac{D'}{k_B T} \frac{\partial U}{\partial x} \frac{\partial p}{\partial x} \quad (2.57)$$

If both D' and μ are constant then Eq. (2.53) can be re-expressed in the form

$$\frac{\partial p}{\partial t} = D' \frac{\partial^2 p}{\partial y^2} - \mu \frac{\partial p}{\partial y} \quad (2.58)$$

In order to numerically solve the stochastic differential equation, the constraint that μ is constant is made, which is satisfactory so long as the time steps used in the simulation remain sufficiently small during interval t and $t + \delta t$. The solutions to Eq. (2.58) has been done by Kolmogorov [13] using different boundary conditions. Due to the extensive use of these Greens' functions in the simulation packages, they have been reproduced below using the four most common boundary conditions.⁴

⁴ Proof of these are shown in the Appendix in Sects. A.4–A.7.

2.3.2.2 Transition Density with No Boundary

$$p(x, y, t) = \frac{1}{\sqrt{4\pi D't}} \exp \left[-\frac{(y - x - \mu t)^2}{4D't} \right]. \quad (2.59)$$

2.3.2.3 Transition Density with a Reflecting Boundary

Boundary condition

$$D' \frac{\partial p}{\partial y} \Big|_a - \mu p(a) = 0 \quad (2.60)$$

$$\begin{aligned} p_{\text{ref}}(x, y, t) = & \frac{1}{\sqrt{4\pi D't}} \exp \left[-\frac{(y - x - \mu t)^2}{4D't} \right] \\ & + \frac{1}{\sqrt{4\pi D't}} \exp[-\mu(x - a)/D'] \exp[-(y + x - \mu t - 2a)^2/4D't] \\ & + \frac{\mu}{2D'} \exp[\mu(y - a)/D'] \text{erfc}[(x + y + \mu t - 2a)/\sqrt{4D't}]. \end{aligned} \quad (2.61)$$

2.3.2.4 Transition Density with an Absorbing Boundary

Boundary condition

$$p(a) = 0 \quad (2.62)$$

$$\begin{aligned} p_{\text{abs}}(x, y, t) = & \frac{1}{\sqrt{4\pi D't}} \left(\exp \left[-\frac{(y - x - \mu t)^2}{4D't} \right] \right) \\ & - \frac{1}{\sqrt{4\pi D't}} (\exp[\mu(a - x)/D'] - \exp[-(y + x - \mu t - 2a)^2/4D't]). \end{aligned} \quad (2.63)$$

2.3.2.5 Transition Density with a Radiation Boundary

Boundary condition

$$D' \frac{\partial p}{\partial y} \Big|_a - \mu p(a) = v p(a) \quad (2.64)$$

Recalling v to measure the reactivity of the surface which has units of velocity, the solution is given as

$$\begin{aligned}
p_{\text{rad}}(x, y, t) = & \frac{1}{\sqrt{4\pi D't}} \exp\left[-\frac{(y-x-\mu t)^2}{4D't}\right] \\
& + \frac{1}{\sqrt{4\pi D't}} \exp[-\mu(y-a)/D'] \exp[-(y+x-\mu t-2a)^2/4D't] \\
& + \frac{2v+\mu}{2D'} \exp[v(x+y+\mu t-2a+vt) + \mu(y-a)/D'] \\
& \times \operatorname{erfc}\left(\frac{x+y-2a+(2v+\mu)t}{\sqrt{4D't}}\right). \tag{2.65}
\end{aligned}$$

2.3.3 Three Dimensional Diffusion

To model diffusion in three dimensions, the stochastic differential equation must be modified to the form

$$d\mathbf{r} = \boldsymbol{\mu}dt + \sigma\sqrt{dt}\mathbf{N}(0, 1) \tag{2.66}$$

with $\boldsymbol{\mu}$ being the drift vector equalling to $D\mathbf{F}/k_{\text{B}}T$ if the species are charged (in this expression D is the diffusion coefficient, \mathbf{F} the external force on the particle, k_{B} the Boltzmann constant and T the temperature). In three dimensional space, Kolmogorov's backward equation becomes

$$\frac{\partial p}{\partial t} = D'\nabla_x^2 p - \frac{D'}{k_{\text{B}}T} \nabla_x U \cdot \nabla_x p \tag{2.67}$$

with the adjoint forward equation taking the form

$$\frac{\partial p}{\partial t} = D'\nabla_y^2 p + \frac{D'}{k_{\text{B}}T} \nabla_y \cdot (p\nabla_y U). \tag{2.68}$$

2.3.4 Other Models of Molecular Motion

The modelling of Brownian motion for molecules in liquids is by no means limited to the Kolmogorov diffusion equation. There are many alternative algorithms available, which make use of the velocity and the force to explicitly calculate the trajectory of the particles. In this section, a brief discussion of the three most commonly used simulations in radiation chemistry are presented. A much more detailed explanation can be found in the references provided.

Molecular dynamics The most successful model which is able to describe molecular motion is molecular dynamics [20–23]. The foundation of molecular dynamics relies on the particles interacting using a predefined potential energy function, which itself is usually calculated from experimental data. The particles move according to the

laws of classical dynamics by integrating Newton's equations of motion. One of the most important functions which can be obtained from this type of simulation is the velocity autocorrelation function (χ) for a single particle, defined as

$$\chi = \frac{\langle \mathbf{v}_c(0) \cdot \mathbf{v}_c(t) \rangle}{\langle \|\mathbf{v}_c(0)\|^2 \rangle} \quad (2.69)$$

with $\mathbf{v}_c(0)$ being the initial velocity and $\mathbf{v}_c(t)$ the velocity at time t . Through the use of the Green-Kubo relation [24, 25], χ can be related to the diffusion coefficient as

$$D = \frac{1}{3} \int_0^\infty \langle \mathbf{v}_c(t) \cdot \mathbf{v}_c(0) \rangle dt \quad (2.70)$$

Unfortunately, molecular dynamics are computationally very expensive which makes simulating radiation kinetics very difficult. This problem is further compounded by the necessity to perform many realisations to obtain statistically significant results; something which is not practical at present. In order to solve the ordinary differential equations of motion to generate a trajectory, a range of finite different methods are available (for example the velocity Verlet algorithm [26]).

Langevin equation Although molecular motion can be entirely described using molecular dynamics, it does have the disadvantages of requiring small time steps and the necessity to model the solvent molecules explicitly. The Langevin equation [27] helps to circumvent these problems to a certain degree. Using Newton's second law of motion, the rate of change of the velocity for a single particle can be described using the relation

$$\frac{dv_c(t)}{dt} = -\frac{\gamma_F v_c(t)}{m} + \frac{1}{m} \xi'(t) \quad (2.71)$$

with $v_c(t)$ being the velocity, m the mass, γ_F the friction coefficient as given by Stokes law and $\xi'(t)$ a stochastic variable representing the collision between the particle and the solvent. The change in the particle's displacement is then simply

$$\frac{dx}{dt} = v_c(t) \quad (2.72)$$

Equation (2.71) is a linear equation whose solution is elementary such that

$$v_c(t) = e^{-t/\tau} v_c(0) + \frac{1}{m} \int_0^t e^{-(t-s)/\tau} \xi'(s) ds \quad (2.73)$$

with $\tau = m/\gamma_F$. The integral in the above equation gives an 'extra' velocity produced by the random noise to prevent the velocity decaying to zero. Unfortunately, $\xi'(s)$ is a fluctuating function and it is not obvious whether any global solution to

Eq. (2.71) exists unless stronger conditions to $\xi'(s)$ are imposed. It can be shown that $\xi'(s)ds$ possesses the properties of a Wiener process $d\mathbf{W}$, which when substituted into Eq. (2.71) gives the stochastic differential equation of the form

$$d\mathbf{v}_c(t) = \frac{\gamma_F}{m}\mathbf{v}(t)dt + \frac{1}{m}d\mathbf{W} \quad (2.74)$$

with the solution to the above equation readily found to be

$$\mathbf{v}_c(t) = e^{-t/\tau} \mathbf{v}_c(0) + \frac{1}{m} \int_0^t e^{-(t-s)/\tau} d\mathbf{W} \quad (2.75)$$

where $\mathbf{v}_c(0)$ is the initial velocity of the particle. The expression for the variance in the velocity is then

$$\langle v_c^2(t) \rangle_{\text{eq}} = \frac{k_B T}{m} \left(1 - \exp\left(-\frac{2\gamma_F}{m}t\right) \right) + v_c^2(0) \exp\left(-\frac{2\gamma_F}{m}t\right) \quad (2.76)$$

where k_B is Boltzmann's constant and T the temperature. The solution for the variance in the position involves multiplying Eq. (2.71) by x and taking the ensemble average. Letting $u = d\langle x^2 \rangle/dt$, Eq. (2.71) can be re-written as⁵

$$\frac{m}{2} \frac{du}{dt} + \frac{\gamma_F}{2} u = k_B T \quad (2.77)$$

The general solution can be readily calculated to be

$$u = C e^{-\gamma_F t/m} + 2 \frac{k_B T}{\gamma_F} \quad (2.78)$$

with C being the constant of integration, which equals to $k_B T/\gamma$. Using the solution for u , the expression for $\langle x^2 \rangle$ finally gives

$$\langle x^2(t) \rangle = \frac{2k_B T m}{\gamma_F^2} \left[\frac{t\gamma_F}{m} - \left(1 - \exp\left(-\frac{t\gamma_F}{m}\right) \right) \right]. \quad (2.79)$$

Fokker-Planck equation The Langevin equation describes the Brownian motion of a single particle which experiences a random force (due to collisions with the solvent particles) causing the velocity to behave in a stochastic way. The Fokker-Planck equation (also known as Kolmogorov forward equation) extends the Langevin equation to an ensemble of identical Brownian particles by finding the probability distribution $P(v, t)$ of N particles in the ensemble having velocities in the interval $(v, v + \delta t)$ at time t . The Fokker-Planck equation can be formally expressed as

⁵ It should be recognised that $\langle \dot{x}x \rangle = \frac{1}{2} \frac{dx^2}{dt}$ and $\langle \ddot{x}x \rangle = \frac{1}{2} \frac{d^2x^2}{dt^2} - u^2$.

$$\frac{\partial}{\partial t} P(v_c, t) = \gamma_F \frac{\partial}{\partial v_c} (v_c P(v_c, t)) + \frac{k_B T \gamma_F}{m} \frac{\partial^2}{\partial v_c^2} P(v_c, t) \quad (2.80)$$

The steady state solution to the Fokker-Planck equation can be readily found to be

$$P(v) = \left(\frac{\gamma_F}{\pi Q} \right)^{1/2} \exp \left(-\frac{\gamma_F v_c^2}{Q} \right) \quad (2.81)$$

with $Q = 2\gamma_F k_B T / m$ which describes the strength of the stochastic force. The time dependence of $P(v_c, t)$, subject to the initial condition $P(v_c, t_0) = \delta(v_c(t) - v_c(0))$ can be obtained using the method of Fourier transformation. A full derivation is not presented here, but can be found elsewhere [28]. The final result yields

$$P(v, t) = \sqrt{\frac{\gamma_F}{\pi Q [1 - \exp[1 - 2\gamma_F(t - t_0)]]}} \exp \left[-\frac{\gamma_F [v_c(t) - v_c(0) \exp[-\gamma_F(t - t_0)]]^2}{Q [1 - \exp[-2\gamma_F(t - t_0)]]} \right] \quad (2.82)$$

Diffusion model used in this work For the purpose of this work the evolution of the particle position is described in terms of the stochastic differential equation. The major problem with using this technique is that the particle velocity cannot be described (since the diffusion sample paths are nowhere differentiable). The central limit theorem does however provide the reassurance that the diffusion equation accurately describes evolution of the transition density. For all chemical systems investigated as part of this work, the transient period occurs on a timescale of tens of picoseconds or possibly even longer. This value is much bigger than typical values of the velocity autocorrelation function, making the use of the diffusion equation justifiable.

2.4 Geminate Recombination

In diffusion controlled kinetics, two different types of reactions can take place, namely geminate recombination and bulk reactions. Geminate recombination arises in isolated spurs, before any significant diffusion has taken place and entails the reaction between isolated pairs of A and B particles. In this case it becomes meaningless to define their concentration. For geminate recombination, the survival probability $\Omega(r, t)$ (or its complement $W(r, t)$), which is the probability of surviving reaction to a time t , given an initial separation r , is one of the most important physical quantities in radiation chemistry.

In this section, the solution to the backward diffusion equation for $\Omega(r, t)$ using two different types of boundary conditions for both neutral and charged species is presented. These solutions will then be used in the next section to demonstrate the link between the bulk reaction rate and the pair survival probability. Before presenting

the discussion, it is worth noticing why $\Omega(r, t)$ (and by extension $W(r, t)$) obeys only the backward diffusion equation rather than the forward diffusion equation.

The expression relating $\Omega(r, t)$ and $p(x, y, t)$ is given by

$$\Omega(r, t) = \int_a^\infty p(x, y, t) dy \quad (2.83)$$

which simply states that the probability of survival is an integral of the probability density function for the interparticle distance up to time t . This integral involves the variable y , so the backward diffusion equation is not affected. However, upon integrating the forward equation one obtains

$$\frac{\partial \Omega}{\partial t} = \left[\frac{\partial}{\partial y} \left(\frac{1}{2} \sigma^2(y) p(x, y, t) \right) - \mu(y) p(x, y, t) \right]_a^b \quad (2.84)$$

which simply states that the rate of reaction is proportional to the diffusive flow over the two boundaries (essentially Fick's law). This is not an expression for the survival probability.

2.4.1 Diffusion Controlled Reactions

2.4.1.1 Neutral Species

In order to find the expression for the reaction probability of two neutral particles it is necessary to return to the backward diffusion equation

$$\frac{\partial W}{\partial t} = D' \left[\frac{\partial^2 W}{\partial r^2} + \frac{2}{r} \frac{\partial W}{\partial r} \right] \quad (2.85)$$

with r being the separation of the pair and W is the reaction probability. Assuming spherical symmetry together with the boundary conditions⁶

$$W(a, t) = 1 \quad (t > 0) \quad (2.86)$$

$$W(r \rightarrow \infty, t) = 0 \quad (2.87)$$

$$W(r, 0) = 0 \quad (r > a) \quad (2.88)$$

the solution to Eq. (2.85) can be found using the Laplace transform method to give

⁶ These boundary conditions are equivalent to Smoluchowski's boundary conditions as discussed earlier.

$$W(r, t) = \frac{a}{r} \operatorname{erfc} \left(\frac{r - a}{\sqrt{4D't}} \right) \quad (2.89)$$

where a is the encounter radius and D' is the mutual diffusion coefficient. The reaction probability $W(r, t)$ is the complement of the survival probability $\Omega(r, t)$ so Eq. (2.89) can be easily reformulated in terms of the survival probability using the relationship $\Omega(r, t) = 1 - W(r, t)$. The asymptotic recombination yield is then easily seen to be

$$W(r, \infty) = \frac{a}{r} \quad (2.90)$$

2.4.1.2 Charged Species

The time-dependent backward diffusion equation for the reaction probability of ions [29, 30] is known to be

$$\frac{\partial W}{\partial t} = D' \left[\frac{\partial^2 W}{\partial r^2} + \frac{(2r + r_c)}{r^2} \frac{\partial W}{\partial r} \right] \quad (2.91)$$

where r_c is the Onsager distance. In order to solve the above diffusion equation, it is necessary to impose some boundary conditions. Assuming the reaction between the species to be diffusion controlled with an absorbing boundary at a (the encounter distance), the required boundary conditions remain the same as shown in Eqs. (2.86)–(2.88). Unfortunately, Eq. (2.91) cannot be solved in closed form with several attempts detailed in the literature which aim to provide an approximate solution [31–37]. The most rigorous of these is the solution obtained by Hong and Noolandi [38], however, the solution is exact only in the Laplace space and cannot be inverted analytically. From their formulation, the survival probability (at long times) is found to be

$$\Omega(t) = [U(r)/U(\infty)] \left(1 + \frac{r_c}{U(\infty)\sqrt{\pi D't}} \right) \quad (2.92)$$

where r is the radical pair separation and $U(r) = \exp(-r_c/r) + (D'r_c/va^2 - 1) \exp(-r_c/a)$ (with r , a and v representing the distance between the ion pair, the encounter radius and reaction velocity respectively). Taking the inverse Laplace transform of Hong and Noolandi's expression (or in general the inverse Laplace transform of any expression) is notoriously numerically unstable. A much better method [39] is to use a numerical solution to the partial differential equation using a standard finite difference method, which is certain to be unconditionally stable.

For high permittivity solvents (when r_c is small), Clifford et al. [32] have obtained an approximate time dependent solution for $W(r, t)$ as

$$W(r, t) = \left(\frac{a'_{\text{eff}}}{r_{\text{eff}}} \right) \operatorname{erfc} \left(\frac{r_{\text{eff}} - a'_{\text{eff}}}{\sqrt{4D't}} \right) \quad (2.93)$$

with the asymptotic form for the reaction probability being

$$W(r, \infty) = \frac{a'_{\text{eff}}}{r_{\text{eff}}} \quad (2.94)$$

In the above expression, r_{eff} and a'_{eff} are defined to be $r_c/(\exp(r_c/r) - 1)$ and $r_c/(\exp(r_c/a) - 1)$ respectively, and are referred to as the natural distance scale for the radial process.

For low permittivity solvents Green et al. [31] have developed an excellent approximation for the reaction probability as

$$W^*(x, a, \tau) \approx \frac{1}{2} \text{erfc} \left(\frac{(x - y)}{\sqrt{2} \left(s(\tau_y)^2 - s(\tau_a)^2 \frac{\tau'_a}{\tau_y^2} \right)^{1/2}} \right) \quad (2.95)$$

with the variables in the above equation defined to be

$$x = \frac{2r}{r_c} \quad (2.96)$$

$$y = \left[6((\tau + \tau_a)^{1/3} - \frac{1}{7}[6(\tau + \tau_a)]^{2/3} \right] \quad (2.97)$$

$$\tau_x = \frac{1}{6} \left[\frac{7}{2} (1 - \sqrt{(1 - 4x/7)}) \right]^3 \quad (2.98)$$

$$\tau'_x = \frac{\frac{1}{2} \left[\frac{7}{2} (1 - \sqrt{(1 - 4x/7)}) \right]^2}{\sqrt{(1 - 4x/7)}} \quad (2.99)$$

$$s^2 = \frac{6\tau}{7} \quad (2.100)$$

where $\tau = 4D't/r_c^2$. Unfortunately, the approximation breaks down if τ is sufficiently large because the normal distribution has a significant part of its density on the wrong side of the reflecting boundary at the origin. This situation arises at longer times because the standard deviation s increases faster than the mean (defined as $m = (6\tau)^{1/3} - (6\tau)^{2/3}/7$). However, in Sect. 4.4.4.1, it will be shown how this error can be partially corrected. The corresponding unconditioned reaction probability can be found using Eq. (2.95) through the relation

$$W(x, a, \tau) = W(x, \infty, \tau) \times W^*(x, a, \tau) \quad (2.101)$$

Using the perturbation treatment [38, 40] for small r and large t , Tachiya [4] has found an approximate expression for $\Omega(r, t)$ as

$$\Omega(r, t) = \frac{e^{-(r_c/r)} - e^{-(r_c/a)}}{1 - e^{-(r_c/a)}} \left[1 + \frac{1}{1 - e^{-(r_c/a)}} \times \frac{r_c}{\sqrt{\pi D' t}} \right] \quad (2.102)$$

with the asymptotic expression for the survival probability found to be

$$\Omega(r, \infty) = \frac{e^{-(r_c/r)} - e^{-(r_c/a)}}{1 - e^{-(r_c/a)}} \quad (2.103)$$

which is the same as that obtained by Clifford et al. [32] [i.e. Eq. (2.94)].

2.4.2 Partially Diffusion Controlled Reactions

2.4.2.1 Neutral Species

As mentioned previously, for partially diffusion controlled reactions the reactivity of the inner boundary can be controlled using the parameter v which has units of velocity. The required inner boundary condition is of the form

$$\left. \frac{\partial \Omega}{\partial r} \right|_{r=a} = \frac{v}{D'} \Omega(a) \quad (2.104)$$

with the outer and initial conditions taking the form

$$\Omega(r \rightarrow \infty, t) = 1 \quad (2.105)$$

$$\Omega(r, 0) = 1 \quad (r > a) \quad (2.106)$$

Using the above boundary conditions, the expression for the survival probability in the absence of any interaction potential can be found to be

$$\begin{aligned} \Omega(r, t) = 1 - \frac{a}{\left(1 + \frac{D'}{va}\right)} & \left(\operatorname{erfc} \left(\frac{r-a}{\sqrt{4D't}} \right) \right. \\ & - \exp \left[\left(\frac{va}{D'} + 1 \right) \left(\frac{r-a}{a} \right) + \left(\frac{vr}{D'} + 1 \right)^2 \left(\frac{D't}{a^2} \right) \right] \\ & \times \operatorname{erfc} \left[\frac{r-a}{\sqrt{4D't}} + \left(\frac{va}{D'} + 1 \right) \frac{\sqrt{D't}}{a} \right] \Bigg) \end{aligned} \quad (2.107)$$

with the asymptotic form of the above to be

$$\Omega(r, \infty) = \frac{1 - (a/r) + (D'/va)}{1 + (D'/va)} \quad (2.108)$$

2.4.2.2 Charged Species

Using the perturbation treatment [38, 40] for small r and large t , together with the boundary conditions given in Eqs. (2.104)–(2.106), Tachiya [4] has arrived at an approximate expression for the survival probability as

$$\Omega(r, t) = \frac{e^{-(r_c/r)} + (\eta - 1) e^{-(r_c/a)}}{1 + (\eta - 1) e^{-(r_c/a)}} \times \left[1 + \frac{1}{1 + (\eta - 1) e^{-(r_c/a)}} \times \frac{r_c}{\sqrt{(\pi D' t)}} \right] \quad (2.109)$$

where $\eta = D' r_c / v a^2$. As expected the above equation decomposes to Eq. (2.102) in the limit $v \rightarrow \infty$. The asymptotic form for the survival probability is then readily found to be

$$\Omega(r, \infty) = \frac{e^{-(r_c/r)} + (\eta - 1) e^{-(r_c/a)}}{1 + (\eta - 1) e^{-(r_c/a)}} \quad (2.110)$$

which unfortunately diverges for short times. A much better approximation has been developed by Green et al. [41], which provides the same asymptotic form as Tachiya's expression, however the function is not divergent for short times. Green et al. [41] solved the backward diffusion equation subject to the inner boundary condition

$$\left. \frac{\partial W}{\partial r} \right|_{r=a} = -\frac{v}{D'} [1 - W(a)] \quad (2.111)$$

with the other boundary conditions given by Eqs. (2.87) and (2.88). The expression for the time-dependent reaction probability was found to be

$$W(r, t) \approx \frac{a'_{\text{eff}}}{r_{\text{eff}}(1 + \delta)} [\text{erfc}(\alpha) + \exp(2\alpha\beta + \beta^2) \text{erfc}(\alpha + \beta)] \quad (2.112)$$

with α , β and δ defined to be

$$\alpha = \frac{r_{\text{eff}} - a'_{\text{eff}}}{\sqrt{4D't}} \quad (2.113)$$

$$\delta = \frac{D' a'_{\text{eff}} e^{r_c/a}}{v a^2} \quad (2.114)$$

$$\beta = (1 + 1/\delta) \frac{\sqrt{D't}}{a'_{\text{eff}}} \quad (2.115)$$

and r_{eff} and a'_{eff} are defined to be $(r_c/\exp(r_c/r) - 1)$ and $(r_c/\exp(r_c/a) - 1)$ respectively. In the limit $v \rightarrow \infty$ Eq. (2.112) reduces to Eq. (2.93) which is to be expected since the surface reactivity is now infinitely fast.

2.5 Bulk Recombination Rate Constant

Bulk reaction is the reaction between two particles, say A and B which are uniformly distributed in the chemical system. In this situation it becomes necessary to define the concentrations c_A and c_B of both species. In this section the bulk reaction rate is derived in terms of the pair survival probability and it is demonstrated how Smoluchowski's time dependent rate constant can be obtained by making use of the independent pairs approximation.

In general the bulk reaction rate k is proportional to both c_A and c_B as

$$-\frac{dc_A}{dt} = -\frac{dc_B}{dt} = kc_Ac_B \quad (2.116)$$

and as previously shown in this work, the usual method to calculate $k(t)$ considers the distribution of B particles around any given A particle. The B particles are assumed to be in excess of the A particles so that the competition of an A particle to capture a B particle is not important. Also the A particles are considered to be effectively independent from one other and therefore the concentration gradients about each surviving A particle do not interfere. The rate constant $k(t)$ is then the inward diffusive flow rate of B particles across the reaction surface at a . Shlesinger [42] has stated in the literature that this formulation for $k(t)$ is not strictly speaking correct. Only the first B particle which diffuses towards the reaction surface will contribute to $k(t)$, and not the diffusive motion of all the B particles towards the reaction surface. This problem is remedied by explicitly using the pair survival probability.

2.5.1 Independent Pairs Approximation

The independent pairs approximation (IPA) plays an important role in describing the kinetics in microscopic nonhomogeneous systems. Rather than formulating a theory based on macroscopic systems, IPA starts with a microscopic description of the geminate pair and extends its applicability to systems of more than two particles. Consider an A particle fixed at the origin, then let the probability density of finding a B particle at distance r_1, r_2 and so on from the A particle be $u(r_1, r_2, \dots, r_N)$ (the joint probability density of N distances). The probability $P(t)$ of the A particle surviving is then the probability of all B particles belonging to A surviving such that

$$P(t) = \int_V \int_V \dots \int_V \Omega(r_1, t) \Omega(r_2, t) \dots \Omega(r_N, t) \\ \times u(r_1, r_2, \dots, r_N) dr_1 dr_2 \dots dr_N \quad (2.117)$$

with V being the volume of the system and $\Omega(r, t)$ the pair survival probability of species A and B.

Uniform distribution The bulk rate constant $k(t)$ for a uniform distribution can now be formulated in a similar manner to Eq. (2.116) using the survival probability of the A particle as follows

$$k(t) = -\frac{1}{c_B} \frac{d \ln P}{dt} \quad (2.118)$$

Letting the B particles be distributed according to a Poisson distribution, the probability that the volume contains N particles is

$$u(N) = e^{-c_B V} \frac{(c_B V)^N}{N!} \quad (2.119)$$

Assuming for simplicity that V only contains one B particle, the survival probability of A is then simply

$$\Omega_1 = 1 - \int_a^R \frac{4\pi r^2}{V} W(r, t) dr \quad (2.120)$$

where $W(t)$ is the reaction probability of particle A and R is the maximum distance between the A–B particle. Now making the *independent pairs approximation* such that

$$P(\text{survival}|N) = P(\text{survival}|1)^N \quad (2.121)$$

which in words states that the probability of the A particle surviving conditioned the volume contains N number of B particles, is equivalent to the probability of all B particles belonging to A surviving. The expression for $P(t)$ can now be rewritten in the form

$$\begin{aligned} P(t) &= \sum_{N=0}^{\infty} u(N) P(\text{survival}|1)^N \\ &= \sum_{N=0}^{\infty} e^{-c_B V} \frac{(c_B V)^N}{N!} (\Omega_1)^N \\ &= [1 - c_B V][1 + c_B V \Omega_1] \\ &= e^{-c_B V(1-\Omega_1)} \\ &= \exp\left(-c_B \int_a^R 4\pi r^2 W(r, t) dr\right) \end{aligned} \quad (2.122)$$

Substituting the expression for $P(t)$ into Eq. (2.118) then gives

$$k(t) = \frac{d}{dt} \int_a^R 4\pi r^2 W(r, t) dr \quad (2.123)$$

Making the assumption that B is in large excess over the A particles and substituting the expression for $W(r, t)$ Eq. (2.89) into Eq. (2.123) finally gives Smoluchowski's time dependent rate constant to be

$$\begin{aligned} k(t) &= 4\pi a \int_a^\infty r \operatorname{erfc} \left(\frac{r-a}{\sqrt{4D't}} \right) dr \\ &= 4\pi a D' \left[1 + \frac{a}{\sqrt{\pi D't}} \right] \end{aligned} \quad (2.124)$$

The rate constant for reactions which are not fully diffusion controlled can also be readily found by substituting the complement of Eq. (2.107) into Eq. (2.123) to give

$$\begin{aligned} k(t) &= \frac{4\pi D'a}{1+\alpha} \left[1 + \frac{va}{D'} \exp \left(\left(\frac{va}{D'} + 1 \right)^2 \left(\frac{D't}{a^2} \right) \right) \right. \\ &\quad \times \left. \operatorname{erfc} \left[\left(\frac{va}{D'} + 1 \right) \frac{\sqrt{(D't)}}{a} \right] \right] \end{aligned} \quad (2.125)$$

where $\alpha = D'/va$. The above expression reduces to Eq. (2.124) for an infinitely fast boundary ($v \rightarrow \infty$). This derivation has shown two important factors: (1) Smoluchowski's first assumption that the central A particle is stationary is equivalent to the independent pairs approximation and (2) Smoluchowski's second assumption that the central sink is indestructible is not necessary in this case (as shown by Steinberg and Katchalski [5] and Tachiya [4]). Other derivations of the above equation have also been presented in the literature [3]. Therefore the usual method used to calculate $k(t)$ is correct, because in Eq. (2.116), the right hand side is multiplied by the concentration of the *surviving* A particles. The concentration of the A particle is only depleted by the inward flow of the *first* B particles and not of all the B particles. Hence only the inward flow of the first B particles contributes to the rate constant.

Thermal distribution From statistical mechanics the thermal distribution is known to take the form

$$u(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{e^{-\beta[\ell_1(\mathbf{r}_1)+\ell_2(\mathbf{r}_2)+\dots+\ell_N(\mathbf{r}_N)]}}{\int \dots \int e^{-\beta[\ell_1(\mathbf{r}_1)+\ell_2(\mathbf{r}_2)+\dots+\ell_N(\mathbf{r}_N)]} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N} \quad (2.126)$$

where $\ell(r) = -e^2/\epsilon_r r$, with ϵ_r being the dielectric constant, e the electron charge and $\beta = 1/k_B T$, with k_B being the Boltzmann constant, T the temperature. The probability of survival of the A particle is then

$$P(t) = \left[\frac{\int_a^V \Omega(r, t) e^{-(\beta\ell(r))} d\mathbf{r}}{\int_a^V e^{-(\beta\ell(r))} d\mathbf{r}} \right]^N \quad (2.127)$$

Under the assumption that

$$\lim_{V \rightarrow \infty} \frac{\int_a^\infty e^{-(\beta \ell(r))} d\mathbf{r}}{V} = 1 \quad (2.128)$$

and $\ell(r)$ to drop with increasing r , the final expression for $P(t)$ yields

$$P(t) = e^{-c_B \int [1 - \Omega(r, t)] e^{-(\beta \ell(r))} d\mathbf{r}} \quad (2.129)$$

Substituting the above expression into Eq. (2.118) then gives the bulk rate constant for a thermal distribution to be [4]

$$k(t) = - \int_a^\infty \frac{\partial \Omega(r, t)}{\partial t} e^{-(\beta \ell(r))} d\mathbf{r} \quad (2.130)$$

2.6 Scavenging Kinetics

2.6.1 Scavenger Concentration and the Inverse Laplace Transform Relationship

In radiation chemistry, experimentalists often use scavengers to intercept the radicals and ions before they recombine. The addition of scavengers often introduces an extra level of complexity into the recombination kinetics since some of the scavenged products might be capable of further reactions. It was first suggested by Monchick and Hummel [43–45] that the kinetics of recombination in a two radical spur can be extracted by observing the concentration dependence of the yields of scavenging and recombination. The yield of scavenged radicals $G(s)$ per 100 eV of absorbed energy can be related to the recombination kinetics in hydrocarbons by the relation

$$G(s) = s \int_0^\infty \exp(-st) G(t) dt \quad (2.131)$$

where s is the pseudo-first order scavenging rate constant (equal to $k[S]$, with k being the steady state scavenging rate constant and $[S]$ the concentration of scavengers) and $G(t)$ the survival yield of radicals per 100 eV in the absence of scavengers. The unknown function $G(t)$ can be obtained by taking the inverse Laplace transform (ILT) of $G(s)/s$. Hence, in order to determine $G(t)$ a knowledge of the function $G(s)/s$ is required from zero up to the point where all the particles are scavenged. Warman et al. [46] have studied the irradiation of hydrocarbon solutions, and have found an expression for $G(s)$ (for low concentrations of $[S]$) to be of the form

$$G(s) = [G(0) - G(\infty)] \frac{(\ell[S])^{1/2}}{1 + (\ell[S])^{1/2}} + G(\infty) \quad (2.132)$$

where $G(0)$ is the initial yield of ions, $G(\infty)$ is the final yield of intra-spur ions and ℓ is a constant which is related to the particular scavenging reaction. The ILT of $G(s)/s$ is then readily found to be

$$G(t) = [G(0) - G(\infty)] \exp(\lambda t) \operatorname{erfc}(t\lambda)^{1/2} + G(\infty) \quad (2.133)$$

with $\lambda = k/\ell$. Hummel has similarly suggested a form for the scavenging of ions to be

$$G(s) = [G(0) - G(\infty)] (1 - \exp(-(\ell[S])^{1/2})) + G(\infty) \quad (2.134)$$

with the ILT of the above expression being

$$G(t) = [G(0) - G(\infty)] \left(1 - \operatorname{erfc} \left(\frac{1}{2(\lambda t)^{1/2}} \right) \right) + G(\infty) \quad (2.135)$$

Both Eqs. (2.132) and (2.134) are functions which can be expressed as

$$G(s) = [G(0) - G(\infty)] \frac{\sum_{i=1}^n (\ell[S])^{i/2}/i!}{\sum_{i=0}^n (\ell[S])^{i/2}/i!} + G(\infty) \quad (2.136)$$

It was found by Pimblott and La Verne [47] that an intermediate function (with $i = 2$ in the above expression) of the form

$$G(s) = [G(0) - G(\infty)] \frac{(\ell[S])^{1/2} + \ell[S]/2}{1 + (\ell[S])^{1/2} + \ell[S]/2} + G(\infty) \quad (2.137)$$

gave a more acceptable fit to experimental data. The ILT of the above expression was found to be

$$G(t) = [G(0) - G(\infty)] \left(2F_f \left(\frac{4\lambda t}{\pi} \right)^{1/2} \right) + G(\infty) \quad (2.138)$$

with F_f representing the auxiliary function for the Fresnel integrals.

2.6.2 Competition Between Scavenging and Recombination

For some of the chemical systems considered in this thesis, geminate recombination competes with scavenging. The fact that the radicals are initially close to one another means that the radicals compete for individual scavengers; this competition leads to an effect on the scavenging rate.

It has been reported in the literature [48] that Smoluchowski's rate constant overestimates the rate of scavenging for a single target that can be hit multiple times (for example DNA). In their work, the authors found that Smoluchowski's rate constant overestimated the scavenging yield in comparison to Monte Carlo random flights simulation (which makes no assumptions on the rate of scavenging as they are explicitly treated). The authors have found that a modification to Smoluchowski's rate constant is required in order to properly take the correlation of reaction times into account; however, the independent pairs approximation is still made.

In their paper [48], they show that the probability distribution for the first reaction time is given by $P_2 = \exp(-cv_L(2t))$, whereas assuming independence of radical-target distances this would be $\exp(-2cv_L(t))$, where c is the target concentration and v_L has the dimension of volume and is defined as $v_L(t) = \frac{4}{3}\pi a^3 + 4\pi D'a(t) + 8a^2\sqrt{\pi D't}$. Comparing the two exponents for a correlated system (Eq. 2.139) and assuming independence of radical-target distance (Eq. 2.140) they obtain the following expressions

$$v_L(2t) = \frac{4}{3}\pi a^3 + 8\pi D'at + 8a^2\sqrt{2\pi D't} \quad (2.139)$$

$$2v_L(t) = \frac{8}{3}\pi a^3 + 8\pi D'at + 16a^2\sqrt{\pi D't} \quad (2.140)$$

In the above equations, the first term representing zero time reaction is overestimated by a factor of two if independence of reaction times is assumed. This is because for a geminate pair, if the scavenger is initially far from one radical then it will also be far from the other radical. Hence there is a second possibility for the other radical to be close to the target and react. However, if the radical-target distances are correlated, and if one radical is far from the target then the other must be as well (as the radicals are close together).

The second term operates in the long time limit when steady state is achieved and any information regarding the initial radical-target correlation is lost. Therefore it is not surprising that both the exponents are the same.

The third term is the most important, as this represents the rate of reaction before a concentration profile is established. It is seen that this term is a factor of $\sqrt{2}$ smaller than what is predicted by Smoluchowski. By slowing the transient term in Smoluchowski's time dependent rate constant, the authors report the modified expression for the correlated system to be

$$k(t) = 4\pi aD' \left(1 + \frac{a}{\sqrt{2\pi D't}} \right) \quad (2.141)$$

The modified rate constant shows that the first radical-target reaction to be slower than what is predicted by Smoluchowski, because as mentioned earlier, if one radical is far from the target the other must be as well (with the converse also being true); whereas assuming independence of radical-target distance, there is a second possibility for the radical to be close to the target. Given that the first reaction time is slower than

what is predicted by assuming independence of distance (assuming radical decay is identical such that each radical is equidistant from the target), it is found by the authors that the second radical-target reaction time must be faster than what is predicted by Smoluchowski. This is found to be true for an indestructible sink, as the second radical is much more likely to react with the same target as the first and this will occur on a much faster timescale than what is predicted by assuming independence of reaction times. Further work conducted by the authors has shown that for a reaction scheme where scavengers are not indestructible, the second reaction is predicted to be slower than Smoluchowski's theory, since the concentration of scavengers is depleted by the first reaction.

2.7 Spin-Controlled Reactions

In order to model spin-dependent reactions it is necessary to introduce a spin statistical factor (σ_S) into Smoluchowski's rate constant to account for the fact that only 1/4 of all interactions will be in a reactive singlet state. The modified Smoluchowski steady state rate constant for spin systems is then [3]

$$k = 4\pi D' a \sigma_S \beta \quad (2.142)$$

where β is $\frac{1}{2}$ for like reactions or unity otherwise. The value of σ_S varies for different chemical systems and is directly related to the spin relaxation time. For radicals whose spin-relaxation time is much longer than the encounter time ($\sim 10^{-8} - 10^{-10}$ s), $\sigma_S = \frac{1}{4}$, however for faster relaxing systems $\sigma_S \rightarrow 1$, reflecting the fact that the spin can re-orient itself whilst still inside the encounter cage. Various σ_S values have been tabulated in the literature [49] based on the observed rate constant for the reaction between the hydrated electron and various radicals; a spin factor of $\frac{1}{4}$ is applicable for $e_{aq}^- + \cdot SO_3^-, CO_3^-, \cdot CO_2^-, \cdot C(CH_3)_2OH, (\cdot CH_2)(CH_3)_2COH, \cdot C_6H_6OH, C_6H_5O\cdot, p-(H_3C)C_6H_4O\cdot$ and $p-OC_6H_4O\cdot^-$, whilst for reactions between $e_{aq}^- + \cdot OH, \cdot N_3, Br_2^{\cdot-}$ and $I_2^{\cdot-}$ the spin factor is found to be close to unity. For the $e_{aq}^- + \cdot OH$ the spin factor is close to unity because of the unquenched orbital angular momentum in linear radicals, which through the spin-orbit coupling mechanism can lead to very fast spin relaxation.

Based on experimental findings by Ichino and Fessenden [49], the authors have suggested that σ_S is also temperature dependent. Assuming the radical pair lifetime to be inversely proportional to the mutual diffusion constant (D') [50], it is found that D' changes by about a factor of three between 298 and 343 K, so the radical pair lifetime should decrease by about the same factor. Therefore, with increasing temperatures, diffusive separation of triplet radical pairs may become a faster process than spin-relaxation, in which case the spin-factor would be lowered. This explanation has been found to be in agreement with experimental findings [49].

A very useful theoretical model developed by Mints and Pukhov [51] allows the relationship between the spin factor and spin relaxation to be analysed. Using the stochastic Liouville equation and a phenomenological approach to treating spin relaxation, the authors arrive at the expression for the ($e_{aq}^- + \text{radical}$) reactions as

$$\sigma_S = \frac{1}{2} \frac{k\tau PQ}{k\tau(P + Q) + 2PQ} \quad (2.143)$$

where

$$\begin{aligned} \tau &= \frac{a'b'}{D'}, \quad P = 2 \left(\frac{1 + \sqrt{2x'}}{2 + \sqrt{2x'}} \right), \quad Q = 1 + \sqrt{y'} \\ x' &= \frac{1}{2T_1} \frac{b'^2}{D'}, \quad y' = \frac{1}{2T_2} \end{aligned} \quad (2.144)$$

Here, k is the rate constant for reaction, τ is the radical pair lifetime, a' is the thickness of the reaction layer, b' is the reaction distance, D' the mutual diffusion coefficient and T_1 and T_2 are the longitudinal and transverse relaxation times of the counter radical. This model neglects any magnetic interactions (i.e. hyperfine and Zeeman) which could possibly influence the observed chemical kinetics.

2.7.1 Recovering Boundary Model

An analytical theory developed by Green et al. [9] replaces the radiation boundary condition, treating encounters and re-encounters differently and is known as *recovering boundary*. The main idea of this theory is that on an unsuccessful encounter the boundary becomes unreactive, which gradually grows back as a function of time. The nature of this recovery can take various analytical forms depending on the type of reaction. In this section only a brief review of the theory is presented which is applicable to this work. A fuller review can be found in reference [9].

The recovery boundary method finds the Laplace transform of the density of the reaction times following an unreactive encounter, which takes the form

$$\begin{aligned} f(t) &= \int_0^t w_2(t_1) w_1(t - t_1) P(t - t_1) dt_1 \\ &+ \int_0^t \int_0^{t_2} w_2(t_1) w_1(t_2 - t_1) (1 - P(t_2 - t_1)) f(t - t_2) dt_1 dt_2 \end{aligned} \quad (2.145)$$

with w_1 and w_2 denoting the first passage density of times from $a + \delta$ to a and a to $a + \delta$ respectively (a being the encounter distance). The first term simply states that for a diffusion process which obtains $a + \delta$ at t_1 , the probability of reacting at time t (which denotes the time taken to diffuse from a to $a + \delta$) is $P(t - t_1)$. The second term accounts for the diffusion process to have attained a at an earlier time t_2 and was found to be unreactive with probability $1 - P(t_2 - t_1)$. Using the strong Markov property, the process starts anew with the probability of reaction at t_2 zeroed, and eventually reacting at a later time t .

Recognising Eq. (2.145) as a convolution, the Laplace transform takes the form

$$\tilde{f}(s) = \frac{\tilde{w}(s)\tilde{v}(s)}{1 - \tilde{w}_2(s)(\tilde{w}_1(s) - \tilde{v}(s))} \quad (2.146)$$

where $\tilde{v}(s)$ contains the recovery function and is related to $v(t)$ by the expression $w_1(t)P(t)$. The authors have found that under most conditions, recovery can start as soon as the boundary is obtained; introducing any delay times (i.e. time to attain $a + \delta$) is deemed unnecessary. In this case taking the limit $\delta \rightarrow 0$ of Eq. (2.146), the authors obtain

$$\tilde{f}(s) = \frac{\tilde{v}(s)}{1 - (\tilde{w}_1(s) - \tilde{v}(s))} \quad (2.147)$$

where $\tilde{v}(s)$ contains the recovery function and is related to $v(t)$ by the expression $w_1(t)P(t)$.

In order to model spin dependent reactivity, where reaction is only possible through the singlet channel, the authors make use of the exponential model of the form $P(t) = p(1 - e^{-\beta t})$ to calculate the probability of reaction. Here, the $P(t)$ relaxes exponentially towards the asymptotic value of p (the probability of being in a singlet state). β in this expression is the inverse of the spin relaxation time. Using the shift theorem of Laplace transform, the authors derive an expression for $\tilde{v}(s)$ to be

$$\tilde{v}(s) = p[\tilde{w}_1(s) - \tilde{w}_1(s + \beta)] \quad (2.148)$$

On substituting this definition for $v(s)$ into Eq. (2.147), the expression for the first passage density of times is

$$\tilde{f}(s) = \frac{p[\tilde{w}_1(s) - \tilde{w}_1(s + \beta)]}{1 - [(1 - p)\tilde{w}_1(0) + p\tilde{w}_1(\beta)]} \quad (2.149)$$

The probability of ultimate reaction can then be simply calculated by using the final value theorem ($s \rightarrow 0$), giving

$$F_\infty = \frac{p[\tilde{w}_1(0) - \tilde{w}_1(\beta)]}{1 - [(1 - p)\tilde{w}_1(0) + p\tilde{w}_1(\beta)]} \quad (2.150)$$

2.7.1.1 Homogeneous Rate Constant

The steady state rate constant can be expressed as

$$k_{\infty} = 4\pi D' a [q + (1 - q) F_{\infty}] \quad (2.151)$$

where q is the probability of reaction on first encounter. The first term of Eq. (2.151) is equivalent to Eq. (2.142) (Smoluchowski's steady state rate constant with a spin statistical factor), with the second term describing the correction for the regrowth of reactivity following each unreactive encounter. The exact solution for $\tilde{w}_1(s)$ (assuming a spherical particle) is shown to be

$$\tilde{w}_1(s) = \frac{a}{a + \delta} \exp(-\delta \sqrt{s/D'}) \quad (2.152)$$

Using the above definition for $\tilde{w}_1(s)$, substituting into Eq. (2.149) and taking the limit $s \rightarrow 0$, the ultimate recombination probability can be expressed as

$$F_{\infty} = \frac{ap\sqrt{\beta/D'}}{1 + ap\sqrt{\beta/D'}} \quad (2.153)$$

Substituting the above expression for F_{∞} into Eq. (2.151) gives the expression for the steady state rate constant to be

$$k_{\infty} = 4\pi D' a \left(\frac{q + ap\sqrt{\beta/D'}}{1 + ap\sqrt{\beta/D'}} \right) \quad (2.154)$$

Whether the recovering boundary or radiation boundary is applicable depends on a detailed model of the dynamics of the system and must be implemented accordingly. For the purposes of this work, the recovering boundary formalism is simply used to estimate the feasibility of certain approximations and is not implemented in any simulation.

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